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ATROPISOMERISM OF SUBSTITUTED 9, 9-PRIME-BITRIPTYCYLS

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ATROPISOMERISM OF SUBSTITUTED 9,9'-BITRIPTYCYLS

BY

CHEN SHEK YU

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment
of the requirements for the degree of Doctor
of Philosophy, The City University of New York.

1979

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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ABSTRACT

Atropisomerism of Substituted 9,9'-Bitriptycyls

by

Chen Shek Yu

Mentor : Professor Leonard H. Schwartz

To demonstrate the presence of atropisomerism in the 9,9'-bitriptycyl system, a number of x,x'-dimethyl-9,9'-bitriptycyls have been synthesized through addition of benzyne to the corresponding x,x'-dimethyl-9,9'-bianthryls. Partial separation of *anti* and *gauche* conformers of 2,2'-dimethyl-9,9'-bitriptycyl (Ib) has been achieved. Attempted thermal equilibration experiments together with nmr spectroscopic analyses have established the non-interconvertibility of these two conformers at temperatures as high as 300°C, indicating a rotational energy barrier of at least 53.8 Kcal/mole.

Likewise, optically active 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih) has also been successfully prepared by the addition of benzyne to optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (IIh). The *anti* and *gauche* conformers of Ih were separated by column and thick layer chromatography. Optical rotation measurements and nmr spectroscopic analyses using a chiral shift reagent, tris-[(3-heptafluoropropylhydroxymethylene)-d-camphorato]europium (III) ($Eu(hfc)_3$), indicated that the specific rotation for the *gauche* Ih is $[\alpha]_D^{23}$ 14.7±0.03 (c 0.375, $CHCl_3$). The results also indicated that 71% racemization of Ih had taken place during the benzyne addition reaction. Such racemization is believed to occur in the half-adduct stage.

Progress has been made towards the synthesis of optically active 2,2'-dicarboxy-9,9'-bitriptycyl (IIg) through a stereospecific route. A key cyclic intermediate, 2,2'-(N,N'-(α,α'-p-xylyl))-dicarboxamido-9,9'-bianthryl (IIm), has been synthesized using a specially designed "Time-controlled Synchronous Constant-volume-addition Double-high-dilution Reaction Apparatus". Addition of benzyne to optically active cyclic intermediate (IIm) could eventually lead to optically active IIg having the same optical purity as IIm.

To Mai Jien

ACKNOWLEDGEMENTS

I am grateful to my dissertation committee, professors William F. Berkowitz, Norman L. Goldman, Jack J. Morrow and Samuel H. Wilen, for their continued guidance and encouragement throughout this research work.

I am particularly in debt and grateful to my mentor, professor Leonard H. Schwartz, for his constant, invaluable criticism, assistance and supports which helped to develop and to bring this research work into fruition. Special thanks is also due to him for the immeasurable amount of time he spent in helping me to prepare this manuscript.

I would also like to take this opportunity to thank the following persons: Messrs. Joe LaRubbio and Miguel Mieles for taking the mass spectra, Hugo Schimatz and Robert Walker for building the glass and electronic parts of the Synchronous Constant Volume Addition Assembly, Barbara Alexander, Emiko Kauz and Sally Mai for helping to complete the final typing of this manuscript.

Finally I like to thank the Chemistry Department of The City College of The City University of New York for their financial support during the work of this research.

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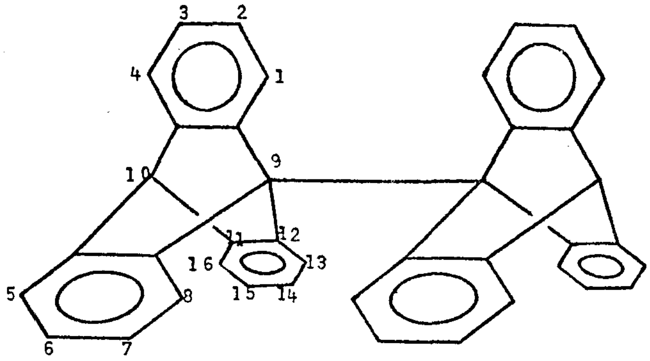
INTRODUCTION

I. Atropisomerism and the 9,9'-Bitriptycyl System

The goal of this research project was to investigate the possibility of atropisomerism in the 9,9'-bitriptycyl system (Fig. I).

Fig. I



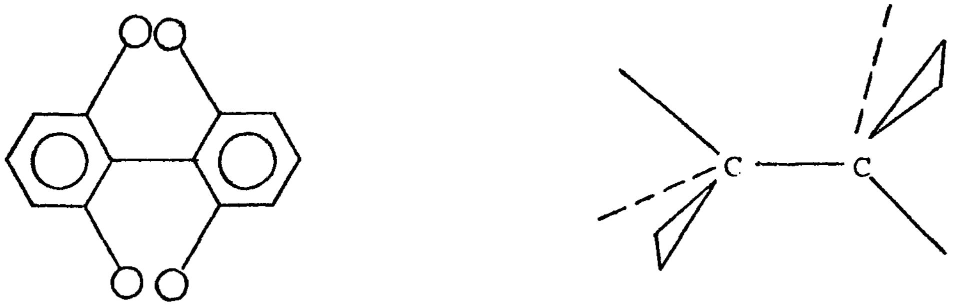
I

Ia; 1,1' = CH_3
b; 2,2' = CH_3
c; 3,3' = CH_3
d; 4,4' = CH_3
e; 1,1',4,4' = CH_3
f; 2,2' = Cl
g; 2,2' = COOH
h; 2,2' = $COOCH_3$

Atropisomerism, as defined by Eliel,[1] is "...any kind of stereoisomerism due to restricted rotation about single bonds where the isomers can actually be isolated." Restricted rotation between carbon-carbon single bonds has long been a field of active interest in organic chemistry. Restricted rotation about single bonds joining two sp^2 hybridized carbon atoms, as in the biaryls, has been thoroughly investigated.

Since the first successful isolation of an optically active biphenyl, 6,6'-dinitro-2,2'-diphenic acid, by Christie and Kenner,[2] numerous ortho-substituted biphenyls have been isolated in optically active form and their barriers to rotation studied.[3] In general, it is believed that the restricted rotation in ortho substituted biphenyls is mainly due to steric factors. An appreciable activation energy is usually required in order to cause the two pairs of opposing ortho-substitutents to pass each other in the planar rotational transition state (Fig. II-A). Steric interference is suggested as the origin of this rotational barrier by the fact that the racemization energies for many biphenyls roughly parallel the known vander Waals radii of their ortho substituents, namely, $I>Br>>CH_3>Cl>NO_2>COOH>>OCH_3>F$.[1,3b,4] The isolation of conformational isomers at or above ambient temperature is possible if the energy barrier to rotation is approximately 23 Kcal/mole or greater.[5]

Fig. II



A

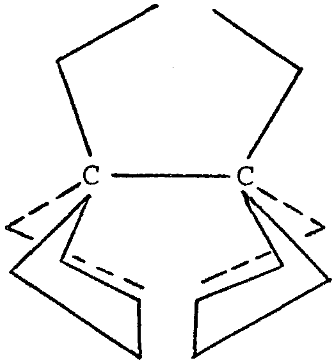
B

In theory, conformers of substituted ethanes could also be isolated, if this energy requirement were met. Rotational barriers of simple substituted ethanes have, in general, been found to be appreciably lower than those of the biphenyls. The pivotal carbon-carbon bonds in biaryls are shorter than the corresponding bonds in substituted ethanes. This factor contributes to the higher rotational barriers in the former system. However, the major factor is the difference in orientation of the substituents bonded to the pivotal carbon atoms. Because the carbon atoms in ethanes are sp^3 hybridized, attached substitutents are necessarily pointing away from each other (Fig. II-B). On the other hand, the ortho substituents of biphenyls are pointing towards each other and are closer together (Fig. II-A). The steric interference between substituents in the transition states of the biphenyls is therefore more severe than in the ethane case.

A simple approach towards the achievement of sufficient steric hindrance for the occurrence of atropisomerism in ethanes is to increase the size of the substituents. Unfortunately, synthetic problems render this approach quite doubtful. As the size of the substituents increases, geminal steric interactions, which would certainly increase more rapidly than the vicinal interactions involved in the rotational barriers, would make such a synthetic pathway futile. Another approach to achieve an increased rotational barrier is to construct a system whose interfering substituents mimic the directional behavior of the substituents in the biphenyls, that is, point towards each other (Fig. III).

9,9'-Bitriptycyl (I)* and its derivatives fit the concept illustrated in Fig. III. A search for atropisomerism in such compounds is the subject of this dissertation. We believe, for reasons to be discussed, that 9,9'-bitriptycyl (I) and its derivatives should posses high rotational energy barriers about the ethane-like linkage joining the 9 and 9' carbon atoms. With properly substituted derivatives, the observation and isolation of conformers (atropisomerism) should be possible.

Fig. III



There are three conformers possible for a x,x'-disubstituted 9,9'-bitriptycyl. The conformers consist of an optically inactive anti form and a pair of enantiomeric gauche forms. These conformers can be best visualized when shown in Newman projections (Fig. IV). If the rotation about the pivotal ethane linkage is sufficiently hindered, the anti conformer should be physically distinguishable and potentially separable from the gauche conformers. With a properly constructed synthetic scheme, an independent synthesis of one or both of the conformers would be possible.

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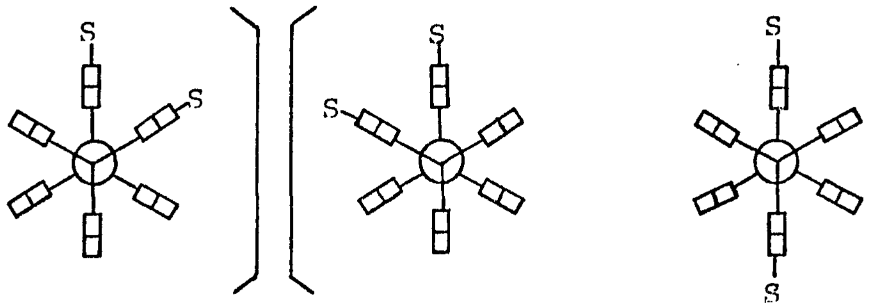
*A list of numbered compounds can be found in Appendix C.

Fig. IV

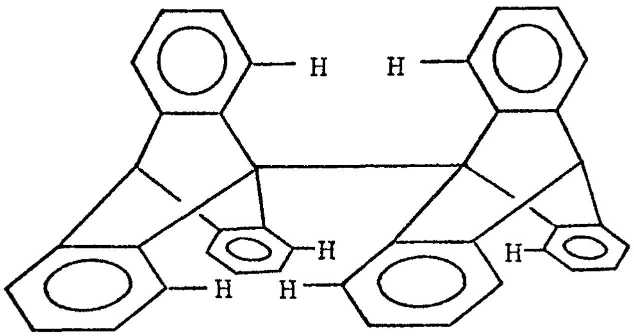


Gauche Gauche Anti

▭ = Sideview of a benzene ring
S = Substituent

In the 9,9'-bitriptycyl (I) system, three aromatic hydrogen atoms on one half of the molecule are directed towards the other half (Fig. V). In the rotational transition state, three pairs of aromatic hydrogen atoms would have to

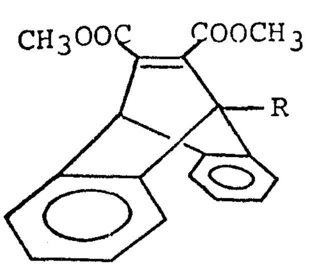
Fig. V



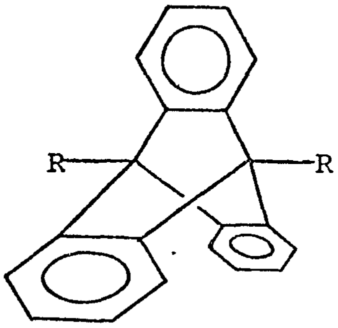
pass each other simultaneously (three benzo-benzo interactions). A recent x-ray crystallographic analysis of 9,9'-bitriptycyl led to the conclusion that, in order for rotation to occur, the benzo hydrogen atoms of one triptycene moiety would have to pass through the midpoints of the benzo carbon-hydrogen bonds of the opposite triptycene.[8] It has been estimated from direct and indirect evidence that a benzo-benzo interaction in the 9,9'-bitriptycyl system (I) would have an energy barrier of approximately 21-29 Kcal/mole.[7] Three such interactions, in the eclipsed transition state of I, would therefore involve an energy barrier in the neighborhood of 63-87 Kcal/mole. Such an energy barrier is well in excess of the energy requirement for the existence of isolable conformers[5](see p. 3).

While this research was in progress, a number of substituted ethanes were reported which exibit relatively high rotational energy barriers about their pivotal carbon-carbon single bonds.[9a-h] In all cases where high rotational energy barriers were detected, the blocking substituents on one part of the molecule were oriented towards the other part- a necessary feature for high rotational energy barriers (see p. 4). A few examples follow. Based on nmr spectroscopic analyses, M. Ōki and co-workers have concluded that rotational energy barriers of 15 Kcal/mole and "no lower than 25 Kcal/mole" exist between the bridgehead substituents, R, and the bicyclic system of compounds 1 (equilibration of diastereomeric methyl group in R through equilibration of *gauche* conformers) and 2, respectively.[9b] An energy barrier of 33 Kcal/mole has been reported for 3 (*anti* conformer → *gauche* conformer).[9c] Subsequently, isolation of all three rotamers (*anti* conformer and *gauche* conformers) of half hydrolyzed 3 (the authors believed that the methyl ester pointing away from the R group was hydrolyzed) was reported.[9h]

Compound 4 has been reported to have a rotational barrier of 37.7 Kcal/mole,[9d] and its *anti* and *gauche* conformers were separated by column chromatography. Compound 5 has been

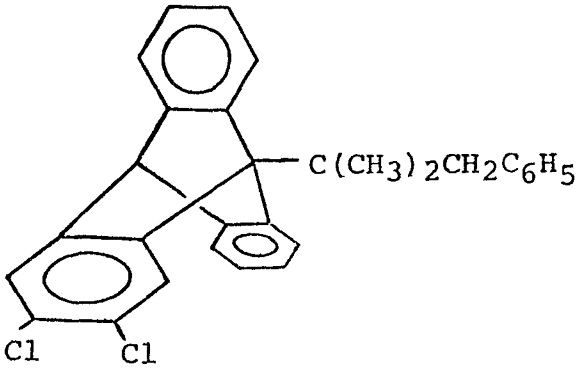


1, R = $CH(CH_3)_2$
2, R = $C(CH_3)_3$
3, R = $C(CH_3)_2(CH_2Ph)$



4, R = $C(CH_3)_2CN$

reported to exhibit an energy barrier of 33.6 Kcal/mole (*anti* conformer → *gauche* conformer).[9g] In this case the two conformers were synthesized separately by stereospecific routes.



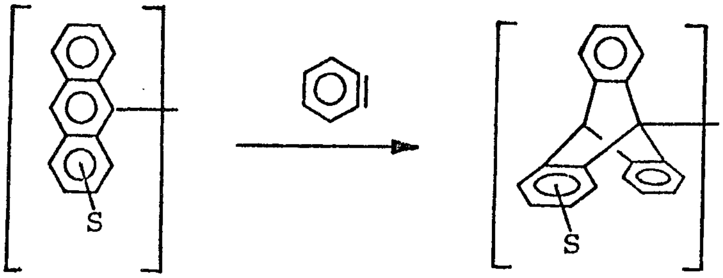
5

Since the steric interaction in the rotational transition state of the 9,9'-bitriptycyl system is due to three benzo-benzo interactions (Fig. V), it should be greater than those of the compounds of the preceding paragraph, and therefore, larger rotational energy barriers should be present.

II. Areas of Research

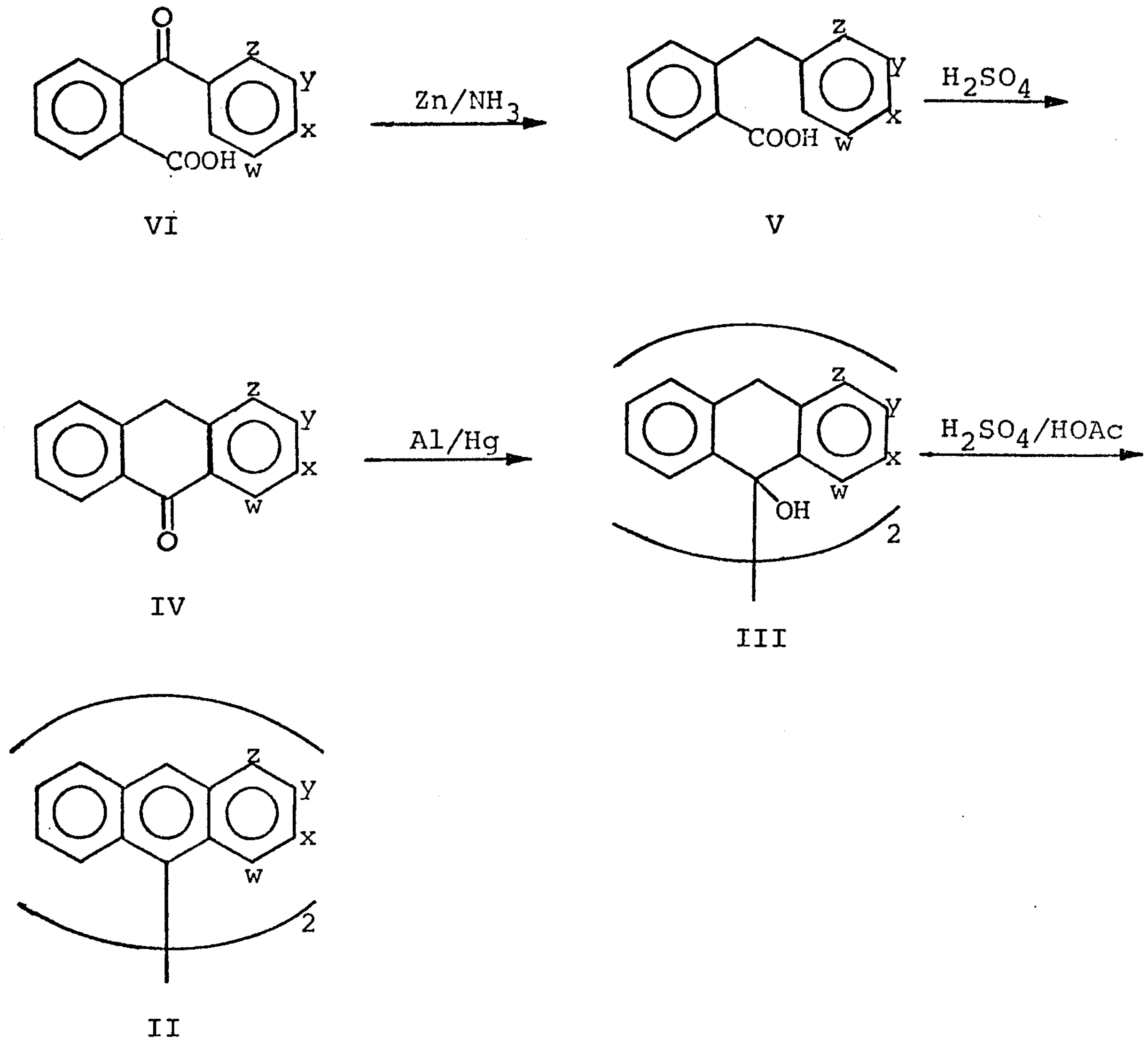
The syntheses of x,x'-disubstituted-9,9'-bitriptycyls have been previously investigated.[7] The bitriptycyls were prepared by the addition of benzyne to the corresponding substituted 9,9'-bianthryls (Scheme I). Benzyne was generated from anthranilic acid and n-butyl nitrite, following the procedure of Friedman and Lagullo.[10] The 9,9'-bianthryls were in turn synthesized from appropriately substituted benzoylbenzoic acids, according to the general synthetic pathway outlined in scheme II (p.10).

Scheme I



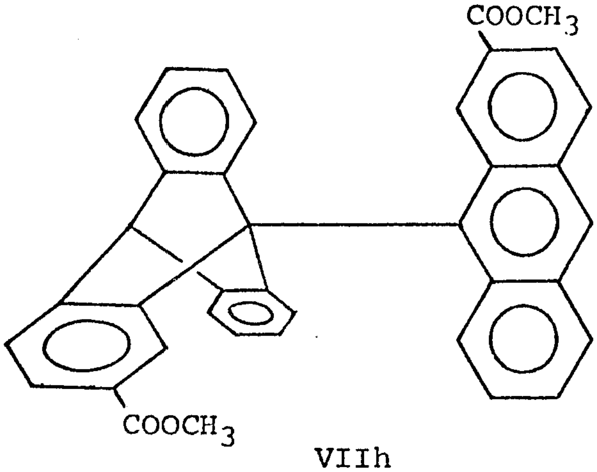
A previous attempt at demonstrating atropisomerism in 9,9'-bitriptycyls was unsuccessful.[7] The approach involved the addition of two benzyne moieties to optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (IIh) according to the general scheme (Scheme I). Arguments were presented that the product, 2,2'-dicarbomethoxy-9,9'-bitriptycyl, Ih, which would be expected to consist of a mixture of anti and gauche conformers, should be optically active, if the conformers were stable to interconversion. No activity was observed in

Scheme II



IIa, IIIa, IVa, Va, VIa, w=CH_3, x=y=z=H
IIb, IIIb, IVb, Vb, VIb, x=CH_3, w=y=z=H
IIc, IIIc, IVc, Vc, VIc, y=CH_3, w=x=z=H
IId, IIId, IVd, Vd, VId, z=CH_3, w=x=y=H
IIe, IIIe, IVe, Ve, VIe, w=z=CH_3, x=y=H
IIf, IIIf, IVf , Vf, VIf, x=Cl, w=y=z=H

the product. A number of possible reasons were offered for this result; the most probable was that rotation had occurred in the mono-adduct, VIIh, prior to the addition of the second benzyne. The rotational transition states of the mono-adduct would each involve only one benzo-benzo interaction. Thus, rotation should be considerably more facile than the rotation in the 9,9'-bianthryl or 9,9'-bitriptycyl systems. No attempt was made in this earlier work to separate the anti and gauche conformers of Ih.



VIIh

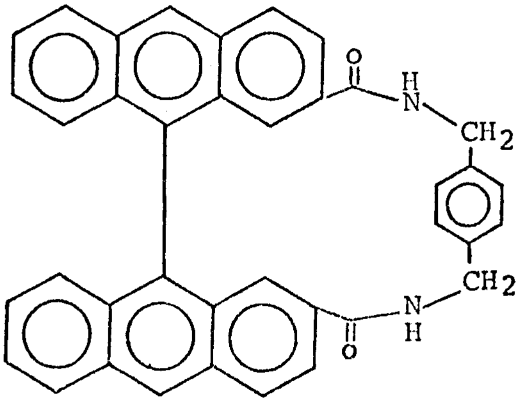
The work reported in this dissertation may be divided into three separate parts.

(A) 2,2'-Dimethyl-9,9'-bitriptycyl (Ib) was synthesized. Its nmr spectrum suggested the presence of non-interconverting conformers. Repeated crystallization yielded two fractions, each considerably enriched in one of the conformers. Experiments were conducted which established the minimum rotational barrier between the two conformers.[66]

(B) The synthesis of 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih) from optically active 2,2'-dicarbomethoxy-9,9'-

bianthryl (IIh) was repeated with a view towards confirming the earlier results and isolating gauche and anti conformers. Repeated column and thick layer chromatography led to the separation and isolation of the conformers. The two conformers were differentiated by optical activity and by nmr experiments using chiral chemical shift reagents.

(C) In an attempt to prevent the relatively rapid rotation in the mono-adduct VIIh, postulated by the earlier work,[7] an optically active bridged 9,9'-bianthryl was sought. The bridge would be expected to maintain the mono-adduct in a relatively stable (non-strained, non-rotating) conformation during the benzyne addition reaction. If rapid rotation in the mono-adduct is the reason for the earlier observed lack of optical activity, removal of the bridge after bitriptycyl formation should lead to an active product. Towards this goal, a method was developed to synthesize the bridged bianthryl, 2,2'-(N,N'-(α,α'-p-xylyl))-dicarboxyamido-9,9'-bianthryl (IIm). A special Synchronous Constant-Volume-Addition Double-High-Dilution System was designed to increase the yield of IIm.



IIm

RESULTS AND DISCUSSION

I. 2,2'-DIMETHYL-9,9'-BITRIPTYCYL (Ib)

A. Background and Statements of The Problem

2,2'-Dimethyl-9,9'-bitriptycyl (Ib) was synthesized by C. Koukotas.[7] However, no attempt was made to demonstrate its atropisomerism. Recently, it was found that the nmr spectrum of an analytical sample of Ib (called Ib' here), previously prepared by Koukotas, exhibited two closely spaced singlets ($\delta = 1.81$ and $\delta = 1.83$) in the methyl region. The absorption intensities of these two singlets were not equal. The low field peak ($\delta = 1.83$) was less intense than the high field peak ($\delta = 1.81$). The peak-height ratio (called R here) was approximately 0.83. When a second sample of Ib, prepared by Koukotas, was purified by preparative tlc (called sample Ib'' here), its nmr spectrum also showed two methyl peaks of unequal intensities. However this time the low field singlet of Ib'' was more intense than the high field one. The peak-height ratio, R, was approximately 2. Upon recrystallization of Ib'', the isolated crystals (Ib''') showed an increase in the high field methyl intensity (R = 1.3) as compared to Ib''. On the other hand, the solid recovered from the mother liquor (Ib"") showed enhancement of the low field signal (R = 2.7). These results indicated the presence of at least two methyl-containing compounds, which could be partially separated by crystallization.

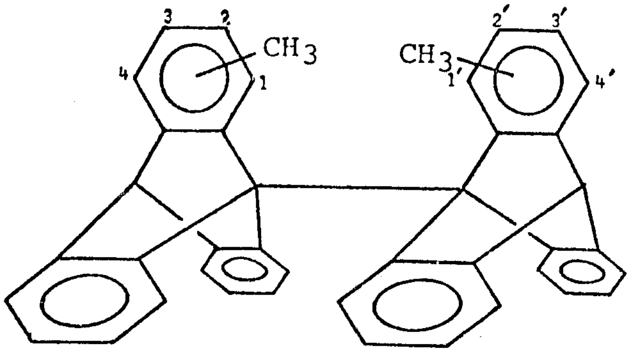
The presence of these methyl-containing compounds in Ib was very interesting. The two methyl peaks could conceivably be due to the presence of two stable diastereomeric conformers of Ib, namely, the anti and the gauche (d, l) forms (Fig. IV, p.6). If this were correct, the existence of restricted rotation in the 9,9'-bitriptycyl system would be established. One of the simplest way to demonstrate the existence of restricted rotation is by means of dynamic nuclear magnetic resonance spectroscopy.[5,11a-d] If at a given temperature (in this case, above room temperature) the two methyl singlets could be made to coalesce the presence of two diastereosmeric conformers would be demonstrated, and the rotational energy barrier could be calculated.

A solution of Ib in 1,1,2,2-tetrachloroethane (b.p. 147°C) was degassed and sealed in a thick-walled nmr tube using hexamethyldisilazane (b.p. 125°C) as internal standard. No coalescence or broadening in the methyl peak intensities was observed at temperature as high as 150°C.

This result, by itself, is not conclusive, since two different interpretations are possible. If the rotational energy barrier is as large as predicted (63-87 Kcal/mole p. 7), no coalescence or even change in the methyl peaks would be observed at the temperature attained. On the other hand, if one of the methyl peaks was due to the presence of an impurity, which somehow survived all attempted purifications, change or coalescence also would not be observed. It was, therefore, necessary to rule out the presence of contaminants in Ib.

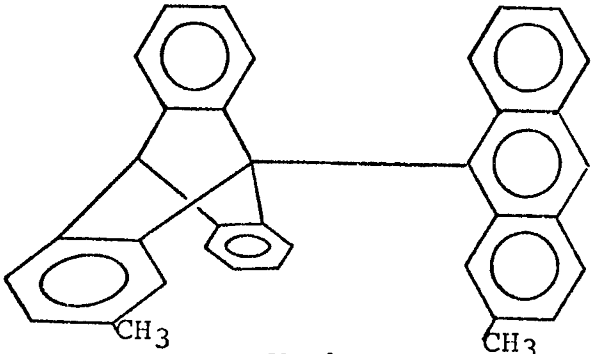
An examination of the synthetic pathway leading to Ib reveals some possible (although not necessarily probable) contaminants that could be present (Fig. VI). The mono-

Fig. VI

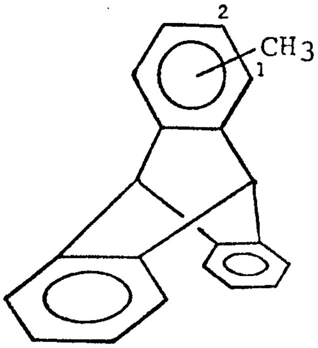


I

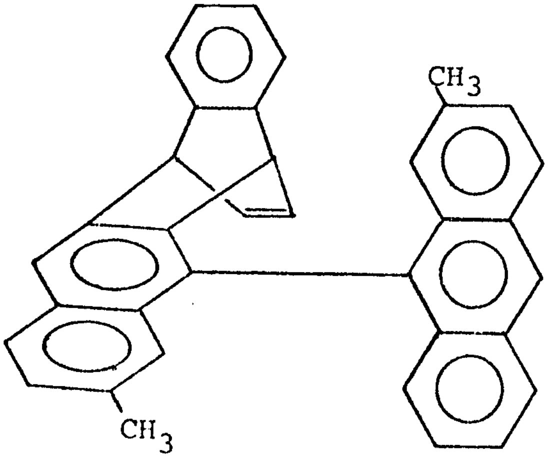
Ia, 1,1' = CH_3
Ib, 2,2' = CH_3
Ic, 3,3' = CH_3
Id, 4,4' = CH_3
Iab, 1,2' = CH_3
Iac, 1,3' = CH_3
Iad, 1,4' = CH_3
Ibc, 2,3' = CH_3
Ibd, 2,4' = CH_3
Icd, 2,4' = CH_3



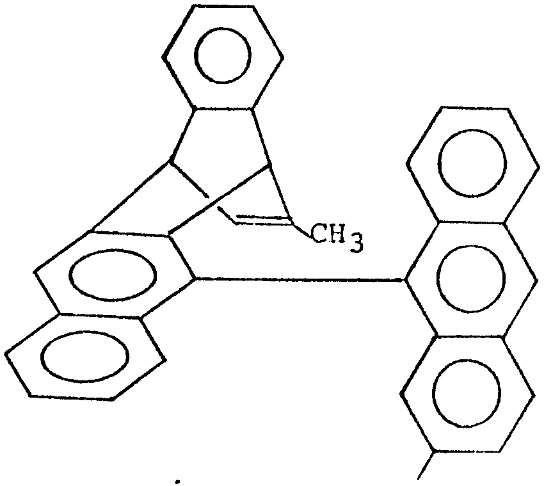
VIIb



IXa, 1 = CH_3
IXb, 2 = CH_3

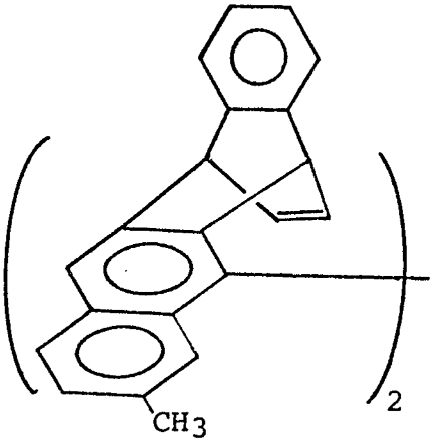


Xa

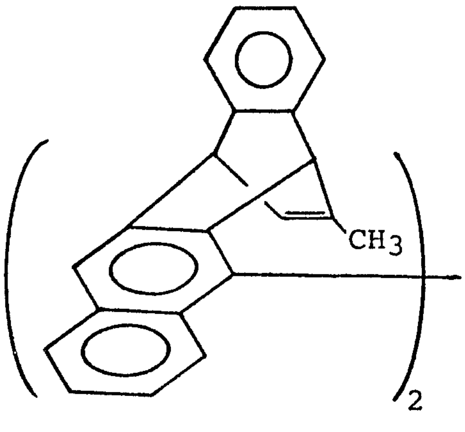


Xb

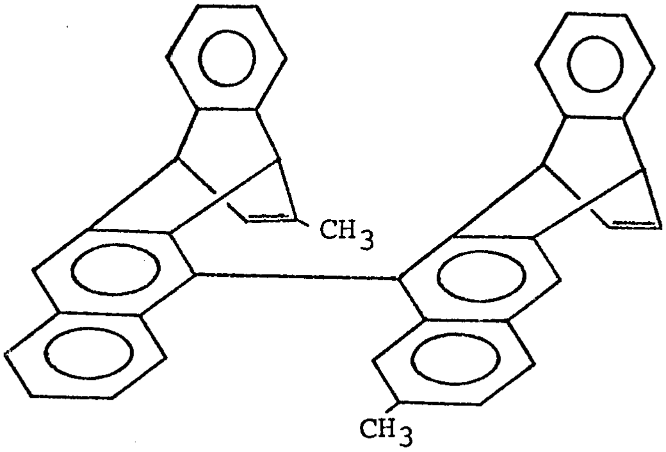
Fig. VI (Continued)



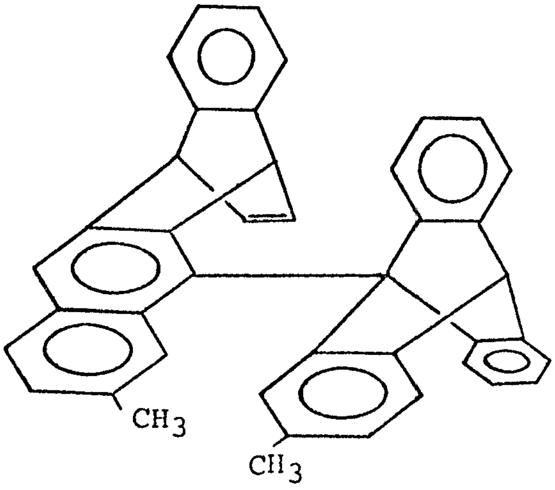
Xc



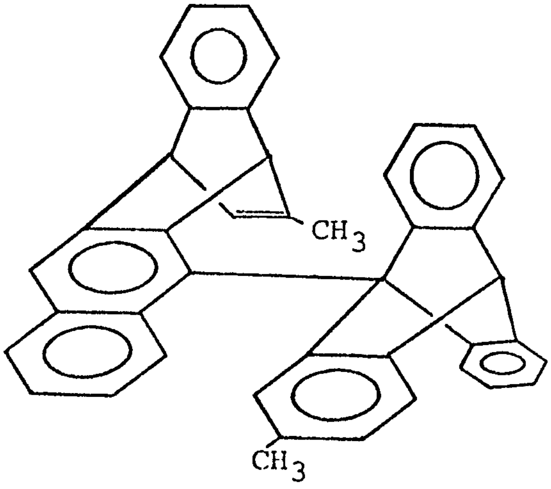
Xd



Xe



Xf



Xg

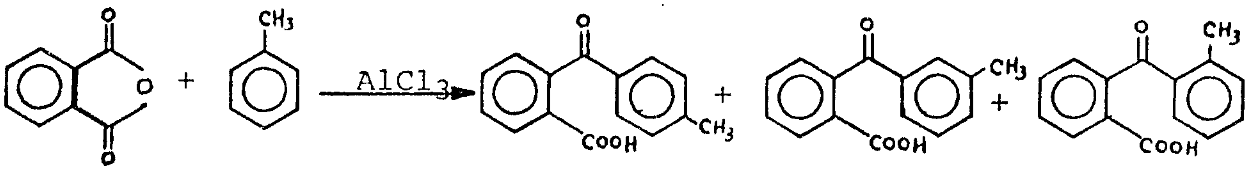
adduct, VIIb, is the expected addition product of only one benzyne molecule to 2,2'-dimethyl-9,9'-bianthryl (IIb). Compounds Xa-g are end-ring adducts formed by the addition of benzyne to the side rings of IIb. Klanderman and Criswell[12] reported that addition of benzyne to substituted anthracenes (including a 9-phenyl derivative) results in the formation of small amounts (a few percent) of end-ring adducts. In view of this study, the formation of small amounts of end-ring adducts such as Xa-g is certainly possible.

There are two possible sources for the occurrence of 1-methyltriptycene (IXa) and 2-methyltriptycene (IXb): a) from the addition of a benzyne to a molecule of 1- or 2-methylanthracene (anthracenes have been shown to be reaction side products in the preparation of x,x'-disubstituted-9,9'-anthrapinacols (pp. 101-109), precusors of the bianthryls, and b) from the cleavage of a dimethylbitriptycyl (an unlikely possibility).

The presence of 9,9'-bitriptycyls containing methyl groups in the 1, 3 and 4 positions (Ia, Iab, Iac, Iad, Ibc, Ibd, Ic, Icd, Id) is also conceivable. o-(p-Methylbenzoyl)-benzoic acid (VIb), the precusor for the synthesis of Ib, was prepared from phthalic anhydride and toluene, under Friedel-Crafts conditions. Some _ortho_ and _meta_ methyl isomers could also have been produced in this synthesis (Scheme III).

According to Scheme II (p. 10), the _ortho_ isomer (VId) would give rise to 4-methylanthrone (IVd), and the _meta_ isomer (VIc) could give rise to both 3-methyl-(IVc) and

Scheme III



VIb VIc VId

1-methylanthrone (IVa). Had IVa, IVc, or IVd not been completely removed, bimolecular reduction could have yielded a product that consisted of any number of the following ten possible dimethylanthrapincols (Scheme IV). Dehydration of this anthrapinacol mixture, and subsequent addition of benzyne to the resulting bianthryls, would yield a mixture of bitriptycyls corresponding to the ten possible dimethyl-9,9'-anthrapinacols (p. 20).

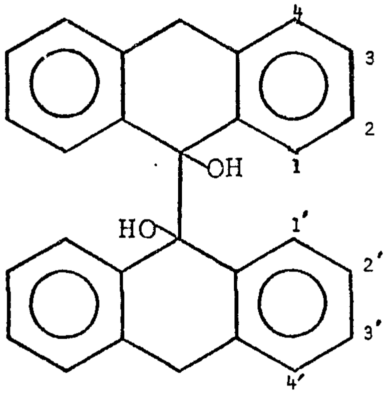
Structurally, the possible contaminants may be divided into two main groups. Compounds in the first group contain one or more naphthalene or anthracene moieties. The mono-adduct (VIIb) and the end-ring adducts (Xa-g) belong to this group. Compounds of the second group (IXa,b, Ia-d, Iab-cd) contain only triptycyl units and thus consist of only isolated phenyl rings. 2,2'-Dimethyl-9,9'-bitriptycyl (Ib), in fact, is a member of the second group.

Because of the presence of a condensed aromatic nucleus, uv spectroscopy would be useful in distinguishing the first group of compounds from Ib, which contains only isolated phenyl rings. However, uv spectroscopy would not be as useful in differentiating the second group of compounds from

Scheme IV

Anthrones Dimethylanthrapinacols

1. IVa + IVa ------------------- IIIa (1,1' = CH_3)
2. IVa + IVb ------------------- IIIab (1,2' = CH_3)
3. IVa + IVc ------------------- IIIac (1,3'-= CH_3)
4. IVa + IVd ------------------- IIIad (1,4' = CH_3)
5. IVb + IVb ------------------- IIIb (2,2' = CH_3)
6. IVb + IVc ------------------- IIIbc (2,3' = CH_3)
7. IVb + IVd ------------------- IIIbd (2,4' = CH_3)
8. IVc + IVc ------------------- IIIc (3,3' = CH_3)
9. IVc + IVd ------------------- IIIcd (3,4' = CH_3)
10. IVd + IVd ------------------- IIId (4,4' = CH_3)



III

Ib. The uv spectra of members of this group would be very similar to Ib. Nmr spectroscopy could be a method for testing the presence of members of the second group of compounds in Ib. Different chemical shift value would be expected for the various methyl groups since their environments are not the same.

B. Synthesis and Fractionation of Ib

To obtain more 2,2'-dimethyl-9,9'-bitriptycyl (Ib), the earlier synthesis was repeated (Scheme I, p. 9 ; II, p. 10).[7] All intermediates leading to Ib were carefully purified. In all but one case the intermediates exhibted a single methyl absorption in the nmr spectrum. Anthrapinacol, IIIb, was the only exception. It had a complex nmr spectrum due to the presence of diastereomers.

2,2'-Dimethyl-9,9'-bitriptycyl (Ib), thus synthesized, had very similar properties to samples prepared by C. Koukotas (p. 14).[7] Each fraction of chromatcgraphed crude Ib, from two independent synthesis, showed two methyl singlets of unequal intensities (δ 1.83 > δ 1.81). The intensity of the high-field singlet was 50-80% of that of the low-field singlet. All the crude 2,2'-dimethyl-9,9'-bitriptycyl fractions obtained were combined and recrystallized from chloroform/acetone. Repeated recrystallization and judicious recombination of fractions according to their nmr spectra gave two major fractions, each enriched in one of the methyl singlets.

The fraction enriched in the δ 1.81 absorption ($R = 0.44 \pm 0.02$, called Ib-A) was less soluble in $CHCl_3$ than the one enriched in the δ 1.83 absorption ($R = 2.10 \pm 0.04$, called Ib-B). The melting point of Ib-A (505°C dec.) was higher than that of Ib-B (473-478°C dec.). The ms fragmentation pattern of the two fractions were identical; both showed intense M^{+} peaks at m/e 534. The uv absorption spectra of

Ib-A and Ib-B were also identical (Fig. VII). The ir (Fig. VIII) and nmr (Fig. IX) spectra of Ib-A and Ib-B were very similar. There were only a few minor differences. The ir spectrum of Ib-A differed somewhat from that of Ib-B in the finger-print region. The absorptions of Ib-A were sharper and better defined. In addition, Ib-A showed two pairs of closely spaced doublets at 620 cm^{-1} and 740 cm^{-1} while two slightly broadened absorptions appeared in the corresponding regions of Ib-B. There was a weak absorption band at 915 cm^{-1} in Ib-B which was absent in Ib-A. The nmr spectrum in the aromatic region of Ib-A differed somewhat from that of Ib-B. The same absorption bands were present in both samples, but they differed in relative intensities. The nmr spectra of both samples are consistent with the structure as a dimethyl-9,9'-bitriptycyl. These spectroscopic results strongly suggest that fractions Ib-A and Ib-B both contain compounds of extremely similar molecular structure.

C. Elimination of Possible Contaminants

To determine whether any of the first group of contaminants is present in Ib-A or Ib-B, the uv absorption spectra of two model compounds, 2,3-benzotriptycene (XII) and 9-(9'-anthracyl)-2,3-benzotriptycene (XIII) were compared with the uv absorptions of Ib-A and Ib-B (Table I, p. 26). Both XII and XIII contain similar structural features to compounds of the first group. XII contains a naphthalene nucleus while XIII contains both naphthalene and anthracene rings. These two compounds were available from C. Koukotas' work.[7]

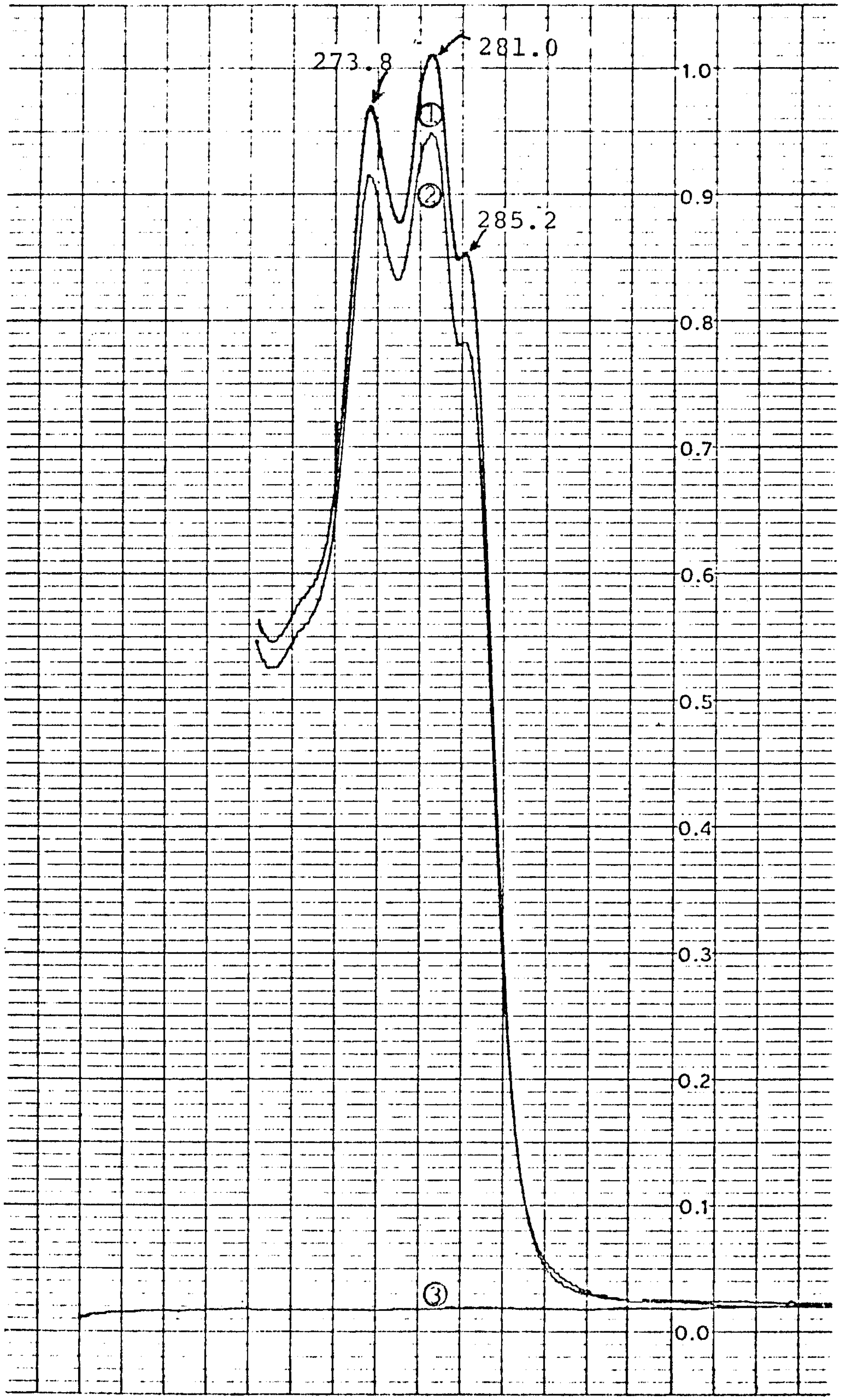


Fig. VII Uv spectra of 2,2'-dimethyl-9,9'-bitriptycyl (Ib)
Curve 1, Sample Ib-A
Curve 2, Sample Ib-B
Curve 3, Solvent($CHCl_3$)

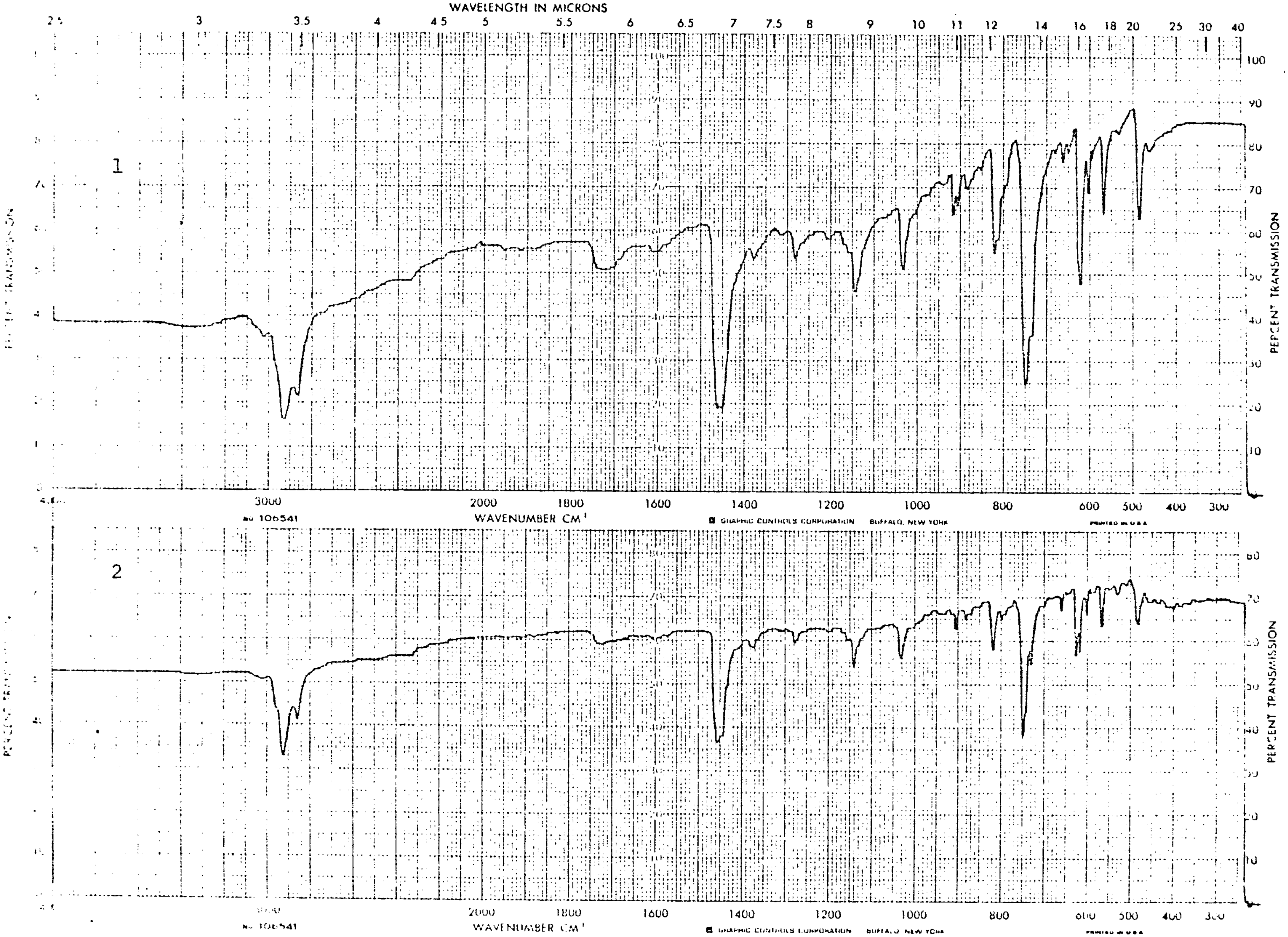


Fig. VIII Ir spectra of 2,2'-dimethyl-9,9'-bitriptycyl (Ib)
Spectrum 1, Sample Ib-B
Spectrum 2, Sample Ib-A

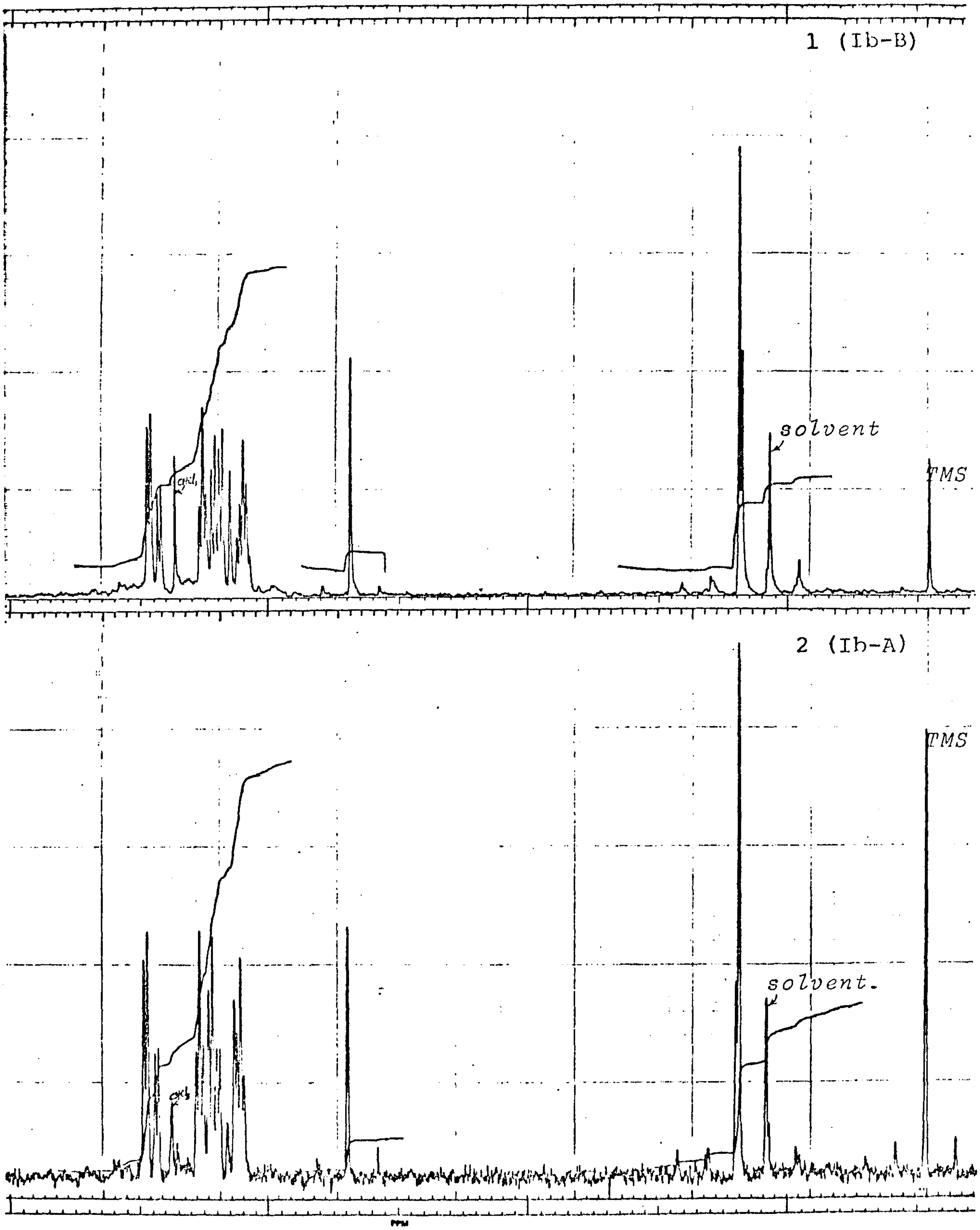
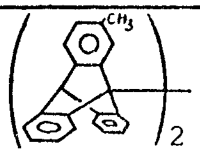
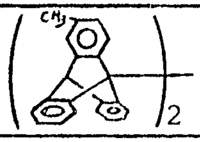
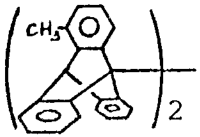
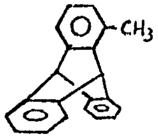
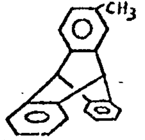
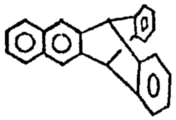
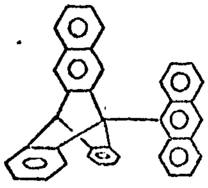
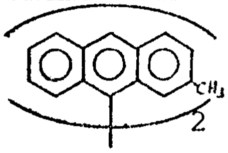
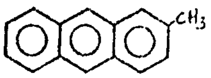


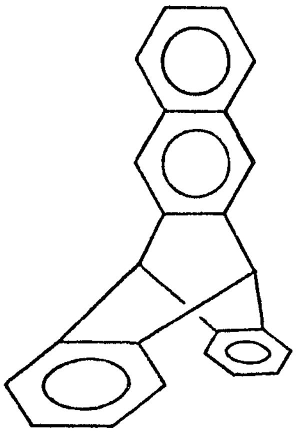
Fig. IX Nmr spectra*of 2,2'-dimethyl-9,9'-bitriptycyl (Ib)
Spectrum 1, Sample Ib-B
Spectrum 2, Sample Ib-A
*Taken with Varian HR 220 MHz nmr spectrometer, continuous wave mode at sweep width 2500 Hz an Fourier Transform mode with 50 pulses.

Table I

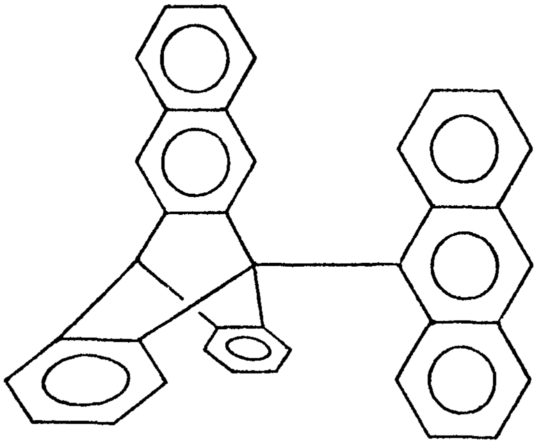
Compounds		UV^a(λmax. (log ε))
	Ib-B	285.2(3.54),281.0(3.62),273.8(3.59)
	Ib-A	285.2(3.57),281.0(3.65),273.8(3.63)
	Ic	282.2(3.73),273.6(3.71),266.1(sh,3.45)
	Id	280.7(3.49),272.7(3.51)
	IXa	279.4(3.53),271.6(3.44),264.2(sh,3.20)
	IXb	283(3.63),280(3.64),273(3.56), 266(sh,3.28)
	XII^b	323(3.20),309(3.09),302(2.80), 289(3.66),277(4.10),268(4.17)
	XIII^b	388, 367, 348, 328, 313, 280, 255 (λmax., Dioxane)
	IIb	394.8(4.34),374.2(4.25),355.0(4.05), 337.5(3.81),320.9(3.52)
	XI	380.4(3.67),359.8(3.72),343.3(3.59), 329.0(3.38),313.8(sh,3.11),269.8(2.99)

a. Uv spectra were taken in $CHCl_3$ except as otherwise stated.

b. From reference 7.



XII

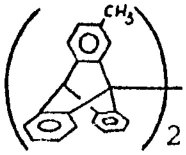
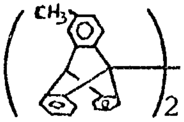
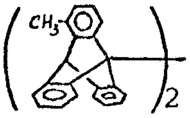
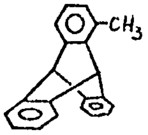
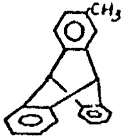
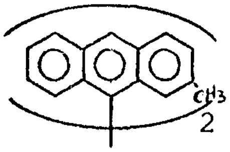


XIII

Table I also contains two other compounds, 2,2'-dimethyl-9,9'-bianthryl (IIb) and 2-methylanthracene (XI) that were used for comparison purposes.

As expected, compounds IIb, XI, XII and XIII exhibit prominent uv absorptions at relatively long wavelengths (300-400 nm). Such absorption is completely absent in the uv spectra of Ib-A and Ib-B. The fact that the uv spectra of Ib-A and Ib-B contain no absorption at wavelengths higher than 285.2 nm precludes the presence of compounds of the first group as major impurities. In order to test for the possible presence of a member of the second group as a major contaminant of Ib-A and Ib-B, chemical shift values of the methyl groups of certain key compounds such as IXa, IXb, Ia, Ic, and Id are needed. 1-Methyltriptycene (IXa) was prepared by the addition of 3-methylbenzyne (generated in situ from 3-methylanthranilic acid and n-butyl nitrite[9]) to anthracene. 3,3'-Dimethyl-9,9'-bitriptycyl (Ic) and 4,4'-dimethyl-9,9'-bitriptycyl (Id) were synthesized following the synthetic scheme outlined on pp. 9-10. 2-Methyltriptycene (IXb) was available from C. Koukotas' work.[7] The chemical shift values of all pertinent hydrogen atoms of IXa, IXb, Ic, and Id together with those of Ib-A and Ib-B are given in Table II.

Table II

Compound		NMR[a] (δ)		
		CH_3	CH	Aromatics-H
	Ib-B	1.81,1.83	5.55(s)	6.4-7.6(m)
	Ib-A	1.81,1.83	5.55(s)	6.4-7.6(m)
	Ic	2.23(s)	5.54(s)	6.3-7.5(m)
	Id	2.65(s)	5.86(s)	6.3-7.6(m)
	IXa	2.44(s)	5.34(s) 5.63(s)	6.6-7.4(m)
	IXb	2.21(s)	5.35(s)	6.6-7.4(m)
	IIb	2.03(s)	8.55(s) (Aromatic, C-10)	6.8-8.1(m)

a. Nmr were taken with a JEOL, JNM-MH 100 spectrometer using $CDCl_3$/TMS.

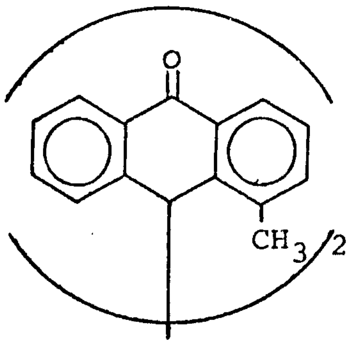
Based on the chemical shift values of the methyl groups the possible presence of IXa or IXb can be easily ruled out. Compounds such as Ic, Id, can be used as models for other 9,9'-bitriptycyls with methyl groups at C-3 and C-4, respectively, since the two methyl groups on each bitriptycyl are far-removed from each other and should not influence each other's chemical shift value. Bitriptycyls Iac, Iad, Ibc, Ibd and Icd all have methyl groups on either C-3 and C-4 and are therefore eliminated. 1,1'-Dimethyl-9,9'-bitriptycyl (Ia) and 1,2'-dimethyl-9,9'-bitriptycyl (Iab) are left to be considered.

Attempts were made to synthesize 9,9'-bitriptycyl with methyl groups at C-1. None of the attempts were successful. The first approach tried was to react 3-methylbenzyne (generated from 3-methylanthranilic acid) with 9,9'-bianthryl. In theory, three bitriptycyls, Ia, Id, Iad, could be produced. Either Ia or Iad would provide a model for a bitriptycyl with a methyl group at the C-1 position. Several reactions were run. In each case, nmr spectroscopy indicated that the product contained only the starting bianthryl and possibly methylacridone (from 3-methylanthranilic acid). No typical triptycene-like bridgehead hydrogen absorption (δ 5.3-6.0, Table II, p. 28) was observed. Under the same reaction conditions, 1-methyltriptycene (IXa) was successfully synthesized from 3-methylbenzyne and anthracene (p. 132). The inability of 3-methylbenzyne to react with 9,9'-bianthryl may reflect the operation of steric factors.[12] This reaction was not further investigated.

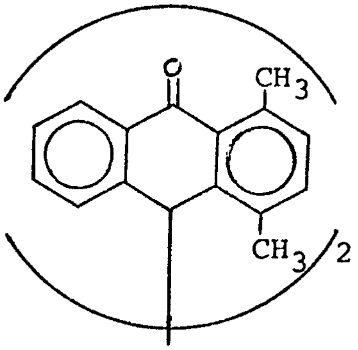
The second approach involved the use of a 1-methyl substituted 9,9'-bianthryl. Such a compound could be reacted with benzyne to give a 9,9'-bitriptycyl, substituted with methyl on C-1. An attempt was made to follow scheme II

(p. 10) starting with o-(2,5-dimethylbenzoyl)benzoic acid (VIe). VIe was prepared by a Friedel-Crafts acylation reaction[13] of p-xylene with phthalic anhydride. This particular synthetic approach turned out to be unsuccessful since the bimolecular reduction of 1,4-dimethylanthrone (IVe) gave, quantitatively, the further reduced product, 1,4-dimethyl-9,10-dihydroanthracene (XIVe), rather than the desired anthrapinacol IIIe. Although the available literature[14,15,16] and our experimental findings have shown that aluminum amalgam is a very useful reagent for promoting the bimolecular reduction of anthrones, it failed in this case. It should also be mentioned in connection with this approach that it has been reported that Zn/HCl, which can condense 2,3- or 2,4-dimethylanthrone to the corresponding bianthryls, fails to do so with 1,4- or 1,4-dimethylanthrone. This has been attributed to the steric interaction of the l-methyl group adjacent to the carbonyl function.[17]

Another approach to the synthesis of a 9,9'-bianthryls containing methyl on C-1 involved the use of 10,10'-bianthrone intermediates. 4,4'-Dimethyl-10,10'-bianthrone (XV)[18] and 1,1',4,4'-tetramethyl-10,10'-bianthrone (XVI)[19] had previously been synthesized from 1-methylanthrone (IVa) and 1,4-dimethylanthrone (IVe), respectively. Reduction of either bianthrone to the corresponding diol and subsequent dehydration would provide a desired bianthryl. Consequently, both XV and XVI were synthesized and subjected to various reduction methods. None of these attempts were successful. Reduction either did not take place or resulted in cleavage to an anthracene (Table III).



XV

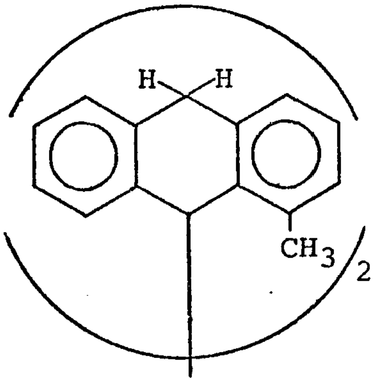


XVI

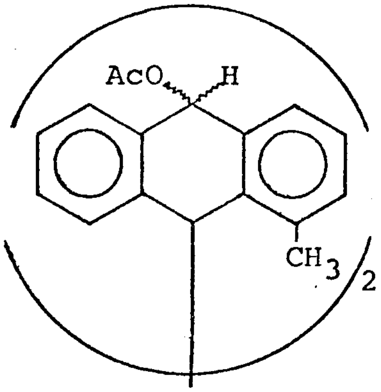
Table III

Bianthrone	Reagent	Product
XVI	$LiAlH_4/Et_2O(N_2$, reflux, 4 hr.)	Starting Material
	$LiAlH_4$/THF(reflux, 40 hr.)	Starting Material
	$LiAlH_4$/Pyridine (RT., 1 hr.)	Mainly 1,4-dimethylanthracene
	$NaAlH_2(OCH_2CH_2OCH_3)_2$/ Benzene (reflux, 1 hr.)	Mainly 1,4-dimethylanthracene
	$NaAlH_2(OCH_2CH_2OCH_3)_2$/ Benzene (R.T., 30 Mins or 20 hr.)	Starting Material
XV	$LiAlH_4/Et_2O$(R.T., 3 1/2 hr. or 48 hr.)	Starting Material
	$LiAlH_4$/THF(60-70°C, 1 hr.)	Mainly 1-methylanthracene

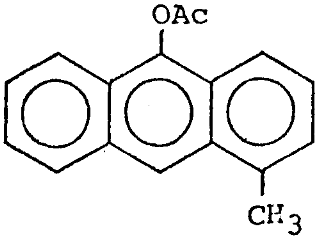
Following the method of Boekelkeide and Hylton,[20] attempts were made to convert XV to XVII by means of $LiAlH_4$/$AlCl_3$/Et_2O and to XVIII by means of Zn/Ac_2O/Et_3N. It was hoped that either XVII or XVIII could be used for the synthesis of 1,1'-dimethylbianthryl (IIa). The nmr spectra of the products revealed that the attempted synthesis of XVII gave 1-methylanthracene (XIa), and the attempted synthesis of XVIII gave, most likely, XIX as major reaction product.



XVII



XVIII



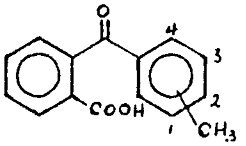
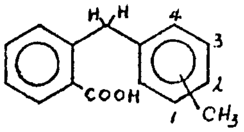
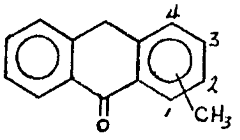
XIX

In the course of the attempt to prepare Ia, Ic, Id, and 1,1'4,4'-tetramethyl-9,9'-bitriptycyl (Ie), a number of methyl-substituted intermediates (methylbenzoylbenzoic acids, methylbenzylbenzoic acids and methylanthrones) were prepared. o-(2-Methylbenzyl)benzoic acid (VId) was prepared from the reaction of o-methylphenylmagnesium bromide and phthalic anhydride. o-(2,5-Dimethylbenzoyl)benzoic acid (VIe) was prepared from phthalic anhydride and p-xylene under Friedel-Crafts conditions. Other corresponding methylbenzylbenzoic acids and methylanthrones were prepared according to scheme II (p. 10). 3-Methylanthrone was obtained from the work of C. Koukotas.[7] The chemical shifts of the methyl groups of these intermediates are listed in Table IV (p. 34).

The values in Table IV indicate that there should be detectable differences in chemical shift values between the 1-methyl compounds and the 2-methyl compounds. The presence of any appreciable amounts of IVa, Va, or VIa in the corresponding 2-methyl compounds (IVb, Vb, or VIb) could have been easily detected by nmr spectroscopy. The fact that intermediates, IVb, Vb and VIb which were used for the synthesis of Ib each contained only a single methyl peak, precludes the presence of any 1-methyl contaminants. Consequently, no bianthryl (IIa, IIab) or bitriptycyls (Ia, Iab) having 1-methyl substitution should have been produced in the synthesis of Ib.

A remaining possibility for the formation of 9,9'-bianthryls and/or 9,9'-bitriptycyls containing a methyl

Table IV: Methyl Group Nmr Chemical Shift Values (δ)

	Position of Methyl Group					
	1-CH$_3$^{a}	2-CH$_3$	3-CH$_3$	4-CH$_3$	1,4-di-CH$_3$	
 VI	2.21	2.39	b	2.58	2.21	2.56
 V	2.25	2.31	b	2.20	2.25	2.18
 IV	2.42	2.36	2.37	2.28	2.42	2.23

a. Estimated values, based on a comparison between the 4-methyl and 1,4-dimethyl compounds, which establishes the δ value corresponding to the C-1 methyl group. The effect of the C-1 methyl group on the chemical shift of the C-4 methyl group in the 1,4-dimethyl compounds is very small. The chemical shifts of the C-1 methyl-substituted compounds are estimated by asssuming that the effect of a C-4 methyl group on a C-1 methyl group will also be very small.
b. Values not available.

substituent at C-1 is that an unexpected methyl migration took place during one of the last three synthetic step (formation and dehydration of the anthrapinacol IIIb, and addition of benzyne to IIb to form Ib). These possibilities are not considered to be very likely. No example of such migration during a benzyne addition to an anthracene has ever been reported. In the present work, addition of benzyne to

1-methyl and to 2-methylanthracene, as well as to 3,3'- and 4,4'-dimethyl-9,9'-bianthryl, proceeded without rearrangement. There is, therefore, no reason to suspect that addition of benzyne to 2,2'-dimethyl-9,9'-bianthryl (IIb) should proceed with rearrangement of the methyl group.

The formation and dehydration of anthrapinacols IIIc and IIId proceeded smoothly and lead to bianthryls IIc and IId, respectively, which contained only a single nmr absorption in the methyl region. The same is true for anthrapinacol IIIb and bianthryl IIb.

The methyl absorptions of IIb, IIc and IId all occur at different δ values. Since IIc and IId each showed only a singlet, no rearrangements occurred in the formation of these compounds. If a rearrangement did occur, more than one singlet would have been present. IIb also showed one singlet in the methyl region. It could be argued that a methyl group on C-1 could absorb in the same place as a methyl group on C-2 and that our IIb contained some IIa or IIab. However, two strong points can be made against this argument. First, there is no reason to expect that a rearrangement of a methyl group on C-2 should be any more facile than rearrangements of methyl groups on C-3 and C-4. Second, rearrangement of a methyl group to C-1 would be highly unfavored on steric grounds. All attempts to form an anthrapinacol with a methyl group on C-1 failed (pp. 29-32). If the supposed rearrangement occurred in the dehydration step, a highly hindered bianthryl, containing a methyl-anthracene peri interaction, would result. On steric grounds, this is highly unlikely.

Another approach that was used in an attempt to eliminate a bitriptycyl with a methyl group on C-1 as a major impurity was to calculate the chemical shift of such a methyl group and compare it to the experimental values (δ 1.81, 1.83).

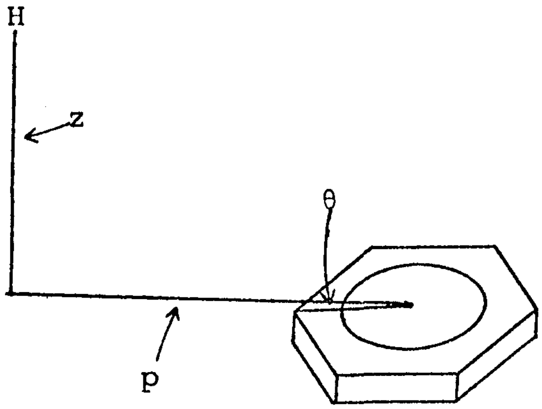
Numerical tables which relate the chemical shift of a hydrogen atom to its spatial relationship to a nearby planar benzene ring have been published by Johnson and Bovey[21a,b] (J & B) and Mallion and Haigh[22] (M & H). The chemical shift value of a hydrogen atom located in the vicinity of a benzene ring can be predicted by the use of either table and the chemical shift value of an appropriate model hydrogen atom (which does not involve the benzene ring in question).

Ia can be considered as being composed of two identical 1-methyltriptycyl units, joined at C-9 by a single bond. The chemical shift of the methyl-hydrogens in 1-methyltriptycene is known (p. 28). If the effect of the adjacent triptycyl group could be predicted, the chemical shift of a methyl group at C-1 of 9,9'-bitriptycyl could be estimated. To a first approximation, triptycene can be considered to be composed of three isolated planar benzene rings. The change in chemical shift of a hydrogen atom due to the influence of a triptycyl unit (i.e. the combined effect of the three benzene rings) should be calculable from either the J & B or the M & H tables.

It should be noted here that care must be exercised in using the chemical shifts calculated from these tables. The values in the J & B table were arrived at using equations derived from semi-classical ring current theory. This table has been critized as overestimating the lateral deshielding effect of the benzene ring.[24,25] The Mallion and Haigh table was obtained from equations derived from modern quantum chemical treatments. Although non-uniform ring current density was considered, the authors cautioned that, because of the inclusion of certain mathematical approximations, the table could substantially underestimate the shielding effect of the benzene ring for hydrogen atoms closed to and above the ring.[22,23,24,25] It was further noted that, for protons in the deshielding region, the M & H table gives better predictions than the J & B table. On the other hand, in the shielding region, the J & B table is superior.[25] For either method, the change in chemical shift values are tabulated in a matrix formed by a series of p and z values. P and z are measured in accordance with figure X (p. 38) and are expressed in terms of benzene carbon-carbon bond units. For the M & H table, values of θ (0°-30°) are also required.

A Drieding model of 1,1'-dimethyl-9,9'-bitriptycyl (Ia) was constructed. The model was fixed in a staggered conformation with copper wire. The Newman projection of the model is shown in Figure XI. This conformation represents the weighted average of all conformations which result from the rapid to-and-fro movement of the two triptycene functions along the (C-9)-(C-9') single bond. The methyl group of one

Fig. X

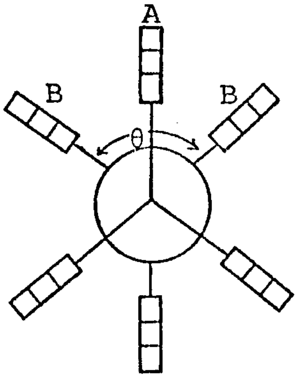


z, The distance between the hydrogen atom in question and the plane of the benzene ring.

p, The length of the perpendicular line drawn from the center of the ring to line z.

θ, The angle (0-30°) between line p and the nearest line drawn from an apex of the benzene ring to the center.

Fig. XI



Benzene ring A bisects the dihedral angle formed by benzene rings B.

triptycyl unit is situated in the plane of one benzene ring and above and between the planes of the other two benzene rings of the opposite triptycyl unit. Values of p, z and θ were measured from the methyl group to each of the three benzene rings of the other half of the molecule, and the change in the chemical shift of the methyl group due to each benzene ring was calculated. The center of the circle described by the three methyl hydrogen atoms was used as the average position of these methyl hydrogens.

In order to compensate for the possible variations associated with Dreiding models, five independent measurements were made. Before each measurement, the molecular model was completely disassembled and reconstructed so that atom interchange occurred. The chemical shift values of the methyl group of Ia calculated according to both the J & B and M & H tables, are listed in Table V (p. 40).

For comparison, and in order to varify the method of calculation, molecular models of Ib, Ic, and Id were likewise constructed, and their methyl chemical shift values calculated (Table V, p. 40).

Generally, good agreement was obtained for calculated and observed values. The correspondence between the calculated and observed values for 3,3'-dimethyl-9,9'-bitriptycyl (Ic) was excellent, using either table.

In the 2,2'-dimethyl-9,9'-bitriptycyl (Ib) case, the methyl groups are situated closer to the interacting benzene rings than in Ic. The J & B table gave a closer result than the M & H Table. This is in line with the fact that, at close proximity, the M & H table underestimates the shielding effect of the benzene ring and thus gives less accurate results (p. 37).

Table V[a]

Compounds	CH_3 δ Values		
	Observed	Calculated	
		J & B	M & H
Ia $(1\text{-}CH_3)$[b]	-	-0.30 ± 0.07	1.50 ± 0.04
Ib $(2\text{-}CH_3)$[c]	1.81 1.83	1.82 ± 0.01	2.06 ± 0.01
Ic $(3\text{-}CH_3)$[c]	2.23	2.21 ± 0	2.20 ± 0
Id $(4\text{-}CH_3)$[b]	2.65	2.44 ± 0	2.44 ± 0

a. For p, z, and θ values and individual calculations, see appendix A.

b. 1-Methyltriptycene (IXa, p. 28) was used as the model compound.

c. 2-Methyltriptycene (IXb, p. 28) was used as the model compound.

The two tables led to significantly different calculated values for 1,1'-dimethyl-9,9'-bitriptycyl (Ia). The value obtained from the J & B table was 1.80 ppm higher than the value obtained from the M & H table. Since the methyl groups on Ia are located in even closer proximity to the relevant interacting benzene rings than the methyl groups of Ib, the M & H table must substantially underestimate the shielding effects of the benzene rings. The chemical shift value (δ −0.30) obtained from the J & B table would therefore be a more reliable estimate.

Since the two methyl peaks of Ib appear at δ 1.83 and 1.81, the calculated methyl chemical shift of Ia clearly suggests that Ib does not contain a methyl group on C-1. The presence of Ia or Iab in Ib can be rejected.

After the completion of the above nmr analyses, x-ray crystallographic data concerning the structure of 9,9'-bitriptycyl became available.[8] The x-ray data show that because of the steric repulsion of the two triptycyl groups, the structure of 9,9'-bitriptycyl is somewhat distorted. Certain carbon-carbon bonds situated in the central portion of the molecule are longer, and the bond angles are larger, than normal values and the values found from Dreiding Models (see Table VI, p. 42).

In order to assess the effect of structural distortion on the calculated methyl chemical shift values (p. 40), Drieding models of Ia and Ib were reconstructed. The bond lengths and angles of the Drieding models were adjusted to reflect the x-ray data. The methyl group chemical shifts were recalculated (see Table VII, p. 43) using both the J & B and M & H tables*.

Table VII shows that except for one case, the chemical shift values do not change significantly from the originally calculated values (p. 40). They are practically within the uncertainty limits of the original calculations. Only when the J & B table is used to determine the chemical shift for a methyl group in close proximity to the interacting benzene rings (as in the case of Ia) is a significant change obtained.

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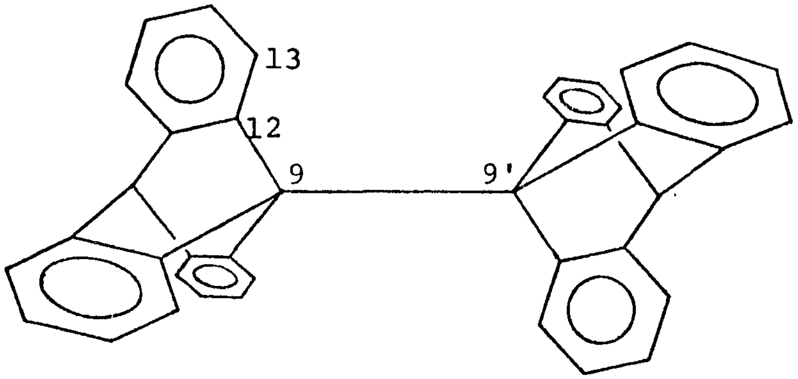
*It is assumed that these tables can be applied to the distorted benzene rings.

Table VI



Bitriptycyl carbon-carbon bonds	x-ray[a] values	Normal values	Drieding Model[f] values
C_9-C_9'(sp^3-sp^3)	1.558 Å	1.54 Å[b]	1.54±0.01 Å
C_9-C_{12}(sp^3-sp^2)	1.565 Å	1.515 Å[c]	1.51±0.004 Å
bond angles			
$C_{9'}$-9-12 (sp^3)	114.7°	109.5°[d]	116.2±0.75°
C_{9}-12-13 (sp^2)	128.0°	120.0°[e]	120.0°
Dihedral angles[h]	116.8° 121.6°	120.0°[e]	120.0°

a. See reference 8. b. Sp^3-sp^3 carbon-carbon single bond.[67] c. Sp^3-sp^2 carbon-carbon single bond.[68] d. Normal sp^3 tetrahedral bond angle. e. Normal sp^2 planar trigonal bond angle. f. Average values from several independent measurements. g. The formation of bicyclo rings widens these sp^3 bond angles in Dreiding models. h. Angle between the planes of two benzene rings of a triptycyl unit in solid state. It is believed that in solution the dihedral angles are all equal.[8]

Table VII

Bitriptycyls	CH_3 δ values	
	J & B	M & H
Ia ($1-CH_3$)	0.01	1.47
Ib ($2-CH_3$)	1.84	2.07

Though the new C-1 methyl chemical shift value differs significantly from the original value, the new value is still distinctively different from the methyl absorptions (δ 1.81, 1.83) observed for Ib. The presence of a C-1 methyl group in Ib remains excluded. The chemical shift change for Ia is merely an indication the extreme sensitivity of the J & B table over the M & H table in a region close to the interacting benzene rings. For the methyl groups located further away from the center of the molecule, as in Ib, the change in chemical shift values, no matter which is used, become insignificant. Since the methyl groups of Ic and Id are located even further away from the center, no change in chemical shift values is expected.

At this point every conceivable contaminant (pp. 16, 17) has been systematically eliminated. It is concluded that the two observed peaks in the methyl region come from stereoisomers of Ib, namely the anti and the gauche conformers.

It would be appropriate here to discuss why the anti and gauche isomers of Ib show different methyl absorptions while the corresponding conformers of Ic and Id do not (Table II, p. 28). Koukotas has shown, in his analysis, that addition of benzyne to the enantiomers of a substituted 9,9'-bianthryl should produce both _gauche_ and _anti_ bitriptycyls (see reference 7, pp. 25-31). Ic and Id should therefore also contain both the _anti_ and _gauche_ conformers.

9,9'-Bitriptycyl is a large molecule with a rigid molecular framework. For a particular x,x'-dimethyl-9,9'-bitriptycyl, the methyl groups of the _anti_ and _gauche_ conformers are situated in essentially identical environments with respect to the aromatic rings. In the absence of a significant methyl-methyl interaction, the methyl groups of both the _anti_ and _gauche_ conformers should experience similar anisotropic effects from the rest of the molecule. Their chemical shift should therefore be identical. Such is the case with Ic and Id where the methyl groups, either in the _anti_ or in the _gauche_ form, are situated far enough apart from each other so that a significant intramolecular methyl-methyl interaction does not take place.

On the other hand, with Ib, the methyl groups of the _gauche_ conformer are situated much closer to each other than the methyl groups of the _anti_ conformer. In this case, the local anisotropy experienced by the _gauche_ methyl groups is apparently different enough from that of the methyl groups of the _anti_ conformer to lead to a difference in chemical shifts.

Since the chemical shift difference between the methyl groups of the _gauche_ and _anti_ conformers of Ib is very small

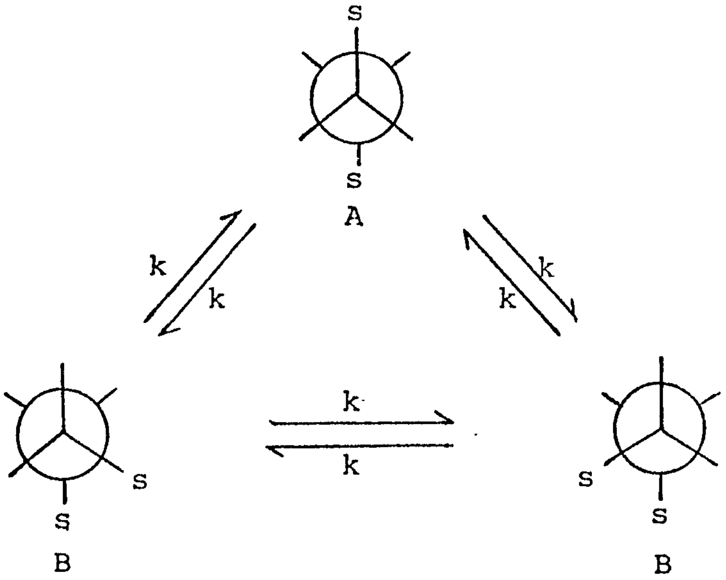
(0.02 ppm, Table V, p. 40), no significant structural difference between these two conformers is expected. If the carbon skeleton of the gauche conformer were significantly distorted from that of the anti conformer, a much larger chemical shift difference would be expected. Since the skeletons of the gauche and anti conformers of Ib appear to be very similar, their ground state energies should be practically the same (this conclusion is used on pp. 47-49 to estimate the rotational barrier of the 9,9'-bitriptycyl system.)

D. Rotational Energy Barrier Determination

In order to determine the rotational energy barrier between the anti and the gauche conformers, thermal equilibration experiments were conducted. It was found that the two conformers could not be equilibrated at temperatures obtainable with the nmr spectrometer. More vigorous equilibration conditions were therefore attempted (see Experimental Section, p. 136). Briefly, the two conformationally enriched samples, Ib-A and Ib-B, were each heated in napththalene solution, under a nitrogen atmosphere in a sealed glass vial at 300±5°C. Sample Ib-A was heated for a total of 171 hours and sample Ib-B was heated for a total of 164 hours. The heating was discontinued when decomposition of the sample was suspected (as evidenced by a slight coloration of the naphthalene solution). Sublimation of the naphthalene gave a quantitative recovery of each sample. The uv and nmr spectra of the heated sample were virtually identical with the spectra taken before heating, except for a very broad weak uv absorption band which was present underneath the original uv absorption bands. This new band apparently was due to the formation of some decomposition product. The shapes of the uv absorption bands remained the same after heating, the extinction coefficient, however, increased slightly (see pages 136 to 138 of the Experimental Section). The 1.83/1.81 peak height ratios, R, for recovered Ib-A and Ib-B were 2.06± 0.05 and 0.42±0.02, respectively, essentially unchanged from the original values. No thermal equilibration has been achieved. We were, however, able to estimate the minimum energy barrier separating the anti and the gauche isomers.

The equilibration involves the interconversion of an anti and two enantiomeric gauche conformers (Scheme V). As

Scheme V

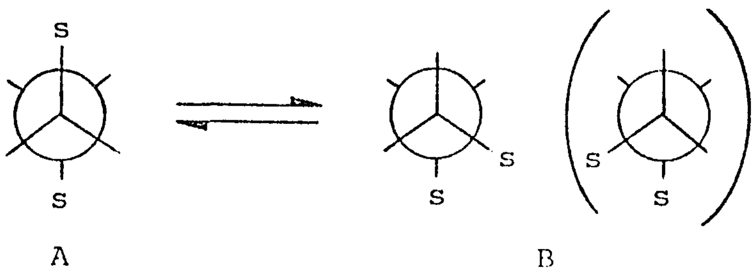


A = Anti Conformer
B = Gauche Conformers

discussed earlier (p.45), the ground state energies of the gauche and anti conformers are expected to be approximately the same. The interconversions of the anti and enantiomeric gauche conformers of Ib all involve, in the transition states, the passing of three C-1 hydrogen atoms on one of the triptycene unit past the three C-1 hydrogen atoms on the other triptycene unit (three benzo-benzo interactions of approximately equal energies). These resulting interactions are the principal contributors to the rotational energy barrier. As estimated earlier (p. 7), the rotational energy should be in the neighborhood of 63-87 Kcal/mole. This high barrier would cause the small contributions to the energy barrier made by the methyl groups on C-2 and C-2' to be insignificant. The transition state energies for all the interconversions shown in Scheme V (P.46) can be regarded as equal. All the rate constants, k, would thus be equal also.

Since nmr spectroscopy can not distinguish between the enantiomeric gauche conformers, the equilibration system can be simplified as shown in Scheme VI. Scheme VI shows a simple first-order reversible system ($A \rightleftharpoons B$). The kinetic

Scheme VI



A

B

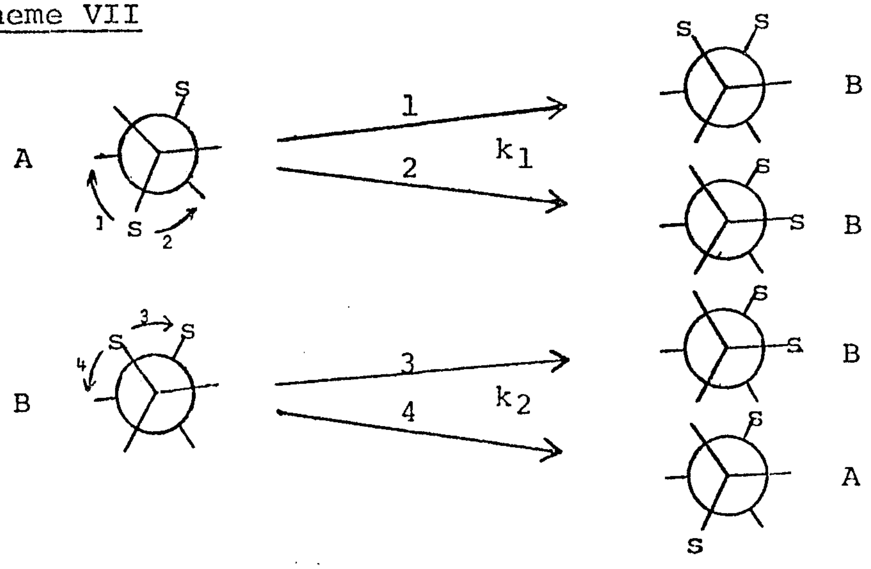
equation of such system is shown in equation 1.

$$\ln \frac{A_o - A_e}{A - A_e} = (k_1 + k_2)t \qquad (1)$$

A_o = concentration of reactant A at time zero.
A_e = concentration of reactant A at equilibrium.
A = concentration of reactant A at time t.

The relationship between k_1 and k_2 can be determined from a consideration of the actual interconversion pathway (Scheme VII) of A and B. Rotation of the front triptycyl unit of the anti conformer, A, 120° in either direction (1 or 2) would produce a gauche conformer, B. Rotation of the front triptycene unit of B 120° results in a gauche conformer in one direction (3) and an anti conformer in the other direction(4). Thus, there are two ways for A to become B and only one way for B to become A. Since all rate constants (k) are considered to be equal (p. 47), statistically, k_1 equals to $2k_2$ (Scheme VI, p. 47).

Scheme VII



*Only one enantiomer of B is demonstrated. The same result would be obtained for the other enantiomer.

For a sample in which the original concentration of A is predominant, the initial equilibration direction would be from A to B (A ⟶ B). Equation I-A would apply. On the other hand, if the original concentration of B is predominant the initial equilibration direction would be from B to A (B ⟶ A). Equation I-B would hold.

$$\ln \frac{A_o - A_o/3}{A - A_o/3} = 1/2\ k_1 t \qquad (1\text{-A})$$

$$\ln \frac{B_o - 2B_o/3}{B - 2B_o/3} = 3k_2 t \qquad (1\text{-B})$$

If the value of either k_1 or k_2 were available the rotational energy barrier of Ib could be calculated using the Arrhenius equation, $k = Ae^{-E_a/RT}$.

Based on our nmr measurements, the uncertainty in a peak-height ratio measurement is estimated to be approximately 2.5%, i.e., a change of 2.5% in the amount of one of the conformers corresponds to our limit of detection. If we substitute this uncertainty for the extent of interconversion of the two conformers, and if we assume an Arrhenius pre-exponential factor of 10^{13},[26] application of equation 1-A (or 1-B) and the Arrhenius equation, for a heating period of 170 hours at 300°C, yields a minimum* energy barrier of 53.8 Kcal/mole. This is the largest rotational barrier between sp^3-hydridized carbon atoms demonstrated to date.[66]

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*The actual energy barrier might be higher.

II. 2,2'-DICARBOMETHOXY-9,9'-BITRIPTYCYL (Ih)

A. Background and Statements of the Problem

The presence of atropisomerism in the 9,9'-bitriptycyl system (I) would be unequivocally demonstrated if optically active 9,9'-bitriptycyl derivatives could be isolated at or above ambient temperatures.

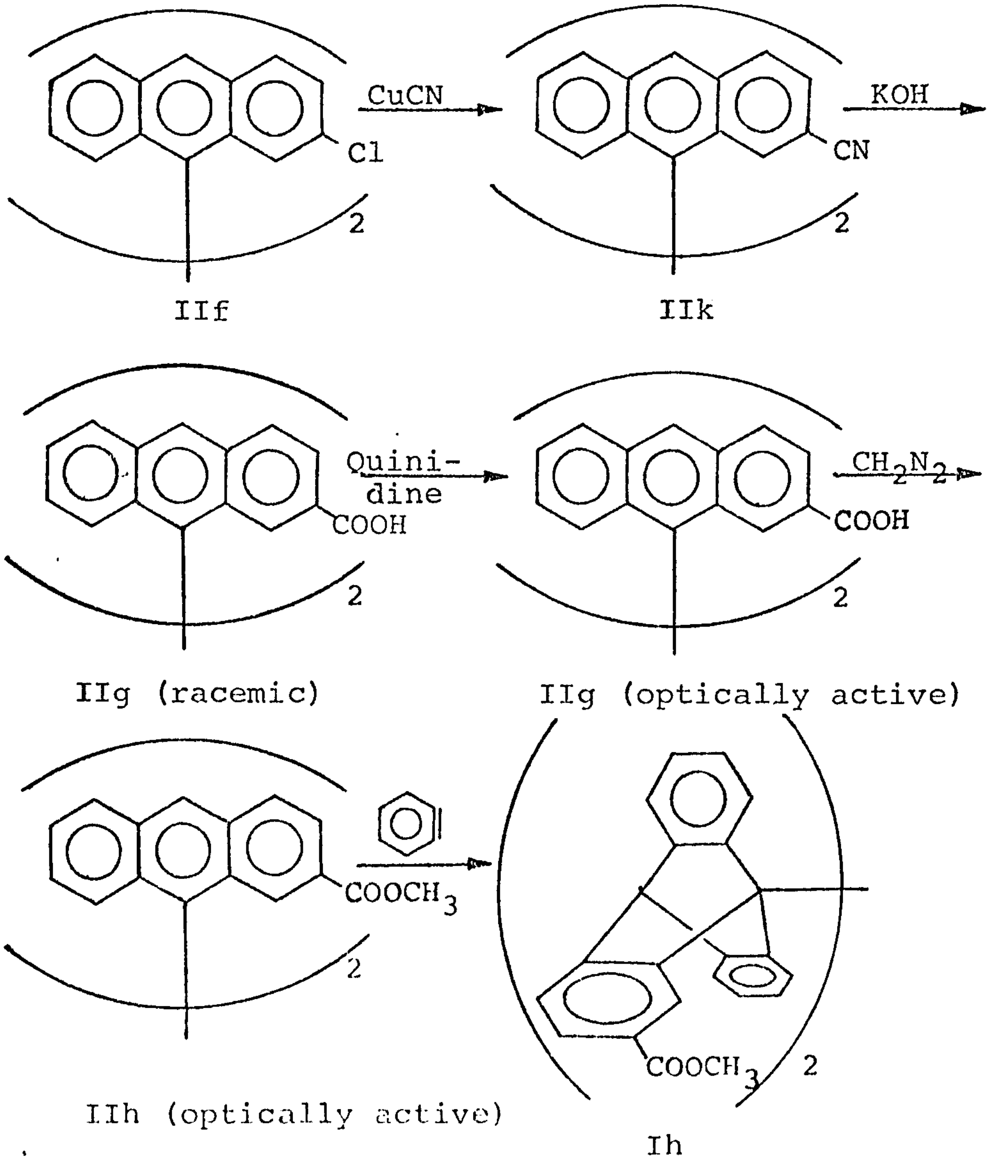
The earlier attempts[7] to synthesize optically active 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih) from optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (IIh) were unsuccessful. The failure was attributed to rapid rotation of the central carbon-carbon bond of the mono-adduct intermediate. This explanation seemed reasonable since, in the mono-adduct, the rotational transition state involves only one benzo-benzo interaction. The energy barrier of such an interaction has been estimated to be in the neighborhood of 21-29 Kcal/mole.[7] If the energy barrier were on the low side of this estimated range (i.e. 21 Kcal/mole), relatively rapid rotation about the carbon-carbon single bond in the mono-adduct could very well be a possible explanation of the inability to isolate an optically active 9,9'-bitriptycyl derivative.

Careful examination of the earlier work revealed that no attempt had been made to quantitatively account for all the Ih that might have been formed. The 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih) isolated from the earlier work was found to be extremely insoluble in most common solvents. It was isolated by repeated washing (acetone/chloroform) of a crude product previously digested with methanol. If the *gauche* form was lost during this work-up and purification process, and only the *anti* form was retained, the lack of optical rotation in the final product would be expected and the question of atropisomerism in the 9,9'-bitriptycyl system would remain unanswered.

B. Synthesis and Isolation of Conformers of Ih

To resolve the question concerning the earlier work, Ih was again synthesized from optically active IIh, according to the developed procedure[7] (Scheme VIII).

Scheme VIII



2,2'-Dichloro-9,9'-bianthryl (IIf) was, in turn synthesized according to the general scheme (Scheme II), outlined on page 10.

The benzyne addition product was initially fractionated by column chromatography. The collected fractions were examined by nmr spectroscopy. Fractions showing bridgehead hydrogen absorption (characteristic of 9,9'-bitriptycyls) were combined and further purified by a combination of digestions, repeated thick layer chromatographies and recrystallizations. The resulting crystalline materials and solid residues from the mother liquors were examined by nmr spectroscopy. Fractions showing the presence of bridgehead hydrogen were retained for further purification and analysis. A complete purification scheme is given in the flow diagrams on pp. 152-157 (Experimental Section).

"Chloroform-insoluble"* white solids, as described by C. Koukotas,[7] were isolated from the early chromatographic fractions upon digestion with solvents such as chloroform/methanol or acetone/methanol. When these white solids were further purified by a series of digestions and recrystallizations, a total of 67.5 mg. of an analytical sample of "chloroform-insoluble" 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih) (called Ih-A here) was obtained. From the combined and concentrated mother liquors of the above purifications, 25.2 mg. of additional "chloroform-insoluble" Ih (called Ih-A' here) was isolated. Finally, thick layer chromatography

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*This is a descriptive term used to differentiate this fraction of Ih from the "chloroform-soluble" fraction, whose solubility in chloroform is distinctively greater.

of the final mother liquor gave 4.6 mg. of additional "chloroform-insoluble" Ih (called Ih-A" here) and 6.5 mg. of "chloroform-soluble" Ih (called Ih-B' here).

From the later chromatographic fractions of the original chromatography, as well as from the mother liquors obtained from the digestions of the early fractions, substantial amounts of bridge-head hydrogen containing compounds were obtained. These compounds were easily soluble in solvents such as chloroform, acetone and ethyl ether. Further purification of these compounds using column and thick layer chromatography and recrystallization gave 101.3 mg. of an analytical sample of "chloroform-soluble" Ih (called Ih-B here). A total of 67.0 mg. additional "chloroform-soluble" Ih (called Ih-B" here) was subsequently recovered from the mother liquors of the above purification.

In addition, 87.4 mg. of material having multiple bridgehead hydrogen absorptions (called Ih-X here) was isolated. Attempts to purify Ih-X by either thick layer chromatography or recrystallization were not successful. Identical nmr spectra were obtained before and after the attempted purifications. The nmr spectrum of Ih-X contained two groups of aromatic multiplets (δ 6.4-7.6, 26 H; 7.7-8.4, 18 H), an aromatic singlet (δ 8.71, 2 H) characteristic of hydrogens on C-9 of bianthryls, three distinguishable bridgehead hydrogen singlets (δ 5.44, 1 H; 5.51, 1 H; 4.88, 2 H, broad) and three methoxyl singlets (δ 3.19, 6 H 3.48, 1 H; 3.72, 6 H). The spectrum did not contain any peaks to indicate the presence of 2,2'-dicarbomethoxy-9,9'bitriptycyl (Ih). Most probably this material was a mixture of the mono-adduct and various end-ring adducts. Identification of the components of this fraction was not pursued.

The uv absorptions (Fig. XII, p. 55) and ms patterns (M^+ ion at m/e 622) of Ih-A and Ih-B are identical. The melting point of Ih-A (m.p. 483-485°C) is much sharper and higher than that of Ih-B (m.p. 340-361°C). The ir spectra (Fig. XIII, p. 56) of these two samples are very similar but not identical. The main difference occurs in the fingerprint region, 1100-1200 cm^{-1}. In this region, Ih-A shows a singlet and a group of three singlets of moderate intensities. The group of three singlets is replaced by a broad band in Ih-B. The nmr spectra of Ih-A and Ih-B are also very similar (Fig. XIV, p. 57). The methoxyl absorption of Ih-A appears at approximately 0.02 ppm lower field than that of Ih-B (Fig. XIV, p. 57 , spectrum No. 3). In the aromatic region, the absorption pattern of the two samples are quite similar. They differ mainly in the relative intensities of some of the peaks, and a shift of one peak in Ih-A at δ 7.46 to δ 7.39 in Ih-B.

Since Ih-A was insoluble in all common solvents, optical rotation measurements could not be performed directly on it. However, it had been shown in the earlier work[7] that the "insoluble" Ih, isolated in a similar fashion to Ih-A was optically inactive. This was accomplished by hydrolysis to the diacid, followed by an optical rotation measurement in basic solution.

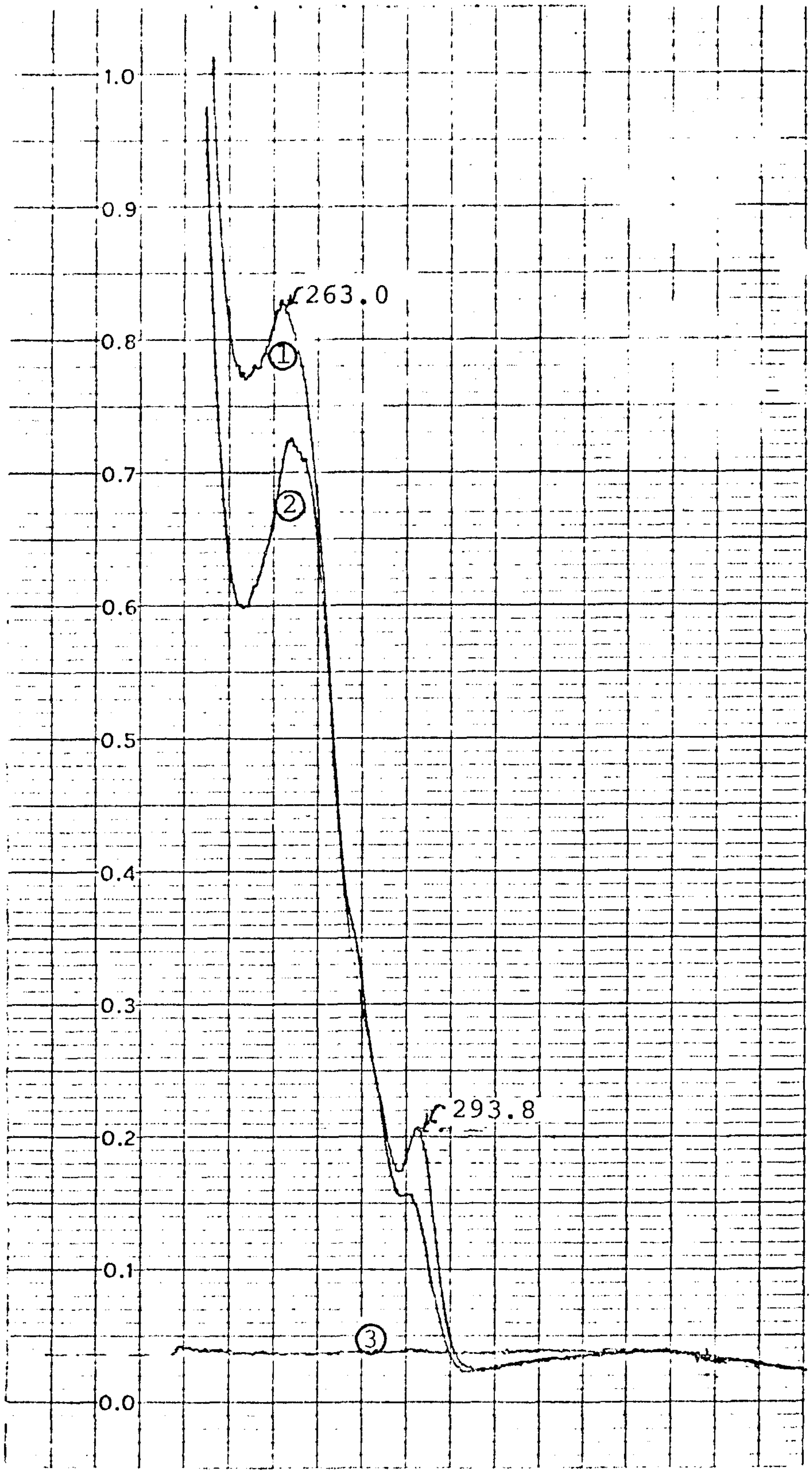

Fig. XII Uv spectra of 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih)
Curve 1, Sample Ih-B (5.4930×10^{-5} mol./l.)
Curve 2, Sample Ih-A (4.5634×10^{-5} mol./l.)
Curve 3, Solvent ($CHCl_3$)

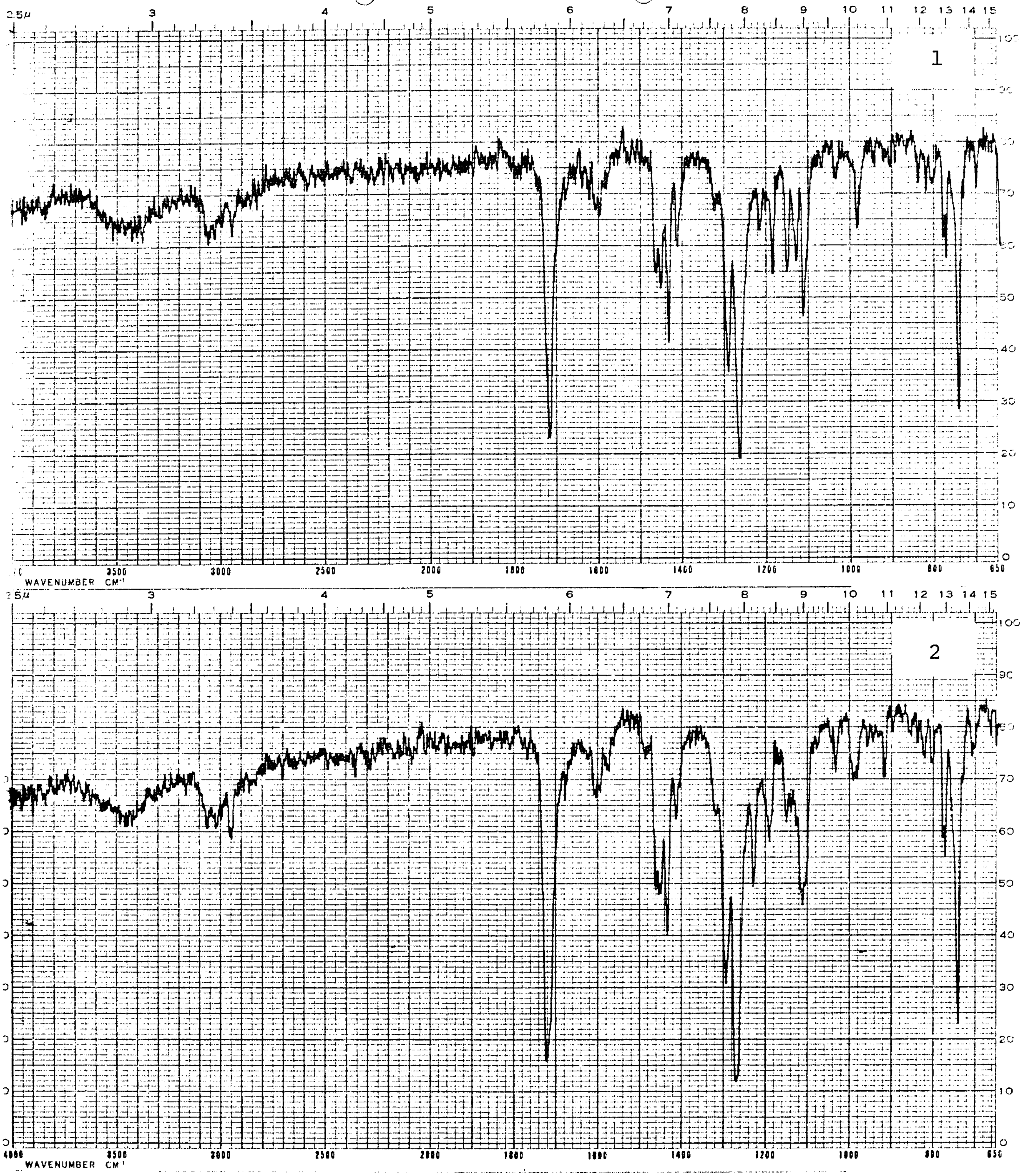

Fig. XIII Ir spectra of 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih)
Spectrum 1, Sample Ih-A
Spectrum 2, Sample Ih-B

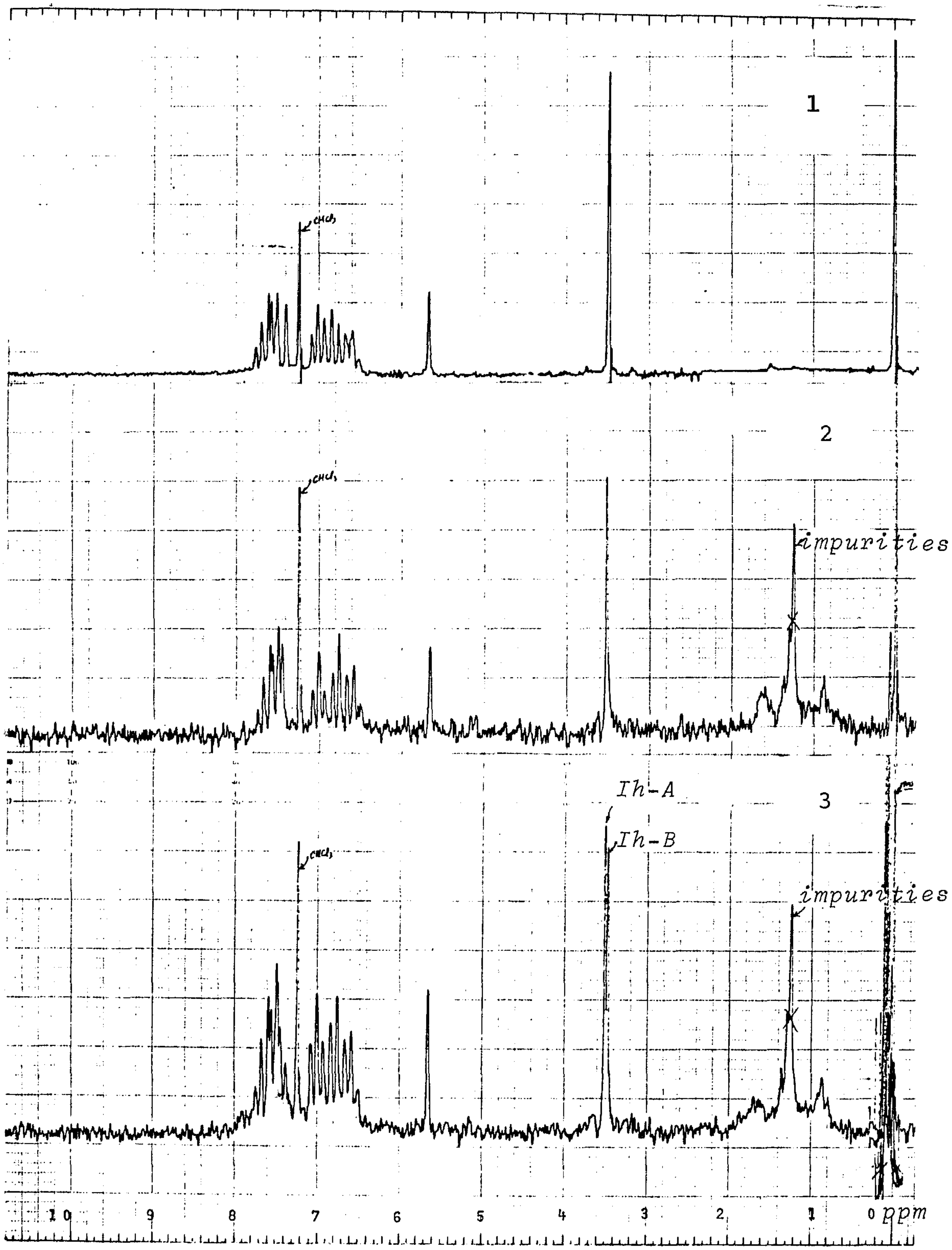

Fig. XIV Nmr spectra of 2,2'-dicarbomethoxy-9,9'-bitriptycyl(Ih)
Spectrum 1, Sample Ih-B
Spectrum 2, Sample Ih-A
Spectrum 3, Sample Ih-A and Ih-B

Because of its greater solubility, the optical rotation of Ih-B could be determined directly. A chloroform solution of Ih-B was found to be optically active, with $[\alpha]_D^{23}$ $-14.7\pm0.03°$ (c 0.375, $CHCl_3$). This finding established the presence of atropisomerism in the 9,9'-bitriptycyl system and revealed that Ih-B was the gauche conformer and Ih-A, the anti conformer. These assignment are consistent with the more symmetrical anti conformer having the higher melting point and lower solubility. The larger melting range for Ih-B is understandable, since it is composed of unequal amounts of the enantiomeric conformers (see below).

To determine the enantiomeric purity of Ih-B, nmr analysis using chiral shift reagents was carried out.[27,28] When a solution of Ih-B ($CDCl_3$) was treated with optically active tris[3-(heptafluoropropylhydroxymethylene)-d-camphorato] europium (III) ($Eu(hfc)_3$, Aldrich Chemical Co., Milwaukee, Wisc.) the methoxyl peak was split into two closely spaced singlets of unequal intensities (Fig. XV, p. 59). The low field singlet was higher, indicating that it corresponded to the levorotatory conformer. The spacing between the two methoxyl peaks widened as the concentration of $Eu(hfc)_3$ was increased. Maximum separation of 0.15 ppm was achieved with about equimolar amounts of Ih-B and $Eu(hfc)_3$. This experiment confirmed that Ih-B was indeed the gauche conformer. Due to the closeness of the two resolved methoxyl peaks, the peak-height ratio (R, low field/high field) had to be used, as in the 2,2'-dimethyl-9,9'-bitriptycyl (Ib) case, to determine

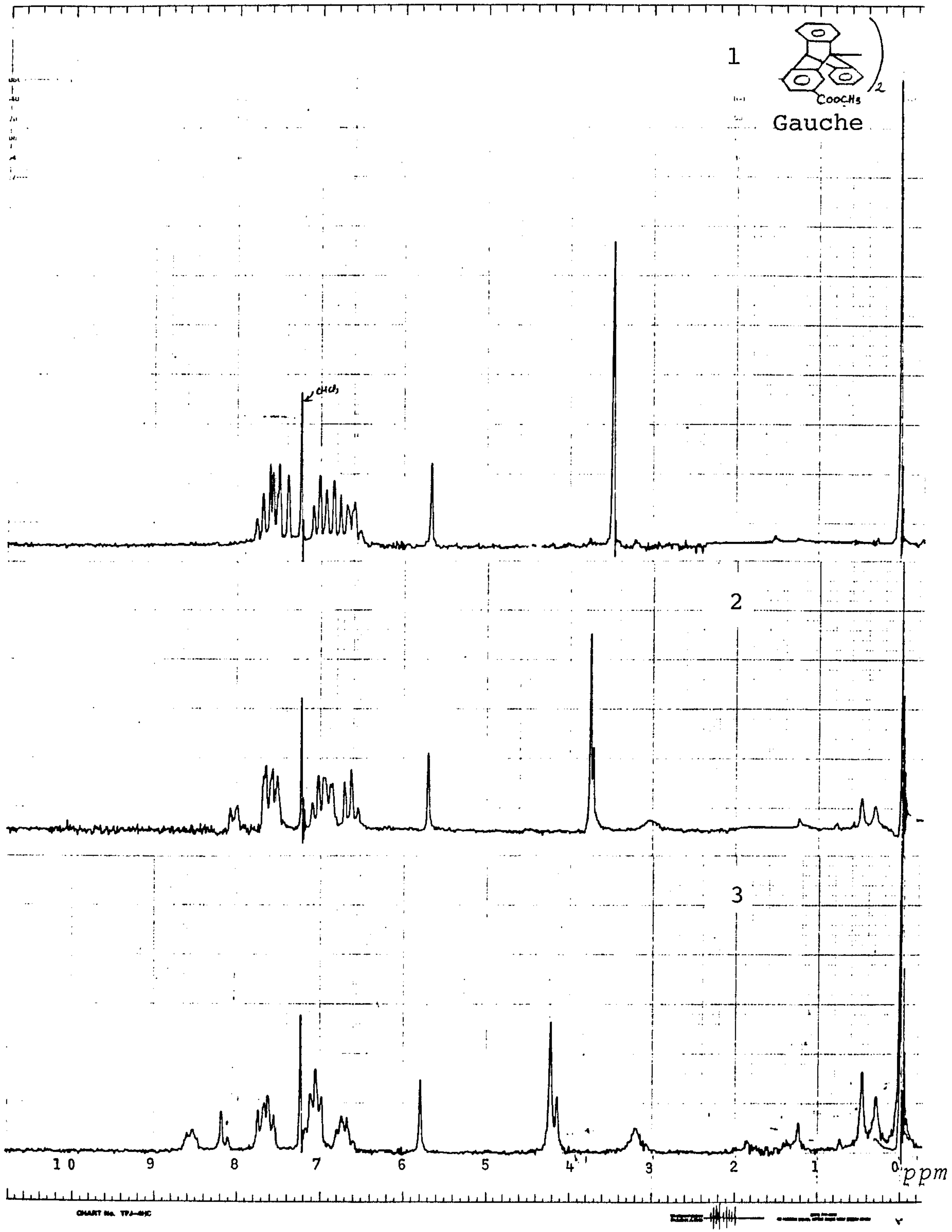

Fig. XV Nmr spectra of Ih-B (gauche conformer), with and without Eu(hfc)$_3$
Spectrum 1, Sample Ih-B
Spectrum 2, Sample Ih-B with Eu(hfc)$_3$;molar ratio (Ih-B/Eu(fhc)$_3$) 5.3
Spectrum 3, Sample Ih-B with Eu(hfc)$_3$;molar ratio (Ih-B/Eu(hfc)$_3$) 2.8

the relative amounts of the two _gauche_ conformers. The measured peak-height ratio, R, was 2.5±0.1, which corresponds to enantiomeric purity of 43%. Consequently, the absolute specific rotation of gauche Ih is approximately 34.2°.

To estimate the relative amounts of the enantiomeric _gauche_ conformers formed in the benzyne addition reaction, Ih-B' and Ih-B" were each treated with Eu(hfc)$_3$ in the same manner as Ih-B. In each case splitting of the methoxyl peak was obtained. As with Ih-B the low field methoxyl peak of both Ih-B' and Ih-B" were higher than the high field ones. The peak-height ratio, R, were 2.0 and 1.22±0.03, respectively. The amounts of anti, d, and l conformers of Ih formed in the benzyne addition reaction are estimated in Table VIII, (p. 61).

According to the analysis in Table VIII, (p. 61) of the total bitriptycyl formed approximately 65% is the _gauche_ conformer. The enantiomeric purity of the _gauche_ conformer is approximately 30%. It should be noted that this analysis is only semiquantitative. Aside from some small mechanical losses, two factors prevent the attainment of more quantitative results. First, not all fractions analyzed were pure analytical samples. Second, the relative amounts of the _gauche_ conformers were determined from the peak-height ratio of two closely overlapping methoxyl peaks rather than the area under the curves.

C. _Conclusion_

The isolation of the _anti_ and optically active _gauche_

Table VIII

Fractions	Weight (mg.)	Peak-height Ratio (low field/high field)	Conformers (mg.)		
			Anti	d	l
Ih-A	67.5	-	67.5	-	-
Ih-A'	25.2	-	25.2	-	-
Ih-A"	4.6	-	4.6	-	-
Ih-B	101.3	2.5	-	28.9	72.4
Ih-B'	6.5	2.0	-	2.2	4.3
Ih-B"	67.0	1.2	-	30.4	36.5
Total (mg)	272.1	-	97.3	61.5	113.2
Percent of total	-	-	36	23	42

conformers of Ih at an ambient temperature (as high as 60°C)* demonstrates unequivocally the existence of atropisomerism in the 9,9'-bitriptycyl system (I). This result also strengthens the conclusion made in the 2,2'-dimethyl-9,9'-bitriptycyl (Ib) case, concerning the independent existence, at elevated temperature, of the <u>anti</u> and <u>gauche</u> conformers.

This isolation of optically active Ih also indicates that the earlier belief[7] of relatively rapid rotation in the mono-adduct stage was incorrect. Substantial rotational barriers are obviously present in the mono-adduct intermediates since an active product is obtained.

However, the low optical purity of the product indicates that a fair amount of racemization could have occurred in the

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*The temperature reached during benzyne addition and recrystallization steps.

the mono-adduct state. To ascertain this possibility requires a comparison of the optical purity with the starting bianthryl (IIh)- for it must be established that there is, in fact, a difference of optical purities between Ih-(B, B', B") and IIh.

Attempts were made to determine the optical purity of the starting IIh by nmr, using chiral shift reagents. Six different commercially available chiral shift reagents* were tried with optically active as well as racemic IIh. Although shifts of the nmr peaks were obtained, the methoxyl peaks were not split. The aromatic absorptions were too complicated to be useful.

Recently the optical rotation of optically pure 2,2'-dicarboxy-9,9'-bianthryl (IIh) was determined by R. K. Gupta.[29] Using (+) α-phenylethylamine (VIII) (Aldrich Chemical Co., Milwaukee, Wisc.) as a diastereomerization reagent, samples of racemic, dextrorotatory and levorotatory IIh were

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* 1. Eu(hfc)$_3$, tris-[3-heptafluoropropylhydroxymethylene)-d-camphorato)europium (II), (Aldrich Chemical Co., Milwaukee, Wisc.).
2. Eu($C_{12}H_{14}F_3O_2$)$_3$, tris-[3-(trifluoromethylhydroxymethylene)-d-camphorato]europium (III), (Alfa Division, Ventron Corp., Davers, Ma.).
3. Pr(tfac)$_3$, tris-[3-(trifluoroacetyl)-d-camphorato] praseodymium (III), (Norell Chemical Co., Inc., Landisville, N.J.).
4. Pr($C_{12}H_{14}F_3O_2$)$_3$, tris[3-(trifluoromethylhydroxymethylene)-d-camphorato]praseodymium (III), (Alfa Division, Ventron Corp., Davers, Ma.).
5. Yb(HFC)$_3$, tris-[3-(heptafluoropropylhydroxymethylene)-d-camphorato]ytterbium (III), (Stohler Isotope Chemical Co., Inc., Rutherford, N.J.).
6. Yb($C_{12}H_{14}F_3O_2$)$_3$, tris-[3-(trifluoromethylhysroxymethylene)-d-camphorato]ytterbium (III), (Ventron Corp., Beverly, Mass.).

Suppliers' chemical abbreviation are used.

independently derivatized according to Scheme IX, (p. 64). The diastereomeric composition of the diamide, IIl , was determined by HPLC. The rotation of optically pure IIh was found to be $[\alpha]_D^{23}$ - 115.3°±0.5° (c 0.5, CH_3OH)*.

In the present work, diacid IIg, having a specific rotation of -115.6° (c 0.5, CH_3OH) was used. The diacid used was therefore 100% optically pure. This finding and the low optical purity of gauche Ih indicate that the benzyne addition reaction must have proceeded with approximately 71% racemization.

C. Koukotas has estimated[7] the ratio of bitriptycyl conformers that should form from the addition of benzyne to a bianthryl enantiomer. The estimate was made using the following assumptions: 1. The addition of the two benzynes occurs one at a time. 2. The addition of the first benzyne is not appreciably influenced by either the dihedral angle or the substituents of the bianthryl. 3. Rotation about the 9,9'-single bond does not occur in the mono-adduct stage. 4. Addition of the second benzyne occurs so as to produce a relatively strain free staggered conformer. Using these assumptions, it was concluded that 75% of the gauche conformer and 25% of the anti conformer would be formed, and that the gauche conformer would be optically pure. In light of the extensive racemization observed in the formation of the gauche conformer of Ih, and the considerably greater amount of the

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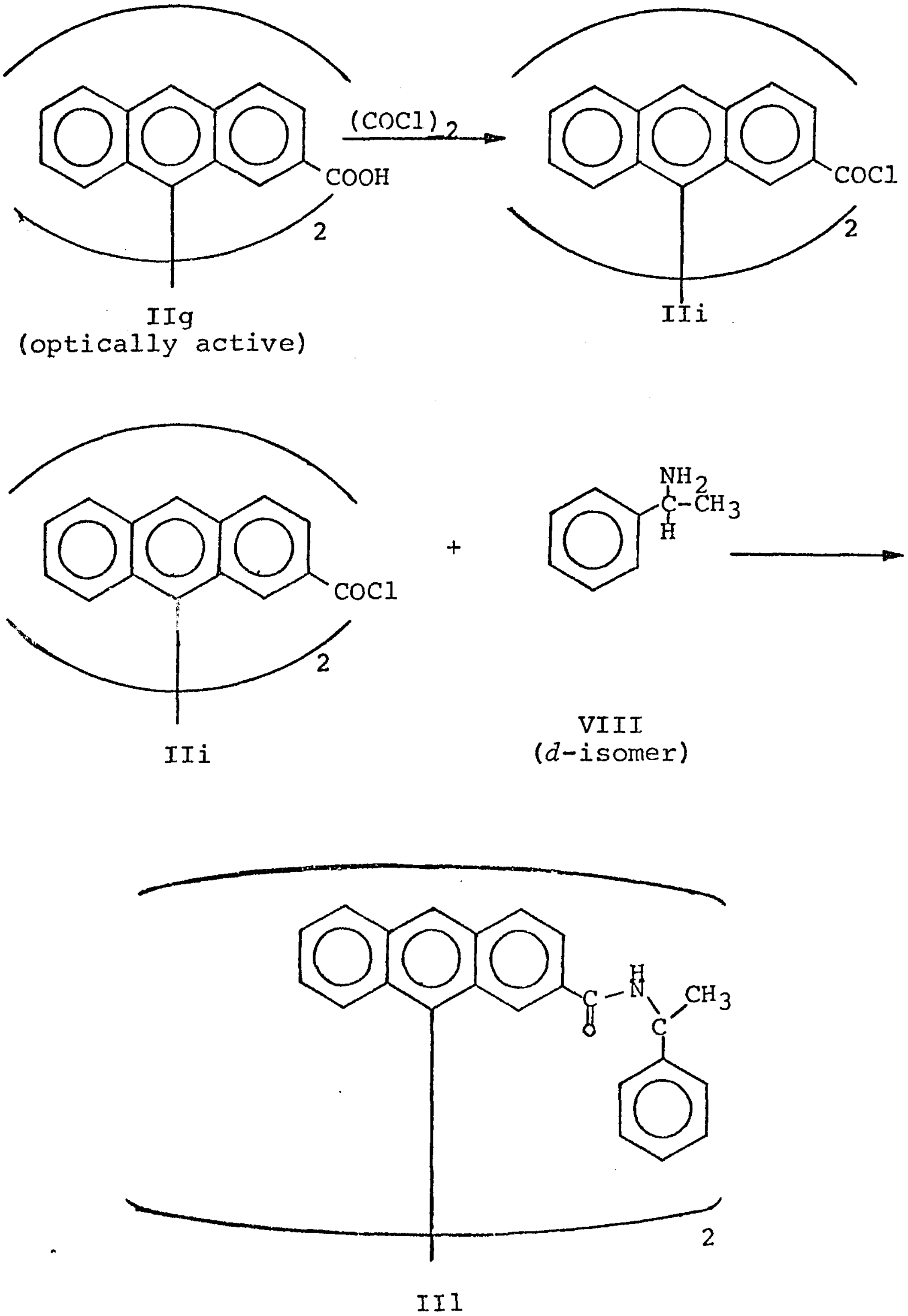
*The absolute rotation obtained from a sample of levorotatory IIh was found to be -115.7°, while that obtained from a sample of dextrotatory IIh was +114.8°. The average value of these two determinations is used.

Scheme IX

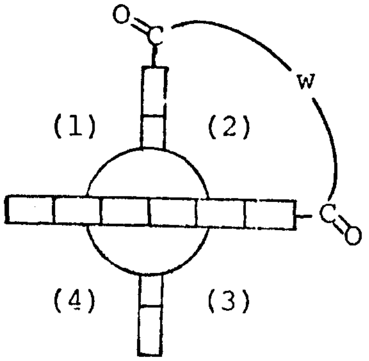

(COCl)$_2$
COOH
2
IIg
(optically active)
COCl
2
IIi
COCl
2
IIi
+
NH$_2$
C-CH$_3$
H
VIII
(*d*-isomer)
C
O
H
N
CH$_3$
C
2
IIl

anti conformer formed (Table VIII, p. 61) than predicted, rotation in the mono-adduct (see assumption 3) appears highly likely. One can not absolutely discount the incorrectness of assumptions 1, 2, and 4, but from the previous detailed analysis (see reference 7, pages 25-31) it is the incorrectness of assumption 3 which seems most likely.

III. SYNTHESIS OF A BRIDGED 2,2'-DICARBOXY-9,9'-BIANTHRYL

A. Bridged, Optically Active 2,2'-Dicarboxy-9,9'-bianthryl (IIw) as Precusor for Optically Active 2,2'-Dicarboxy-9,9'-bitriptycyl (Ig).

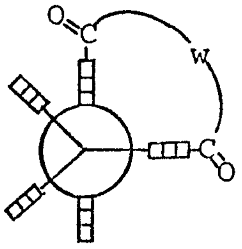
The earlier work[7] from our laboratories suggested that rotation of the single bond in the mono-adduct intermediate, VIIh, was the most probable cause for the failure to obtain optically active 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih) from the reaction of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (IIh) with benzyne. While the earlier work was being repeated (pp. 50 to 65), methods were also sought to prevent this rotation. An approach involving the use of a removeable bridge was envisioned. In this approach a proper organic bridge would be built across the two anthracene units of the starting bianthryl. The bridge would remain throughout the benzyne addition reaction to prevent the rotation in the mono-adduct intermediate. The bridge would later be removed after the bridged bitriptycyl was isolated. With a proper bridge that prevented rotation completely, an optically active bitriptycyl of the same optical purity as the starting bianthryl should be obtained. Let IIw represent a bridged 2,2'-dicarboxy-9,9'-bianthryl. A benzyne molecule can approach the front anthracene unit of IIw from one of the four indicated general directions. The approach from each direction may not be equally probable, due to the nature of the dihedral angle of the bridged bianthryl (IIw) and/or the presence of the bridging group. However, it will be seen from the following analysis that these factors will not affect the final results and therefore need not be considered.



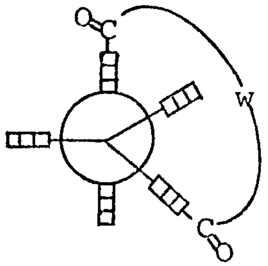
IIw

One enantiomer shown
w = bridging group
▯▯▯▯▯= side view of anthracene unit

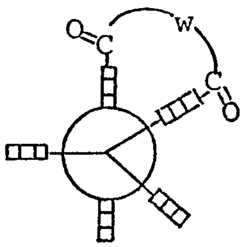
Depending on the direction of approach, mono-adducts VIIw, VIIw', or VIIw" could be produced. Addition from



VIIw



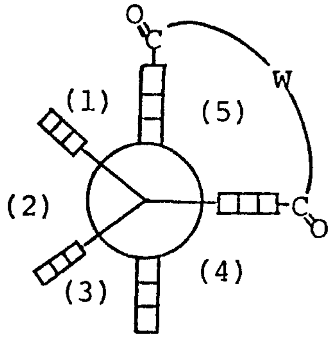
VIIw'



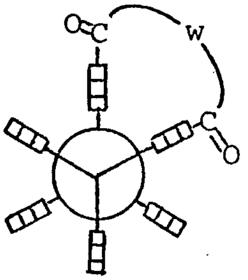
VIIw"

directions (1) or (4) would give VIIw. Addition from direction (2) and (3) would give VIIw' and VIIw", respectively. The formation of VIIw' would require a longer and more flexible bridge than the formation of VIIw and VIIw". A properly chosen bridging group would prevent the formation of VIIw'. The addition of the first benzyne to the back anthracyl unit would give the same results.

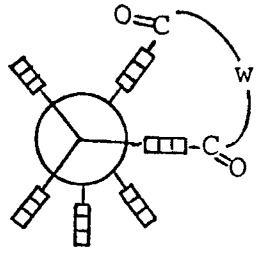
The second benzyne may approach VIIw, VIIw' and VIIw" from five general directions. Consider the addition of a second benzyne to VIIw. Addition from (2) would give Iw, a staggered, bridged bitriptycyl. Addition from directions (3) and (4) would give Iw'. Addition from direction (1) and (5) would give Iw" and Iw"', respectively. Conformers Iw',



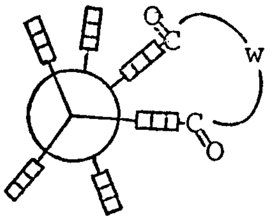
VIIw



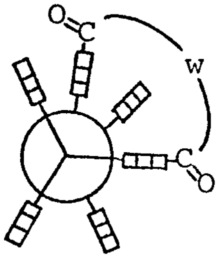
Iw



Iw'



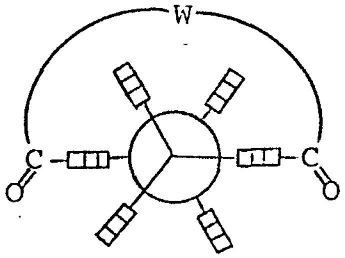
Iw"



Iw"'

Iw" and Iw"' contain extremely distorted bond angles and compressed benzo groups, and should be considerably less stable than Iw. The transition state leading to the formation of the bridged bitriptycyl should reflect this strain, and result in the formation of only Iw. If, however, some Iw', Iw", or Iw"' did form, the end result would still be the formation of only Iw.

To release the steric and the angle strain, the benzo groups of Iw' and Iw" would realign themselves to assume a thermodynamically more stable, staggered conformation. The realignments would consist of bond rotations involving only one benzo-benzo interaction. Because the relative positions of the two carbonyl groups are fixed by the bridge, realignments of the crowded benzo groups in Iw' and Iw" would give Iw as the only staggered conformer. For Iw", two routes are possible to release the steric and angle strain. The crowded, bridged benzo group (of the back triptycyl unit) could rotate counterclockwise to form a bridged anti conformer Iw"". However, the formation of Iw"" would be highly improbable unless the bridging group was sufficently lengthy and flexible. The other route involves two shifts of benzo groups. The crowded, unsubstituted benzo group (back,right) could rotate clockwise and consequently force the benzo group, originally pointing down, to also rotate clockwise and thus reach a staggered conformation. This staggered conformer is Iw.



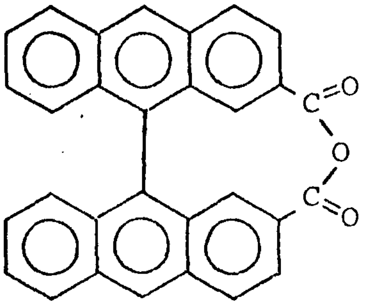
Iw""

Similar consideration for VIIw' and VIIw" leads to the conclusion that Iw would be the only conformer formed.

The above analysis would be equally valid for the enantiomer of the bridged bianthryl considered here. In that case, a bridged bitriptycyl enantiomeric to Iw (p. 68) would be the only conformer formed. The conclusion that can be drawn from this analysis is that a properly bridged, optically active 2,2-dicarboxy-9,9'-bianthryl (IIg) would give an optically active 2,2'-dicarboxy-9,9'-bitriptycyl (Ig). The optical purity of the resulting Ig would be the same as that of the starting bianthryl (IIg).

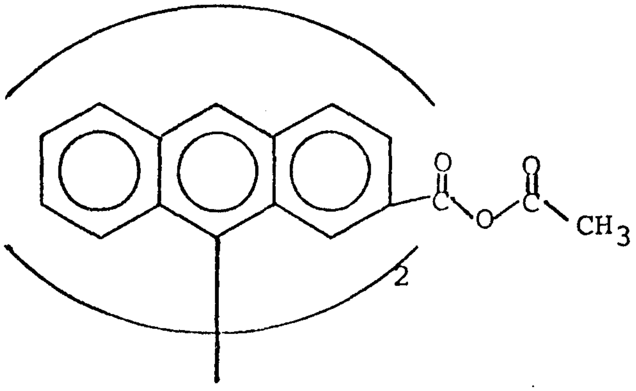
Accordingly, proper bridging groups and bridging methods were sought to bridge IIg. A suitable bridging group would have to be: (1) easily attached to the starting bianthryl (IIg); (2) easily removed from the bridged bitriptycyl (Iw); (3) the proper size to allow for a stable (non-strained) bridged bianthryl (IIw), bridged mono-adduct (VIIw or VIIw") and bridged bitriptycyl (Iw); (4) rigid enough to not allow rotation in the mono-adducts or the formation of conformers such as VIIw' and Iw'".

Initially, attempts were made to prepare the intramolecular anhydride of IIg, with the hope that the anhydride bridge would serve our purpose. A conventional method of anhydride formation,[30] by heating the diacid, IIg, in acetic anhydride did not give the desired intramolecular anhydride,



IIj

IIj Nmr and mass spectroscopy indicated that the mixed anhydride, IIs, had been obtained.*



IIs

Based on Dreiding models, α,α'-diamino-p-xylene (XXIa) and α,α'-dihydroxy-p-xylene (XXIb) (p. 72) were thought to be promising bridging compounds. These two compounds appeared to satisfy all the requirements previously mentioned on page 70. Reaction of either XXIa or XXIb with the diacid

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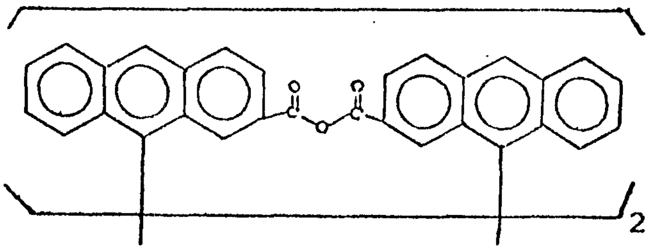
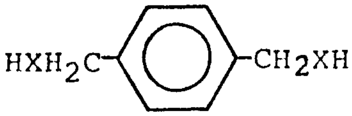
*The mixed anhydride IIs was rather unstable. Purification could only be accomplished with freshly prepared absolute $CHCl_3$. Recrystallization of IIs from ordinary reagent grade $CHCl_3$ or CH_3CN gave the diacid (IIg) and other products which were not investigated further. Recrystallization of IIs from benzene or acetone gave a high melting (m.p.>450°d) insoluble crystalline solid which was shown to be IIt by ir and mass spectroscopy. A quantitative recovery of diacid, IIg was obtained when IIt was hydrolyzed with an aqueous solution of KOH/MeOH. Heating decomposed (foaming) IIs to form the same high melting, insoluble solid. Since a Dreiding model of the intramolecular anhydride appeared to be quite strained, this synthetic goal was abandoned.



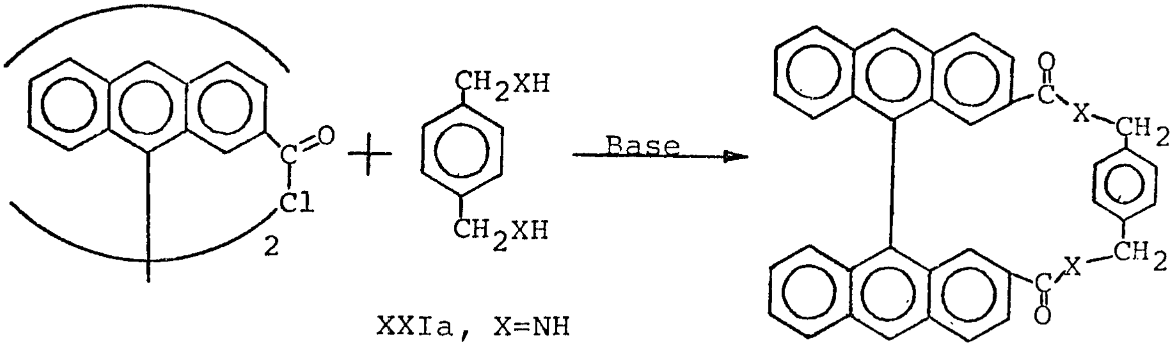
IIt



XXIa, X = NH
b, X = O

chloride of IIg, 9,9'-bianthracene-2,2'-dicarbonyl dichloride (IIi), would produce the desired bridged bianthryls, IIm and IIn, respectively (Scheme X).

Scheme X



IIi

XXIa, X=NH
b, X=O

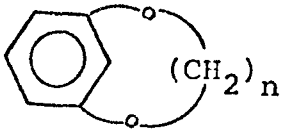
IIm, X=NH
n, X=O

B. Double High Dilution Reaction. Synthesis of 2,2'-(N,N'-(α,α'-p-Xylyl))dicarboxyamido-9,9'-bianthryl (IIm).

The reactions shown in Scheme X both involve intermolecular cyclization of two reactants, each having two equivalent reactive sites. A major difficulty inherent in this type of synthesis is the prevention of the formation of open chain and cyclic polymers. Various high-dilution reaction methods have been previously developed to deal with reactions analogous to those in Scheme X.[31]

Lüttringhaus[32] employed a two-step synthesis to prepare

6 from 7 and 8. First, a simple condensation reaction of 7 and 8 using an ordinary experimental procedure was used. The reaction mixture was purified, and the open-chain dimer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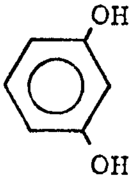
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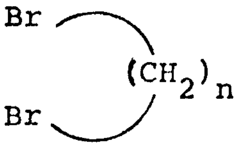
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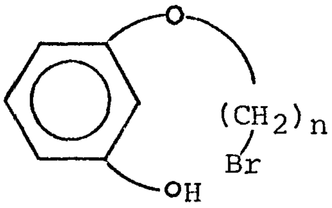
9 was isolated. The dimer 9, was subjected to a one-component-high-dilution reaction (IC-VP)* in which the concentration of the dimer was kept extremely low so that an intramolecular


9

cyclization reaction was favored.

This approach is tedious, since it involves the isolation and purification of the open-chain dimer from the other reaction products. It is also wasteful. The polymeric products must be isolated and discarded or the monomers regenerated from them. This method is not attractive when a precious starting material, such as our optically active 2,2'-dicarboxy -9,9'-bianthryl (IIg), is to be used.

Ruggli[33] employed a one-step two-component-high-dilution reaction (2C-VP)* to prepare compound 10 from 11 and 12. The key operation of this 2C-VP synthesis involved the

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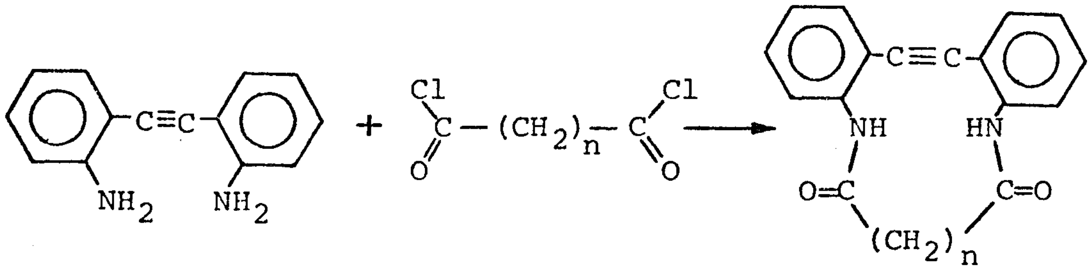
*Terminology adopted from Vögtle.[31]

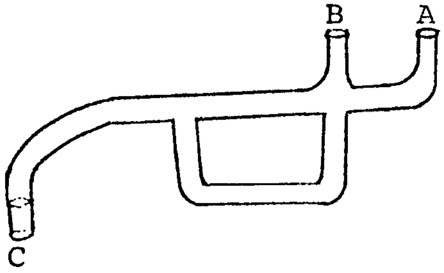
separate addition of the two reactants, simultaneously, into a large reaction volume so that two single-unit reactants would meet and react to form the two-unit cyclic product.



11 12 10

Improvements were later made on the high-dilution technique and on the 2C-VP reaction by Leonard and Sentz[34] and Stetter and Marx.[35] To increase the dilution, Leonard and Sentz made use of high-dilution side arms (Fig. XVI).

Fig. XVI

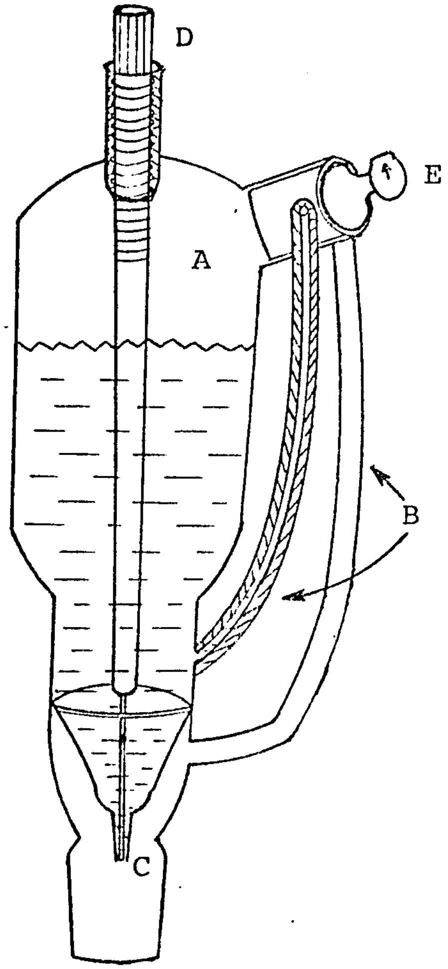


A High-Dilution Side Arm

The high-dilution side arm is attached to the addition funnel at point A and the reaction flask at point C. An efficient reflux condenser is attached at point B. The reaction solvent is heated to reflux in order to form a continous, lively, stream of solvent condensate dropping from the condenser. When the reactant is dropped into the high-dilution side arm, it is carried down into the reaction flask through the loop by the solvent stream. In this manner the reactant is diluted by the solvent before it enters the reaction flask.

To have better control over the addition of the reactants, Stetter and Marx[35] developed the "Constant Addition Funnel". A modern version of this addition funnel is shown in Fig. XVII.[36]

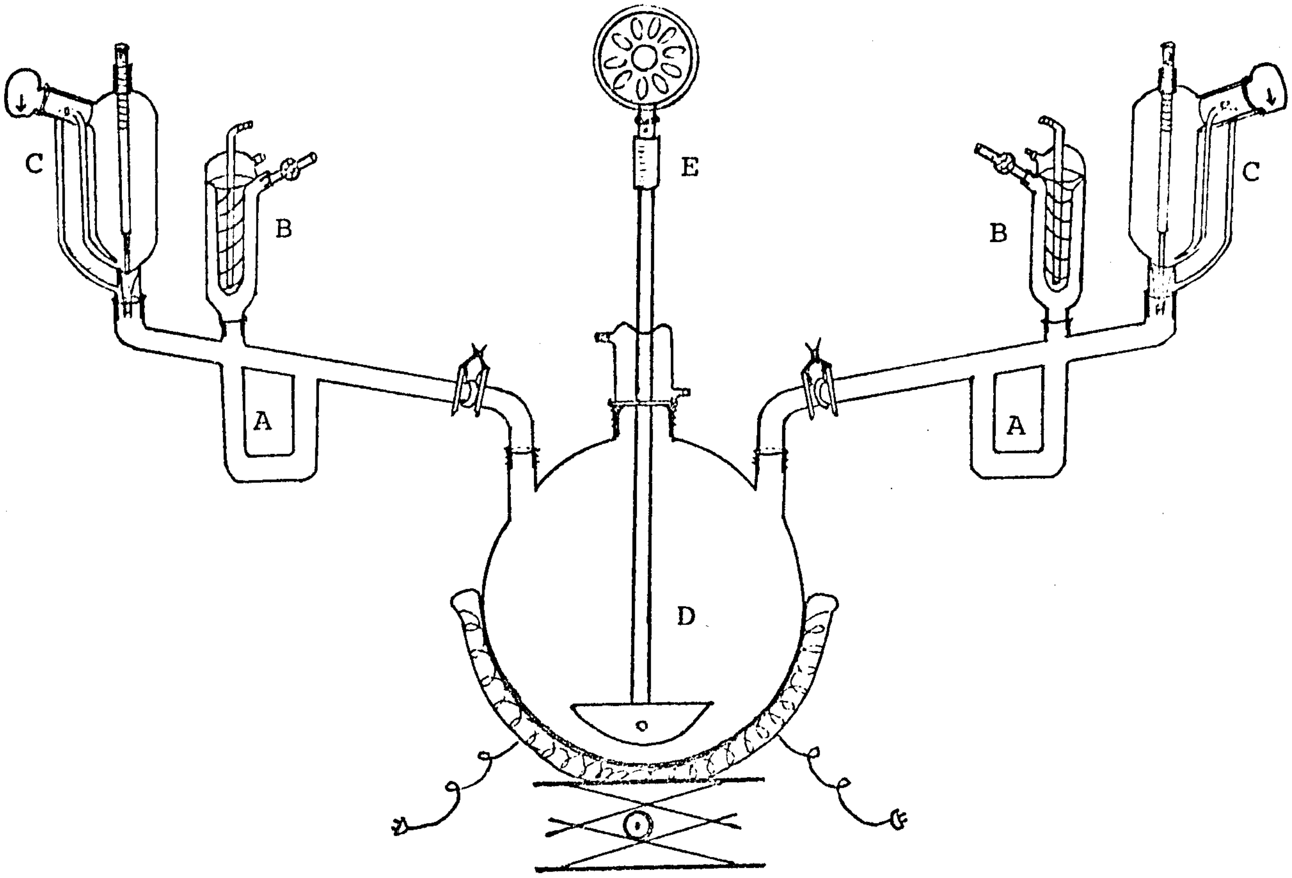
Fig. XVII



The funnel is made of three parts: 1) the main glass body with reservoir(A), pressure equalization side arms(B), and drip tip (C), 2) a teflon tipped probe(D), and 3) a ground glass stopper with a T-bore (E). In operation, the funnel is filled with liquid with stopper E removed and the probe D at the shut-off position (fully down). The stopper E is then replaced so that the T-bore is open to the side arms and the reservoir A allowing the pressure in reservoir A to come to equilibrium with the external system. When equilibrium is achieved, the stopper is rotated 180° thus isolating the reservoir from the external system but leaving the side arms connected. The probe D is slowly backed out to allow liquid to drop into the reaction system through drip tip C. As liquid drops out of the reservoir, the pressure in the reservoir above the liquid is reduced. Gas (or air) will be drawn from the external system down the capillary side arm until it bubbles into the reservoir. The liquid level affecting the drop rate is the volume contained between the capillary side arm opening and the drip tip. As long as the pressure of the external system remains constant, the addition rate should not change, except at the very end when the level of the stock solution gets below the capillary opening.

A 2C-VP reaction assembly, incorporating the ideas of Leonard and Sentz[34] and Stetter and Marx[35] (Fig. XVIII, p. 77) was explored for the synthesis of IIm and IIn. The synthesis of 2,2'-(N,N'-α,α'-p-xylyl))dicarboxamido-9,9'-bianthryl (IIm) was first attempted (Scheme X, p. 72). 2,2'-Di-(chlorocarbonyl)-9,9'-bianthryl (IIi) was prepared according to Scheme XI. It was found that pure IIi could only be obtained from the reaction of IIg and excess oxalyl chloride. Other common reagents, $SOCl_2$ and PCl_5, also chlorinated the aromatic rings. The

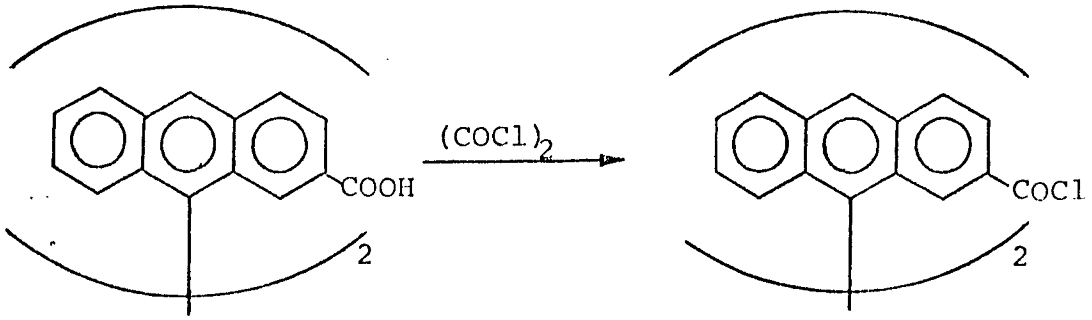
Fig. XVIII



DOUBLE HIGH DILUTION SYSTEM (2C-VP)

A. High-Dilution Side Arms.
B. Reflux Condensers.
C. Constant-rate Addition Funnels.
D. 12-Liter Reaction Flask.
E. Heavy Duty Stirring Assembly.

Scheme XI



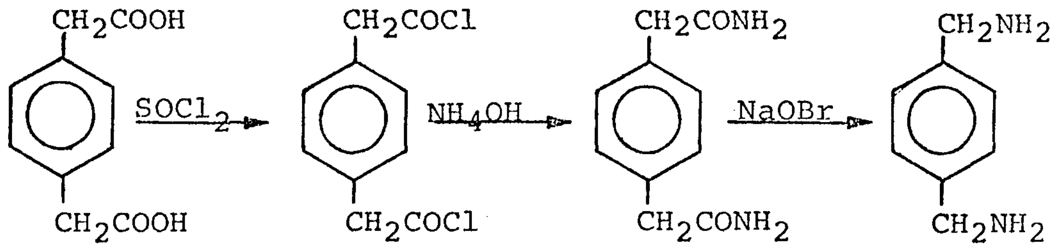
IIg

IIi

mass spectra of the bis-acid chloride products, using $SOCl_2$ or PCl_5, indicated the presence of bis-acid chlorides containing zero, one and two extra chlorine atoms. Mass spectra of the diacids from the hydrolysis of the above acid chlorides confirmed this conclusion.

α,α'-Diaminoxylene (XXIa) was synthesized according to Scheme XII.

Scheme XII

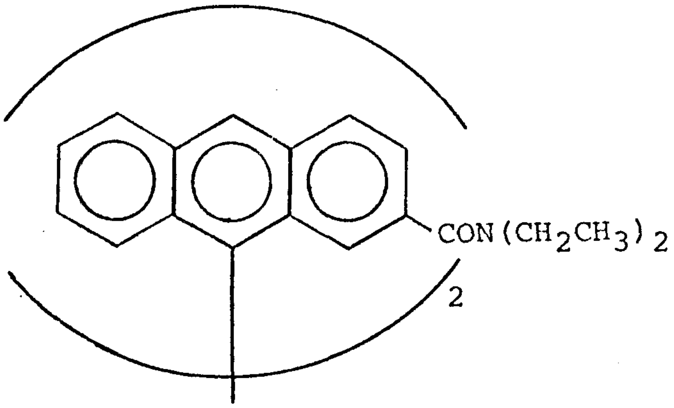


XXIe XXId XXIc XXIa

α,α'-Diaminoxylene was found to be extremely hygroscopic and reactive. It should be handled at all times under a dry N_2 atmosphere.

A number of high-dilution reactions using equimolar amounts of IIi and XXIa were tried in the high dilution apparatus shown in Fig. XVIII, (p. 77). Either benzene or carbon tetrachloride was used as solvent and either triethylamine (TEA) or pyridine was used, in 2-10 fold excess, as catalyst. In the case where carbon tetrachloride and triethylamine (TEA) were used, the only significant product that could be isolated was identified (by nmr, ms, ir) as

2,2'-bis-(N,N-diethylamido)-9,9'-bianthryl* (IIo).



IIo

It accounted for about 46% of the IIi employed in the reaction.

Before use, primary and secondary amines were removed from the TEA by treatment with p-toluenesulfonyl chloride.[37] IIo could be a direct reaction product of IIi and TEA, or, IIo could be the reaction product of IIi with newly formed diethylamine which arose from the reaction of TEA and CCl_4.[38]

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*The nmr spectrum of IIo in $CDCl_3$ is interesting. At room temperature the methylene groups appear as a broad singlet at δ 3.09 and the methyl groups appear as two broad singlets at δ 0.98 and δ 0.31. At lower temperature (-10°C) the broad methylene singlet becomes two quartets of equal intensity while the two methyl singlets become two triplets of equal intensity. At higher temperature (75-90°C), a single quartet for the methylene groups and a broad triplet for the methyl groups are observed. These results indicate that the rotation of the amide bond in IIo is not free, and that the two ethyl groups on each amide nitrogen are not equivalent. A space-filling model of IIo indicates that in order to accommodate two ethyl groups on the same nitrogen atom, one of the ethyl groups must bend toward an anthracene unit so as to have its methyl group closer to the aromatic shielding region. The nmr spectra are in agreement with the model requirements. The most probable conformation of IIo would be as shown (p. 80).

In the case where pyridine and benzene were used, dicarboxybianthryl (IIg) and other unidentified products were isolated.

Only when TEA and benzene were used was a small amount of the bridged bianthryl, 2,2'-(N,N'-(α,α'-p-xylyl))dicarboxamido-9,9'-bianthryl (IIm), obtained. The crude yields from three such syntheses were quite variable (3-20%) and depended on the mechanical behavior of the high dilution apparatus (Fig. XVIII, p. 77). After months of work, only about 75 mg of IIm was obtained from the above three separate syntheses.

The major mechanical difficulty was the irregular behavior of the constant addition funnels (parts C Fig. XVIII, p. 77). It was found that the balance of the constant addition funnel was too delicate to be practical for reactions requiring vigorous reflux and stirring conditions over an extended period of time. The balance was easily destroyed by slight vibrations and changes in temperature and pressure of the reaction system. In addition, when solutions of solid

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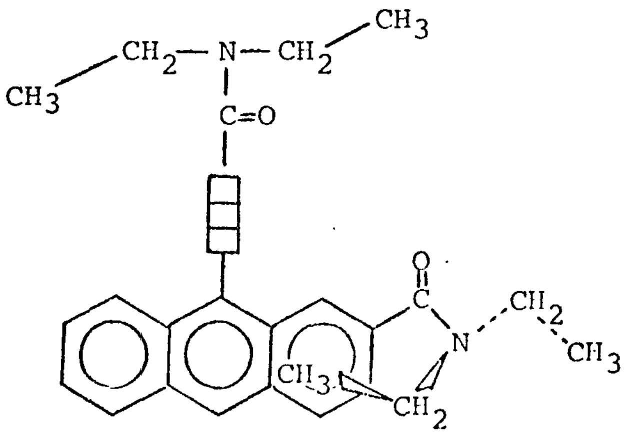

IIo

▤ = side view of an anthracene unit

reactants such as IIi and XXIa were used, slow addition over a longer period of time often resulted in an accumulation of solid at the drip tip. The addition rate was thus altered and eventually stopped. Satisfactory addition could not be obtained from both funnels for more than a few hours. Large discrepancies often occurred in the amount of reactants added. A better and more reliable means of addition was necessary.

C. Synchronous Constant Volume Addition Assembly

Accordingly, a Synchronous Constant Volume Addition Assembly (Fig. XIX, p.82) was designed to replace the constant addition funnels. The assembly contains ten major parts: a timer* (A), a relay* (B), two automatic dispensers* (C), two primary reservoirs (D), two secondary reservoirs (E), and two capillary delivery probes (F). The stock solutions are stored (air tight) in the primary reservoirs (D) which have outlet tubes open to the secondary reservoirs (E). The liquid levels and therefore the weight of the reactant solution in each secondary reservoir E is controlled and maintained by the length of the outlet probe extending from D to E. The capillary delivery probes (F) are attached to the high dilution side arms (part A, Fig. XVIII, p.77), and to the secondary reservoirs (E). To insure against leakage, the latter attachments are secured with springs (H). Since the probes (F) are exchangeable, different sizes may be used.

In operation, the signal from the timer (A) is trans-

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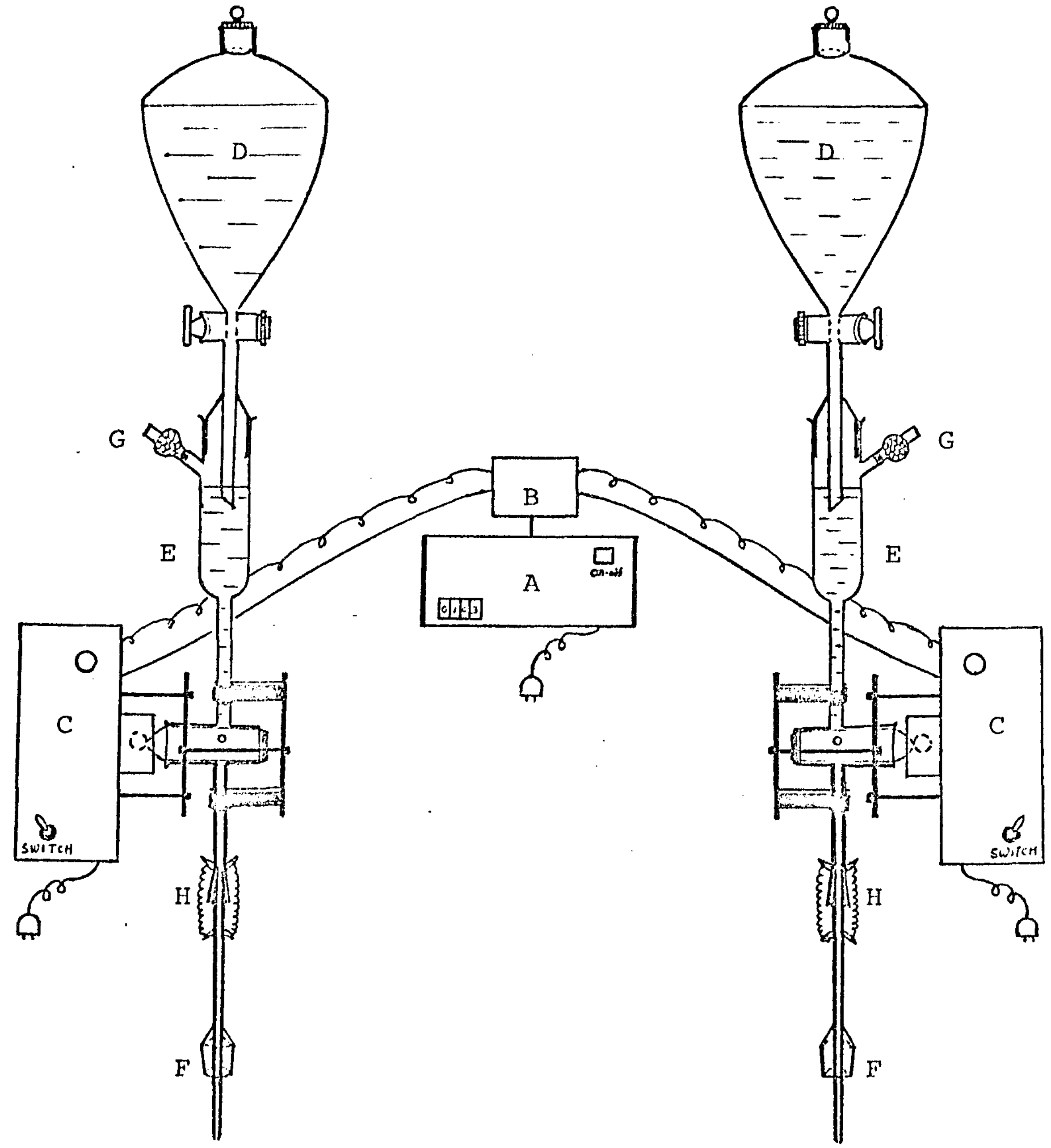
*Electronic circuitry of each unit is shown in Appendix B.

Fig. XIX Synchronous Constant Volume Addition Assembly



A. Timer
B. Relay
C. Automatic Dispensers
D. Primary Reservoirs
E. Secondary Reservoirs
F. Capillary Delivery Probes
G. Drying Tubes
H. Springs

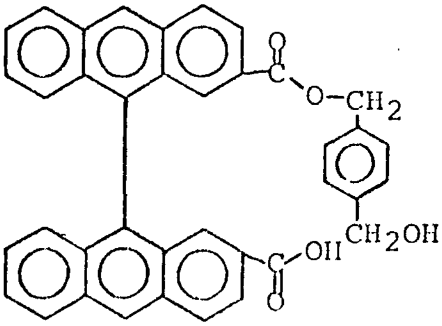
mitted, through the relay (B), simultaneously to both dispensing units (C) which control the drive-motors. The drive-motors rotate the stopcocks (G) in the secondary reservoirs (E) 180°. During the rotation, solutions from reservoirs E are discharged into the reaction system through the delivery probes (F) by gravity. The amount of each reactant solution delivered is controlled by: (1) the liquid level (the weight of the solution) in E, (2) the rotation speed of the stopcock (G) (determined by the rotation of the dispenser drive-motor), (3) the bore size of the capillary delivery probe (F). Since each of these parts can be independently adjusted, the volume of solution delivered can be pre-set.

It is not easy to preset the two dispensing units to deliver exactly the same volume. Nevertheless, this does not prevent the attainment of the addition of the desired amount of each reactants. The volume delivered from each dispensing unit is premeasured, and the concentrations of the stock solutions adjusted so that the delivered volumes contain the right amount of each reactant.

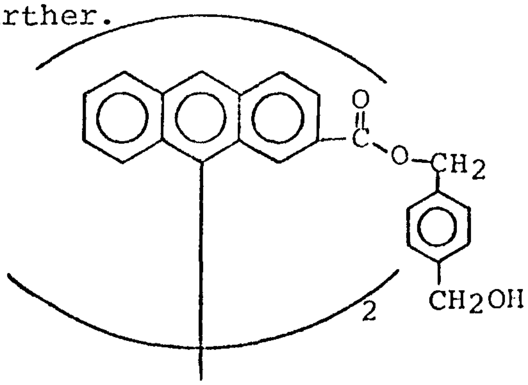
The addition units, thus assembled, gave good addition results. Two runs using these addition units were tried. Discrepancies of 8% and 9% between the two addition units were observed at the end of the runs. These discrepancies could be actually due to human errors in calibrating and adjusting the volume of the original stock solution rather than to nonreproducibility of the apparatus.

The two indpendent runs, above, gave 32% and 34% yields of IIm (total yield 300 mg. of IIm). In one of the runs 1,8-bis-(dimethylamino)naphthalene (Proton Sponge®, Aldrich Chemical, Milwaukee, Wisc.) was used as the base instead of TEA. No significant improvement in the overall yield was obtained.

Using the Synchronous Constant Volume Addition Assembly (p. 82), attempts were made to prepared the cyclic diester, IIn from IIi and XXIb, in benzene. Both TEA and 1,8-bis-(dimethylamino)napththalene were tried as catalysts. The syntheses were unsuccessful. No cyclic diester could be isolated. In the TEA case, the major isolable product was 2,2'-bis-(N,N'-diethylamino)-9,9'-bianthryl (IIo) (see p. 80). It accounted for about 50% of the IIi used in the reaction. This time the product IIo could only come from reaction of IIi and TEA (see p. 79). However, the reaction mechanism was not studied. With 1,8-bis-(N,N'-dimethylamino)-naphthalene the product mixtures, as analyzed by nmr, ms and ir, appeared to contain the diacid IIg, the monoester IIp, the diester IIq, and polymers. The synthesis of cyclic diester IIn was not pursued further.



IIp



IIq

At this point, the presence of atropisomerism in 9,9'-bitriptycyl system was successfully demonstrated through other methods (see Section I and II, pp. 2-65). The synthesis of optically active 9,9'-bitriptycyl to achieve the same goal, through a bridged 9,9'-bianthryl, became unnecessary. Further work along this bridged-bianthryl route was therefore stopped.

It came to our attention, after the construction of the Synchronous Constant-Volume-Addition Assembly (Fig. XIX, p. 82), that there were other instruments which could be easily adapted for the same purpose. A fluid metering pump (FMI LAB PUMP, Fluid Metering Inc., Oyster Bay, N.Y.) which can deliver liquid from 0.01 ml. per minute to 1 l. per minute with reproducibility of better than 1%[39] and an automatic dilutor/dispenser (Dilutrol 2™, Dilutrol 3™, Manostat, New York, N.Y.) which can deliver liquid from 50 microliters to 30 ml per stroke with accuracy of ±0.3%[40] are commercially available. Dilutrols are designed to allow for outside signal actuation via an electrical connection. It is conceivable that a pair of metering pumps of dilutor/dispensers with capabilities mentioned above could be synchronized and used as an addition assembly for high dilution reactions.

EXPERIMENTAL SECTION

ANALYSES

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921. Melting points, unless otherwise indicated, were determined using a Thomas-Hoover apparatus in open capillary tubes and are corrected. Boiling points are uncorrected. Infrared spectra were taken using either a Beckman IR-20A or a Perkin-Elmer 137 spectrophotometer. Absorption position are expressed in reciprocal centimeters (cm^{-1}). Proton magnetic resonance spectra, unless otherwise indicated, were taken using a JOELCO JNM-MH-100 spectrometer. Chemical shifts are expressed in ppm (δ) downfield from internal tetramethylsilane. Integration experimental values within ±5% of the expected values are recorded as integers. Mass spectra were taken using a Varian CH-5 Mass Spectrometer at 70 ev, under direct sample inlet and linear mass scan conditions. Ultraviolet spectra were taken using a Cary 15 spectrophotometer. Uv absorption maxima are expressed in log ε. Optical rotations were measured using a Perkin-Elmer 141 polarimeter. Values are reported as the average of three measurements.

(I) Preparation of Substituted Benzoylbenzoic Acids.

A. Preparation of o-(2-Methylbenzoyl)benzoic Acid (VId). Reaction of o-Methylphenylmagnesium Bromide with Phthalic Anhydride.

In a 300-ml "Grignard flask" (a three-necked flask equipped with a sintered-glass filter and a stopcock at the bottom) were placed 12.2 g. (0.501 mole) Mg turnings, 120 ml. anhydrous ether and a few crystals of I_2. The mixture was stirred under a N_2 atmosphere at room temperature for 15 min. until the distinct I_2 color disappeared. Approximately 2-3 g of o-bromotoluene was added, and the mixture was warmed gently for 2 min. to initiate an exothermic reaction. With the heat source removed, the remainder of the o-bromotoluene (a total of 77 g., 0.45 mole) was added dropwise at a rate to sustain a gentle reflux. After complete addition, the reaction mixture was heated at reflux for an additional 30 min. The reaction mixture become too viscous to be filtered through the sintered-glass filter of the Grignard flask. Therefore, it was necessary to transfer it to a pressure-equalizing addition funnel. This Grignard mixture was then added slowly to a stirred mixture of 62 g. (0.42 mole) phthalic anhydride, 300 ml. benzene and 100 ml. ether at 0°C. The reaction mixture was stirred at room temperature for an additional 1 hr. and then heated at reflux for another 30 min. All of the above operations were performed under a N_2 atmosphere. After cooling, 200 g. of ice was added, followed by 100 ml. 1:1 HCl. This mixture was stirred vigorously for 10 min. and steam distilled to remove the organic solvents. The pot residue yielded an oily organic layer which became semi-solid on cooling. The semi-solid was boiled in benzene (300-400 ml.), and the insoluble phthalic acid was removed by filtration. The benzene solution was concentrated to approximately 100 ml. and 60 ml. of hexane was added. The solution deposited 42 g. of crystals on cooling. These crystals were purified again with benzene and hexane in the same manner as above to give 39.3 g. of white crystals, m.p. 126-129°. The nmr spectrum was consistent with o-(2-methylbenzoyl)benzoic acid (VId). When the residue from the evaporation of the mother liquor of the first crystallization was dissolved in $CHCl_3$ and precipitated by the addition of hexane, an additional 11.6 g. of o-(2-methylbenzoyl)benzoic acid (VId) was obtained. The product thus obtained was used for the synthesis of o-(2-methylbenzyl)benzoic acid (Vd) without further purification. A sample of VId was recrystallized again from benzene/hexane to give white crystals; m.p. 129-131° (lit.[41] 129.6-132.6°, lit.[42] 128-129°); ir (KBr), 2800-3100 (COOH), 1715 (sh) and 1700 (CO) $cm.^{-1}$; nmr ($CDCl_3$) δ 2.58 (s, 3 H, CH_3), 7-8 (m, 8 H, aromatic-H), 11.73 (s, 1 H, COOH).

B. Preparation of o-(2',5-Dimethylbenzoyl)benzoic Acid (VIe). Friedel-Crafts Acylation of p-Xylene with Phthalic Anhydride.

In a one-liter three-necked flask, equipped with a mechanical stirrer and a reflux condenser, were placed 32 g. (0.22 mole) of powdered phthalic anhydride and 290 g. (2.74 mole) of p-xylene (99%). The mixture was heated to 60-65° C. Aluminum chloride (55 g., 0.41 mole) was added slowly, in portions. An exothermic reaction took place, and the reaction mixture turned orange-red. Additional phthalic anhydride (30 g., 0.20 mole) was added. After 30 min., an additional 27 g. (0.22 mole) of $AlCl_3$ was added. The mixture was then stirred at 85-90°C for 2 hr. After cooling, 250 ml. of 1.2 M. HCl solution was added with thorough mixing. The aqueous layer was isolated and washed twice with 100 ml. portions of benzene. The organic layer, after being combined with the benzene solution was washed once with water, and then extracted four times with 200 ml. portions of 8% aqueous Na_2CO_3 solution. The aqueous extract was acidified to pH<1 to give 75 g. of a white precipitate. Recrystallization from 1200 ml. $HOAc/H_2O$ (2:3), and then from benzene/hexane (3:2), gave 46 g. (43%) o-(2,5-dimethylbenzoyl)benzoic acid (VIe); m.p. 145-147° (lit.[13] 149°, lit.[43] 149-150°); ir (KBr), 3200-2200 (COOH), 1680-1650 (COOH, CO) cm.$^{-1}$; nmr ($CDCl_3$), δ 2.21 (s, 3 H, CH_3 at C-5), 2.56 (s, 3 H, CH_3 at C-2), 6.8-8.2 (m, 7 H, aromatic-H), 11.32 (s, 1 H, COOH); mass spec., m/e (rel. intensity using linear mass scan) 254 (65), 235 (100), 218 (5, metastable).

(II) Preparation of Substituted Benzylbenzoic Acids.

A. Preparation of o-(2-Methylbenzyl)benzoic Acid (Vd). Reduction of o-(2-Methylbenzoyl)benzoic Acid (VId).

In a 3-l. three-necked flask, equipped with two reflux condensers and a mechanical stirrer, were placed 50.8 g. (0.212 mole) of o-(2-methylbenzoyl)benzoic acid (VId) (p.88), 148 g. (2.26 g-atoms) of zinc dust, 520 ml. of concentrated ammonium hydroxide (28-30%), and 6 ml. of saturated cupric sulfate solution. The mixture was refluxed for 1.5 hr. A 100 ml. portion of 10% sodium carbonate solution was added. The mixture was refluxed for a total of 50 hr. and filtered while warm. The metallic residue was washed with a few portions of 10% ammonium hydroxide solution. The filtrate and washings were combined and acidified with concentrated HCl to pH<1 to precipitate out 45.6 g. (95%) of white solid which was shown to be pure o-(2-methylbenzyl)benzoic acid (Vd) by nmr spectroscopy. This material was used for the synthesis of 4-methylanthrone (IVd) without further purification. A sample was recrystallized from benzene/hexane to give off-white crystals; m.p. 129-131° (lit.[41] 128-131°, lit.[18] 128-128.5°); ir (KBr), 3300-2000 (COOH), 1710 (COOH), 1390 (CH_3) $cm.^{-1}$; nmr ($CDCl_3$), δ 2.20 (s, 3 H, CH_3), 4.40 (s, 2 H, CH_2), 6.80-8.80 (m, 8 H, aromatic-H), 12.26 (s, 1 H, COOH).

B. Preparation of o-(4-Methylbenzyl)benzoic Acid (Vb). Reduction of o-(4-Methylbenzoyl)benzoic Acid (VIb).

The procedure on p. 91 for the preparation of o-(2-methylbenzyl)benzoic acid (Vd) (p. 91) was followed, using 100 g. (0.416 mole) of o-(4-methylbenzoyl)benzoic acid (VIb) (prepared by C. K. Koukotas of this laboratory[7]) 280 g. (4.28 g-atoms) of zinc dust, 1030 ml of concentrated ammonium hydroxide (28-30%), 11 ml. of saturated cupric sulfate solution, and 320 ml. of 10% sodium carbonate solution. Following the same work-up procedure as described on p. 91, a white precipitate was obtained. Upon recrystallization from benzene/hexane (45:55), 70.9 g. (75.5%) of o-(4-methylbenzyl)benzoic acid (VIb) was obtained; m.p. 133.5-135.5° (lit.[44] 133.5-134.0°); ir (KBr), 3100-2500 (COOH), 1680 (COOH) cm.$^{-1}$; nmr ($CDCl_3$), δ 2.31 (s, 3 H, CH_3), 4.46 (s, 2 H, CH_2), 7.12 (s, 4 H, $C_6H_4CH_3$), 7.30-8.17 (m, 4 H, C_6H_4COOH), 11.62 (broad s, 1 H, COOH).

C. Preparation of o-(2,5-Dimethylbenzyl)benzoic Acid (Ve). Reduction of o-(2,5-Dimethylbenzoyl)benzoic Acid (VIe).

The procedure on p. 91 for the preparation of o-(2-methylbenzyl)benzoic acid was followed, using 60 g. (0.24 mole) of o-(2,5-dimethylbenzoyl)benzoic acid (VIe) (p. 90), 368 g. (5.63 g-atoms) of zinc dust, 645 ml. of ammonium hydroxide (28-30%), 200 ml of 10% sodium carbonate solution and 6 ml. of saturated cupric sulfate solution. The reaction mixture was refluxed for a total of 28 hr. and was worked-up using the same procedure as described on p. 91, to give 55.1 g. (77.5%) of white solid (m.p. 130-133°) which was shown to be rather pure o-(2,5-dimethylbenzyl)benzoic acid (Ve) by nmr spectroscopy. Recrystallization from benzene/cyclohexane (1.5:1) gave 45.7 g. of o-(2,5-dimethylbenzyl)-benzoic acid (Ve); m.p. 134-136° (lit.[13] 136°); ir (KBr), 3200-2200 (COOH), 1680 (COOH) cm.$^{-1}$; nmr ($CDCl_3$), δ 2.18 (s, 3 H, CH_3 at C-5), 2.25 (s, 3 H, CH_3 at C-2), 4.41 (s, 2 H, CH_2), 6.76-8.20 (m, 7 H, aromatic-H), 11.95 (broad s, COOH); mass spec., m/e (rel. intensity using linear mass scan) 240 (73), 222 (100), 207 (72).

D. Preparation of o-(4-Chlorobenzyl)benzoic Acid (Vf). Reduction of o-(4-Chlorobenzoyl)benzoic Acid (VIf).

The procedure on p. 91 for the preparation of o-(2-methylbenzyl)benzoic acid was followed using 735 g. (2.83 moles) of o-(4-chlorobenzoyl)benzoic acid (VIf)(Aldrich Chemical Co., Inc., Milwaukee, Wisc.), 1953 g. (29.87 moles) of zinc dust, 7280 ml. of 28% ammonium hydroxide solution, 70 ml. of saturated cupric sulfate solution and 1137 ml. of 20% sodium carbonate solution. The reaction mixture, after being refluxed for 30 hr., was worked-up using the same procedure as described on p. 91 to give 685.6 g. of white solid. The white solid, was recrystallized twice from benzene/hexane (1:1) to give 559.3 g. (80.5%) of o-(4-chlorobenzyl)benzoic acid (Vf); m.p. 131-132° (lit.[45] 130-132°, lit.[46] 132°); ir (KBr), 3300-2100 (COOH), 1665 (COOH) cm.$^{-1}$; nmr ($CDCl_3$), 4.40 (s, 2 H, CH_2), 7.0-8.2 (m, 8 H, aromatic-H), 12.17 (broad s, 1 H, COOH).

(III) Preparation of Substituted Anthrones.

A. Preparation of 2-Methylanthrone (IVb). Intramolecular Acylation of o-(4-Methylbenzyl)benzoic Acid (Vb).

To 300 ml. of cold (ice bath) concentrated H_2SO_4 was added 73.1 g. (0.324 mole) of pulverized and pre-cooled (-10°C) o-(4-methylbenzyl)benzoic acid (Vb) (p. 92). The mixture, after being stirred in the ice bath for 6 hr., was poured onto crushed ice to give a yellow precipitate which was filtered and washed with water to give 50.9 g. (75.5%) of crude product. The nmr spectrum indicated the crude product to be rather pure 2-methylanthrone (IVb). Recrystallization from methanol gave 37 g. (55%) of yellow-green IVb ; m.p. 98-101° (lit.[44] 99.5-100°, lit.[47] 103°, lit.[48] 100°); ir (KBr), 1645 (CO) $cm.^{-1}$; nmr ($CDCl_3$), 2.36 (s, 3 H, CH_3), 4.10 (s, 2 H,CH_2), 7.08-8.40 (m, 7 H, aromatic-H).

Attempts to recover additional product from the mother liquor by concentration or evaporation of solvent under reduced pressure gave a solid mixture of 2-methylanthrone (IVb), 2-methylanthraquinone (XXIIb), and, most probably, 2,2'-dimethyl-10,10'-bianthrone (XXIII). Although the isolation of XXIII was not attempted, this conclusion is based on similar experiences with other anthrones (pp. 96,97) where the corresponding bianthrones have been isolated and identified. The nmr spectrum of the mixture showed a group of aromatic absorptions at δ 6.6-6.8 and a singlet methine absorption at δ 4.58 that are characteristic of bianthrones (see pp.129,130).

B. Preparation of 4-Methylanthrone (IVd). Intramolecular Acylation of o-(2-Methylbenzyl)benzoic Acid (Vd).

A mixture of 43 g. (0.19 mole) of o-(2-methylbenzyl)-benzoic acid (Vd) (p. 91) and 650 ml. of 80% H_2SO_4 was heated at 80-90°C for 1.5 hr. with stirring. The dark-red solution was cooled to room temperature and poured into approximately 1000 g. of ice. The yellow precipitate obtained was washed consecutively with water, 5% sodium carbonate solution and water to give 40.7 g. of yellow solid. Its nmr spectrum was consistent with 4-methylanthrone (IVd). Recrystallization from MeOH gave 19.5 g. (49%) of 4-methylanthrone (IVd); m.p. 123-126° (lit.[41] 125.5-129.5°, lit.[18] 126°); ir (KBr), 1640 (CO) $cm.^{-1}$; nmr ($CDCl_3$), δ 2.28 (s, 3 H, CH_3), 3.88 (s, 2 H, CH_2), 7.0-7.6, 8.0-8.3 (m, 7 H, aromatic-H).

A mixture (7.2 g.) of 4-methylanthrone (IVd) and 4,4'-dimethyl-10,10'-bianthrone (XV) was obtained as the second crop by partial evaporation of the solvent (a similar phenomenon is discussed on p. 95). Evaporation of the resulting mother liquor gave an additional 5.1 g. of solid, which was shown to have an even higher percentage of the bianthrone (XVa) than the second crop, by nmr analysis. A sample of this mixture, when recrystallized from benzene, gave 4,4'-dimethyl-10,10'-bianthrone (XV), whose nmr and ir spectra were identical with that of an authentic sample prepared by a known method (p. 129).

C. Preparation of 1,4-Dimethylanthrone (IVe). Intramolecular Acylation of o-(2,5-Dimethylbenzyl)-benzoic Acid (Ve).

A mixture of pulverized o-(2,5-dimethylbenzyl)benzoic acid (Ve) (p. 93) (40.17 g., 0.17 mole) and 80% H_2SO_4 (650 ml.) was heated at 75-80°C for one hour with stirring. The solution, after being cooled to room temperature, was poured onto 1000 g. of crushed ice. The resulting yellow precipate was washed with 5% sodium carbonate solution and throughly with water to give 35.5 g. of crude product. Its nmr spectrum was consistent with 1,4-dimethylanthrone (IVe). Recrystallization from MeOH gave 24.3 g. (65%) of yellow 1,4-dimethylanthrone (IVe); m.p. 114-116° (lit.[49] 113°, lit.[13] 116°); ir (KBr), 1640 (CO) $cm.^{-1}$; nmr ($CDCl_3$), δ 2.23 (s, 3 H, CH_3 at C-4), 2.42 (d, 3 H, CH_3 at C-1), 3.86 (s, 2 H, CH_2), 6.8-8.2 (m, 6 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 222 (100), 207 (60).

A solid mixture (4.3 g.) of 1,4-dimethylanthrone (IVe) and 1,1'4,4'-tetramethyl-10,10'-bianthrone (XVI) was obtained as a second crop by concentration of the mother liquor. Further concentration gave 2.8 g. of 1,1'4,4'-tetramethyl-10,10'-bianthrone (XVI), which had identical nmr and ir spectra to that of an authentic sample prepared by an independent method (p. 130).

D. Preparation of 2-Chloroanthrone (IVf). Intramolecular Acylation of o-(4-Chlorobenzyl)benzoic Acid (Vf).

The procedure on (p. 95) for the preparation of 2-methylanthrone was followed using 80 g. (0.33 mole) of o-(4-chlorobenzyl)benzoic acid (Vf) (p. 94) and 300 ml. of concentrated H_2SO_4. The yellow precipitate obtained was thoroughly washed with water and recrystallized from 95% alcohol to give 60 g. (81%) of 2-chloroanthrone (IVf); m.p. 153° (lit.[46] 155°, lit.[45] 154-155°); ir (KBr), 1660 (CO) $cm.^{-1}$; nmr ($CDCl_3$), 4.2 (s, 2 H, CH_2), 7.2-8.4 (m, 7 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 230 (1.6), 228 (4.5), 214 (94), 179 (100).

An attempt to obtain a second crop of 2-chloroanthrone (IVf) by concentration of the mother liquor gave a mixture of solids. One of these solids was almost insoluble in most of the common solvents and could easily be separated. The soluble solid was shown to be 2-chloroanthrone (IVf) by nmr spectroscopy. The insoluble solid was recrystallized from a large volume of benzene to give white crystals; m.p. above 250° (dec.); ir (KBr), 1670 (CO) $cm.^{-1}$; nmr ($CDCl_3$), 4.72 (s, CH), 6.70-6.96, 7.32-7.52, 7.80-8.0 multiplets (m, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 454 (2.25), 452 (2.5), 229 (45), 227 (100), 175 (metastable).

The insoluble solid was most likely 3,3'-dichloro-10,-

10'-dianthrone (XX) perhaps formed during the recrystallization of 2-chloroanthrone (IVf). When a sample of once-recrystallized 2-chloroanthrone (IVf) was boiled in 95% alcohol for several hours, a large amount of the above solid was obtained. Barnett[19] has reported the preparation of 3,3'-dichloro-10,10'-dianthrone (XX) M.P. 240° (darkens) by oxidation of 2-chloroanthrone (IVf) with $FeCl_3$.

(IV) Preparation of 9,9'-Anthrapinacol (III) and Substituted 9,9'-Anthrapinacols.

Bimolecular Reduction of Anthrone and Substituted Anthrones.

A. Preparation of 9,9'-Anthrapinacol (III).

Aluminum amalgam was prepared according to the procedure of Schreibmann.[52] A mixture of 30 g. (1.1 g-atoms) of aluminum powder (20 mesh and finer), 15 g. of $HgCl_2$ (56 mmole.), and 150 ml. of THF was heated at reflux with stirring for 30 min. in a 3-l. three-necked flask equipped with a mechanical stirrer and reflux condenser. After cooling, the THF solution was carefully poured off, and the metallic residue was washed with small portions of THF and benzene in the original reaction flask. After pouring off the wash solvent, the wet aluminum amalgam was used immediately.

Anthrone (50 g., 0.258 mole) was dissolved in 600 ml. hot benzene. The benzene solution was filtered hot in order to remove a small amount of insoluble material (probably 3,3'-dichloro-10,10'-dianthrone (XX) (p.99)) and mixed with the aluminum amalgam prepared above. The mixture was heated to reflux with stirring for 30 min. With the heat source removed, 150 ml. of absolute alcohol was added over a period of 25 min. An exothermic reaction took place immediately. The reaction mixture turned green after 5 min. and became dark green and viscous within 30 min. The reaction mixture was refluxed for an additional 20 hr. and was then cooled to room temperature. Dilute HCl solution (2.4 M, 300 ml.) was added slowly with good stirring. The organic layer was isolated and washed with H_2O. White crystals began to form in the organic layer during washing. The organic layer was allowed to stand at room temperature overnight to complete crystallization. The white crystals (12.4 g.) obtained were shown to be pure 9,9'-anthrapinacol (III) by nmr and tlc analysis. Second and third crops (total 22.3 g.) were obtained by further concentration of the organic layer. However, they were shown to be mixtures of anthrone, anthracene, and 9,9'-anthrapinacol (III) by nmr and tlc analysis. Upon final evaporation of the resulting mother liquor under reduced pressure, additional yellow solid (12 g.) was obtained. This was shown to consist of mainly 9,10-dihyroanthracene with minor amounts of 9,9'-anthrapinacol and anthrone. The first crop of white crystals was recrystallized twice from benzene to yield pure 9,9'-anthrapinacol (III); m.p. 184-186° (lit.[50] 185.2-186.0°); ir (KBr), 3560, (OH) $cm.^{-1}$; nmr $CDCl_3$), δ 1.76, 1.96, 3.14, 3.34 (AB, J 20 Hz, 4 H, CH_2), 3.37 (s, 2 H, OH), 6.80-7.44 (m, 16 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 372 (44.3), 354 (100).

B. Preparation of 2,2'-Dimethyl-9,9'-anthrapinacol (IIIb). Bimolecular Reduction of 2-Methylanthrone (IVb).

In a 3-l. three-necked flask equipped with a mechanical stirrer and reflux condenser, aluminum amalgam was prepared as described on p. 100, using 40 g. (1.48 g.-atoms) of Al powder, 52 g. (0.19 mole) $HgCl_2$ and 250 ml. THF.

A mixture of 2-methylanthrone (IVb, 23 g., 0.11 mole), 800 ml. benzene and the aluminum amalgam was heated at reflux for 30 min. With the heat source removed, 150 ml. of absolute alcohol was added over a period of 10 min. The reaction mixture turned green in 15 min. and became dark green and viscous in 3 hr. More benzene (300 ml.) and aluminum amalgam (prepared from 6 g. Al powder, 10 g. $HgCl_2$ and 30 ml. THF) were added. The reaction mixture was kept at reflux for an additional 3.5 hr. After cooling to room temperature, 500 ml. of 2 M HCl was added, and the mixture was stirred vigorously for 15 min. The organic layer was washed with water, dried over $MgSO_4$, and evaporated under reduced pressure to give 22.6 g. of crude product.

The crude product was dissolved in 20 ml. $CHCl_3$ and 60 ml. benzene and chromatographed on 800 g. of silica gel (100-200 mesh) packed in a 4.2 cm. I.D. column. The column was eluted with benzene, and 20 ml. fractions were collected using an automatic fraction collector. Fractions were combined according to their tlc (silica gel GF, C_6H_6, UV visualization) behavior and nmr spectra. A mixture

(5.0 g.) of 2-methylanthracene (XIb), 2-methyl-9,10-dihydroanthracene (XIVb) and some unknown materials were collected, followed by 13.5 g. of 2,2'-dimethyl-9,9'-anthrapinacol (IIIb) (approx. 65-70% by nmr) contaminated with a small amount of 2-methylanthrone (IVb) and probably some 2-methylanthraquinone (XXIIb). After most of the 2,2'-dimethyl-9,9'-anthrapinacol (IIIb) was collected, the column was eluted with acetone to give 3.7 g. of yellow-brown solid which was shown by nmr spectroscopy to be a mixture of 2-methylanthrone (IVb) and probably 2,2'-dimethyl-10,10'-bianthrone (XXIII). The anthrapinacol (IIIb) thus obtained was used directly for the preparation of 2,2'-dimethyl-9,9'-bianthryl (IIb) without further purification. A sample of the chromatographed 2,2'-dimethyl-9,9'-anthrapinacol (IIIb) was repeatedly recrystallized from benzene to give a white solid; m.p. 164-165.5°; ir (KBr), 3540 (OH) cm.$^{-1}$; nmr ($CDCl_3$), δ 1.67, 1.86, 3.02, 3.21 (AB, J 19 Hz, 4 H, CH_2), 3.26 (s, 2 H, OH), 2.10, 2.18 (2 s, 6 H, CH_3), 6.60-7.20 (m, 14 H, aromatic-H).

C. Preparation of 3,3'-Dimethyl-9,9'-anthrapinacol (IIIc). Bimolecular Reduction of 3-Methylanthrone (IVc).

Aluminum amalgam was prepared as described on p. 100 using 12 g. Al, 5.0 g. $HgCl_2$ and 150 ml. THF.

A mixture of 13 g. 3-methylanthrone (IVc), 400 ml. benzene, and the aluminum amalgam was heated to reflux with stirring in a 2-l. three-necked flask, equipped with a mechanical stirrer and reflux condenser, for 30 min. With the heat source removed, 60 ml. of absolute ethanol was added slowly. A vigorous exothermic reaction took place immediately. The reaction mixture began to turn green and viscous. The heat source was replaced, and the reaction mixture was heated at reflux with stirring for an additional 20 hr. The viscous dark-green reaction mixture was cooled to room temperature and 300 ml. of HCl (2.4 M) was added slowly with good stirring. The organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated under reduced pressure to give 12.4 g. of solid which was purified by column chromatography.

A 20 g. sample of crude product from three different syntheses was chromatographed according to the procedure on p.   using 550 g. silica gel (100-200 mesh) and benzene. Three major fractions were obtained. Based on nmr spectra, the first fraction (2.43 g.) was a mixture of 2-methylanthracene (XIb) and 2-methyl-9,10-dihydroanthracene (XIVb). The second fraction (2.22 g.) was a mixture of 3,3'-dimethyl-9,9'-anthrapinacol (IIIc), 3-methylanthrone (IVc) and a small amount of unknown material. The third fraction (10.6 g.) was a mixture of 3,3'-dimethyl-9,9'-anthrapinacol (IIIc) and probably 3,3'-dimethyl-10,10'-bianthrone (XXIV). The second and third fractions were used without further purification for the preparation of 3,3'-dimethyl-9,9'-bianthryl (IIc) (p. 113).

A sample of the chromatographed 3,3'-dimethyl-9,9'-anthrapinacol (IIIc) was further purified by recrystallization from $CHCl_3$/hexane (with treatment of activated carbon) to give light yellow crystals. These crystals were digested with 95% EtOH at room temperature to give white crystalline, 3,3'-dimethyl-9,9'-anthrapinacol (IIIc); m.p. 165-167° (lit.[53] 166°); ir (KBr) 3640 (OH) $cm.^{-1}$; nmr ($CDCl_3$), δ 2.71, 2.90, 3.07, 3.26 (AB, J 19 Hz, 4 H, CH_2), 3.20-3.33 (s, 2 H, OH), 2.29 (s, 6 H, CH_3), 6.20-7.60 (m, 14 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 400 (50.1), 382 (100).

D. Preparation of 4,4'-Dimethyl-9,9'-anthrapinacol (IIId). Bimolecular Reduction of 4-Methylanthrone (IVd).

Aluminum amalgam was prepared as described on p. 100 using 8.5 g (0.31 g-atom) Al, 4.3 g (16 mmole.) $HgCl_2$, and 120 ml. THF.

The procedure on p.104 for the preparation of 3,3'-dimethyl-9,9'-anthrapinacol (IIIc) was followed using 15 g. (0.072 mole) of 4-methylanthrone (IVd) (p. 96), 300 ml. of benzene, and 60 ml. of absolute alcohol. The reaction mixture was refluxed for an additional 4.5 hr. after the addition of ethanol was completed. The reaction mixture, after work-up in the same manner as on p.103, gave 16.1 g. of crude product.

The crude product was dissolved in 30 ml. $CHCl_3$ and coated on 30 g. of silica gel (100-200 mesh) by evaporation of the solvent. The solid mixture was placed on top of a silica gel column (400 g., 100-200 mesh, packed dry in 4.2 cm. I.D. glass tube) and eluted with benzene. Approximately 20 ml. fractions were collected using an automatic fraction collector. The fractions were combined according to their tlc behavior and their nmr spectra to give three major fractions. The first fraction (1.65 g.) was a mixture of 1-methylanthracene (XIa) and 1-methyl-9,10-dihydroanthracene (XIVa). The second fraction (7.53 g.) was a mixture of 4-methylanthrone (IVd) (approx. 50%), and 4,4'-dimethyl-9,9'-anthrapinacol (IIId) (approx. 50%). The third fraction, which was eluted with acetone, was a mixture of 4-methylanthrone (IVd) (approx. 30%), a small amount of 4,4'-dimethylanthrapinacol (IIId) (approx. 10%) and a large amount of 4,4'-dimethyl-10,10'-bianthrone (XV) (approx. 60%).

The third fraction, when digested with hot hexane, gave 1.1 g. of an insoluble solid, which had an identical nmr spectrum to an authentic sample of 4,4'-dimethyl-10,10'-bianthrone (XV), prepared by a known method[18] (p. 129).

The second fraction, after digestion with 5% benzene/hexane at reflux, gave a white solid (6.37 g.) which was used for the synthesis of 4,4'-dimethyl-9,9'-bianthryl (IId) without further purification.

Attempts to purify a sample of 4,4'-dimethyl-9,9'-anthrapinacol (IIId) for analysis by recrystallization (benzene) or preparative thick layer chromatography (silica gel GF, 2000 microns, benzene/hexane (20:80) were unsuccessful. According to nmr spectroscopy, 4-methylanthrone could not be completely removed.

E. Preparation of 2,2'-Dichloro-9,9'-anthrapinacol (IIIf). Bimolecular Reduction of 2-Chloroanthrone (IVf).

Aluminum amalgam was prepared as described on p. 100 using 6.0 g. (0.22 g-atom) Al powder, 2.0 g. (7.4 mmole.) $HgCl_2$ and 80 ml. THF.

The procedure on p. 104 for the preparation of 3,3'-dimethyl-9,9'-anthrapinacol (IIIc) was followed using 10.0 g. (43.9 mmole.) 2-chloroanthrone (IVf) (p. 98), 300 ml. benzene, and 60 ml. absolute alcohol. The reaction mixture was refluxed for 6 hr. after the addition of absolute alcohol. To the cold reaction mixture was added 150 ml. of 7.5% HCl with good stirring. The aqueous layer was washed twice with 50 ml. portions of benzene. All organic layers were combined and washed three times with 100 ml. portions of H_2O. The organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give a solid. The solid was digested twice with 100 ml. portion of refluxing cyclohexane to give 6.7 g. (67%) of 2,2'-dichloro-9,9'-anthrapinacol (IIIf), suitable for the synthesis of 2,2'-dichloro-9,9'-bianthryl (IIf). Recrystallization from benzene/cyclohexane (1:1) gave an analytical sample of 2,2'-dichloro-9,9'-anthrapinacol (IIIf); m.p. 182-184°; ir (KBr), 3560 (sh), 3510 cm.$^{-1}$ (OH); nmr ($CDCl_3$), δ 1.86, 2.06, 3.19, 3.39 (AB, J 20 Hz, CH_2), 3.25 (s, OH), 6.8-7.4 (m, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 444 (10), 442 (44), 440 (62), 426 (6), 424 (24), 422 (37), 231 (36), 230 (54), 229 (100), 228 (100).

Anal. Calcd for $C_{28}H_{20}O_2Cl_2$: C, 73.21; H, 4.39; Cl, 15.44. Found: C, 73.03; H, 4.31; Cl, 15.44.

F. Attempted Preparation of 1,1'4,4'-Tetramethyl-9,9'-anthrapinacol (IIIe).

Bimolecular Reduction of 1,4-Dimethylanthrone (IVe).

Aluminum amalgam was prepared as described on p. 100 using 2.9 g. (0.17 g-atom) Al powder, 1.54 g. (5.6 mmole.) $HgCl_2$, and 50 ml. THF.

The procedure on p.104 for the preparation of 3,3'-dimethyl-9,9'-anthrapinacol (IIIc) was followed, using 5 g. (22.5 mmole.) 1,4-dimethylanthrone (IVe), 25 ml. absolute ethanol and 250 ml. benzene. The reaction mixture did not change color or become viscous after 2 hr. More Al(Hg), prepared from 2.9 g. (0.17 g-atom) Al powder, 1.54 g. (5.6 mmole.) $HgCl_2$, and 50 ml. THF, was added to the reaction mixture. The reaction was continued for a total of 20 hr. No obvious change in color or viscosity (as observed in the successful preparations of 9,9'-anthrapinacols) was observed. The reaction mixture, after work-up following the usual procedure (p.104), gave 4.7 g. of yellow liquid, which solidified upon cooling. The solid was shown to be 1,4-dimethyl-9,10-dihydroanthracene (XIVe) by nmr and mass spectroscopy. Recrystallization from 95% ethanol gave white crystalline needles; m.p. 59-60°; nmr ($CDCl_3$), δ 2.21 (s, 6 H, CH_3), 3. 73 (s, 4 H, CH_2), 6.8 (s, 2 H, aromatic-H) 7.06 (broad s, 4 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 208 (100), 206 (149).

(V) Preparation of 9,9'-Bianthryl (II) and Substituted 9,9'-Bianthryls.

A. Preparation of 9,9'-Bianthryl (II). Dehydration of 9,9'-Anthrapinacol (III).

9,9'-Anthrapinacol (III) (p.100) (10 g., 22 mmole.), acetic acid (190 ml.) concentrated sulfuric acid (130 ml.) and water (60 ml.) were placed in a 500-ml. three-necked flask equipped with a magnetic stirrer and a reflux condenser. The mixture was heated at 95-100°C for 5 hr. White-green crystals gradually formed. The mixture, after cooling to room temperature, was poured into 300 ml. of cold water to give a green precipitate. Recrystallization from benzene gave 7.16 g. (76.5%) of light green 9,9'-bianthryl (II); m.p. 323-325° (lit.[54] 300°, lit.[55] 308°); nmr ($CDCl_3$), δ 7.0-7.6 (m, 12 H, aromatic-H at C-1, 2,3,6,7,8 and 1',2',3',4', 5',6',7',8'), 8.07, 8.15 (d, J 8 Hz, 4 H, aromatic-H at C-4, 5 and 4',5'), 8.58 (s, 2 H, aromatic-H at C-9, 10); mass spec., m/e (rel. intensity using linear mass scan) 354 (100), 337 (8.24).

B. Preparation of 2,2'-Dimethyl-9,9'-bianthryl (IIb). Dehydration of 2,2'-Dimethyl-9,9'-anthrapinacol (IIIb).

The procedure on p. 111 for the preparation of 9,9'-bianthryl (II) was followed, using 7 g. (16.7 mmole.) of 2,2'-dimethyl-9,9'-anthrapinacol (IIIb) (p.102), 200 ml. 70% H_2SO_4 and 200 ml. HOAc. The tan-colored precipitate obtained was recystallized from acetonitrile to give 3.1 g. (48%) of light yellow 2,2'-dimethyl-9,9'-bianthryl (IIb); m.p. 278-280° (lit.[7] 273.8-275.0°); nmr ($CDCl_3$), δ 2.03 (s, 6 H, CH_3), 6.82-8.09 (m, 14 H, aromatic-H), 8.55 (s, 2 H, aromatic-H at C-9, 10); uv ($CHCl_3$), λmax (log ε) 394.8 (4.34) 374.2 (4.25), 355.0 (4.05), 337.5 (3.81), 320.9 sh. (3.51); mass spec., m/e (rel. intensity using linear mass scan) 382 (100), 365 (6), 364 (4), 351 (11), 350 (9), 337 (3).

C. Preparation of 3,3'-Dimethyl-9,9'-bianthryl (IIc). Dehydration of 3,3'-Dimethyl-9,9'-anthrapinacol (IIIc).

The procedure on p. 111 for the preparation of 9,9'-bianthryl (II) was followed, using 8.5 g. (20.3 mmole.) 3,3'-dimethyl-9,9'-anthrapinacol (IIIc) (p. 104), 100 ml. 70% H_2SO_4, and 100 ml. HOAc. The precipitate obtained was recrystallized twice from acetone/MeOH (1:1) to give 1.64 g. of pale yellow 3,3'-dimethyl-9,9'-bianthryl (IIc); m.p. 258-261° (lit.[55] 268°); nmr ($CDCl_3$), δ 2.44 (s, 6 H, CH_3), 6.80-8.04 (m, 14 H, aromatic-H), 8.44 (s, 2 H, aromatic-H at C-9,10); mass spec., m/e (rel. intensity using linear mass scan) 382 (100), 365 (5), 364 (10), 351 (6), 350 (9), 337 (5).

The activated carbon used in the recrystallization had removed quite a large amount of 3,3'-dimethyl-9,9'-bianthryl (IIc). The activated carbon was extracted with $CHCl_3$. The dark red chloroform solution was evaporated under reduced pressure to give 1.85 g. of dark solid. This solid was chromatographed on 85 g. of alumina (dry column) using hexane/benzene (75:25) as eluent to yield 1.18 g. of 3,3'-dimethyl-9,9'-bianthryl (IIc), m.p. 258-261°. The total yield of IIc in this preparation was 36.6%.

D. Preparation of 4,4'-Dimethyl-9,9'-bianthryl (IId). Dehydration of 4,4'-Dimethyl-9,9'-anthrapinacol (IIId).

The procedure on p. 111 for the preparation of 9,9'-bianthryl (II) was followed using 4.0 g. (9.5 mmole.) of 4,4'-dimethyl-9,9'-anthrapinacol (IIId) (p. 106), 100 ml. 80% H_2SO_4, and 80 ml. HOAc. The crude product (3.5 g.) was dissolved in $CHCl_3$ and coated on 30 g. of silica gel (100-200 mesh) by evaporation of the $CHCl_3$ under reduced pressure. The resulting solid was placed on top of a column of silica gel (170 g., 2.7 cm. I.D., packed dry). Using benzene/hexane (30:70) as eluent, 2.8 g. of an off-white solid (m.p. 302-305°) was obtained. This solid was further purified by recrystallization from $CHCl_3$/acetone (1:1) and then $CHCl_3$ to give an analytical sample of 4,4'-dimethyl-9,9'-bianthryl (IId); m.p. 303-306°; nmr ($CDCl_3$), δ 2.92 (s, 6 H, CH_3), 6.8-8.2 (m, 14 H, aromatic-H), 8.74 (s, 2 H, aromatic-H at C-9,10); uv ($CHCl_3$), λmax (log ε) 321.0 sh. (3.46), 338.1 (3.78), 355.6 (4.06), 374.5 (4.33), 396.0 (4.43); mass spec., m/e (rel. intensity using linear mass scan) 382 (100), 365 (10), 364 (8), 351 (17), 350 (10), 337 (5).

Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found; C, 94.21; H, 5.77.

E. Preparation of 2,2'-Dichloro-9,9'-bianthryl (IIf). Dehydration of 2,2'-Dichloro-9,9'-anthrapinacol (IIIf).

In a 250-ml. three-necked flask equipped with a magnetic stirrer and a reflux condenser were placed 3.0 g. (6.6 mmole.) of 2,2'-dichloro-9,9'-anthrapinacol (IIIf) (p. 108), 30 ml. acetic acid and 30 ml. 70% H_2SO_4. The reaction mixture was heated at 98-99° (oil bath) for 5 hr. After cooling to room temperature, 200 ml. of water was added, and the yellow solid was isolated. The yellow solid, after being washed with a large amount of water, was digested with 150 ml. refluxing 95% alcohol. The mixture was filtered while still warm, and the solid was washed with several portions of cold alcohol until the washings became colorless. The tan-colored 2,2'-dichloro-9,9'-bianthryl (IIf) (2.19 g., 80%, m.p. 280-282°) obtained was suitable for the synthesis of 2,2'-dicyano-9,9'-bianthryl (IIk). Recrystallization from EtOH/benzene (2.5:1) gave pure 2,2'-dichloro-9,9'-bianthryl (IIf); m.p. 296-298° (lit.[56] 289°); nmr ($CDCl_3$), δ 8.68 (s, 2 H, aromatic-H at C-10), 8.0-8.2 (two sets of d, J 9.5 Hz, 4 H, aromatic-H at C-4,5), 6.8-7.7 (m, 10 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 426 (14.4), 424 (70.2), 422 (100).

F. Preparation of 2,2'-Dicyano-9,9'-bianthryl (IIk). Reaction of 2,2'-Dichloro-9,9'-bianthryl (IIf) with CuCN.

In a 2-l. three-necked flask equipped with a mechanical stirrer, reflux condenser and heating mantle were placed 20 g. (0.045 mole) of 2,2'-dichloro-9,9'-bianthryl (IIf) (p. 115), 48 g. (0.54 mole) of cuprous cyanide and 450 ml. of N-methyl-2-pyrrolidinone. The reaction mixture was heated to reflux with continuous stirring. A thin coat of brown solid possibly metallic copper) was observed on the reaction flask after 24 hr. of reflux. The reaction mixture was refluxed for 72 hr. and cooled to room temperature. A ferric chloride solution (prepared from 250 g. $FeCl_3 \cdot (H_2O)_6$, (0.93 mole), 65 ml. HCl, and 400 ml. H_2O), was added. The mixture was heated at 75-80°C with stirring for 1.5 hr. Two liters of water was added which precipitated a black product. The black precipitate was isolated and washed with a large volume of water, followed by warm 95% ethanol until the ethanol washings became nearly colorless. This material was air-dried and mixed with 340 ml. $CHCl_3$. After removal of $CHCl_3$- insoluble material by filtration, the $CHCl_3$ solution was treated with approximately 50 g. of activated carbon to give a yellow $CHCl_3$ solution. Evaporation of the $CHCl_3$ under reduced pressure gave 9.5 g. of yellow, crude product. Recrystallization from $CHCl_3$/95% EtOH (1:2) yielded yellow crystals; m.p. 341-346°C. Mass spectral analysis indicated the presence of 2-chloro-2'-cyano-9,9'-bianthryl (IIr) which could not be removed by further repeated recrystallization.

A 10 g. sample of recrystallized 2,2'-dicyano-9,9'-bianthryl (IIk) was chromatographed on 350 g. silica gel (100-200 mesh) packed as slurry in a 3 cm. I.D. column using $C_6H_6/CHCl_3$ (1:1) as eluent. Fractions of 20 ml. each were collected and combined according to their tlc (silica gel GF, $C_6H_6/CHCl_3$ (1:1), uv visualization) behavior. The tlc behavior and ir spectroscopy of the first material (0.24 g.) eluted from the column was identical to that exhibited by a known sample of 2-chloro-2'-cyano-9,9'-bianthryl (IIr). The ms of this sample also gave a mass value of 413 (the molecular weight of IIr). This material was followed by a mixture of IIr and 2,2'-dicyano-9,9'-bianthryl IIk Dicyano-9,9'-bianthryl (IIk) (7.01 g.) was then collected. Other material (0.6 g.) collected after IIk was not identified. The chromatographed 2,2'-dicyano-9,9'-bianthryl (IIk) was recrystallized from benzene, to give greenish-yellow crystals; m.p. 342.5-345.5° (a sample from the work of reference 7 showed a m.p. of 341-345°); ir (KBr), 2250 cm.$^{-1}$ (CN); nmr ($CDCl_3$), δ 6.96-7.60 (m, 10 H, aromatic-H), 8.12-8.28 (m, 4 H, aromatic-H), 8.74 (s, 2 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 404 (100), 378 (13), 377 (15).

G. Preparation of 2,2'-Dicarboxy-9,9'-bianthryl (IIg). Hydrolysis of 2,2'-Dicyano-9,9'-bianthryl (IIk).

2,2'-Dicyano-9,9'-bianthryl (IIk) (p. 116) (3 g., 7.4 mmole.) 375 ml. MeOH, 100 ml. H_2O and 94 g. KOH were placed in a 500-ml. three-necked flask, equipped with a mechanical stirrer, reflux condenser and a heating mantle. The mixture was heated at reflux with stirring for 28 hr. Water (300 ml.) was added to the cooled reaction mixture, and the mixture was filtered to remove a small amount of insoluble material. The filtrate was acidified with concentrated HCl to give a yellow precipitate which was washed with a large volume of water and recrystallized from 800 ml. of acetic acid to yield 2.55 g. (from three crops) of 2,2'-dicarboxy-9,9'-bianthryl (IIg); m.p. 412-417° (lit.[7] 419.5-420.5° dec.); ir (KBr) 3600-2400 (COOH), 1680 (COOH) cm.$^{-1}$; mass spec., m/e (rel. intensity using linear mass scan) 442 (100), 398 (32), 350 (28).

H. Preparation of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (IIh). Reaction of (-)2,2'-Dicarboxy-9,9'-bianthryl (IIg) with Diazomethane.

Into a 200 ml. one-necked flask equipped with magnetic stirrer and a Claisen distillation adaptor, was placed an alcoholic potassium hydroxide solution consisting of 5 g. KOH, 25 ml. 95% ethanol and 8 ml. H_2O. On top of the straight arm of the Claisen distillation adaptor was placed a pressure equalizing addition funnel containing 19 g. (88.7 mmole.) of Diazald (N-methyl-N-nitroso-p-toluenesulfonamide, Aldrich Chemical Inc., Milwaukee, Wisc.) dissolved in 200 ml. of anhydrous ether. The take-off arm of the adaptor was connected to a water-cooled condenser, which was attached to a 2-l. Erlenmyer flask through a vacuum distillation head. In the Erlemyer flask, which was equipped with a magnetic stirrer, was placed 4.0 g. (9.1 mmole.) of (-)2,2'-dicarboxy-9,9'-bianthryl* $[\alpha]_D^{23}$ -115.6 (c 0.5, CH_3OH) dissolved in 1200 ml. dioxane.

The Diazald solution was added slowly to the vigorously stirred, hot (60±3°C) alcoholic KOH solution. The diazomethane generated was distilled directly into the stirred (-)2,2'-dicarboxyl-9,9'-bianthryl solution (at room temperature). Slight bubbling was observed during distillation. The original yellow fluorescence began to disappear to give a yellow solution. A deep yellow solution was obtained after two-thirds of the Diazald solution had been added, in 2 hr.

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* Prepared by Mr. C. H. Chen of these laboratories, following the pattern of C. Koukotas.[7]

The generation of diazomethane was stopped and the excess diazomethane in the reaction solution was destroyed by the addition of 10 ml. HOAc. Upon evaporation of the solution under reduced pressure, a yellow-brown solid was obtained. This solid, dissolved in $CHCl_3$, was coated on 30 g. silica gel (100-200 mesh), using a rotatory evaporator to remove the solvent. The coated silica gel was placed on top of a column of 250 g. of silica gel (100-200 mesh, packed dry in a 3.6 cm I.D. glass tube). The column was developed with $C_6H_6/CHCl_3$ (1:1). After 3-l. of solvent was passed through, a distinct yellow band near the bottom of the column was observed. This yellow band was cut out and extracted with $CHCl_3$. Upon evaporation of the chloroform under reduced pressure, 3.95 g. (92.5%) of (-)2,2'-dicarbomethoxy-9,9'-bianthryl (IIh) was obtained; m.p. 235-237°; ir (KBr), 1715 cm.$^{-1}$ (COOMe); nmr ($CDCl_3$), δ 3.62 (s, 6 H, CH_3O), 6.8-8.2 (m, 14 H, aromatic-H), 8.63 (s, 2 H, aromatic-H at C-10 and C-10'); uv ($CHCl_3$, λmax (log ε) 329.8 (3.62), 345.6 (3.83), 366.0 (3.98), 388.9 (4.10), 411.8 (4.21); mass spec., m/e (rel. intensity using linear mass scan) 470 (100), 439 (18), 411 (8), 350 (64), 337 (7); $[\alpha]_D^{23}$ -149.2° (c 0.3, $CHCl_3$); -139° (c 0.3, acetone).

I. Preparation of 2,2'-Di-(chlorocarbonyl)-9,9'-biantbryl (IIi).

Reaction of Oxalyl Chloride with 2,2'-dicarboxy-9,9'-bianthryl (IIg).

A mixture of 1.3 g. (2.9 mmole.) 2,2'-dicarboxyl-9,9'-bianthryl (IIg) (p. 118), 40 ml. oxalyl chloride and 300 ml. benzene (dried over Na) was refluxed with stirring for 72 hr. After cooling, the yellow solution was filtered, and the filtrate was evaporated under reduced pressure to give a yellow solid. The solid was dried under vacuum (0.75-1 mm Hg) at 120°C over-night and recrystallized (with treatment with activated carbon), twice from CCl_4 to give 1.12 g. (two crops, 80%) of 2,2'-Di-(chlorocarbonyl)-9,9'-bianthryl (IIi). Repeated recrystallization of IIi from CCl_4 always gave yellow crystals which, upon heating, began to melt in the range of 256-262°, resolidified at 263-264°, and melted again at 275-279°: ir (KBr), 1750 (CO) $cm.^{-1}$; nmr ($CDCl_3$), δ 7.04-8.48 (m, aromatic-H), 8.92 (s, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 482 (15.8), 480 (66.9), 478 (100), 445 (37.0), 443 (91.2).

Anal. Calcd for $C_{30}H_{16}Cl_2O_2$: C, 75.17; H, 3.36; Cl, 14.79. Found: C, 74.07; H, 3.54; Cl, 16.72.

J. Preparation of 2,2'-(N,N'-(α,α'-p-xylyl)dicarboxamido-9,9'-bianthryl (IIm).

1. Preparation of p-Phenylenediacetamide (XXIc).

A mixture of 15.5 g. (79.9 mmole.) p-phenylenediacetic acid (Aldrich Chemical Co., Inc., Milwaukee Wisc.), 56.0 g. (512 mmole.) $SOCl_2$ and 360 ml. absolute ether was refluxed, with magnetic stirring, for 24 hr. The yellow reaction solution was filtered and the filtrate evaporated under reduced pressure to give a yellow-brown liquid that solidified upon cooling. The solid,* p-phenylenediacetyl dichloride (XXId) was dissolved in 100 ml. acetone (dried over $MgSO_4$), and the acetone solution was added slowly into 150 ml. of vigorously stirred NH_4OH (28%) solution to give a white precipitate. To this reaction mixture was added 100 ml. of H_2O. The white precipitate, was isolated by filtration, washed with a large volume of water, rinsed with acetone, and recrystallized from n-propanol/water (1:1) to give 8.1 g. (52.8%) of p-phenylenediacetamide (XXIc) (m.p. 294-303°) which was used for the synthesis of α,α'-diaminoxylene (XXIa) without further purification. Two recrystallizations of a small quantity from n-propanol/water (1:1) gave white p-phenylenediacetamide (XXIc); m.p. 308-312° (lit.[59] >290°, lit.[60] 294-298°); ir (KBr), 3170, 3350 (NH_2), 1635, 1660 ($CONH_2$), 1410 (CH_2) cm.$^{-1}$; mass spec., m/e (rel. intensity using linear mass scan) 192 (26), 149 (100), 105 (100).

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*A small quantity was sublimed (50°C, 4 mm Hg) to give a white solid; m.p. 62-64°C; ir (KBr) 1780, 1700 (sh) (COCl) cm.$^{-1}$; nmr (acetone-d_6), 4.36 (s, 4 H, CH_2), 7.36 (s, 4 H, aromatic-H).

2. Preparation of α,α'-Diaminoxylene (XXIa). Hoffmann Rearrangement of p-Phenylenediacetamide (XXIc).

Into a cold (ice bath) NaOH solution (24 g., 0.60 mole NaOH, 240 ml. H_2O) was added, dropwise, 10.2 g. (63.7 mmole.) of Br_2 to produce a pale yellow NaOBr solution. With continuous stirring, p-phenylenediacetamide (XXIc) (p. 122) (6.2 g. 32 mmole.) was added to this solution in small portions. The mixture was stirred at 0°C for 30 min., and the temperature was slowly raised to 55-60°C over a period of 30 min. The mixture was kept at this temperature for 45 min. After cooling to room temperature, the solution was filtered and extracted ten times with 30-ml. portions of $CHCl_3$. The $CHCl_3$ solution gave a light yellow solid upon evaporation under reduced pressure. The solid was sublimed (45-50°C, 0.8 mm Hg, alcohol, at 6°C, was circulated through the condenser) to give 1.91 g. (45%) α,α'-diaminoxylene (XXIa); m.p. 60-62° (lit.[61] 60°); nmr ($CDCl_3$), δ 1.46 (s, 4 H, NH_2), 3.88 (s, 4 H, CH_2), 7.36 (s, 4 H, aromatic-H).

α,α'-Diaminoxylene (XXIa) is very hydroscopic and appears to rapidly react with the CO_2 in the atmosphere. When a sample of XXIa was exposed to the atmosphere, it became wet immediately. Upon exposure to dry air in a dry box, XXIa turned into a white solid which had a m.p. of 164-173°C and was insoluble in inorganic solvents but soluble in H_2O. The white solid dissolved readily and gave off gas when treated with HCl(20%). A white solid residue (m.p. 300°C) was obtained when the HCl solution was evaporated in an oven at

80°C. The white solid obtained from the reaction of XXIa and air was most likely the carbonate of XXIa, and the white solid from the reaction with HCl solution was most likely the amine hydrochloride. It is a well known fact that alkylamines are reactive to CO_2 in air.[64] α,α'-Diaminoxylene (XXIa) reacted with benzoyl chloride (using triethylamine as catalyst) in CH_2Cl_2 or CCl_4 at room temperature to give the dibenzamide, which was recrystallized from 95% EtOH to give fluffy crystals; m.p. 198-200° (lit.[62] 196-196.5°); ir (KBr), 3320 (NH), 1635 (CONH) $cm.^{-1}$; mass spec., m/e (rel. intensity using linear mass scan) 344 (2), 239 (3), 224 (60), 223 (85), 105 (100).

3. Reaction of 2,2'-Di-(chlorocarbonyl)-9,9'-bianthryl (IIi) with α,α'-Diaminoxylene (XXIa).

The synthesis of 2,2'-(N,N'-(α,α'-p-xylyl)dicarboxamido-9,9'-bianthryl (IIm) was carried out using a Synchronous Constant Volume Addition Double High Dilution apparatus (pp. 81 - 83). Since the preliminary calibrations indicated that the volume ratio delivered by the two dispensing units was 1.44, 592.3 mg. (1.239 mmole.) of 2,2'-di-(chlorocarbonyl)-9,9'-bianthryl (IIi) (p. 121) and 178.3 mg. (1.313 mmole.) of α,α'-diaminoxylene (p. 123) were each dissolved in 500 ml. benzene (dried over Na), and their benzene solutions were filtered and diluted to exactly 1,440 ml. and 1,000 ml., respectively. The two solutions were placed in the corresponding dispensing units and added simultaneously to the Double High Dilution system, which contained 7.5 l. of refluxing benzene (dried over Na) and 2.5 g. (11.7 mmole.) of 1,8-bis-(dimethylamine)napththalene (porton sponge, Aldrich Chemicals Co., Inc., Milwaukee, Wisc.). The addition time interval was set at 1.5 min. The total addition time was 142 hr. After five days, a small amount of white solid was found forming on the wall of the high-dilution side arm of the α,α'-diaminoxylene (XXIa) branch. The white solid was found to be the hydrochloride salt of α,α'-diaminoxylene (XXIa). More "proton sponge" (1.0 g., 4.7 mmole.) was therefore added to the reaction mixture. At the end of the diamine (XXIa) addition, 133 ml. (9.3%) of 2,2'-di-(chlorocarbonyl)-9,9'-bianthryl (IIi) solution was left unadded. The reaction mixture was refluxed for an additional 30 min., cooled to room temperature, and filtered to remove a yellow insoluble solid (157 mg.). The filtrate was concentrated by distillation to 400 ml. and stored at room temperature over-night to yield 126 mg. of yellow crystals. The filtrate was evaporated under reduced pressure to dryness to yield a yellow, oily, semi-solid which, after being digested with hexane, gave an additional 312 mg. more of yellow crystals. The two crops of yellow crystals were combined and dissolved in 150 ml. $CHCl_3$. The $CHCl_3$ solution was washed with dilute HCl and water, dried over $MgSO_4$, and concentrated to approximately 20 ml. A small portion (5 ml.) of cyclohexane was added. The solution, after cooling to room temperature, was allowed to remain at -10°C for several days to yield 0.2 g. (30%)

of yellow crystals whose ir and mass spectra were consistent with IIm. A sample of the yellow crystals was further purified by thick layer chromatography (alumina, 2,000 micron, $CHCl_3$) and several recrystallizations from $CHCl_3$ at -10°C to give an analytical sample of 2,2'-(N,N'-(α,α'-p-xylyl)dicarboxyamido-9,9'-bianthryl (IIm); m.p. 370-375° dec.; ir (KBr), 3200-3600 (broad NH), 3050 (aromatic-CH), 2940 (CH_2), 1640 (amide-CO) cm.$^{-1}$; mass spec., m/e (rel. intensity using linear mass scan) 542 (100), 514 (7.2) 424 (43.1), 271 (9.9).

Anal. Calcd for $C_{38}H_{26}N_2O_2$: C, 84.11; H, 4.83; N, 5.16. Found: C, 83.98; H, 4.62; N, 5.04.

Reactions using either triethylamine (TEA) or pyridine as base and either benzene or carbon tetrachloride as solvent were tried. In the case of TEA/benzene, similar yield of IIm was obtained. The other combinations were unsatisfactory. In some cases, 2,2'-bis-(N,N-diethylamido-9,9'-bianthryl (IIo) was isolated as the major product (see discussion section, P. 79).

K. Attempted Preparation of 2,2'-(Oxydicarbonyl)-9,9'-bianthryl (IIj).

Dehydration of 2,2'-Dicarboxy-9,9'-bianthryl (IIg) with Acetic Anhydride.

In a 500-ml. one-necked flask, equipped with a reflux condenser, were placed 5.0 g. of 2,2'-dicarboxy-9,9'-bi anthryl (IIg) and 150 ml. acetic anhydride. The mixture was heated at reflux for 1 hr. acetic acid and acetic anhydride was distilled off until approximately 50 ml. of solution remained. The solution was cooled to room temperature and placed in a refrigerator at 10°C, to give 5.6 g. (two crops) of yellow solid. This solid was recrystallized again from acetic anhydride (filtered at 10°C) to give 5.1 g. (two crops) of yellow crystals; m.p. 203-205° (foaming); ir (KBr), 1798, 1720 (CO-O-CO), 1610 (aromatic) cm.$^{-1}$; nmr ($CDCl_3$), δ 2.03 (s, CH_3), 7.0-8.4 (m, aromatic-H), 8.80 (s, aromatic-H at C-10, 10'); mass spec., m/e (rel. intensity using linear mass scan) 526.

The above spectral data indicate that the yellow crystals were the mixed anhydride, 9,9'-bianthracene-2,2'-dicarboxylic diacetic anhydride (IIs), from 2,2'-dicarboxy-9,9'-bianthryl (IIg) and acetic acid. Based on the amount of IIg used, the yield was 85%. The mixed anhydride, IIs, was found to be very unstable. Attempts to recrystallized a sample of it from other solvents, for analysis, gave erratic results. Acetone, acetonitrile and chloroform, pre-dried over Na_2SO_4, gave the hydrolysis product, 2,2'-dicarboxy-9,9'bianthryl

(IIg). Only once were yellow crystals (m.p. 210-211°C) of the mixed anhydride (IIs) obtained. This was with freshly prepared absolute chloroform (method of Morgan and Lowry[63]). Other attempts using absolute $CHCl_3$ gave unexplained results. When benzene was used as the recrystallizing solvent, yellow crystals formed very slowly which had the following physical properties; m.p. >450° dec., ir (KBr) 1770, 1715 (CO-O-CO), 1618 (aromatic) $cm.^{-1}$ (the fingerprint region was different from that of IIs); mass spec., m/e (rel. intensity using linear mass scan) 848 (100), 804 (32), 732 (55), 350 (90); insoluble in most of the common solvents. When these crystals were heated in aqueous potassium methoxide, and the resulting solution acidified, a quantitative yield of 2,2'-dicarboxyl-9,9'-bianthryl (IIg) was obtained. These yellow crystals were most likely the cyclic, dimeric anhydride of 2,2'-dicarboxy-9,9'-bianthryl (IIt). This cyclic anhydride, IIl, could also be obtained (based on ir analysis) by heating a sample of mixed anhydride, IIs, at 250°C for 2 hr.

(VI) Preparation of Substituted 10,10'-Bianthrones.

A. Preparation of 4,4'-Dimethyl-10,10'-bianthrone (XV). Oxidative Coupling of 4-Methylanthrone (IVd).

A mixture of 1.5 g. (7.2 mmole.) 4-methylanthrone (IVd) (p. 96), 1.4 g. (8.6 mmole.) $FeCl_3$ (anhydrous), and 20 ml. HOAc was refluxed with magnetic stirring for 1.5 hr. The resulting dark-red solution was poured into 200 ml. H_2O. The precipitate formed was washed with water, dilute HCl and water to give 1.31 g. of dark solid. This solid was dissolved in acetone, and the acetone solution was treated with activated carbon and evaporated under reduced pressure to give a pink solid. The pink solid was recrystallized once from C_6H_6/hexane (1:3) and once from C_6H_6 to give a white solid; m.p. 220-223° (lit.[18] 233°); ir (KBr), 1650 (CO) cm.$^{-1}$; nmr ($CDCl_3$), δ 2.01 (s, 1 H, CH_3), 2.71 (s, 5 H, CH_3), 4.83 (s, 2 H, CH) 5.91, 5.99 (d, J 8 Hz, 2 H, aromatic-H), 6.8-7.8 (three m, 12 H, aromatic-H), (C_6D_6 with a small amount of $CDCl_3$ to assist dissolution, 1.66 (s), 2.22 (s), 4.52 (s), 4.55 (s), 5.74, 5.81 (d, J 7 Hz), 6.6-7.2 (m), 7.8-8.2 (m); mass spec., m/e (rel. intensity using linear mass scan) 414 (100), 398 (35).

B. Preparation of 1,1'4,4'-Tetramethyl-10,10'-bianthrone (XVI).

Oxidative Coupling of 1,4-Dimethylanthrone (IVe).

The procedure on p. 129 for the preparation of 4,4'-dimethyl-10,10'-bianthrone (XV) was followed using 1.45 g. (6.5 mmole.) of 1,4-dimethylanthrone (IVe) (p. 97), 1.4 g. (8.6 mmole.) of anhydrous $FeCl_3$, and 20 ml. of HOAc. The black precipitate isolated was washed with water, dilute HCl, water and air-dried. The air-dried solid was washed with ether until the ether washings became colorless. A tan-white solid (0.73 g.) was obtained. The dark ethereal wash was decolorized with activated carbon and evaporated to give some additional tan-white solid (0.57 g.). The solids were combined and recrystallized from MeOH to give 0.9 g. (47.4%, from two successive crops) of white, crystalline, 1,1',4,4'-tetramethyl-10,10'-bianthrone (XVI); m.p. 215-217° lit.[19] 216°); ir (KBr), 1660 (CO) $cm.^{-1}$; nmr ($CDCl_3$), δ 2.0 (s, 3 H, CH_3), 2.44 (s, 9 H, CH_3), 4.76, 4.78 (2 s, 2 H, CH), 6.12, 6.20 (d, 1 H, aromatic-H), 6.78 (m, 1 H, aromatic-H), 6.1-7.8 (m, 10 H, aromatic-H), (C_6D_6), 1.72 (s, CH_3), 2.11 (s, CH_3), 2.70 (s, CH_3), 4.59, 4.64 (2 s, CH), 5.99, 6.06 (d, aromatic-H), 6.48-8.04 (m, aromatic-H).

A sample of XVI (2 g.) was chromatographed on 250 g. of neutral alumina (packed dry in 2 cm. I.D. column) using benzene as the eluent. Fractions of approximately 100 ml. each were collected and combined according to their tlc (alumina GF, C_6H_6) behavior to give two major fractions. The first fraction, after evaporation of the solvent and washing with acetone, gave 0.9 g. of a tan-white solid; m.p. 215-218°; ir (KBr), 1658 (CO) $cm.^{-1}$; nmr ($CDCl_3$), 2.0 (s, 6 H, CH_3), 2.46 (s, 6 H, CH_3), 4.82 (s, 2 H, CH), 6.8-7.8 (m, 12 H, aromatic-H), (C_6D_6), 1.72 (s, 6 H, CH_3), 2.70 (s, 6 H, CH_3), 4.65 (s, 2 H, CH), 6.52-8.04 (m, 12 H, aromatic-H). Attempts to further purify this solid by recrystallization (benzene) gave crystals having the same nmr spectrum as the original unchromatographed material.

The second fraction, after evaporation of the solvent under reduced pressure and washing with acetone, gave 0.38 g. of a tan-white solid; m.p. 203-205°; ir (KBr), 1660 (CO) $cm.^{-1}$; nmr ($CDCl_3$), δ 2.45 (s, 12 H, CH_3), 4.81 (s, 2 H, CH), 6.18, 6.26 (d, J 8 Hz, 2 H, aromatic-H), 6.9-7.8 (m, 10 H, aromatic-H), (C_6D_6), 2.11 (s, 6 H, CH_3), 2.69 (s, 6 H, CH_3), 4.60 (s, 2 H, CH), 6.00, 6.07 (d, J 7 Hz, aromatic-H), 6.68-8.02 (m, 10 H, aromatic-H). When this sample was boiled in benzene, a solid showing the same nmr spectrum as the original unchromatographed material was again obtained.

The ir spectra of the two chromatographed solids were nearly identical in the functional group regions. However, some differences were observed in the fingerprint region.

(VII) Preparation of Methyltriptycenes.

A. Preparation of 1-Methyltriptycene (IXa).

Addition of 3-Methylbenzyne to Anthracene.

The procedure on p. 134 for the preparation of 2,2'-dimethyl-9,9'-bitriptycyl (Ib) was followed using 0.55 g. (3.5 mmole.) anthracene, 60 ml. 2-butanone, 0.86 g. (5.7 mmole.) 3-methylanthranilic acid dissolved in 40 ml. 2-butanone, and 1.26 g. (12 mmole.) n-butyl nitrite dissolved in 40 ml. 2-butanone. The addition was completed in 2 hr. The reaction mixture was heated for an additional 4 hr. after the completion of addition. The reaction solution was worked-up in the same manner as described on p. 134, for 2,2'-dimethyl-9,9'-bitriptycyl (Ib) to give a brown-colored solid. No chromatography was necessary for the purification of this reaction product. The crude solid obtained was thoroughly washed with 70% ethanol to give a light brown solid (0.17 g.). It nmr spectrum indicate it to be pure 1-methyltriptycene (IXa). The ethanol filtrate was evaporated to give 0.29 g. of brown residue. Its nmr spectrum indicated the presence of mainly 1-methyltriptycene (IXa) and some aliphatic impurities. No unreacted anthracene was detected. Recrystallization of the above light brown solid from EtOH/H_2O (3:1), using decolorizing carbon, gave white crystals of 1-methyltriptycene (IXa); m.p. 190-192° (lit.[10] 190.5-192.5°), nmr ($CDCl_3$), δ 2.44 (s, 3 H, CH_3), 5.34 (s, 1 H, CH at C-10), 5.63 (s, 1 H, CH at C-9), 6.6-7.4 (m, 11 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan 268 (67), 253 (100), 239 (44, metastable).

B. Preparation of 1,4-Dimethyltriptycene (IXe). Addition of 3,6-Dimethylbenzyne to Anthracene.

The procedure on p.134 for the preparation of 2,2'-dimethyl-9,9'-bitriptycyl (Ib) was followed using 0.5 g. (2.8 mmole.) of anthracene, 2.6 g. (16 mmole.) of 3,6-dimethylanthranilic acid (ROC/RIC Research Organic/Inorganic Chemical Corp., Belleville, New Jersey) and 1.9 g. (18 mmole.) of n-butyl nitrite. The reaction solution was worked-up in the same manner as described on p.134 for 2,2'-dimethyl-9,9'-bitriptycyl (Ib). However, no chromatography was necessary. The crude brown solid (0.93 g.) obtained, in $CHCl_3$, was treated repeatedly with small portions of activated carbon to remove most of the dark brown color. The $CHCl_3$ was evaporated under reduced pressure and the solid was recrystallized once from 95% EtOH and once from $CHCl_3$/EtOH to give 0.32 g. (40%) of 1,4-dimethyltriptycene (IXe); m.p. 255-256° (lit.[57] 253-255.5°, lit.[10] 249-251°); nmr ($CDCl_3$), δ 2.44 (s, 6 H, CH_3), 5.62 (s, 2 H, CH), 6.69 (s, 2 H, aromatic-H at C-2,3), 6.84-7.45 (m, AA'BB', 8 H, aromatic-H); mass spec., m/e (rel. intensity using linear mass scan) 282 (83.1), 267 (100), 252 (41.4).

(VIII) Preparation of Substituted 9,9'-Bitriptycyls.

Substituted 9,9'-bitriptycyls were prepared by the addition of benzyne to the corresponding 9,9'-bianthryls. Benzyne was generated from anthranilic acid and n-butyl nitrite. All glassware was dried in an oven at 95-100° before use. The solvent, 2-butanone, was kept over $CaSO_4$ and filtered before use. The adition of the anthranilic acid and n-butyl nitrite solutions were controlled so that there was always an excess of n-butyl nitrite present in the reaction mixture.

A-1. Preparation of 2,2'-Dimethyl-9,9'-bitriptycyl (Ib).

2, 2'-Dimethyl-9,9'-bianthryl (IIb) (p. 112) (1.2 g., 3.1 mmole.) was dissolved in 80 ml. 2-butanone. A few drops of n-butyl nitrite were added. The solution was heated to reflux in an oil bath with stirring. Into this stirred solution, anthranilic acid (6.4 g., 47 mmole.) dissolved in 105 ml. 2-butanone and n-butyl nitrite (5.3 g., 51.1 mmole.) dissolved in 105 ml. 2-butanone were simultaneously added, dropwise, at a constant rate over a period of 4 hr. The reaction mixture was refluxed for an additional 1/2 hr., cooled, and evaporated under vacuum to give a semi-solid residue. The residue was thoroughly mixed with 200 ml. of $CHCl_3$. The chloroform-insoluble material was filtered off, and the $CHCl_3$ solution was washed repeatedly with 5% NaOH until the aqueous washings became nearly colorless. The $CHCl_3$ solution was then washed with water, dilute HCl, and water. After drying with $MgSO_4$, the $CHCl_3$ solution was evaporated under reduced pressure to give a red-brown solid, which was further purified by column chromatography (silica gel, 100-200 mesh, 90 g., packed as slurry in a 2 cm. I.D. column, eluent, benzene/hexane (25:75)).

The crude product was initially dissolved in a minimum amount of $CHCl_3$, and placed on the silica gel column. Fractions of approximately 20 ml. were collected and combined according to their tlc behavior and their nmr spectra. The first combined fraction (0.72 g.) was, according to the nmr spectra, a mixture of 2,2'-dimethyl-9,9'-bianthryl (IIb) (70-80%) and a small amount of 2,2'-dimethyl-9,9'-bitriptycyl (Ib) (10-15%) and unknown impurities (10-15%). The second fraction (0.28 g.) was a mixture of 2,2'-dimethyl-9,9'-bitriptycyl (Ib) (55-65%), 2,2'-dimethyl-9,9'-bianthryl (IIb) (5-10%) and unknown material (35-45%). The second fraction was washed repeatedly with small portions of hexanes to give 63.4 mg. (3.8%) of a tan-white solid. Its tlc behavior and uv, ir and mass spectra were identical with that of a known sample of 2,2'-dimethyl-9,9'-bitriptycyl (Ib).[7]

The nmr spectrum of this sample contained two singlets of unequal intensities in the methyl region, at δ 1.81 and 1.83. Sample of Ib from two preparations were combined and recrystallized repeatedly from chloroform/acetone (20:80). By judicious recombination and recrystallization of fractions according to their nmr spectra, two white solids were collected. The solid enriched in the low field methyl singlet (δ 1.83) (Ib-B) had m.p. 473-478° dec.; uv ($CHCl_3$), λmax (log ε) 285.2 (3.54), 281.0 (3.62), 273.8 (3.59); nmr

($CDCl_3$), δ 1.81, 1.83 [2 s, CH_3, peak-height ratio[a] (1.83/1.81) 2.10±0.04], 5.55 (s, CH), 6.4-7.6 (m, aromatic-H). The solid enriched in high field methyl singlet (δ 1.81) (Ib-A) had m.p.>505° dec.; uv ($CHCl_3$), λmax (log ε) 285.2 (3.57), 281.0 (3.65), 273.8 (3.63); nmr ($CDCl_3$), δ 1.81, 1.83 [2 s, CH_3, peak-height ratio[b] (1.83/1.81), 0.44±0.02], 5.55 (s, CH), 6.4-7.6 (m, aromatic-H).

A-2. Attempted Thermal Equilibration of Conformers of 2,2'-Dimethyl-9,9'-bitriptycyl (Ib)

2,2'-Dimethyl-9,9'-bitriptycyl fraction Ib-B (13 mg.) was sealed with 0.7 g. of twice-sublimed napthalene, under a nitrogen atmosphere (1 atm.) in a 1-ml. glass ampoule. The ampoule was completely submerged in a silicone bath (A.H. Thomas Co., Philadelphia, Pa., U.S.A., Cat. No. 6407-J, EDP No. 6428-R15) contained in a 300 ml. three-necked flask, equipped with a reflux condenser (to minimize the escape of vapor into the atmosphere), a submerged thermometer and a heating mantle. The silicone fluid was heated to 300±5°C

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[a] The nmr spectroscopy of this methyl region was recorded with a JOEL JNM-MH-100 spectrometer (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan) with the following settings; sweep width, 540 Hz: sweep time, 500 sec.; amplitude, 400: filter, 5; RF, 0.1. The peak-height ratio was the average of eight different measurements. The methyl region of this same sample was also scanned by a Varian HR 220 MHz nmr spectrometer (Varian Associate, Palo Alto, Ca.) using continuous wave mode spectrometry at sweep width 2500 Hz and 250 Hz, and Fourier Transform mode (50 pulses) at sweep width 2500 Hz, and 250 Hz. The average peak-height ratio (δ 1.83/δ 1.81) from fifteen different measurements was 2.0±0.09.

[b] The nmr spectroscopy of this methyl region was recorded with a JOEL JNM-MH-100 spectrometer (see a.) at settings: sweep width, 540 Hz; sweep time, 250 sec.; amplitude, 500; filter, 5; RF, 0.3. The peak-height ratio was the average of twenty-three different measurements.

in 1 hr., and the temperature was maintained for 74 hr. A slight yellowing of the naphthalene solution was observed after 24 hr. Upon cooling, the glass ampoule was opened, and the solid mixture was dissolved in a minimum amount of chloroform. The chloroform solution was transferred into the sample cup of a micro sublimator, and the chloroform was evaporated in an oven at 60°C. The solid residue was placed under vacuum (0.05-0.08 mm. Hg, 50°C) to remove the naphthalene by sublimation. A tan-colored residue (Ib-B', 14 mg.) was obtained. The nmr spectrum of Ib-B' was identical with that of Ib-B. The methyl region of Ib-B' was scanned eighteen times using a JEOL, JNM-MH-100 at the same settings as that of Ib-B (footnote a., p. 136). The average peak-height ratio (δ 1.83/δ 1.81) was 2.00 ± 0.05, uv ($CHCl_3$), λmax (log ε), 285.0 (3.69), 381.1 (3.76), 273.8 (3.76).

Sample Ib-B' was recovered completely and equilibrated again in the same manner as described above using 0.5 g. of twice-sublimed napththalene. The sample was heated at 285-295°C for 97 hr. A dark brown solution resulted. After removal of the naphthalene by sublimation, a dark brown solid (Ib-B'', 12.3 mg.) was obtained. The nmr spectrum of Ib-B'' was identical with that of Ib-B. The methyl region of Ib-B'' was recorded twenty-one times using a JEOL, JNM-MH-100 at settings: sweep width, 540 Hz: amplitude, 500; filter, 10; sweep time, 250 sec. The average peak-height ratio of δ 1.83 to 1.81 was 2.00 ± 0.05; uv ($CHCl_3$), λmax (log ε), 285.0 (3.86), 281.0 (3.89), 273.8 (3.89).

Fraction Ib-A (10 mg.) in 0.9 g. of twice-sublimed naphthalene was treated in the same manner as Ib-B. After 72 hr. of heating the light tan-colored residue (Ib-A', 9.7 mg.) obtained gave an identical nmr spectrum to that of Ib-A. The methyl region was recorded twenty-three times using a JEOL, JNM-MH-100 at the same settings as that of Ib-A (note b., p. 136). The average peak-height ratio (1.83/ δ 1.81) was 0.49± 0.03; uv ($CHCl_3$), λmax (log ε) 285.1 (3.62), 280.1 (3.67), 273.7 (3.67).

Sample Ib-A' was recovered and equilibrated again in the same manner as Ib-B' above (p. 137), at 290-300°C for 92 hr. The residue (Ib-A'') showed an identical nmr spectrum to that of Ib-A. The methyl region was recorded thirty times at the same settings as that of Ib-A (note b., p.136). The average peak-height ratio (δ 1.83/δ 1.81) was 0.42±0.02; uv ($CHCl_3$), λmax (log ε) 285.3 (3.81), 281.3 (3.84), 274.0 (3.85).

B. Preparation of 3,3'-Dimethyl-9,9'-bitriptycyl (Ic).

The procedure on p.134 for the preparation of 2,2'-dimethyl-9,9'-bitriptycyl (Ib) was followed, using 1.1 g. (2.9 mmole.) 3,3'-dimethyl-9,9'-bianthryl (IIc) (p. 113), 2.37 g. (17.3 mmole.) anthranilic acid dissolved in 60 ml. 2-butanone, 1.96 g. (19.0 mmole.) n-butyl nitrite dissolved in 60 ml. 2-butanone and 70 ml. 2-butanone. The addition took 6.5 hr. After work-up in the same manner as described on p. 134, the semi-solid crude product was further purified by chromatography.

The crude product, dissolved in $CHCl_3$, was coated on 35 g. of neutral alumina using a rotatory evaporator to remove the solvent. The coated alumina was placed on top of a column of 300 g. neutral alumina, packed dry in a 2.5 cm. I.D. column. The column was eluted with benzene/hexane (1:4). Fractions, of approximately 20 ml. were collected and combined according to their tlc behavior and nmr spectra.

Fractions	Weight (g.)	Analysis (tlc, nmr)
1-10	---	No material
11-25	0.46	3,3'-Dimethyl-9,9'-bianthryl (IIc)
26-45	0.44	IIc (approx. 30%) Ic (approx. 40%) and unknown bridgehead containing compound (approx. 20%).
46-70	0.05	IIc (approx. 20%) Ic (approx. 30%), unknown bridgehead containing compound (approx. 30%), and other unknown (approx. 20%).

The solid from fractions 26-45 was dissolved in $CHCl_3$, and the solid was treated with activated carbon. After removal of the activated carbon by filtration, a large volume of 95% alcohol was added and the solution was concentrated by distillation until a slight cloudiness appeared. The solution was allowed to cool to room temperature to give 70.5 mg. (4.6%) of white solid. One recrystallization from 95% EtOH/$CHCl_3$, and several recrystallizations from acetone/ $CHCl_3$ provided an analytical sample of 3,3'-dimethyl-9,9'-bitriptycyl (Ic); m.p. 473-476° dec.; nmr ($CDCl_3$), 2.23 (s, CH_3), 5.54 (s, CH), 6.33-7.53 (m, aromatic-H); uv ($CHCl_3$), λmax (log ε) 282.2 (3.73), 273.6 (3.71), 266.1 (sh, 3.45); mass spec., m/e (rel. intensity using linear mass scan) 534 (100), 519 (3), 267 (10).

Anal. Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.17; H, 5.73.

C. Preparation of 4,4'-Dimethyl-9,9'-bitriptycyl (Id).

The procedure on p. 134 for the preparation of 2,2'-dimethyl-9,9'-bitriptycyl (Ib) was followed, using 1.0 g. (2.6 mmole.) 4,4'-dimethyl-9,9'-bianthryl (IId) (p. 114), 4.0 g. (29 mmole.) anthranilic acid dissolved in 60 ml. 2-butanone, 3.2 g. (32 mmole.) n-butyl nitrite dissolved in 60 ml. 2-butanone and 90 ml. 2-butanone. The crude product was chromatographed according to the procedure on p. 139 for the purification of 3,3'-dimethyl-9,9'-bitriptycyl (Ic), using 250 g. of neutral alumina, to give three major fractions. According to their nmr spectra, the first fraction (0.57 g.) contained essentially unreacted starting material, IId. The second fraction (0.25 g.) was a mixture of 4,4'-dimethyl-9,9'-bitriptycyl (Id), 4,4'-dimethyl-9,9'-bianthryl (IId) and unknown impurities in an approximate ratio of 15:15:70. The third fraction (49 mg.) was essentially pure 4,4'-dimethyl-9,9'-bitriptycyl (Id). The second fraction was recrystallized from $CHCl_3$/acetone to give 37 mg. 4,4'-dimethyl-9,9'-bitriptycyl (Id). All crude samples of 4,4'-dimethyl-9,9'-bitriptycyl (Id) were combined and recrystallized repeatedly from $CHCl_3$/acetone to give an analytical sample; m.p. 510° dec.; ir (KBr), 1378 $cm.^{-1}$; nmr ($CDCl_3$), δ 2.65 (s, CH_3), 5.86 (s, CH), 6.32-7.60 (m, aromatic-H); uv ($CHCl_3$), λmax (log ε) 280.7 (3.49), 272.7 (3.51); mass spec., m/e (rel. intensity using linear mass scan) 534 (100), 519 (8), 267 (100).

Anal. Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.27; H, 5.63.

D. Preparation of Optically Active 2,2'-Dicarbomethoxy-9,9'-bitriptycyl (Ih).

Addition of Benzyne to (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (IIh).

The procedure on p. 136 for the preparation of 2,2'-dimethyl-9,9'-bitriptycyl (Ic) was followed, using 1.0 g 2.12 mmole.) (-)2,2'-dicarbomethoxy-9,9'-bianthryl (IIh) ($[\alpha]_D^{23}$ -149.2° (c 0.3, $CHCl_3$)), 2.90 g (21.2 mmole.) anthranilic acid dissolved in 60 ml. 2-butanone, 2.40 g (23.3 mmole.) n-butyl nitrite dissolved in 60 ml. 2-butanone and 60 ml. 2-butanone. The reaction temperature was kept at 60°C (oil bath). The addition took 4.5 hr. The reaction mixture was maintained at 60°C for an additional 0.5 hr., cooled, and evaporated under reduced pressure to give a dark-brown semi-solid. This semi-solid was dissolved in 200 ml. of warm $CHCl_3$. A small amount of chloroform-insoluble material (most probably acridone, as evidenced by its ir spectrum) was removed by filtration. Evaporation of the filtrate gave a viscous brown residue. Nmr spectroscopy of this residue indicated the presence of unreacted starting bianthryl, a small amount of bridgehead hydrogen-containing compounds and some other impurities. The chloroform filtrates of three similar reaction mixtures were combined and evaporated. The semi-solid residue was further purified as follows. (The procedure is outlined in schemes XIII (pp. 152-154), XIV (p. 155), and XV (p.156). The residue was dissolved in a minimum amount of chloroform and coated on 50 g.of silica gel (100-200 mesh) using a rotary evaporator to remove solvent. This coated silica gel was placed on top of a column of dry silica gel (200 g., 100-200 mesh, 4 cm.I.D.). The column was eluted with $C_6H_6/CHCl_3$ (1:1.5). Fractions were collected manually. Uv light was used to assist in approximation of band separation.

Fractions	(ml.)	Solid Weight (g.)	Analysis (nmr)
Ia.	1200	0.240 (semi-solid)	Anthracene type of compounds and some aliphatic materials.
Ib.	2800	2.01 (semi-solid)	Mixture of unknown impurities and small amount of 2,2'-dicarbomethoxy-9,9'-bianthryl. No obvious triptycene-like bridgehead hydrogen.
Ic.	700	1.02 (yellow)	(-)2,2'-Dicarbomethoxy-9,9'-bianthryl ($[\alpha]_D^{23}$ -98.8°, $CHCl_3$).
Id.	800	1.32 (yellow)	(-)2,2'-Dicarbomethoxy-9,9'-bianthryl, triptycene-like bridgehead hydrogen.
Ie.	230	0.55 (yellow)	(-)2,2'-Dicarbomethoxy-9,9'-bianthryl and other impurities.
If.	600	0.53 (light brown)	Aromatic compounds and a small amount of dicarbomethoxy-bianthryl, no triptycene-like bridgehead hydrogen.
Ig.	1550	0.63 (dark-brown, semi-solid)	Aromatic compounds and some aliphatics, no dicarbomethoxy-bianthryl nor triptycene bridgehead hydrogen.

Fraction Ib was digested with 30 ml hexane/chloroform (3:1) to give 37 mg.of an insoluble white solid. Upon addition of more hexane to the filtrate, 0.50 g.of 2,2'-dicarbomethoxy-9,9'-bianthryl (IIh) was obtained. The hexane/chloroform solution, upon evaporation under reduced pressure, gave a viscous brown liquid residue (1.5 g.). This material had a complicated nmr spectrum which indicated the presence of unknown aromatics, aliphatics, and a small amount of the bianthryl. Thick layer chromatography did not lead to the isolation of material with an nmr spectrum consistent with 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih). Fraction Id was digested with methanol/chloroform (3:1) to give a small amount of an insoluble white solid (6.8 mg.). The filtrate, after evaporation at reduced pressure, gave a dark brown solid. Its nmr spectrum indicated the presence of a significant amount of triptycyl-containing compounds, unreacted bianthryl and other unknown by-products. This dark brown solid was combined with Ic, Ie and 2,2'-dicarbomethoxy-9,9'-bianthryl obtained from fraction Ib. When the combined solid was mixed with 100 ml of 2-butanone, small amounts of insoluble white solids (5 mg.) were isolated. The 2-butanone solution was divided into two equal portions. Each portion was subjected to a benzyne addition reaction, as described on p. 142 , using 3.5 g. (25.5 mmole) anthranilic acid dissolved in 70 ml. 2-butanone, and 2.8 g. n-butyl nitrite dissolved in 70 ml. 2-butanone. The addition took 5 hr. The two crude reaction products were combined and chromatographed in the same manner as described on p. 143, using 350 g. silica gel (100-200 mesh) and $C_6H_6/CHCl_3$ (2:1). Fractions were collected visually using a uv lamp for detection.

Fractions (ml.)		Solid Weight (g.)	Analysis (nmr)
IIa.	1800	---	Mixture of unknown impurities.
IIb.	2500	3.9	Mainly 2,2'-dicarbomethoxy-9,9'-bianthryl, small amount of bridgehead hydrogen containing compounds and impurities.
IIc.	2000	1.2	Mainly unknown impurities, little 2,2'-dicarbomethoxy-9,9'-bianthryl and bridgehead hydrogen containing compounds.
IId.	1500	0.5	Unknown aromatic side products.

Fraction IIb was dissolved in a minimum amount of acetone and an equal amount of methanol was added. On remaining at room temperature overnight, 60 mg. of white solid precipitated. This white solid was combined with all the "insoluble white solids" (designated VIII-Da). Evaporation of the filtrate gave 3.34 g. of yellow-brown solid which was coated on 20 g. of silica gel and chromatographed in the same manner as described on p. 143, using 300 g. of silica gel (100-200 mesh, 2.8 cm. I.D.) and 1:2 chloroform/benzene as eluent.

Fractions (ml.)		Solid Weight (g.)	Analysis (nmr)
IIIa.	250	0.3 (oily solid)	---
IIIb.	300	0.01 (oily solid)	---
IIIc.	850	0.01	Aliphatic unknowns; silicone grease.
IIId.	2200	0.02	Aliphatic unknown; silicone grease.
IIIe.	700	0.08 (yellow-brown oily solid)	---
IIIf.	1800	0.02 (light yellow solid)	---
IIIg.	550	0.04 (yellow-orange)	Unknown aromatics and aliphatics.
IIIh.	500	0.24 (yellow-orange)	2,2'-Dicarbomethoxy-9,9'-bianthryl.
IIIi.	1150	0.88 (yellow)	2,2'-Dicarbomethoxy-9,9'-bianthryl.
IIIj.	150	0.47 (yellow-orange)	2,2'-Dicarbomethoxy-9,9'-bianthryl; bridgehead hydrogen containing compounds.
IIIk.	300	0.61 (brown)	Mainly bridgehead hydrogen containing compounds; small amount of 2,2'-dicarbomethoxy-9,9'-bianthryl and impurities.
IIIl.	500	0.04 (brown)	Unknown aromatics.

Fraction IIc was dissolved in $CHCl_3$. No insoluble solid was observed. The $CHCl_3$ solution was chromatographed using 130 g. of silica gel (100-200 mesh) $C_6H_6/CHCl_3$ (2:1) as eluent to give three major fractions.

Fractions (ml.)	Solid Weights (g.)	Analysis (nmr)
IVa. 2120	0.003 (oily solid)	---
IVb. 1030	0.34	Unknown aromatics and aliphatics.
IVc. 500	0.50	2,2'-Dicarbomethoxy-9,9'-bianthryl and bridgehead hydrogen containing compounds.

Fractions IIIk and IVc were combined and coated on 20 g. silica gel. The coated silica gel was placed on a dry-packed silica gel (130 g., 100-200 mesh) column (2.8 cm.I.D.) and eluted with petroleum ether. An insignificant amount of oily solid was obtained from 600 ml. of petroleum ether. The eluent was then changed to 2:1 $C_6H_6/CHCl_3$, and 20 ml. fractions were collected using an automatic fraction collector. Based on tlc (silica gel GF, 250 micron, CH_2Cl_2, uv visualization) analysis, fractions were combined for nmr analysis and for further purification.

Fractions	Solid Weight (g.)	Analysis (nmr)
Va. 1-59	0.020	No significant absorption.
Vb. 60-164	0.021	Silicone grease.
Vc. 165-175	0.041 (yellow)	2,2'-Dicarbomethoxy-9,9'-bianthryl and bridgehead hydrogen containing compound.
Vd. 176-180	0.075 (yellow-orange)	Same as Vc, bridgehead hydrogen absorption more intense.
Ve. 181-219	0.497 (yellow-orange)	Same as Vd.

Vf.	220-245	0.082 (yellow)	Complicated, several singlets at bridgehead hydrogen region, several singlets at methoxy region and other aliphatics.
Vg.	246-305	0.692 (yellow-brown)	Unknown aliphatics.

Fraction Vc, Vd and Ve were combined. The solid was dissolved in a minimum amount of $CHCl_3$ (ca. 5 ml.) and spotted on four thick layer plates (silica gel GF, 2000 micron). After four developments with CH_2Cl_2, six bands were isolated from each plate (uv 12 detector). Corresponding bands were combined and extracted with chloroform. Evaporation of the chloroform extracts over a steam bath gave the following results:

Bands	Solid Weight (mg.)	Analysis (nmr)
VIa.	173.1	2,2'-Dicarbomethoxy-9,9'-bianthryl (IIh) and some unknown impurities.
VIb.	101.3	Same as band I.
VIc.	88.2	2,2'-Dicarbomethoxy-9,9'-bitriptycyl.
VId.	172.8	2,2'-Dicarbomethoxy-9,9'-bitriptycyl.
VIe.	58.3	Same as Vf.
VIf.	80.4	Same as Vf.

The solids from bands VIe and VIf were combined and digested with a small amount of 95% alcohol. A small amount of tan-white solid (VIg) was obtained. Evaporation of the alcoholic filtrate gave a yellow-brown solid with an nmr spectrum similar to Vf. This solid and Vf were combined and chromatographed on thick layer plates (silica gel GF, 2000 micron) with CH_2Cl_2. Each plate was developed six times to give four major bands.

Bands	Solid Weight (mg.)	Analysis (nmr)
VIIa.	90	No significant absorption.
VIIb.	8.4	2,2'-Dicarbomethoxy-9,9'-bitriptycyl and some impurities.
VIIc.	5	Same as Vf.
VIId.	87.4	Same as Vf.

Fractions VIc, VId and VIIb were combined to give VIII-Db for further purification (Scheme XV, p. 156). The solid from VIg was later incorporated into the purification Scheme of VIII-Db. The solids from VIIc and VIId were combined. Thin layer chromatography using silica gel plate (GF, 250 micron and various solvents; hexane, benzene, ether, chloroform, methanol) did not give distinct separation of bands. Recrystallization of this material from ether/hexane gave a yellow powdery solid having the same nmr spectrum as Vf. Nmr ($CDCl_3$), δ 3.19 (s, 6 H), 3.48 (s, 1 H), 3.72 (s, 6 H), 4.88 (s, broad, 2 H), 5.44 (s, 1 H), 5.51 (s, 1 H), 6.4-7.6 (m, 20 H), 7.7-8.4 (m, 18 H), 8.71 (s, 2 H); mass spec., m/e (rel. intensity using linear mass scan) 546.

Solid VIII-Da was further purified by digestions and repeated recrystallizations according to Scheme XIV to give an analytical sample (67.5 mg.) of anti-2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih-A); m.p. 483-485°; ir (KBr), 2950 (CH_3), 1720 ($COOCH_3$); nmr ($CDCl_3$), δ 3.51 (s, OCH_3), 5.66 (s, CH), 6.4-8.0 (m, aromatic-H); uv ($CHCl_3$), λmax (log ε) 292.1 (3.48), 264.8 (4.18), 239.3 (4.59); mass spec., m/e (rel. intensity using linear mass scan) 622 (100).

<u>Anal</u>. Calcd for $C_{44}H_{30}O$: C, 84.87; H, 4.86; O, 10.2 Found: C, 84.72; H, 4.93; O, 10.35 (by difference).

Ih-A was very insoluble in chloroform and other common organic solvents. Concentration of the recrystallization mother liquor gave additional, less pure, Ih-A (total 25.2 mg.). In addition, thick layer chromatography of the final mother liquor gave 4.6 mg. Ih-A and 6.5 mg. chloroform soluble Ih which was later shown to be <u>gauche</u> 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih-B) by nmr, using a chiral shift reagent (Eu(hfc)) (see below). The peak-height ratio (low field/high field) of the two resolved methoxy peaks of the chloroform soluble Ih was 2:1.

Solid VIII-Db was likewise purified by repeated recrystallization according to Scheme XV to give an analytical sample (101.3 mg.) of <u>gauche</u> 2,2'-dicarbomethoxy-9,9'-bitriptycyl (Ih-B); m.p. 340-361°; ir (KBr), 2950 (CH_3) 1720 ($COOCH_3$); nmr ($CDCl_3$), δ 3.48 (s, OCH_3), 5.66 (s, CH), 6.4-8.0 (m, aromatic-H); uv ($CHCl_3$), λmax (log ε) 293.6 (3.51), 263.1 (4.16) 238.8 (4.55); $[\alpha]_D^{23}$-14.7 (c 0.375, $CHCl_3$); mass spec., m/e (rel. intensity using linear mass scan) 622 (100).

Anal. Calcd for $C_{44}H_{30}O$: C, 84.87; H, 4.86, O, 10.27 Found: C, 84.70; H, 4.84; O, 10.46 (by difference).

The nmr spectrum of a sample of Ih-B treated with the chiral nmr shift reagent tris-((3-heptafluoropropylhydroxymethylene)-d-camphorato) Europium (III) (Eu(hfc), Aldrich Chemical Co. Inc., Milwaukee, Wisc.) showed two methoxy absorption peaks of unequal intensities. The maximum peak separation ($\Delta\delta$, 0.15) was found at a molar ratio (Ih-B/ Eu(hfc)) of 0.98. The peak-height ratio of the low field peak to the high field peak was 2.5±0.1.[a] Five additional, less pure, samples of Ih-B were recovered from the recrystallization mother liquors. Each of the recovered samples, when treated with Eu(hfc), gave a separation into two methoxy peaks of unequal intensities. These samples were combined and further purified with thick layer chromatography to give 67.0 mg. of Ih-B which, when treated with Eu(hfc), gave a methoxy peak-height ratio (low field to high field) of 1.22±0.03.[b]

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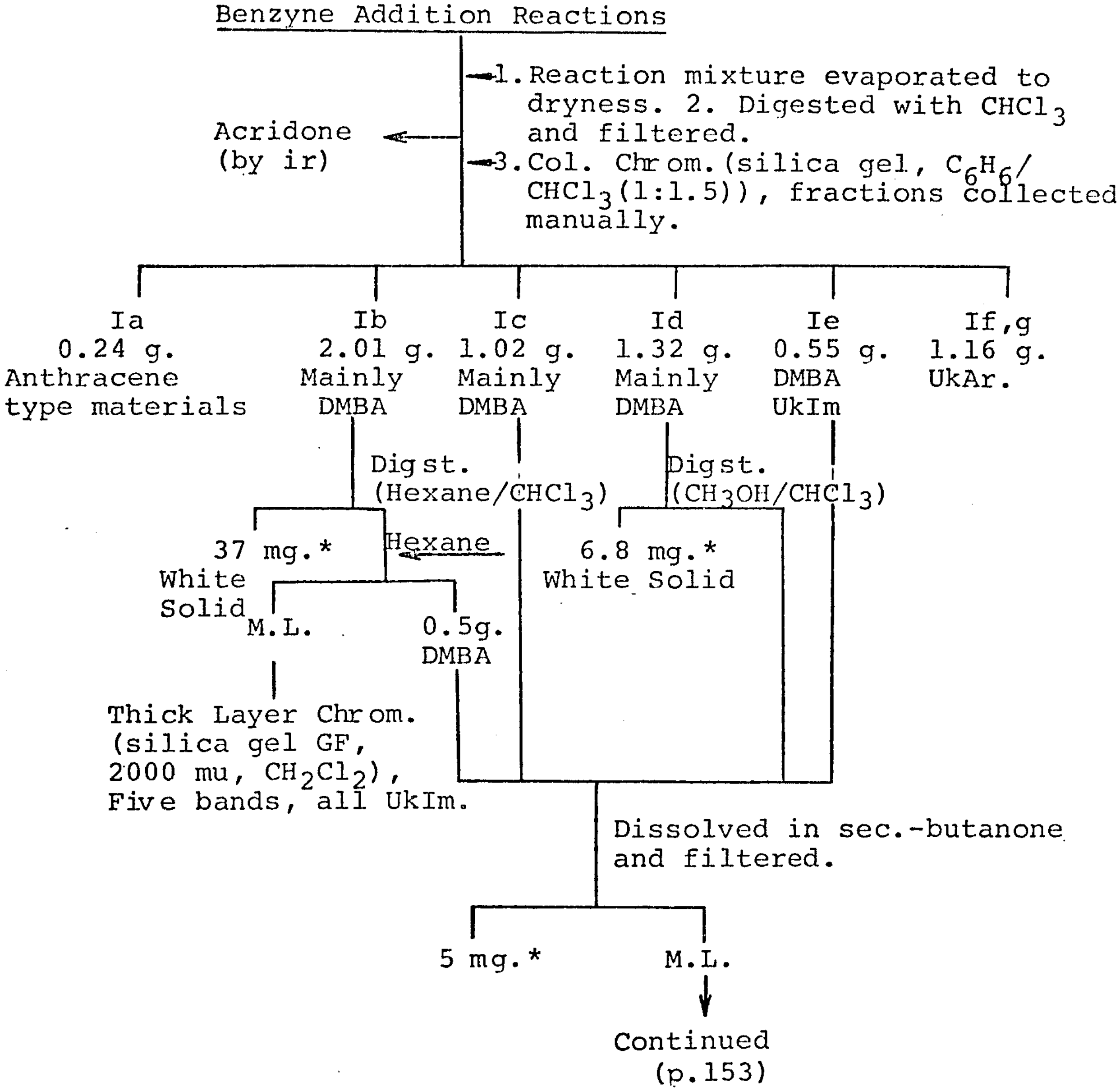
a. The nmr spectrum of the methoxy region was recorded with JEOL, JNM-MH-100 (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan) spectrometer at settings: sweep width, 540 Hz; sweep time 250 sec.; amplitude 600; filter, 2; RF, 0.1. The peak-height ratio was the average of nine measurements.

b. Same instrument as (a.) at settings: sweep width, 1080 Hz; sweep time, 250 sec.; amplitude 250; filter, 10; RF, 0.1. The peak-height ratio was the average of nine measurements.

Scheme XIII : Isolation Scheme of 2,2'-Dicarbomethoxy-9,9'-bitriptycyl (Ih)

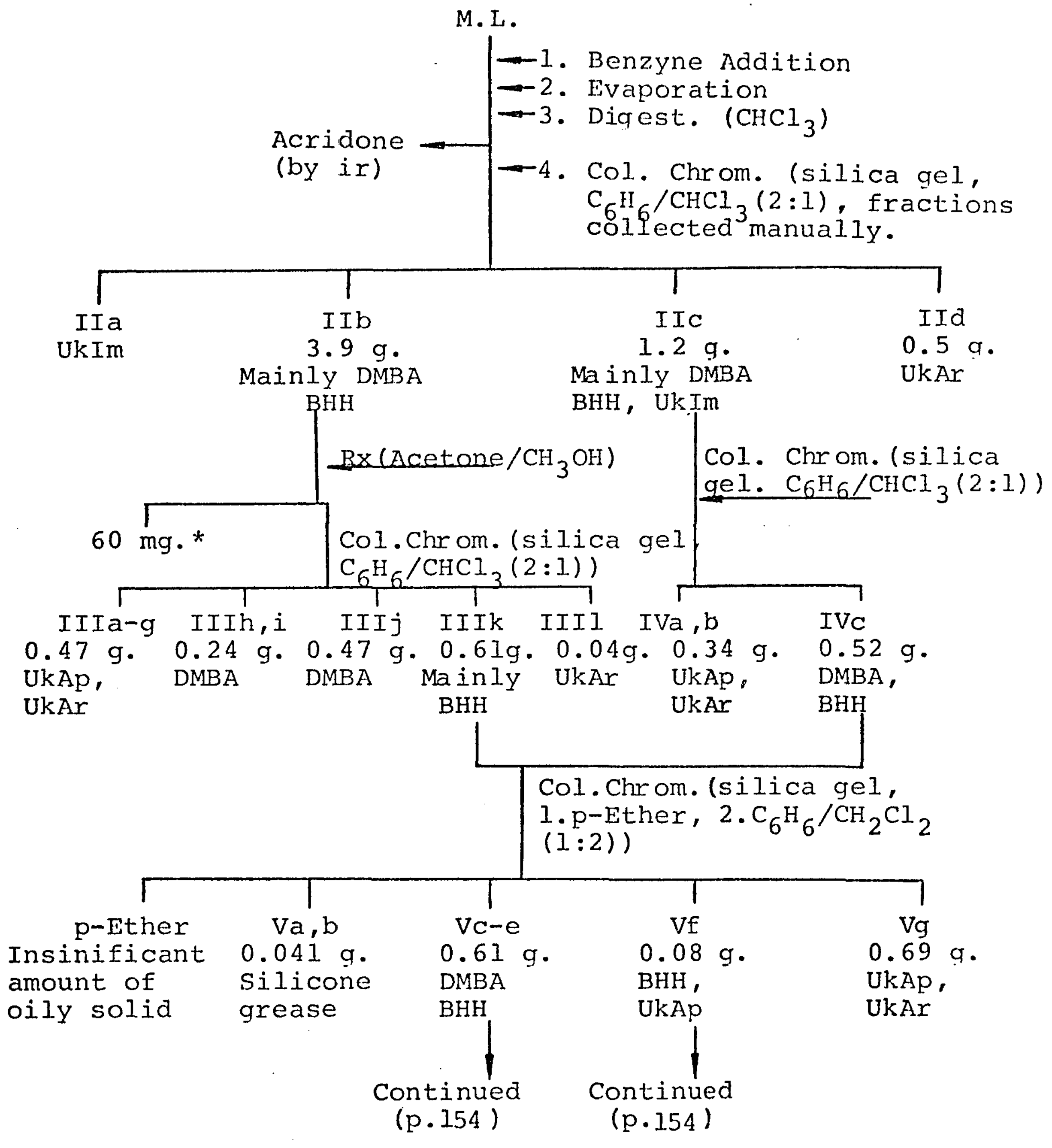


Keys to abbreviations

DMBT = 2,2'-Dicarbomethoxy-9,9'-bitriptycyl
DMBA = 2,2'-Dicarbomethoxy-9,9'-bianthryl
UkAr = Unknown Aromatics
UkIm = Unknown Impurities
Digst. = Digestion (solvent)
M.L. = Mother Liquor

* These solids were combined (designated as VIII-Da) and purified according to Scheme XIV (p. 155).

Scheme XIII : Isolation Scheme of 2,2'-Dicarbomethoxy-9,9'-bitriptycyl (Ih) (Continued)

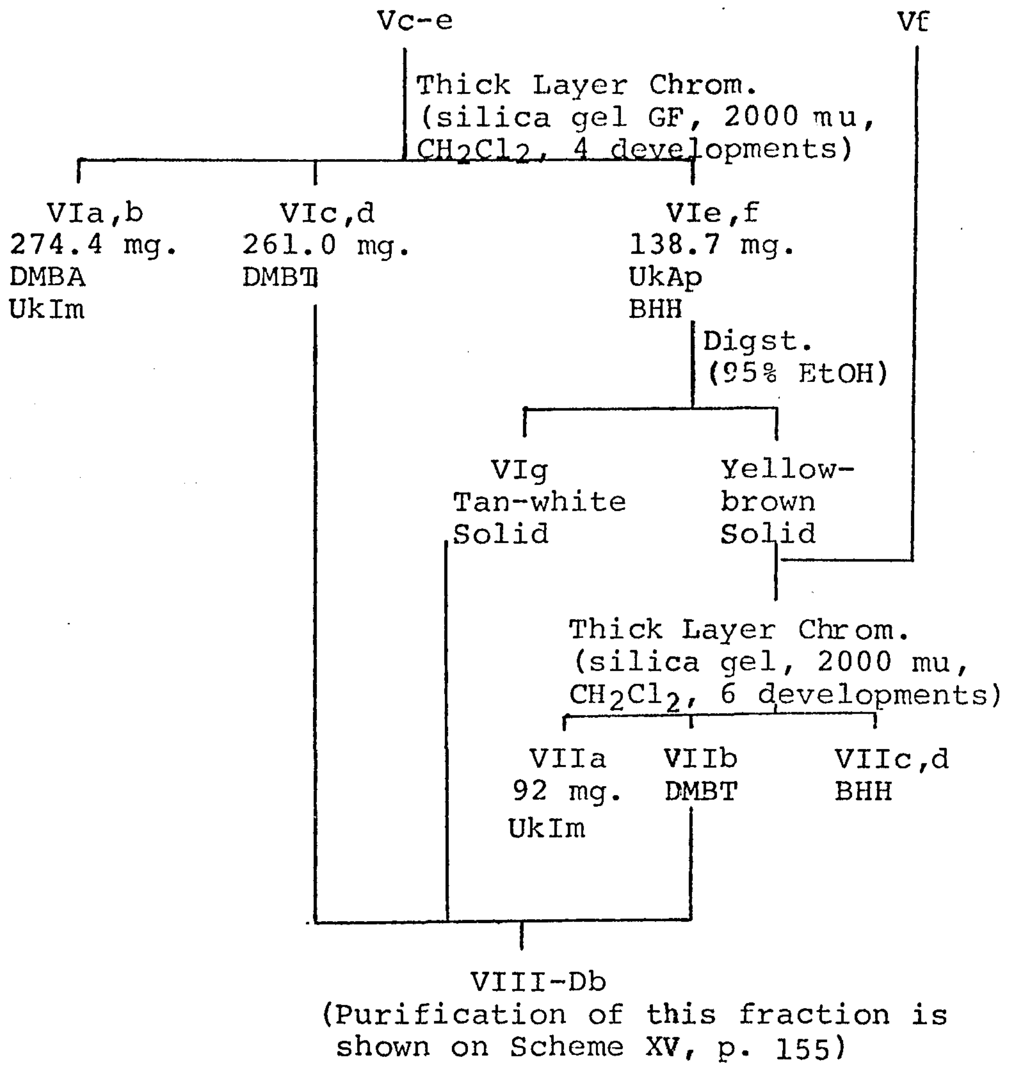


Keys to Abbreviations

DMBA = 2,2'-Dicarbomethoxy-9,9'-bianthryl
UkAp = Unknown Aliphatics
UkAr = Unknown Aromatics
UkIm = Unknown Impurities
BHH = Bridgehead Hydrogen Containing Compounds
Rx = Recrystallization (solvent)

* See footnote on previous page (p.152).

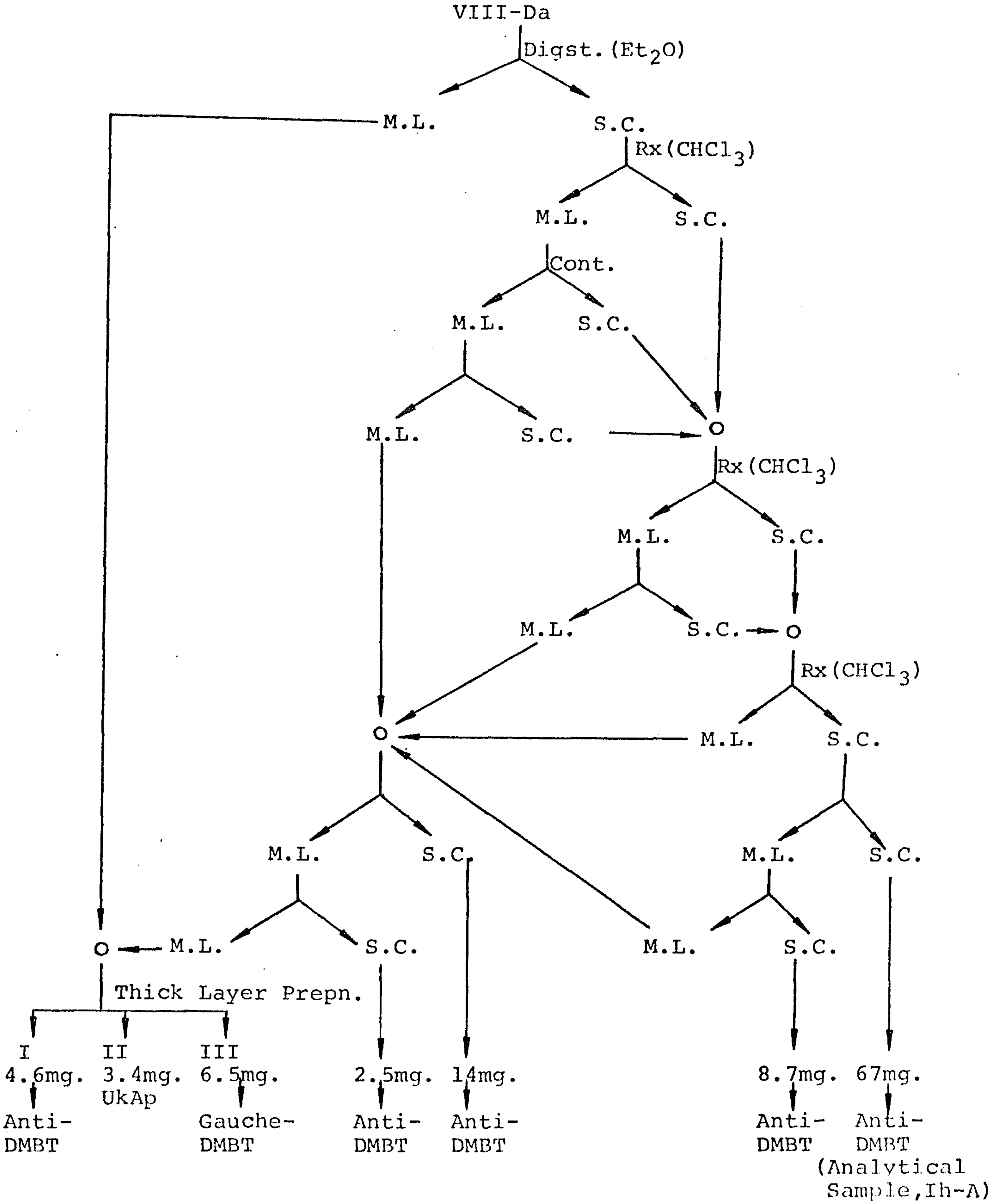
Scheme XIII : Isolation Scheme of 2,2'-Dicarbomethoxy-9,9'-bitriptycyl (Ih) (Continued)



Keys to abbreviations

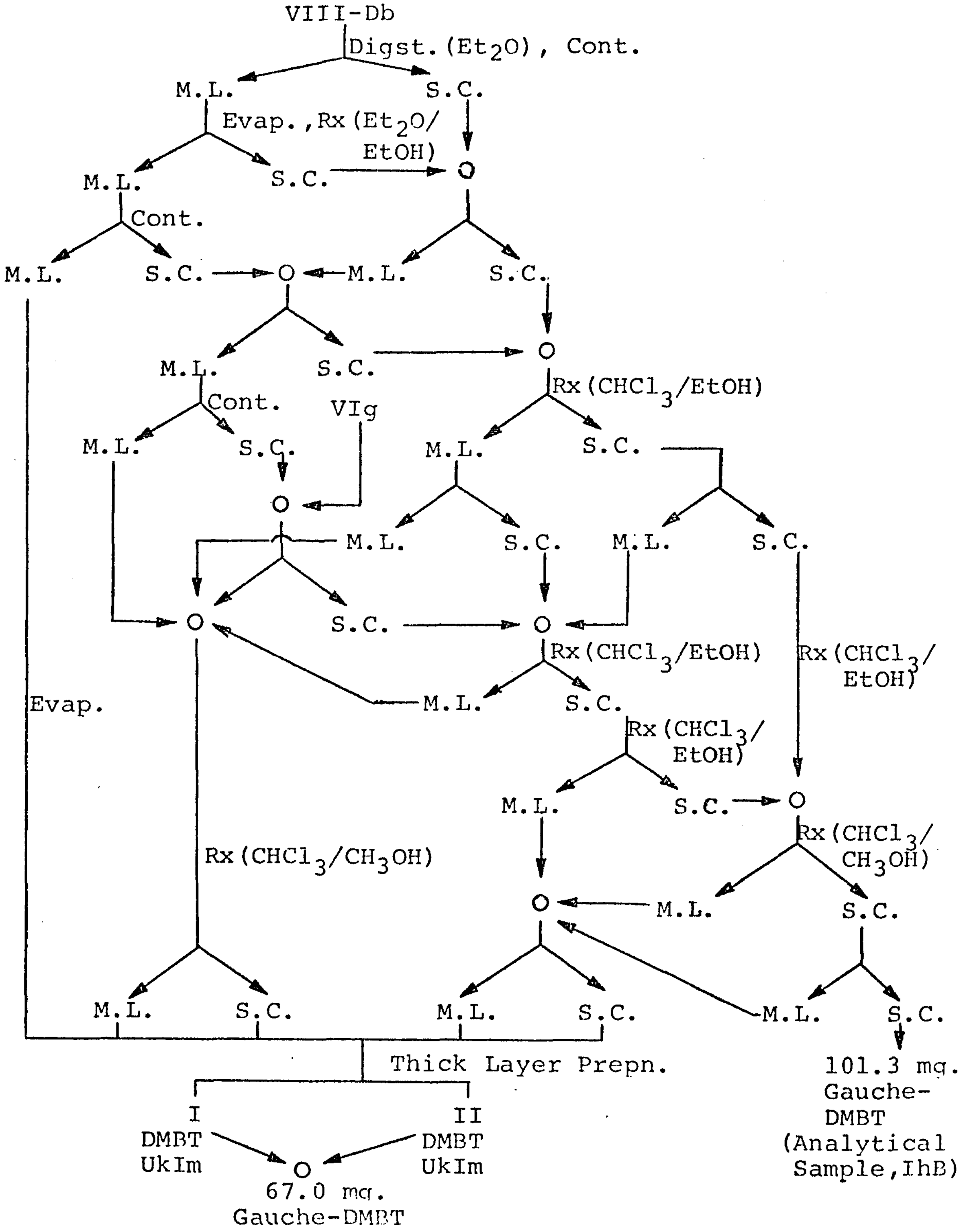
DMBA = 2,2'-Dicarbomethoxy-9,9'-bianthryl
DMBT = 2,2'-Dicarbomethoxy-9,9'-bitriptycyl
UkAp = Unknown Aliphatics
UkIm = Unknown Impurities
BHH = Bridgehead Hydrogen Containing Compounds
Digst. = Digestion (solvent)

Scheme XIV : Purification of VIII-Da*



* Keys to abbreviations given on p. 157.

Scheme XV : Purification of VIII-Db*



*Keys to abbreviations given on p. 157.

Keys to Abbreviations for Scheme II and Scheme III

DMBT = 2,2'-Dicarbomethoxy-9,9'-bitriptycyl

UkIm = Unknown Impurities

UkAp = Unknown Aliphatics

UkAr = Unknown Aromatics

S.C. = Solid Crystals

M.L. = Mother Liquor

Cont. = Concentration of Mother Liquor

Digst. = Digestion (Solvent)

Rx = Recrystallization (Solvent)

O = Combination of

APPENDIX A

Individual p, z, and θ measurements and chemical shift calculations for methyl groups of n,n'-dimethyl-9,9'-bitriptycyls.

Measured[a] p, z, and θ Values and Calculated Chemical Shift Values for Methyl Groups of Dimethyl-9,9'-bitriptycyls

Bitriptycyls	Trials	p		z		θ		Δδ Calcd.		δ Calcd.	
		Out[b]	In[c]	Out[b]	In[c]	Out[b]	In[c]	J & B	M & H	J & B	M & H
Ia[d]	1	1.12	3.74	1.59	0	6	22	-2.89	0.93	-0.45	1.39
	2	1.15	3.97	1.62	0	5	23	-2.75	0.89	-0.31	1.55
	3	1.16	3.76	1.64	0	8	21	-2.67	0.84	-0.23	1.57
	4	1.15	3.74	1.59	0	7	21	-2.72	0.90	-0.28	1.55
	5	1.12	3.79	1.65	0	6	23	-2.84	1.00	-0.21	1.44
Ib[e]	1	2.00	6.05	3.47	0	3	14	-0.39	0.15	1.82	2.06
	2	1.91	6.00	3.53	0	5	15	-0.42	0.16	1.79	2.05
	3	2.06	6.18	3.53	0	3	14	-0.37	0.14	1.85	2.07
	4	1.97	6.12	3.56	0	4	15	-0.38	0.14	1.83	2.07
	5	2.00	6.09	3.47	0	3	14	-0.39	0.15	1.82	2.06
Ic[e]	1	4.50	7.21	3.35	0	0	4	0	0.01	2.21	2.20
	2	4.71	7.29	3.65	0	1.5	5	0	0.01	2.21	2.20
	3	4.32	7.21	3.68	0	3	4	0	0.01	2.21	2.20
	4	4.59	7.24	3.53	0	1	5	0	0.01	2.21	2.20
	5	4.53	7.29	3.50	0	0	6	0	0.01	2.21	2.20
Id[d]	1	5.65	6.76	1.76	0	13	22	0	0	2.44	2.44
	2	5.73	6.71	1.85	0	12	22	0	0	2.44	2.44
	3	5.68	6.79	1.74	0	12	20	0	0	2.44	2.44
	4	5.59	6.74	1.79	0	12	21	0	0	2.44	2.44
	5	5.74	6.76	1.71	0	14	22	0	0	2.44	2.44

a. Method of measurement see pp. 37 - 38. P and z values are measured in units of benzene ring radii (1.39 Å). When the p and/or z values exceed the values listed in J & B or M & H table, no correction in chemical shift value is made.

b. Values measured from the methyl group to the benzene rings out of plane of the methyl group. There are two such interacting benzene rings.

c. Values measured from the methyl group to the benzene ring in plane of the methyl group. There is one such interacting benzene ring.

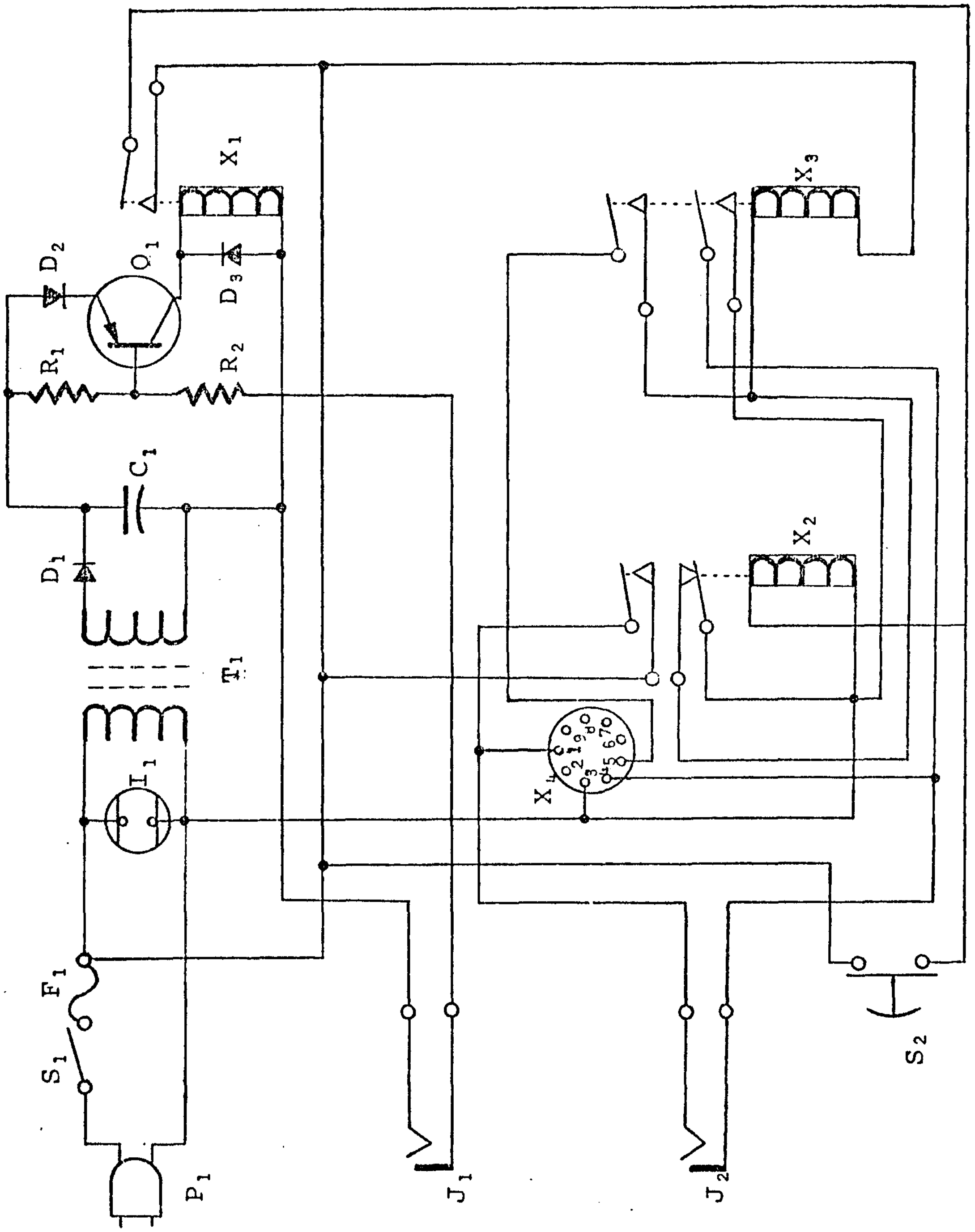
d. Reference standard, δ 2.44 (from 1-methyltriptycene, IXa).

e. Reference standard, δ 2.21 (from 2-methyltriptycene, IXb).

APPENDIX B

Electronic Circuitries of Timer (A), Relay (B) and Automatic Dispensers (C) of Synchronous Constant Volume Addition Assembly.

Fig. XX Timer Unit*



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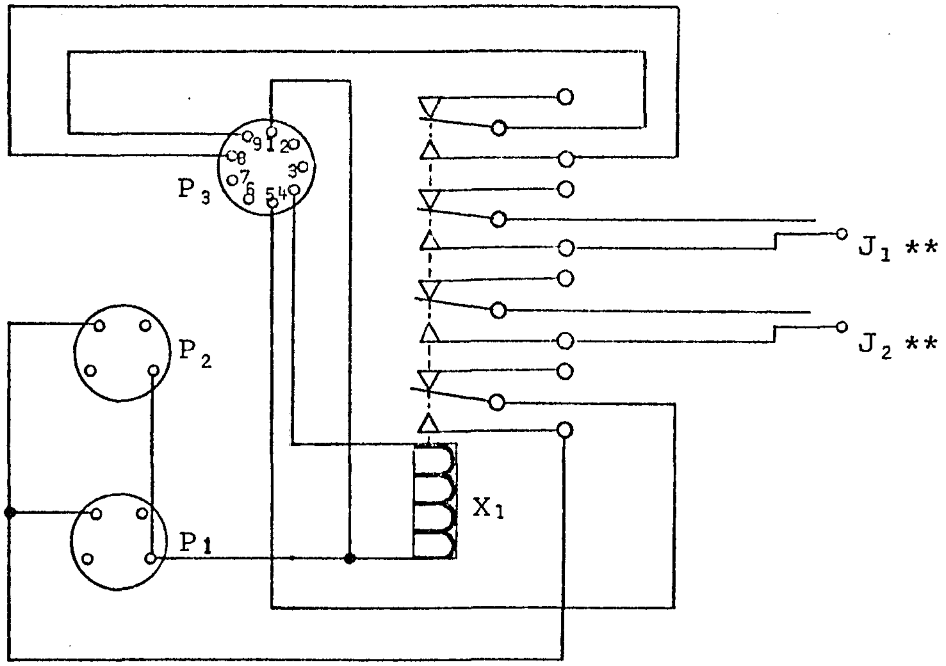
* Converted from Tri-purpose Fraction Collector Activator (# 3-4010, Buchler's Instruments Division[65]).
Conversion made by Mr. R. Walker of The City College of New York.
Components list on page 164.

Fig. XXI Relay Unit*



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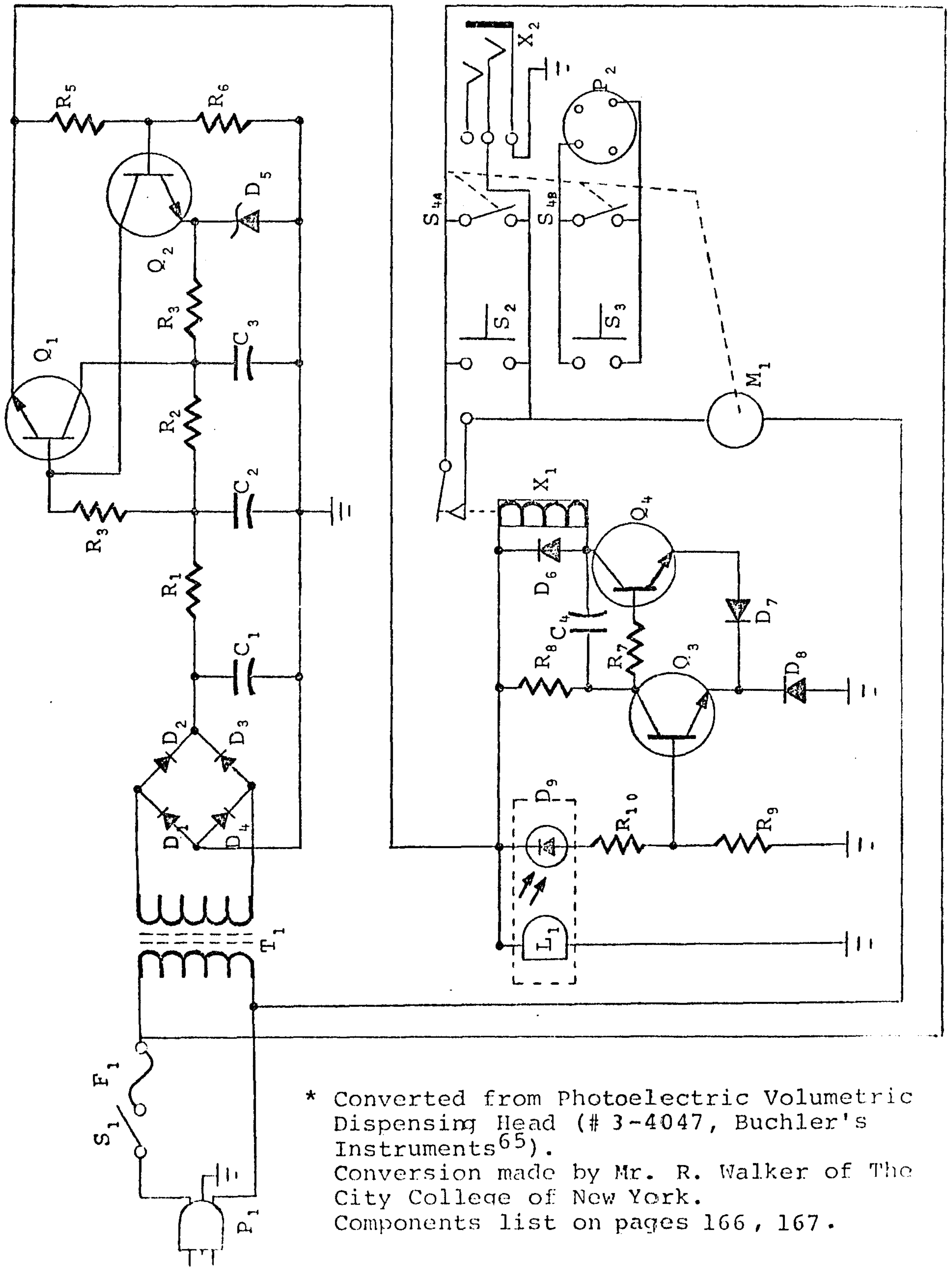
* Designed and made by Mr. R. Walker of The City College of New York.
Components list on page 165.
**No ground connection made to these plugs.

Fig. XXII Automatic Dispenser Unit*



* Converted from Photoelectric Volumetric Dispensing Head (# 3-4047, Buchler's Instruments[65]).
Conversion made by Mr. R. Walker of The City College of New York.
Components list on pages 166, 167.

COMPONENTS LIST FOR TIMER UNIT (Fig. XX)

1. C_1, 50 uF 25 volts capacitor
2. D_1, D_2, D_3, 1N1487 diode
3. F_1, 3AG 3 amp SB Fuse
4. I_1, Neon Lamp and Resistor for Pilot Lamp
5. J_1, Volume Jack
6. J_2, Event Marker Jack
7. Q_1, 2N4872 transistor
8. R_1, 47 KΩ 1/2 watt resistor
9. R_2, 220 KΩ 1/2 watt resistor
10. S_1, SPST On-off Power Switch
11. S_2, SPST Momentary-on Push Button Switch
12. T_1, 117 vac PRI, 12.6 vac sec. Power Transformer
13. X_1, SPST N.O. Relay Coil Resistance 2500
14. X_2, X_3, DPDT Relay 117 vac Coil
15. X_4, 9 Pin Socket to Relay Unit (Fig. XXI)

COMPONENTS LIST FOR RELAY UNIT (Fig. XXI)

1. P_1, P_2, Stereo Phone Plugs (To Automatic Dispenser Unit, Fig. XXII)
2. P_3, 9 Pin Plug (To Relay Unit, Fig. XXI)
3. J_1, J_2, 4 Pin Sockets (To Automatic Dispenser Unit, Fig. XXII)
4. X_1, 4 PDT 115 V 60 cps Relay

COMPONENTS LIST FOR AUTOMATIC DISPENSER UNIT (Fig. XXII)

1. C_1, C_2, C_3, 50 uF 50 volts
2. C_4, .002 uF Disc
3. D_1, D_2, D_3, D_4, D_6, D_7, D_8, 1N4004
4. D_5, Si 1 Volt Zener Diode
5. D_9, Photo Sensitive Diode
6. F_1, 3AG 3 amp Fuse
7. L_1, 16 volt Lamp
8. M_1, Motor to drive SPST cam switches (S_{4A} and S_{4B}) and turn stop
9. P_1, 115 V AC out type plug
10. P_2, 4 Pin Plug (To Relay Unit, Fig. XXI)
11. Q_1, Q_2, Q_4, 2N1711
12. R_1, 100Ω 5 watt
13. R_2, 47Ω 2 watt
14. R_3, R_7, 4.7 KΩ 1/2 watt
15. R_4, 3.9 KΩ 1/2 watt
16. R_5, 1.6 KΩ 1 watt
17. R_6, 820Ω 1 watt
18. R_8, 10 KΩ 1/2 watt
19. R_9, 22 KΩ 1/2 watt
20. R_{10}, 50 KΩ 1/2 watt
21. S_1, SPST On-off Power Switch
22. S_2, SPST Momentary "ON" Push Button Switch
23. S_3, SPST Momentary "OFF" Push Button Switch

24. S_4, See M_1

25. T_1, Power Transformer Buchlor # UV-3 or 94x

26. X_1, SPDT Relay 2500Ω

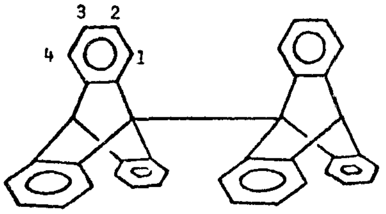
27. X_2, Stereo Phone Jack

APPENDIX C

List of Compounds

List of Compounds

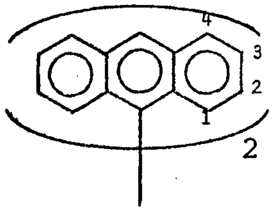
I

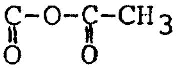


Ia 1,1' = CH_3
b 2,2' = CH_3
c 3,3' = CH_3
d 4,4' = CH_3
e 1,1' 4,4' = CH_3
f 2,2' = Cl
g 2,2' = COOH
h 2,2' = $COOCH_3$

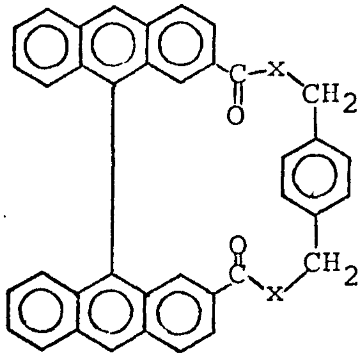
Iab 1,2' = CH_3
ac 1,3' = CH_3
ad 1,4' = CH_3
bc 2,4' = CH_3
cd 3,4' = CH_3

II

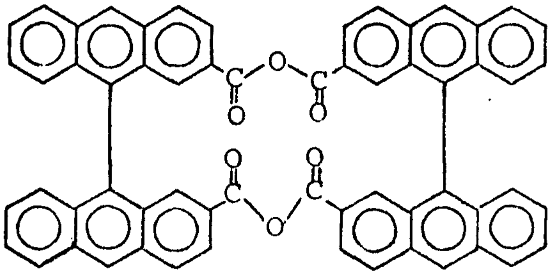


IIa 1,1' = CH_3
b 2,2' = CH_3
c 3,3' = CH_3
d 4,4' = CH_3
e 1,1' 4,4' = CH_3
f 2,2' = Cl
g 2,2' = COOH
h 2,2' = $COOCH_3$
i 2,2' = COCl
j 2-C=O
O
2'-C=O
k 2,2' = CN
l 2,2' = $CONHCH(CH_3)C_6H_5$
m See Figure
n See Figure
o 2,2' = $CON(C_2H_5)_2$
p 2 = COOH, 2' = $COOCH_2(C_6H_4)CH_2OH$
q 2,2' = $COOCH_2(C_6H_4)CH_2OH$
r 2 = CN, 2' = Cl
s 2,2' = 
$\underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-CH_3$
t See Figure
w 2-w-2'

IIab 1,2' = CH_3
ac 1,3' = CH_3
ad 1,4' = CH_3
bc 2,4' = CH_3
cd 3,4' = CH_3

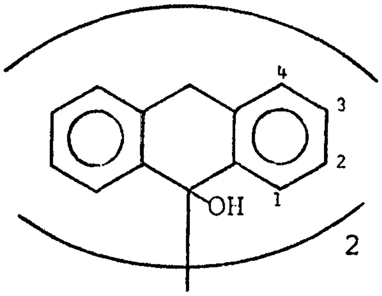


IIm x = NH
n x = O



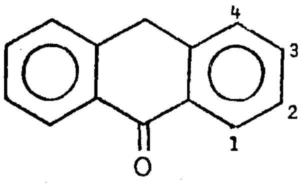
IIt

III



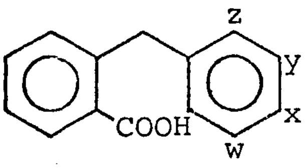
IIIa 1 = CH_3
b 2 = CH_3
c 3 = CH_3
d 4 = CH_3
e 1,1'4,4' = CH_3
f 2 = Cl

IV



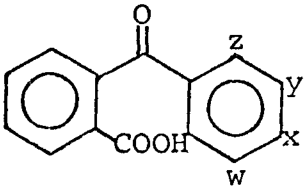
IVa 1 = CH_3
b 2 = CH_3
c 3 = CH_3
d 4 = CH_3
e 1,4 = CH_3
f 2 = Cl

V



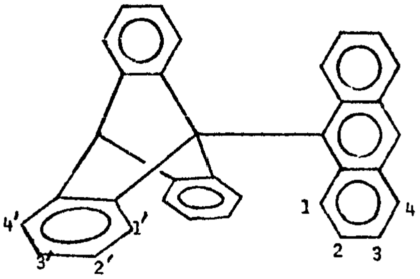
Va w = CH_3
b x = CH_3
c y = CH_3
d z = CH_3
e w,z = CH_3
f x = Cl

VI



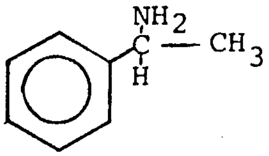
VIa w = CH_3
b x = CH_3
c y = CH_3
d z = CH_3
e w,z = CH_3
f x = Cl

VII



VIIb 2,2' = CH_3
h 2,2' = $COOCH_3$
w 2-w-2'

VIII



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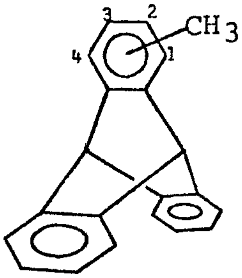
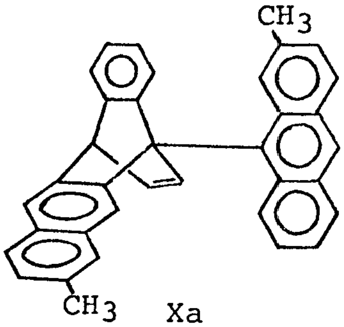


IXa, 1 = CH_3

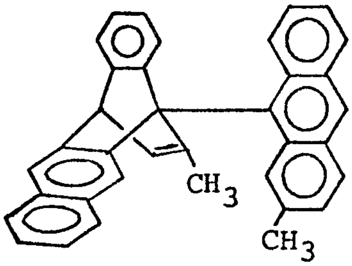
b, 2 = CH_3

e, 1, 4 = CH_3

X



Xa



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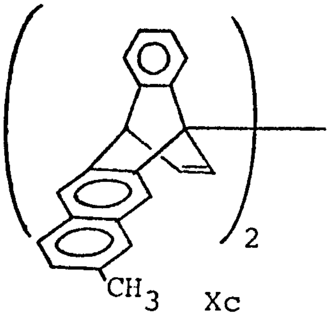
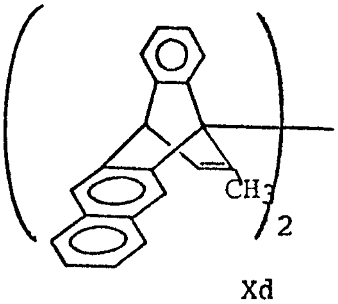
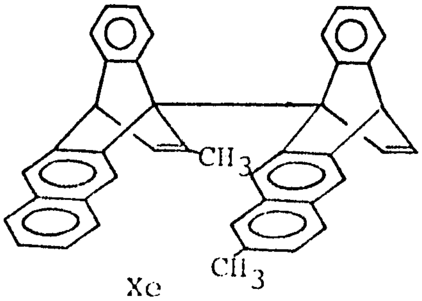


Xc

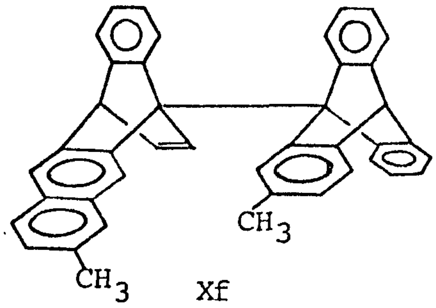


Xd



Xe

X



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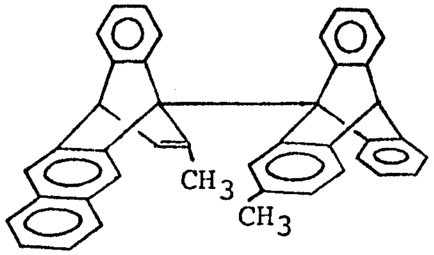
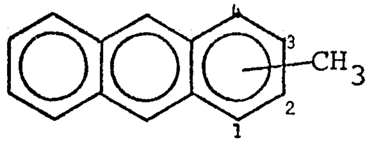


Xg

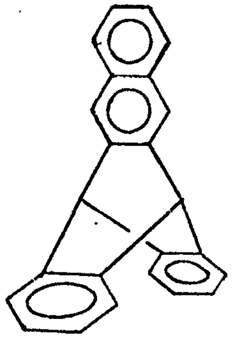
XI



XIa, 1 = CH_3

b, 2 = CH_3

XII



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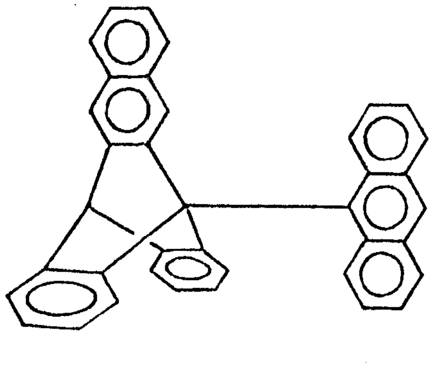

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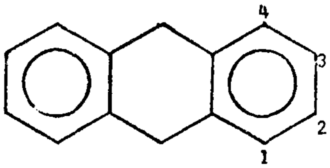
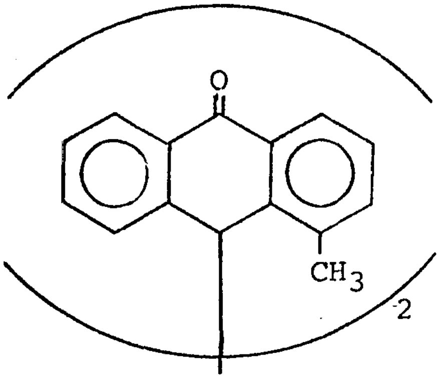


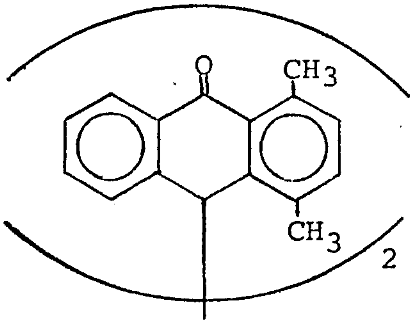
XIVb, 2 = CH_3

e, 1,4 = CH_3

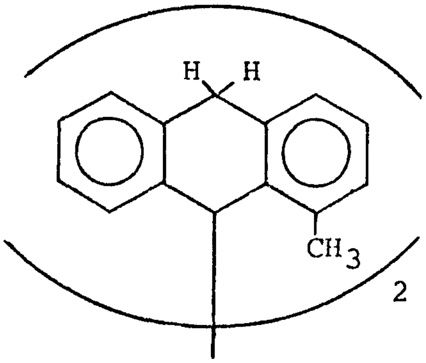
XV



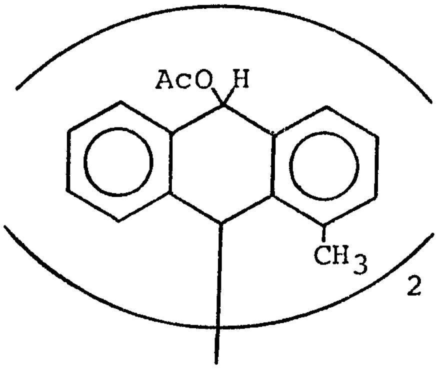
XVI



XVII



XVIII



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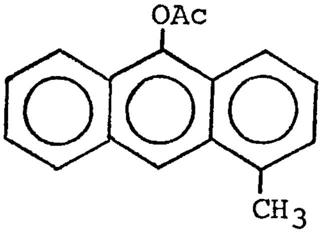
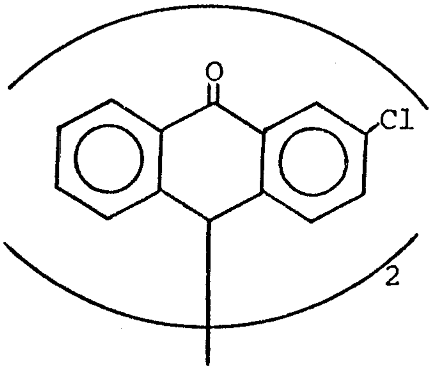
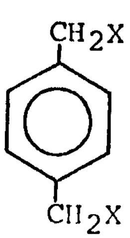


XX

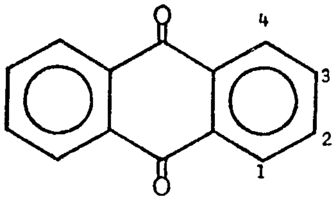


XXI



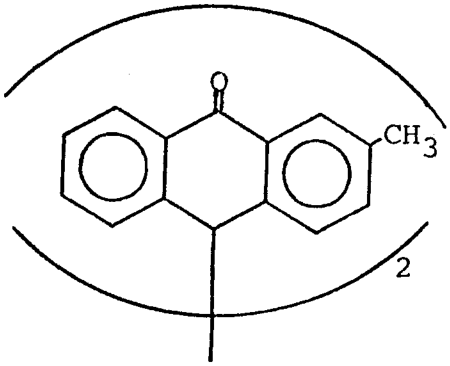
XXIa, x = NH_2
b, x = OH
c, x = $CONH_2$
d, x = COCl
e, x = COOH

XXII

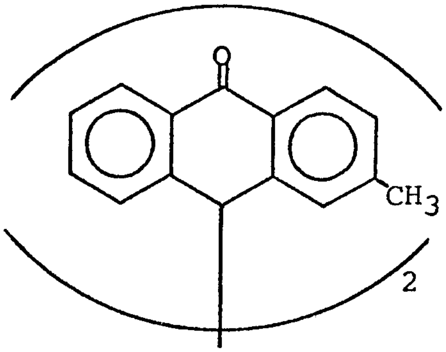


XXIIa, 1(4) = CH_3
b, 2(3) = CH_3
e, 1, 4 = CH_3

XXIII



XXIV



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