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# RESTRICTED ROTATION ABOUT THE
# CARBON-CARBON SINGLE BOND

by

CONSTANTINE KOUKOTAS

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment of
the requirements for the degree of Doctor of
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1968

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To my brother Stephen

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# ABSTRACT

## Restricted Rotation About The Carbon-Carbon Single Bond

by

Constantine Koukotas

Adviser: Leonard H. Schwartz

To date, no stereoisomers resulting from restricted rotation about a $sp^3$-$sp^3$ carbon-carbon bond have been obtained. Exceptions to this involve cases where the atoms of the single bond in question are further connected to each other by a bridge, the properties of the bridge being responsible for the atropisomerism.

In this dissertation the 9,9'-bitriptycyl system is proposed to study restricted rotation about a $sp^3$-$sp^3$ carbon-carbon single bond. A suitably substituted 9,9'-bitriptycyl such as 2,2'-dicarboxy-9,9'-bitriptycyl resembles a 1,2-disubstituted ethane such as n-butane in terms of the number of conformers and the stereochemical relationships among them. It is estimated that the barrier to rotation in 9,9'-bitriptycyl would be high enough so that substituted 9,9'-bitriptycyls would be conformationally stable at ambient temperatures. Various approaches to demonstrate this conformational stability are discussed. The approach chosen for investigation consists of the addition of benzyne to an optically active 2,2'-disubstituted-9,9'-bianthryl. If the resulting 2,2'-disubstituted-9,9'-bitriptycyl were found to be optically active, conformational stability would be established.

Various 2,2'-disubstituted-9,9'-bianthryls have been synthesized. 2,2'-Dicarboxy-9,9'-bianthryl has been resolved into its optical enantiomers. In the process of determining the activation parameters of the racemization of 2,2'-dicarbomethoxy-9,9'-bianthryl, it was discovered that oxygen catalyses this racemization. Various 2,2'-disubstituted-9,9'-bitriptycyls have been synthesized by the addition of benzyne to 2,2'-disubstituted-9,9'-bianthryls. The corresponding 2-substituted triptycenes have also been synthesized. Infrared, mass spectra and ultraviolet data of 9,9'-bitriptycyls and triptycenes are presented; mass spectra are discussed. The addition of benzyne to optically active 2,2'-dicarbomethoxy-9,9'-bianthryl yielded 2,2'-dicarbomethoxy-9,9'-bitriptycyl. After hydrolysis, the resulting 2,2'-dicarboxy-9,9'-bitriptycyl was found to be optically inactive. Possible reasons for this lack of optical activity are discussed.

# Introduction

Stereoisomerism due to restricted rotation about single bonds (atropisomerism) has been recognized for some time. The successful resolution of 6,6'-dinitrodiphenic acid provided the first such case.[1] Since then, numerous substituted biphenyls and binaphthyls have been obtained in optically active form.[2]

The major factor responsible for restricted rotation in biaryls is believed to be steric in origin, although other effects have also been recognized. Thus, in biphenyl atropisomerism, it is the "bulkiness" of the ortho substituents which mainly determines the energy barrier to rotation. This is supported by the fact that the order of interference of ortho substituents as determined by racemization studies, $Br \gg CH_3 > Cl > NO_2 > CO_2H \gg OCH_3 > F$, roughly parallels their van der Waals radii.[3]

The theoretical basis for the steric nature of atropisomerism in

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[1] G.H. Christie and J. Kenner, J. Chem. Soc., 121, 614 (1922).

[2] (a) J. Grundy, "Stereochemistry," Butterworths and Co. Ltd., Washington, D.C., 1964, chap.8; (b) E.L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co.Inc., 1962, chap.6; (c) M.M. Harris, in W. Klyne and P.B.D. de la Mare, ed., "Progress in Stereochemistry," vol.2, 1958, chap.5; (d) R. Adams and H.C. Yuan, Chem. Rev. 12, 261 (1933).

[3] See ref. 2(b), p 161.

biphenyls was provided by Westheimer and coworkers.[4] They calculated, with good agreement[3] with experimental values, the enthalpies of activation for the racemization of 2,2'-dibromo-5,5'-dicarboxybiphenyl, 2,2'-diiodo-5,5'-dicarboxybiphenyl and 2,2', 3,3' -tetraiodo-5,5'-dicarboxybiphenyl. These calculations were based on van der Waals radii and the stretching- and bending-force constants of the bonds involved in a planar transition state.

The energy of racemization ($E_{rac}$) is the difference between the transition state energy ($E_{tr}$) and the ground state energy ($E_{gs}$).

$$E_{rac} = E_{tr} - E_{gs}$$

For biaryls, the transition state energy will be a composite of two opposing factors: (a) a net non-bonded repulsive interaction (steric) between ortho substituents and (b) the gain in resonance energy ($E_{res}$) in going from a non-planar ground state to a planar transition state. Harris and Chua[5] have expressed the energy of racemization as a function of three parameters:

$$E_{rac} = E_{ster} - E_{res} - E_{gs}$$

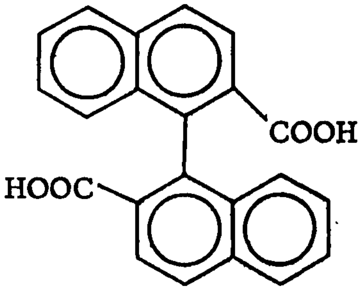
The validity of any racemization energy calculation will depend

[4] F.H. Westheimer and J.E. Mayer, J. Chem. Phys., 14, 733 (1946); F.H. Westheimer, ibid., 15, 252 (1947); M. Rieger and F.H. Westheimer, J. Am. Chem. Soc., 72, 19 (1950); F.H. Westheimer, in M.S. Newman, ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, 1956, chap. 12.

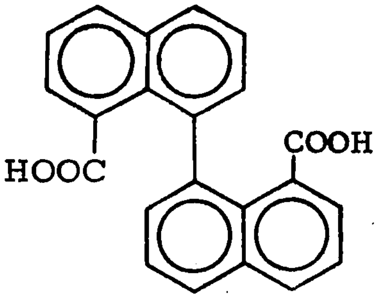
[5] C.K.L. Chua and M.M. Harris, J. Chem. Soc. 1825 (1964).

on the accuracy of estimating these parameters. Howlett, using 6.95 kcal mole$^{-1}$ for the resonance stabilization term and a revised van der Waals potential function, obtained good agreement for 2,2'-dibromo- and 2,2'-diiodobiphenyl with the experimental values.[6] Mislow and coworkers used a value of 4 kcal mole$^{-1}$ for $E_{res}$ in 2,2'-bridged biphenyls.[7]

The ground state energy factor, which is generally ignored for biphenyls since they are relatively strainless in the ground state, may assume importance in strained molecules. The minimum energy planar racemization transition states for compounds I and II involve the same interactions. In addition, the resonance stabilization factor is expected to be approximately the same for both. It would therefore be



I



II

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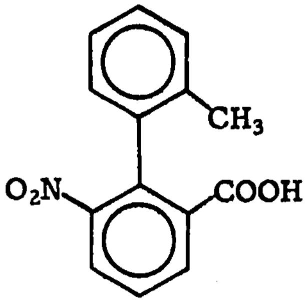
[6] K.E. Howlett, J. Chem. Soc. 1055 (1962).

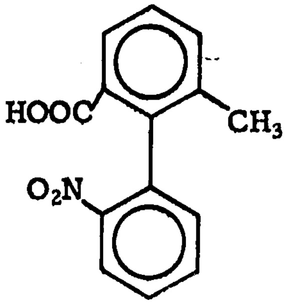
[7] K. Mislow, S. Hyden and H. Schaefer, J. Am. Chem. Soc., 84, 1449 (1962).

expected that both compounds would have very similar racemization energies. Experimentally, it is found that I does not racemize in boiling N-methylformamide at 175° or in boiling tetralin for 2 hr.[8] In contrast, II has a half-life of 51.5 minutes at 50° in N,N-dimethylformamide.[9] Harris and coworkers have attributed the ease of racemization of II to its higher ground state energy, due to the peri interactions between the 8-and 8'-carboxyl groups and the adjacent naphthalene nuclei.[9,10]

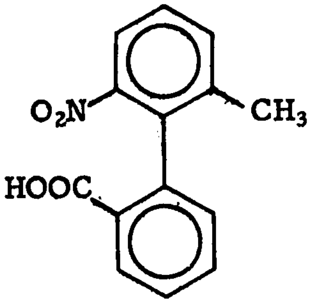
That factors other than steric are also operative and contribute to the energy barrier of rotation can be seen from the optical stabilities of III, IV and V.[11] On steric grounds alone, the predicted order of optical stability would be III > IV ≈ V (see p 2). However, the order of optical stability was found to be V > IV > III.



III



IV



V

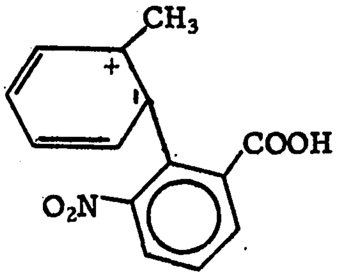
[8] D.M. Hall and E.E. Turner, J. Chem. Soc., 1242 (1955).

[9] A.S. Cooke and M.M. Harris, J. Chem. Soc., 2365 (1963).

[10] Y. Badar, A.S. Cooke and M.M. Harris, J. Chem. Soc., 1412 (1965).

[11] R. Adams and G.C. Finger, J. Am. Chem. Soc., 61, 2828 (1939).

Baddely has proposed that if out-of-plane bending about the 1,1'-bond could take place, it would facilitate racemization.[12] This bending would depend on the availability of electrons to stabilize structures such as VI. The bent structure would require more $sp^3$-like



VI

character for $C_1$ and thus would be favored by a high electron density. It may be noted that the electron densities in the upper rings of compounds III, IV and V parallel the rates of racemization. Crawford and Smyth suggested that in the racemization of biquinolyls and bi-isoquinolyls, hydrogen ions attack the pivotal carbon and change the hybridization from $sp^2$ to $sp^3$.[13] Neither of these proposals received wide acceptance in the past. Recently, Harris has revived these ideas by suggesting that the transition state to racemization of biphenyls may not be planar as previously assumed, but that the 1,1'-bond is

[12] G. Baddeley, Nature, 157, 694 (1946).

[13] M. Crawford and I.F. B. Smyth, Chem. and Ind., 346, (1946); J. Chem. Soc. 3464 (1954).

bent.[5,9,10,14] According to this proposal, racemization would occur by two consecutive ortho-ortho interactions rather than by two simultaneous interactions.

Substituents, other than at ortho positions also effect the barrier to rotation. In general, meta substituents increase the barrier to rotation.[15] This is attributed to the "buttressing effect." In the transition state, meta substituents impede the backward motion of the ortho substituents, forcing them forward. This serves to increase the effective interference size of the ortho groups.

Para substituents make a small contribution to the rotational barrier in comparison with meta substituents. The effect seems to be electronic in nature and parallels their effect on electrophilic aromatic substitution.[5,10] That is, electron donating groups decrease the barrier to rotation while the opposite is true for electron withdrawing groups.

A rotational barrier is associated with all single bonds. Ethane has a barrier of about 3 kcal/mole[16] and although, to date, no conformationally stable ethane has been reported, this only reflects the

[14] M.M. Harris and L.K. Cheung, Chem. and Ind., 1378 (1962).

[15] (a) P.B.D. de la Mare, in W. Klyne, ed., "Progress in Stereochemistry," vol. 1, Butterworths, London, 1954; (b) Ref 2(b), p 163.

[16] K. Pitzer, Disc. Faraday Soc., 10, 66 (1951) gives a value of 2.875 ± 0.125 kcal $mole^{-1}$.

low energy barrier to rotation.

The cause of the rotational barrier in ethane is not completely understood. Eyring and coworkers have calculated that the contribution of the steric factor to the rotational barrier in ethane should amount to only 0.36 kcal mole$^{-1}$.[17] Wilson concluded that neither van der Waals interactions between the hydrogen atoms nor electrostatic interactions between the CH bonds could account for the potential barrier.[18] Recently, Dale has proposed a qualitative model based on two factors, the repulsion between the four substituents or lone pairs of electrons of a tetrahedral atom, and the polarizability of the single C-C bond along the bond direction.[19] However, by his own admission, the model proposed "may not furnish the final theory of restricted rotation in single bonds."

In recent years, N.M.R. spectroscopy has been very valuable in detecting restricted rotation and in the measurement of rotational barriers. For example, 1,2-dineopentyl-tetramethylbenzene shows an AB pattern at room temperature, assigned to the methylene protons, which coalesces into a singlet above room temperature.[20] The observed activation energy

[17] H. Eyring, G.H. Stewart and R.P. Smith, Proc. Natl. Acad. Sci. U.S.A., 44, 259 (1958).

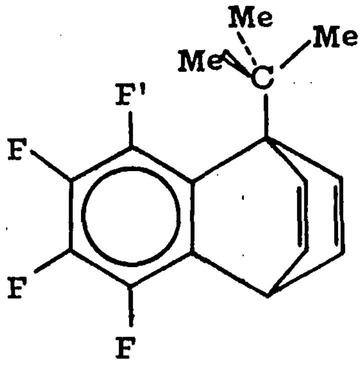
[18] E.B. Wilson, ibid., 43, 816 (1957); Adv. Chem. Phys. (Interscience), 2, 367 (1959).

[19] J. Dale, Tetrahedron, 22, 3373 (1966).

[20] D.T. Dix, G. Fraenkel, H.A. Karnes and M.S. Newman, Tetrahedron Letters, 517 (1966).

of 11.5 ± 0.6 kcal is too small to effect conformational stability[21] at room temperature. The activation energy must still be smaller for the 1,4- and 1,3-dineopentyl derivatives for these isomers do not show such behavior.

An ethane-like molecule which appears to have an appreciable rotational barrier is VII. Coupling is observed between F' and the hydrogens of two of the methyl groups.[22] At room temperature a doublet (6H) is observed at 8.6 $\tau$ (J (F'-H) 2.9 cps) and a singlet (3H) at 8.8 $\tau$ . These signals begin to collapse at 120°. At 180° a doublet (9H) at 8.42 $\tau$ (J (F'-H) ~ 2.1 cps) begins to form. When the sample is



VII

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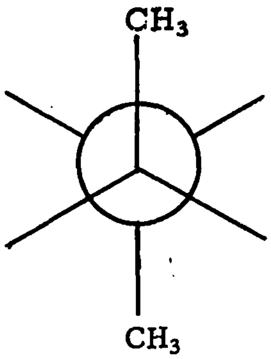
[21] The term "conformational stability" is used here and elsewhere to denote stereoisomerism due to restricted rotation. Thus, ortho substituted biphenyls obtained in an optically active form are conformationally stable. n-Butane (see subsequent discussion, p 10) would be conformationally stable if more than one isomer (due to restricted rotation) were isolable.

[22] J.P.N. Brewer, H. Heaney and B.A. Marplus, <u>Chem</u>. <u>Comm.</u>, 27 (1967).

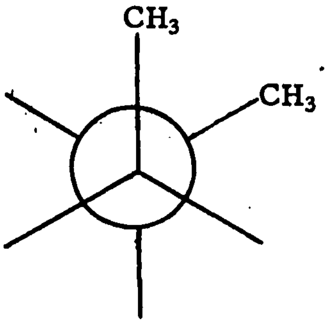
cooled to room temperature, the original spectrum is again observed.

Let us briefly consider the stereochemical consequences of restricted rotation in a substituted ethane such as n-butane. n-Butane exists as an equilibrium mixture of three minimum energy conformations (VIII, IX and X).

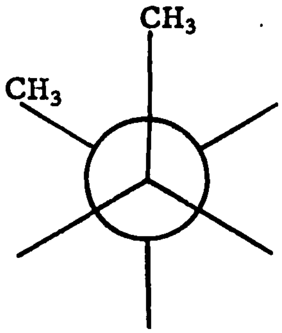


VIII

anti-parallel



IX



X

syn-skew

If the barrier to rotation were high enough, then n-butane would exist as two distinct diastereomers. Accordingly, the physical properties (boiling points, dipole moments, spectra, optical activity, etc.) would differ. The fact that only one n-butane is known reflects the low interconversion energy barrier of these conformers.[23] This

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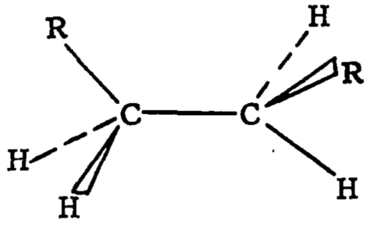
[23] The conformational stability of an ethane depends not only on the energy barrier but also on the Arrhenius pre-exponential factor, "A" (related to entropy). For biphenyls[15a] "A" is of the order of 10" $sec^{-1}$ while for binaphthyls[10] it is of the order of $10^{12}$. Some bridged biphenyls and binaphthyls have higher "A" values (D.M. Hall and M.M. Harris, J. Chem. Soc., 490 (1960)). Assuming an A factor of $10^{12}$ and an energy barrier of 25 kcal $mole^{-1}$ the half-life of racemization would be approximately 1.5 hr at $50^{\circ}$.

barrier[24] has been estimated to be approximately 2.9 - 3.5 kcal mole$^{-1}$ for the conversion of VIII to IX and 3.6 - 5.2 kcal mole$^{-1}$ for the interconversion of IX and X by way of the eclipsed conformation involving a methyl-methyl interaction.

Somewhat higher barriers to rotation are found with the halogenated ethanes.[20,25] Apparently the steric factor comes into play, raising the barrier to rotation. In principle, the rotational barrier may be increased by increasing the steric size of the groups attached to the carbon atoms. However, because of the tetrahedral nature of the carbon atom, the substituents on most ethanes are directed away from each other (XI).



XI

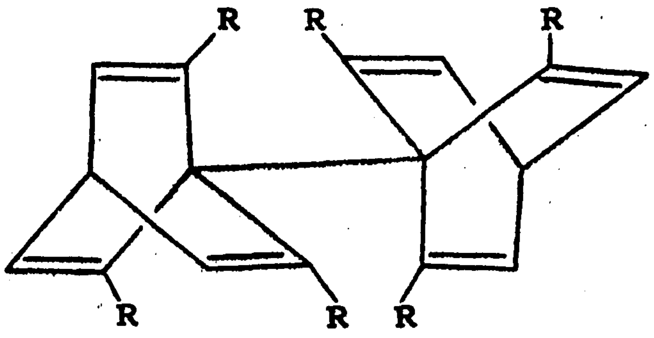
Furthermore, increasing the size of the substituents introduces not only vicinal interactions but also geminal interactions. Thus, not only the transition state energy is raised but also the ground state energy. Aside

[24] Ref 2(a), p 54; 2(b), p 125.

[25] R. A. Newmark and C.H. Sederholm, J. Chem. Phys., 43, 602 (1965).

from energy considerations, synthetic problems of increasing difficulties are certain to be encountered as the groups become larger.

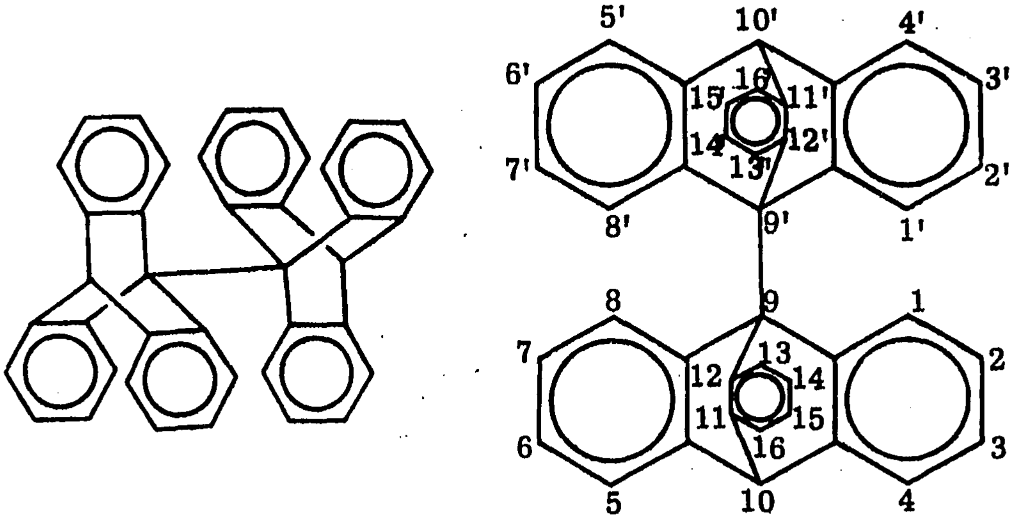
To maximize rotational barriers and minimize synthetic difficulties the interfering groups should be directed towards each other along the rotational bond axis. A substituted bibarrelene (XII) would provide such an ideal case.



XII

Unlike with most other substituted ethanes, here the substituents (R) are directed toward each other.

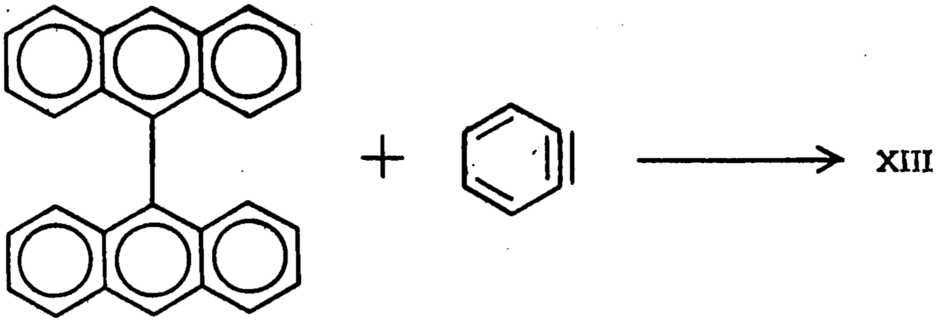
9,9'-Bitriptycyl (XIII) should also possess such directional inter-



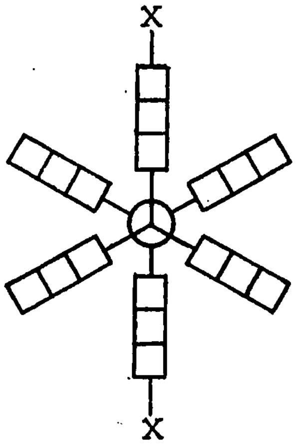
XIII

ference along the rotational axis.

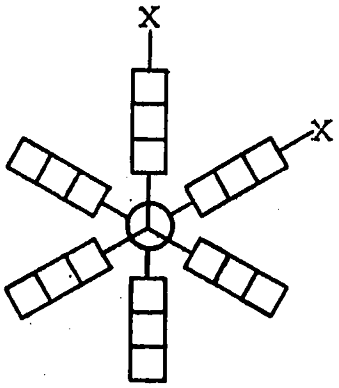
We have synthesized 9,9'-bitriptycyl by the addition of benzyne to 9,9'-bianthryl (see p 94).[26] Substituted bitriptycyls can be synthesized



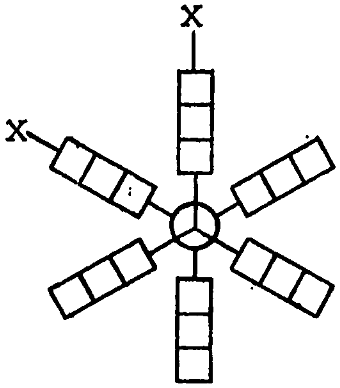
using substituted 9,9'-bianthryls or substituted benzynes. The conformational problem in a substituted 9,9'-bitriptycyl such as 2,2'-dimethyl-9,9'-bitriptycyl is comparable to n-butane. Thus, we have three staggered conformers, an antiparallel (XIV) and two enantiomeric syn-skew (XV, XVI).



XIV



XV



XVI

▭▭▭ = side view of benzene ring

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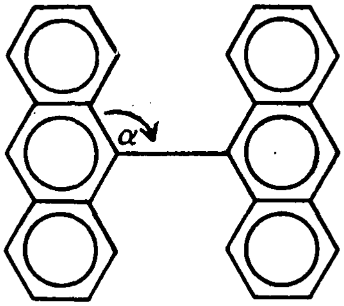
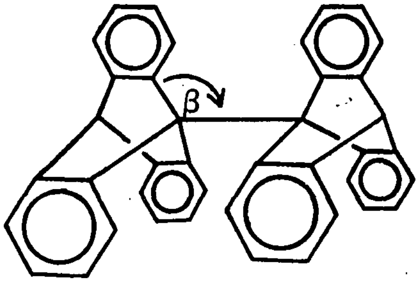
[26] C. Koukotas, S.P. Mehlman and L.H. Schwartz, J. Org. Chem., 31, 1970 (1966).

Although molecular models indicate a high degree of interference of the benzo groups in the transition state to rotation, the magnitude of such interactions cannot be estimated with any degree of accuracy. In principle, the barrier to rotation could be estimated if the magnitude of the benzo-benzo interaction and the ground state energy were known. Unfortunately, neither is known. Using the 1,1'-binaphthyl system as a model, a crude estimate of the benzo-benzo interaction in 9,9'-bitriptycyl can be made. Differences due to different central carbon-carbon bond lengths are assumed to be of minor importance. It is necessary to make this assumption, and it may very well be justifiable to a degree. Due to differences in hybridization, the central carbon-carbon bond in 9,9'-bitriptycyl is probably somewhat longer than the central bond in 9,9'-bianthryl. However, angle $\beta$ in 9,9'-bitriptycyl is smaller than angle $\alpha$ in 9,9'-bianthryl. This smaller angle in 9,9'-bitriptycyl will cause the benzo groups on opposite halves of the molecule to be closer, compensating in part for the difference in central carbon-carbon bond distances.

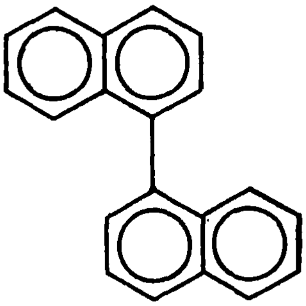


9,9'-bianthryl

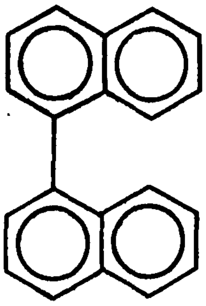


9,9'-bitriptycyl

The energy of racemization of 1,1'-binaphthyl is 22.5 kcal mole$^{-1}$.[9] The transition state is certainly XVII, which does not involve a benzo-benzo interaction and not (XVIII) which does.

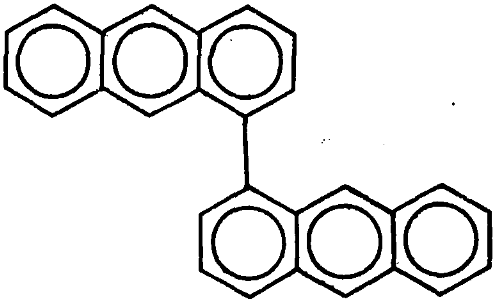


XVII

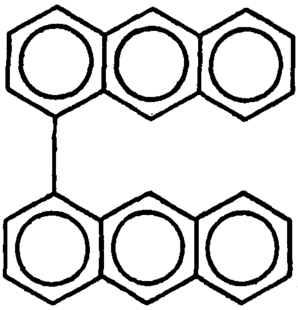


XVIII

This is supported by the fact that 1,1'-bianthryl[27] has a half-life of approximately 1 hr in boiling chloroform, indicating a transition state (XIX) involving the same interactions as in 1,1'-binaphthyl rather than XX.



XIX

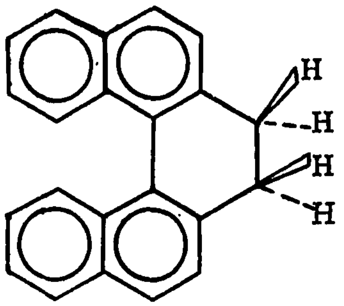


XX

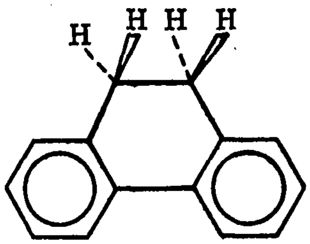
[27] F. Bell and D.H. Waring, *J. Chem. Soc.*, 1579 (1949).

It may therefore be concluded that a benzo-benzo interaction plus the hydrogen-hydrogen interaction of the 2,2'-positions is greater than 22.5 kcal mole$^{-1}$. Subtracting one-half the calculated racemization energy of biphenyl (4 kcal mole$^{-1}$)[28] the minimum value for the benzo-benzo interaction is estimated to be 20.5 kcal mole$^{-1}$.[29] In this analysis ground state differences have been assumed to be of minor importance, and a planar transition state has been assumed.

The bridged 1,1'-binaphthyl XXI has been obtained in an optically active form.[30] This molecule, which may also be looked upon as a conformationally stable ethane, has an energy barrier of racemization of 30.8 kcal mole$^{-1}$.[31] This barrier can be assumed to



XXI



XXII

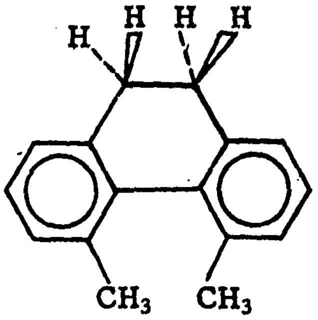
[28] K.E. Howlett, *J. Chem. Soc.*, 1055 (1960).

[29] F.J. Adrian, *J. Chem. Phys.*, *88*, 606 (1958), gives a value of 0.5 kcal mole$^{-1}$ for the racemization energy of biphenyl. Using this value the minimum benzo-benzo interaction would be 22.3 kcal mole$^{-1}$.

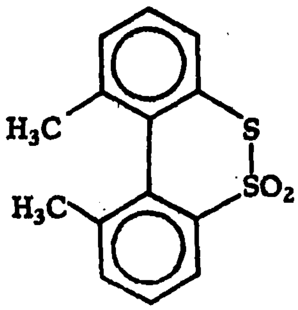
[30] D.M. Hall and E.E. Turner, *J. Chem. Soc.*, 1242 (1955).

[31] D.M. Hall and M.M. Harris, *J. Chem. Soc.*, 490 (1960).

be the sum of two factors: the benzo-benzo interaction and the contribution of the bridge. Howlett calculated the energy of racemization of 9,10-dihydrophenanthrene (XXII) to be 1.4 kcal mole$^{-1}$.[32] Mislow and Hopps[33] determined the energy of racemization of XXIII to be 23 kcal mole$^{-1}$. From the energy barrier (31 kcal mole$^{-1}$) of XXIV and the calculated contribution of the bridging (10 kcal mole$^{-1}$), 21 kcal mole$^{-1}$ was assigned to a methyl-methyl interaction. Assuming this to be the value of the methyl-methyl interaction in XXIII, this leaves about 2 kcal mole$^{-1}$ for the contribution of the bridge to the racemization energy of XXIII.



XXIII



XXIV

Therefore, the barrier in the bridged 1,1'-binaphthyl (XXI) is almost entirely due to the benzo-benzo interaction. Subtracting the contribution of the bridge (2 kcal mole$^{-1}$) from the total energy of

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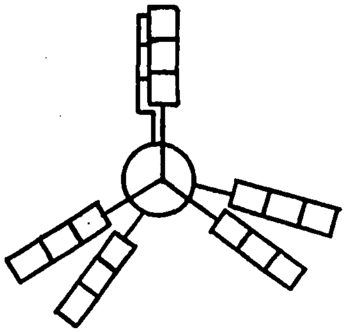
[32] K.E. Howlett, J. Chem. Soc., 1249 (1955).

[33] K. Mislow and H.B. Hopps, J. Am. Chem. Soc., **84**, 3018 (1962).

racemization (31 kcal mole$^{-1}$), a value of 29 kcal mole$^{-1}$ is obtained for the benzo-benzo interaction. This value is probably on the low side compared to the corresponding unbridged compounds which probably have lower ground state energies. In this analysis the resonance energy factor has been ignored. If this factor were considered, a higher estimated value would be obtained.

9,9'-Bitriptycyl would involve three benzo-benzo interactions in the transition state to rotation. A transition state involving less than three benzo-benzo intractions can also be imagined (XXV). However, it would be accompanied by considerable angle deformation.

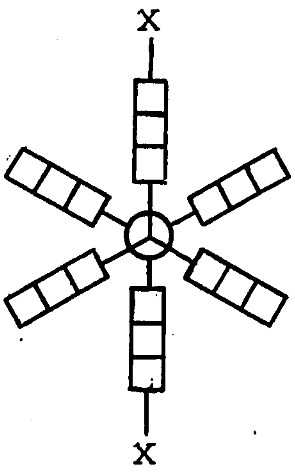


XXV

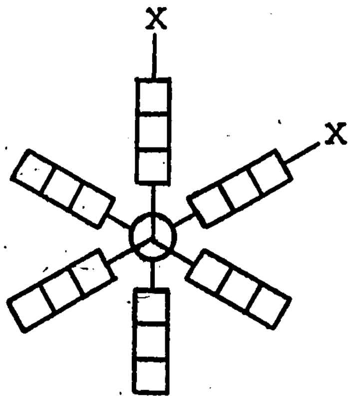
The resonance energy factor can be ignored. Of possible importance, however, is the ground state energy. 9,9'-Bitriptycyl appears from molecular models to be considerably strained in the staggered conformation (ground state). However, because of the three benzo-benzo interactions in the transition state, the ground state energy would have to be enormous to permit interconversion of the rotational isomers at room temperature. Three benzo-benzo interactions would amount to 3(29) = 87 kcal mole$^{-1}$. The value of 29 kcal mole$^{-1}$ is taken from a system with considerable ground state energy. To effect interconversion of the rotational isomers at ambient temperatures a value of more than 50 kcal mole$^{-1}$ would have to be assigned to the ground state strain energy. It may therefore be concluded that a substituted 9,9'-bitriptycyl will be conformationally stable at ambient temperatures. Whether rotation about the single bond, and thus interconversion of the isomers, can be effected at higher temperatures or not is difficult to predict. A rotational barrier of 50 kcal mole$^{-1}$ or greater would prevent interconversion of the isomers in normal high boiling solvents (200 - 250$^{\circ}$).[34]

There are a number of routes available for demonstrating conformational stability in the 9,9'-bitriptycyl system. These routes are based on the stereochemical relationships among the possible conformers of a substituted bitriptycyl. The first two discussed below, (1) and (2), are based on the diastereomeric relationship between conformers XIV and XV or XVI, and the other, (3), on the enantiomeric relationship between XV and XVI.

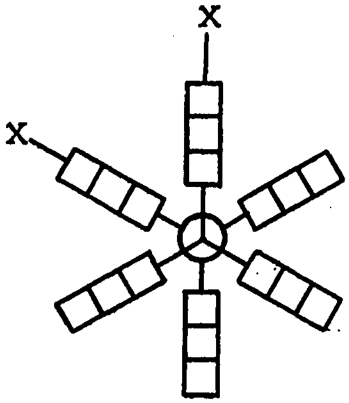
[34] For the interconversion of two isomers A→B or B→A which have the same ground state energy, the rate constant for the process is given by the Arrhenius equation $k = Ae^{-E/RT}$. The half life ($t_{1/2}$) of either A or B will be $t_{1/2} = \frac{0.69}{k}$. For a rotational barrier of 50 kcal mole$^{-1}$ and an "A" value of $10^{13}$ (possibly a large value, see ref (23)), at 250$^{\circ}$ $t_{1/2} \simeq 2 \times 10^{4}$ hr.



XIV



XV



XVI

(1) A difference in physical properties should exist between the diastereomeric conformers. Separation, based upon differences in properties such as solubility, thin layer chromatographic behavior, etc., may be possible. Such a separation would demonstrate conformational stability and restricted rotation.

However, because the substituents constitute a very small portion of the molecule and are well separated, the differences in properties might be too small to be useful.

If the separation were accomplished, thermal interconversion of the conformers to an equilibrium mixture would yield the activation parameters. This assumes that the barrier to rotation is low enough to effect thermal equilibration.

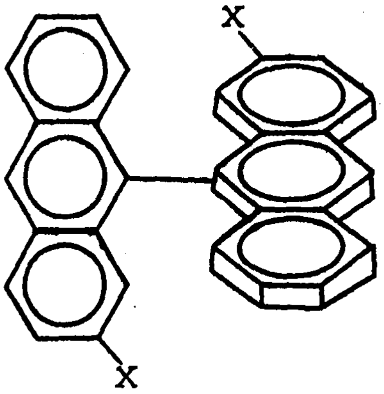
(2) If the formation of the substituted bitriptycyl were kinetically controlled, the thermal equilibration to the thermodynamic equilibrium mixture of diastereomeric conformers, which hopefully would be accomplished by some observable change in physical properties of the

mixture, would prove conformational stability. For example if the spectral properties of the mixture were examined before and after such an equilibration, differences might be observed. The underlying assumptions in this approach are: (a) The free energies of activation for the formation of the two diastereomeric conformers are sufficiently different to cause a detectably different kinetically controlled product composition from that of the equilibrium mixture. (b) The barrier to rotation is small enough to allow thermal equilibration.

(3) Resolution of the mixture of conformers would prove conformational stability. However, failure to resolve the mixture would be inconclusive, since we might not be using the correct resolving agent, the active material might not have a detectable rotation, or a less likely possibility, only conformer XIV might be present.

Another approach would be to start with an optically active 9,9'-bianthryl such as 2,2'-dicarbomethoxy-9,9'-bianthryl. If addition of benzyne yielded an optically active bitriptycyl, conformational stability would be established. An inactive product would again be inconclusive.

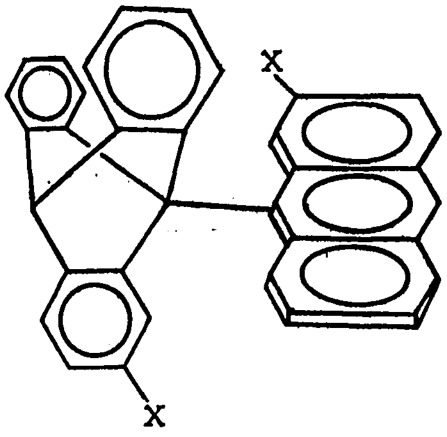
That an optically active product is to be expected can be seen from the following analysis. We will make the reasonable assumption that benzyne will add to an optically active 9,9'-bianthryl (XXVI) one molecule at a time. The first product formed would be a 9-anthracyl-9'-triptycene (mono-adduct) derivative.



XXVI 2,2'-di-x-9,9'-Bianthryl
One Enantiomer

Addition of benzyne to either ring of XXVI would produce either XXVII, XXVIII or XXIX depending on the direction of approach of the benzyne. Consider addition to the left anthracyl unit. Attack from either the front or the back of the plane of the left anthracyl unit and from above the plane of the right anthracyl unit would produce conformer XXVII. Attack from below the plane of the right unit but from the front of the left unit would produce conformer XXVIII. Attack from the back of plane of the left unit and below the plane of the right unit would give conformer XXIX. Similar considerations for the addition of benzyne to the right anthracyl unit lead to the formation of the same three species. The statistical ratio of conformers XXVII, XXVIII and XXIX would therefore be 2:1:1.

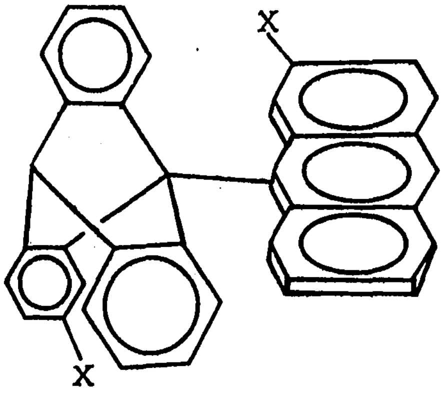
A. Attack of benzyne from the front and downwards.



XXVII

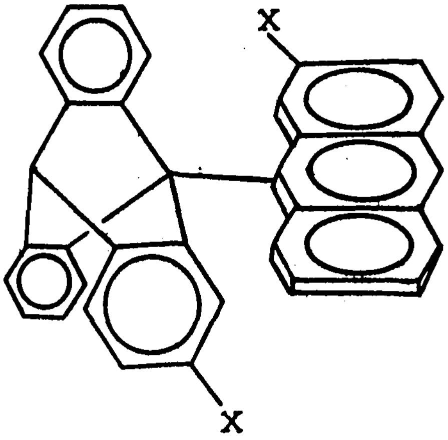
B. Attack of benzyne from the back and downwards will give the same product, XXVII.

C. Attack of benzyne from the front and upwards



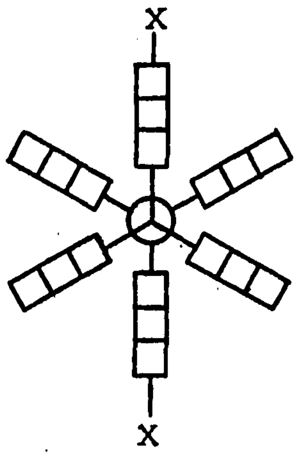
XXVIII

D. Attack of benzyne from the back and upwards

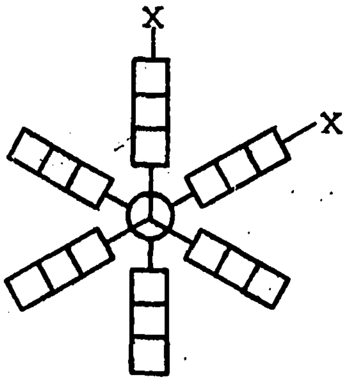


XXIX

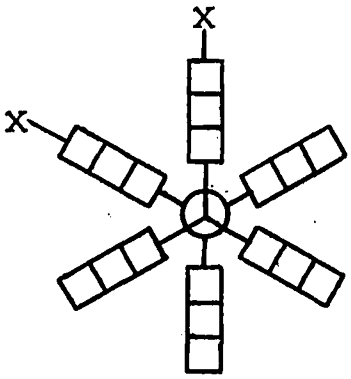
However, the four possible modes of addition are not necessarily equally probable. The conformation (dihedral angle) of the disubstituted bianthryl could have an effect on the direction of addition, as could also the substituent "X". The magnitude and direction of these effects cannot readily be assessed, e.g., whether "X" primarily attracts the incoming benzyne or repels it cannot be established at the present time. The important conclusion to be derived at this stage is that no matter what the relative population of the resulting adducts, all would be optically active provided that rotation about the 9,9'-single bond did not occur. Whether racemization of these conformers occurs or not depends on the barrier to rotation. The transition state to racemization requires only one benzo-benzo interaction. If racemization occurs, upon the addition of a second molecule of benzyne the resulting bitriptycyl would be optically inactive. If, however, there is no interconversion of the mono-adducts (XXVII, XXVIII, XXIX) or if the interconversion is slow compared to the addition of the second benzyne molecule, the resulting bitriptycyl would be optically active. The optical purity would depend on the relative amounts of conformers XIV, XV and XVI produced, which in turn would depend on the direction of benzyne addition to, and the relative amounts of, XXVII, XXVIII and XXIX.



XIV

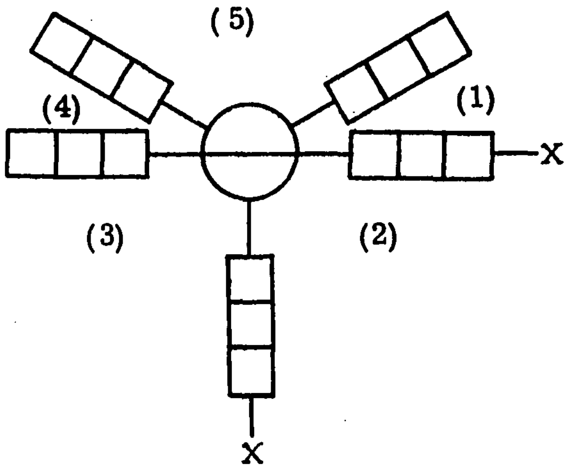


XV



XVI

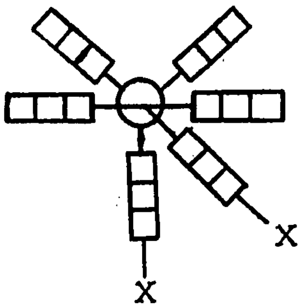
Let us represent the mono-adduct XXVII as follows:



XXVII

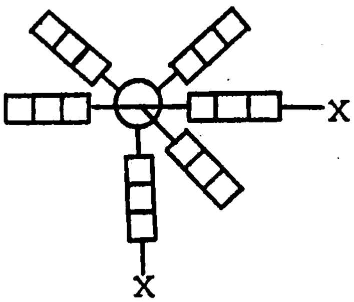
There are five directions (numbered 1 - 5) from which a second benzyne molecule could approach the mono-adduct to give a bitriptycyl. The approach of benzyne from direction (5) is energetically favored over the others, because it involves the least steric hindrance, and of possible greater importance, the transition state to addition resembles the staggered conformation.

The following conformations would be obtained if benzyne added to XXVII from directions (1), (2), (3), (4) and (5).



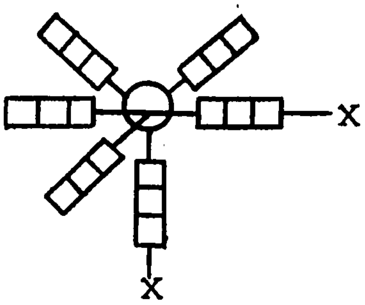
(from 1)

XXX



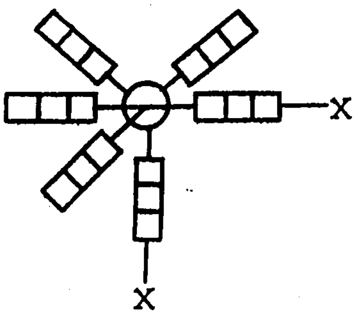
(from 2)

XXXI



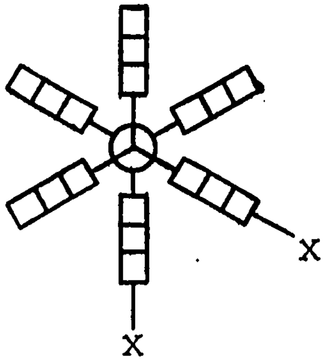
(from 3)

XXXII



(from 4)

XXXIII

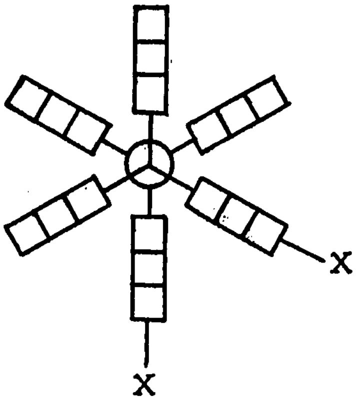


(from 5)

XV

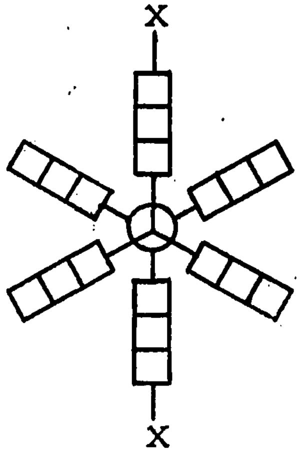
XXXII ≡ XXXIII

Conformations XXX, XXXI, XXXII and XXXIII, because of severe angle deformations and steric hindrance are less stable than XV. In order to assume their normal bond angles a rotation of benzo groups past each other would be necessary. The following conformers would be produced.



from XXX, XXXII and XXXIII

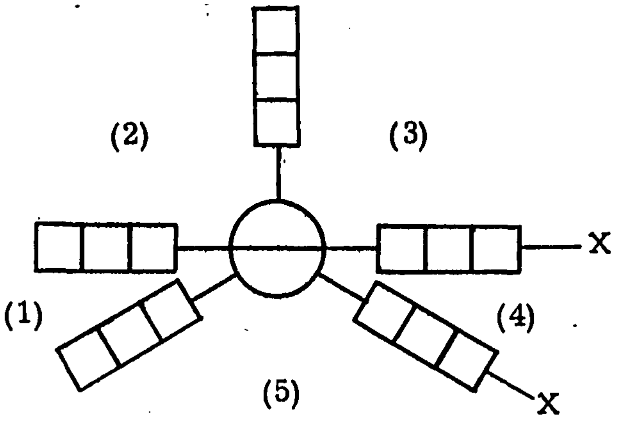
XV



from XXXI

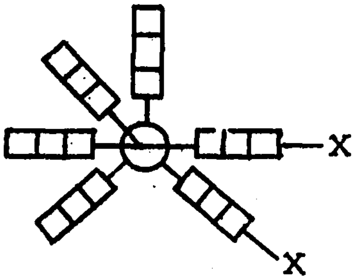
XIV

Consider now the addition of benzyne to mono-adduct XXVIII.



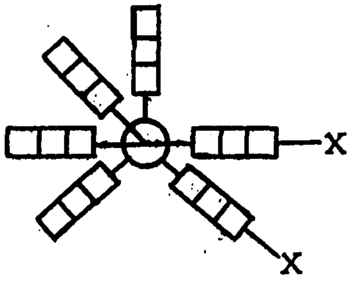
XXVIII

The following conformations would be obtained by benzyne attack from directions (1), (2), (3), (4), and (5).



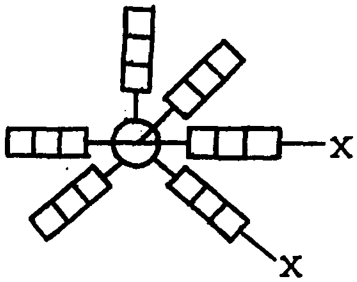
(from 1)

XXXIV



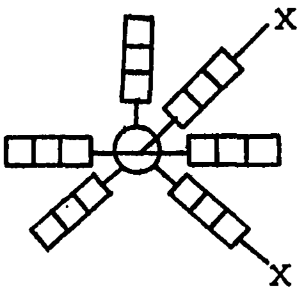
(from 2)

XXXV



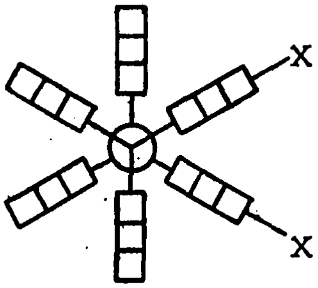
(from 3)

XXXVI



(from 4)

XXXVII

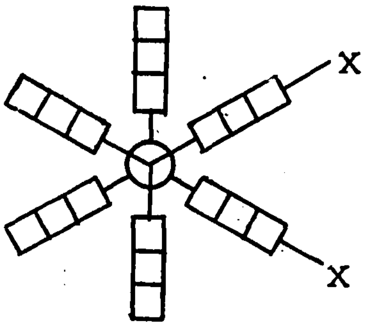


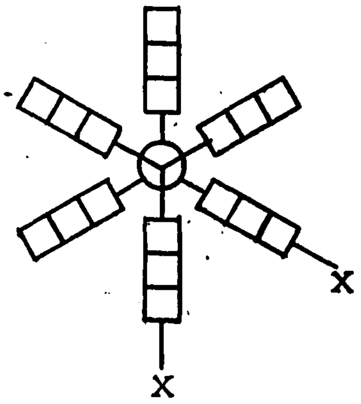
(from 5)

XV

XXXIV ≡ XXXV

Here again the formation of conformer XV would be favored over the others. Release of angle deformation would yield the following conformers from XXXIV, XXXV, XXXVI and XXXVII.





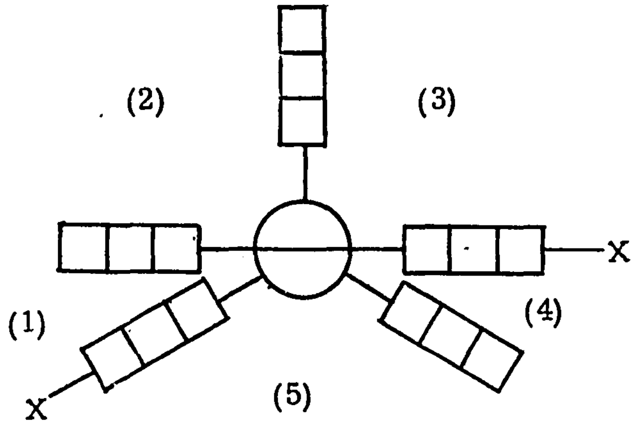
from XXXIV, XXXV and XXXVII

from XXXVI

XV

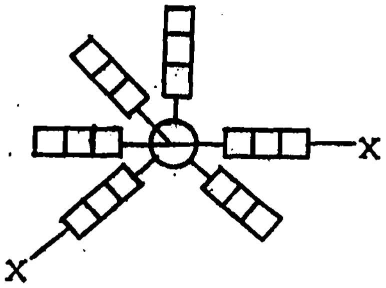
XVI

Finally, let us consider the addition of benzyne to mono-adduct XXIX.



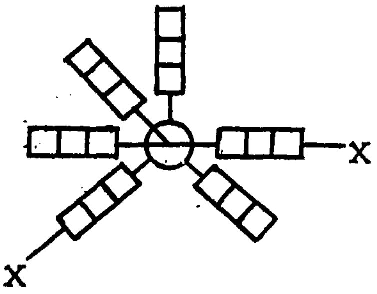
XXIX

Addition of benzyne from directions (1), (2), (3), (4) and (5) leads to the following conformations.



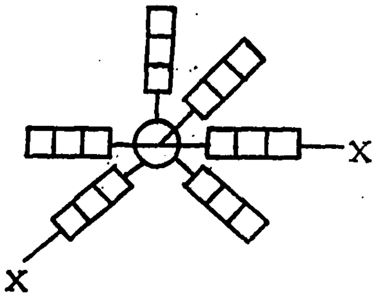
(from 1)

XXXVIII



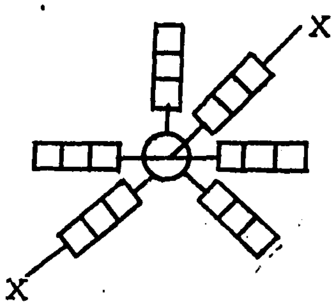
(from 2)

XXXIX



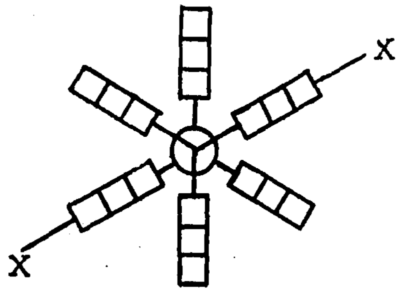
(from 3)

XL



(from 4)

XLI

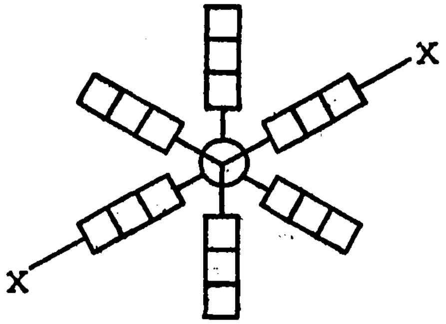


(from 5)

XIV

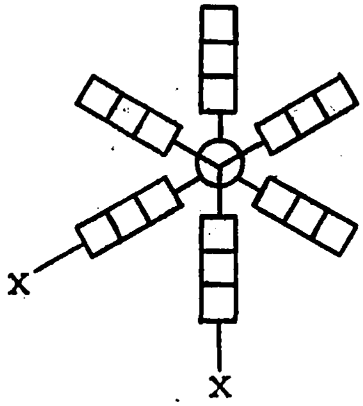
XXXVIII ≡ XXXIX

Upon release of angle deformation, the following conformers would be obtained.



from XXXVII, XXXIX and XLI

XIV



from XL

XV

Table I. Conformers Obtained From the Addition of Benzyne to XXVI

| Addition Direction (pp 22 - 24) | XIV | XV | XVI |
|---|---|---|---|
| A | 1 | 4 | |
| B | 1 | 4 | |
| C | | 4 | 1 |
| D | 4 | 1 | |
| Total | 6 | 13 | 1 |

Assuming equal probability for each direction of benzyne addition there would be 70% syn-skew (XV and XVI), and 30% anti-parallel conformers. The optical purity of the syn-skew conformer would be 86%. If benzyne added only from the favored direction (5), then from XXVII and XXVIII only XV would be formed, while from XXIX the symmetrical conformer XIV would be obtained. Here, the percent syn-skew conformer would be 75%; it would be optically pure.

## Experimental

Microanalyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside 77, New York. Melting points, unless otherwise indicated, were determined on a Thomas-Hoover apparatus and are corrected; boiling points are uncorrected.

Infrared spectra were determined on a Perkin-Elmer Infracord 137 spectrophotometer, ultraviolet spectra on a Cary 14 Spectrophotometer and nuclear magnetic resonance spectra on a Varian A-60 spectrometer. Mass spectra were determined on Hitachi RMU-6 Mass Spectrometer by Morgan-Schaeffer Corp., Montreal, Canada.

Because of water absorption, bands above 3200 $cm^{-1}$ are not reported for infrared spectra taken in KBr.

Optical rotations, unless otherwise indicated, were measured with a Rudolph 80 Polarimeter.

## (A) Preparation of 9,9'-Bianthryl Derivatives

### (1) Preparation of 3,3'-Dimethyl-9,9'-bianthryl

### (a) Preparation of 3-Methylanthrone. Reduction of 2-Methylanthraquinone[35]

To a solution of 100 g (0.45 mole) of 2-methylanthraquinone in 900 ml of concentrated sulfuric acid (d=1.84), 20 ml of water was added. The temperature rose to 30 - 35°. Aluminum powder (18.0 g, 0.67 g-atom) was slowly added, with stirring, over a period of 4 hr. The addition of aluminum was sufficiently exothermic to maintain the reaction temperature at 30 - 40°. Stirring was continued for an addition 6 hr. As previously noted[35], when the reduction was completed, foaming occurred.

The reaction mixture was poured onto ice, and a yellow solid precipitated. The solid was recrystallized (15 - 20 times) to constant mp, from methanol, to yield 7.81 g (8.3%) of the yellow solid, 3-methylanthrone: mp 99.2 - 101.2° (lit [35,36] 101°, 102°); IR (KBr): 3030 (w, aromatic C-H), 2900 (w, aliphatic C-H), 1670 (s, carbonyl), 1620 (s), 1490 (m) (aromatic nucleus), 1335 (m), 1310 (s) (aromatic ketone, due to -C-(CO)-C- bending and stretching), 842 (m,

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[35] E. De Barnett and N.F. Goodway, J. Chem. Soc., 1754 (1929).

[36] F. Bell and D.H. Waring, J. Chem. Soc., 2689 (1949).

1,2,4-trisubstituted aromatic), 730 (s, 1,2-disubstituted aromatic). The bands at 865 and 815 present in 2-methylanthrone (p 41) are notably absent even in the crude reduced 2-methylanthraquinone.

### (b) Preparation of 3,3'-Dimethyl-9,9'-anthrapinacol. Bimolecular Reduction of 3-Methylanthrone[37]

In a 250-ml flask, equipped with two reflux condensers and a mechanical stirrer, were placed 7.79 g (0.0375 mole) of 3-methylanthrone (p 33), 40 ml of dry benzene and 56 ml of absolute ethanol.

To the refluxing solution, 3.42 g (0.127 g-atom) of aluminum foil (freshly scratched, cut into ½ inch squares, and ground with approximately ½ g of mercuric chloride) was added, with stirring, over a period of 1¼ hr. To the resulting green viscous mixture, 35 ml of absolute alcohol was added, and refluxing was continued for an additional 3 hr.

The reaction flask was cooled in an ice bath, and 100 ml of 1:3 hydrochloric acid was slowly added. The reaction solution was extracted with 300 ml of benzene. The benzene extract was evaporated to give a light yellow solid. This solid was extracted with 200 ml of methanol. Evaporation of the methanol solution yielded 4.75 g of a light yellow solid which was free of 2-methylanthracene, as evidenced by comparison of its infrared spectrum with that of an authentic sample. IR (KBr): 3030 (m, aromatic C-H), 2910 (m, aliphatic C-H), 1620 (m), 1490 (s) (aromatic nucleus), 1030 (s, broad, characteristic of all the

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[37] Patterned after M.S. Newman, J. Am. Chem. Soc., 62, 1683 (1940).

9,9'-anthrapinacols prepared), 826 (m), 795 (w) (1,2,4-trisubstituted aromatic), 740 (s, 1,2-disubstituted aromatic).

This solid was dehydrated to yield 3,3'-dimethyl-9,9'-bianthryl (p 37) without further purification.

### (c) Preparation of 3,3'-Dimethyl-9,9'-bianthryl. Dehydration of 3,3'-Dimethyl-9,9'-anthrapinacol[36]

In a 250-ml flask, equipped with a reflux condenser, were placed 4.75 g of 3,3'-dimethyl-9,9'-anthrapinacol (p 35), 100 ml of 70% (v/v) sulfuric acid and 115 ml of glacial acetic acid. The reaction solution was heated with stirring at 98 - 100° for $5\frac{1}{2}$ hr.

The reaction mixture was diluted with water, filtered, and the collected solid washed with water. Recrystallization from benzene/heptane yielded 2.25 g (31%, based on 3-methylanthrone) of the yellow solid, 3,3'-dimethyl-9,9'-bianthyl: mp 261 - 263° (lit[35] 268°); IR (KBr): 3030 (w, aromatic C-H), 2915 (w, aliphatic C-H), 1640 (m), 1520 (w), 1480 (w), 1450 (m), 1010 (m), 947 (w), 918 (w), 893 (s), 855 (w), 838 (m), 810 (s), 776 (w), 740 (s).

## (2) Preparation of 2,2'-Dimethyl-9,9'-bianthryl

### (a) By the Dehydration of 2,2'-Dimethyl-9,9'-anthrapinacol

### (a') Preparation of o-(p-Toluoyl)benzoic Acid. Friedel-Crafts Reaction of Toluene with Phthalic Anhydride[38]

Into a 1-liter three-necked flask, equipped with a mechanical stirrer and a reflux condenser (connected to a trap containing 10% aqueous NaOH) were placed 50.0 g (0.340 mole) of phthalic anhydride and 231 ml (4.55 moles) of toluene. The flask was cooled in an ice bath and 100 g (0.75 mole) of anhydrous $AlCl_3$ was rapidly added. Stirring was started immediately, and the ice bath was removed. The reaction mixture became warm and pink-red in color. When the evolution of HCl subsided (10 - 15 min), the reaction flask was heated in a water bath at 89 - 91$^{o}$ for 2.5 hr.

The reaction mixture was cooled with an ice bath, and crushed ice was slowly added, with stirring, until the dark mass was decomposed. Concentrated hydrochloric acid (75 ml) was added to precipitate the crude product. The excess toluene was removed by steam distillation. The flask was cooled and the dark red solid was separated by filtration. Hot 10% $NaCO_3$ solution (500 ml) was added to the solid, and steam was passed through the mixture until solution occurred.

The solution was filtered while hot, leaving a small amount of tar on the filter paper. The filtrate was acidified with 35 ml of concentrated hydrochloric acid. The organic acid precipitated as a viscous oil which soom crystallized to a white solid. The solid was collected by suction filtration and air-dried to yield 80.3 g of o-(p-toluoyl) benzoic acid: mp 134 - 139° (lit[38] mp 138 - 139°).

o-(p-Toluoyl) benzoic acid forms a hydrate.[38] The melting point varied according to the degree of dryness. A sample was dissolved in acetone, and dried over $MgSO_4$. After filtration, the acetone was evaporated to yield a white solid: mp 137.0 - 139.0°; IR (KBr): 3100 - 2500 (m, carboxylic acid), 1690 (doublet, m, carbonyl), 1615 (s), 1580 (m), 1495 (w) (aromatic), 1450, 1420 (m, methyl, methylene), 1380 (w, methyl), 769 (s), 741 (s), 712 (s), (aromatic C-H, out of plane bending).

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[38] L.F. Fieser, "Organic Syntheses," Coll. Vol.I, A.H. Blatt, ed., John Wiley and Sons, Inc., New York, N.Y.1955, p 181.

### (b') Preparation of o-(p-Methylbenzyl)benzoic Acid. Reduction of o-(p-Toluoyl)benzoic Acid[39]

In a 2-liter flask, equipped with a reflux condenser, were placed 80.0 g (0.354 mole) of o-(p-toluoyl)benzoic acid (p 38), 220 g (3.36 g-atoms) of zinc dust, 800 ml of concentrated ammonia (d = 0.899) and 8 ml of saturated cupric sulfate solution. The mixture was refluxed for 2.5 hr. Aqueous sodium carbonate solution (260 ml, 10%) was added, and refluxing was continued for an additional 36 hr.

The reaction mixture was filtered while hot, and the colorless filtrate was acidified with concentrated hydrochloric acid to yield a white solid. Two recrystallizations from benzene/hexane yielded 58.1 g (73%) of o-(p-methylbenzyl)benzoic acid: mp 133.0 - 133.7° (lit[39] 133.5 - 134.0°); IR (KBr): 3100 - 2500 (carboxylic acid), 1680 (s, aromatic carbonyl), 1580 (w), 1520 (w), 1490 (w) (aromatic nucleus), 920 (w, broad, carboxylic acid), 830 (w), 805 (w), 772 (w), 752 (w), 744 (m).

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[39] E.D. Bergmann and E. Loewenthal, Bull. Soc. Chim. France, 61 (1952).

### (c') Preparation of 2-Methylanthrone. Intramolecular Acylation of o-(p-Methylbenzyl) benzoic Acid[39]

o-(p-Methylbenzyl)benzoic acid (18.1 g, 0.0794 mole) (p 40) was cooled in a dry-ice acetone bath to approximately -30°. Concentrated sulfuric acid (55 ml, d 1.84) was cooled to about -15° and added to the o-(p-methylbenzyl) benzoic acid. The mixture was allowed to warm to room temperature overnight . The resulting dark solution was poured onto crushed ice. A yellow solid precipitated which was collected by suction filtration. After washing this solid with water, it was recrystallized from methanol to constant mp to yield 8.20 g (50%) of the yellow solid, 2-methylanthrone: mp 99.5 - 101.5° (lit[39,35,40] mp 99.5 - 100°, 103°, 100°; IR (KBr): 3030 (w, aromatic C-H), 2900 (w, aliphatic C-H), 1670 (s, carbonyl), 1620 (s), 1490 (m) (aromatic nucleus), 1320, 1295 (s, aromatic ketone, due to -C-(CO)-C- bending and stretching), 865, 815 (m, 1,2,4-trisubstituted aromatic), 731 (s, 1,2-disubstituted aromatic).

[40] H. Limpricht, Ann., 314, 237 (1901).

### (d') Preparation of 2,2'-Dimethyl-9,9'-anthrapinacol. Bimolecular Reduction of 2-Methylanthrone.[37]

In a 500-ml three-necked flask, equipped with two reflux condensers and a mechanical stirrer, were placed 14.8 g (0.0712 mole) of 2-methylanthrone (p 41), 134 ml of dry benzene and 187 ml of absolute ethanol.

To the refluxing reaction solution, 7.24 g (0.268 g-atom) of aluminum foil (freshly scratched, cut into ½ inch squares and ground with 1.5 g mercuric chloride) was added over a period of 1 ¼ hr. The reaction solution became green and viscous. Absolute ethanol (20 ml) was added and refluxing was continued for an additional 3 hr.

The reaction flask was cooled in an ice bath, and 70 ml of 1:3 hydrochloric acid was added. Benzene (100 ml) was added, and the organic layer was separated. The aqueous layer was extracted with benzene. The extracts were combined with the organic layer and dried over $MgSO_4$. After filtration, the solvent was evaporated to yield 13.8 g of a light yellow solid.

This yellow solid was chromatographed on 500 g of silica gel (100 - 200 mesh) as described below.

| FRACTION | SOLVENT | VOLUME (ml) | WEIGHT(g) | DESCRIPTION |
|---|---|---|---|---|
| 1 | Benzene | 1,000 | 3.19 | white solid. |
| 2 | Benzene | 1,110 | 0.25 | yellow semi-solid |
| 3 | Acetone | 300 | 9.33 | light yellow solid. |

Fraction 1 was identified as 2-methylanthracene by comparison of its infrared spectrum with an authentic sample. Fraction 2 was not identified. Fraction 3 appeared to be 2,2'-dimethyl-9,9'-anthrapinacol contaminated with a little 2-methylanthraquinone (probably from the oxidation of 2-methylanthrone). IR (KBr): 3050 (w, aromatic C-H), 2930 (m, aliphatic C-H), 1610, 1500, 1480(m) (aromatic nucleus), 1030 (m, broad, characteristic of all 9,9'-anthrapinacols prepared), 740 (s).

Fraction 3 was dehydrated, without further purification,to yield 2,2'-dimethyl-9,9'-bianthryl (p 44 ).

## (e') Preparation of 2,2'-Dimethyl-9,9'-bianthryl. Dehydration of 2,2'-Dimethyl-9,9'-anthrapinacol[41]

In a 500-ml flask, equipped with a reflux condenser, and containing a magnetic stirrer, were placed 9.32 g (0.022 mole) of 2,2'-dimethyl-9,9'-anthrapinacol (p 42), 140 ml of glacial acetic acid and 110 ml of 70% (v/v) sulfuric acid. The solution was heated at 98 - 99$^{\circ}$ for 6½ hr. Within 20 minutes, a yellow solid began to precipitate.

The reaction mixture was diluted with water, and the yellow precipitate was collected by suction filtration and washed with water and methanol. Three recrystallizations from benzene/hexane yielded 5.82 g (43%, based on 2-methylanthrone) of the yellow solid, 2,2'-dimethyl-9,9'-bianthryl: mp 273.8 - 275.0$^{\circ}$; IR (KBr) (p 123): 3030 (m, aromatic C-H), 2910 (m), 2850 (w) (aliphatic C-H), 1640 (s), 1590 (w), 1520 (w), 1490 (w), 1450 (m), 1400 (w), 1380 (w, methyl), 1020 (m), 952 (w), 913 (m), 885 (s), 854 (w), 840 (w), 790 (m), 770 (m), 740 (s).

Anal. Calcd for $C_{30}H_{22}$: C, 84.20; H, 5.80. Found: C, 93.95; H, 5.70.

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[41] Patterned after F. Bell and D.H. Waring, J. Chem. Soc., 2689 (1949).

### (b) By the Direct Bimolecular Reduction of 2-Methylanthrone

#### (a') Bimolecular Reduction of 2-Methylanthrone. Impure 2,2'-Dimethyl-9,9'-bianthryl[42]

In a 250-ml three-necked flask, equipped with a mechanical stirrer, reflux condenser and an addition funnel, were placed 10.0 g (0.0481 mole) of 2-methylanthrone (p 41), 160 ml of glacial acetic acid and 20.0 g (0.306 g-atom) of zinc dust.

To the refluxing solution, 40 ml of concentrated hydrochloric acid (sp gr 1.19) was added over a period of 40 minutes. A yellow solid precipitated after 7 - 8 ml of hydrochloric acid had been added. Refluxing was continued for an additional 45 minutes.

The cooled reaction mixture was diluted with 100 ml of water. The precipitated yellow solid was collected by filtration. This solid was dissolved in benzene, and the benzene solution was washed with 10% aqueous potassium hydroxide solution, water, and dried over $Na_2SO_4$.

Evaporation of the solvent yielded 9.92 g of impure 2,2'-dimethyl-9,9'-bianthryl which was further purified by treatment with maleic anhydride to remove 2-methylanthracene (p 46).

[42] Patterned after (a) E. De Barnett, Chem. Ber., 65, 1563 (1932). (b) E. De Barnett and M.A. Matthews, J. Chem. Soc., 2549 (1923).

### (b') Treatment of Impure 2,2'-Dimethyl-9,9'-bianthryl with Maleic Anhydride

A solution of 9.91 g of impure 2,2'-dimethyl-9,9'-bianthryl (p 45) and 15.0 g of maleic anhydride in 80 ml of xylene (bp 137 - 140°) was refluxed for 40 minutes.

The xylene was removed with a rotary evaporator to yield a yellow-red tar to which 100 ml of 15% aqueous potassium hydroxide was added. The mixture was heated, with stirring, at 80° for ½ hr. The cooled suspension was extracted with 250 ml of benzene. The benzene solution was washed several times with 10% aqueous potassium hydroxide solution, water, and dried over $MgSO_4$. After filtration, the benzene was evaporated to yield 7.56 g of a yellow solid contaminated with some dark material. This solid was chromatographed on 170 g of Woelm alumina (acidic, activity grade I) using benzene as the eluting solvent. The first fluorescent yellow fraction gave after evaporation of the eluent 7.47 g of a yellow solid. Six recrystallizations from benzene/heptane yielded 1.26 g (15%, based on 2-methylanthrone) of the yellow solid, 2,2'-dimethyl-9,9'-bianthryl: mp 273.5 - 274.6°. The IR spectrum is identical to 2,2'-dimethyl-9,9'-bianthryl prepared by the dehydration of 2,2'-dimethylanthrapinacol (p 44). The mother liquors were combined and evaporated to yield a yellow solid which upon two recrystallizations from benzene/heptane yielded an additional

0.30 g of 2,2'-dimethyl-9,9'-bianthryl: mp 272.0 - 273.0°. The mother liquors of this solid when concentrated, precipitated two types of solids (yellow and white), as observed in the preparation of 2,2'-dichloro-9,9'-bianthryl by the same method (p 53). The white solid was not identified.

## (3) Preparation of 2,2'-Dichloro-9,9'-bianthryl

### (a) By the Dehydration of 2,2'-Dichloro-9,9'-anthrapinacol

### (a') Preparation of o-(p-Chlorobenzyl)benzoic Acid. Reduction of o-(p-Chlorobenzoyl)benzoic Acid[43]

In a 2-liter flask, equipped with a reflux condenser, were placed 105 g (0.402 mole) of o-(p-chlorobenzoyl)benzoic acid (Aldrich Chem. Co., Milwaukee, Wisconsin), 279 g (4.27 g-atoms) of zinc dust, 1,040 ml of concentrated ammonia (d = 0.899) and 10 ml of saturated cupric sulfate solution. The mixture was refluxed (oil bath) for 2 hr and 325 ml of 10% aqueous sodium carbonate solution was added. Refluxing was continued for an additional 23 hr. During the first few hours, the oil bath had to be removed occasionally to avoid excessive foaming.

The reaction mixture was filtered while hot, and the colorless filtrate was acidified with concentrated hydrochloric acid. The white precipitate obtained was collected by suction filtration. Two recrystallizations from ethanol yielded 83.9 g (80%) of o-(p-Chlorobenzyl)benzoic acid: mp 130.6 - 132.3° (lit[43,44] 130 - 132°, 132°); IR (KBr): 3100 - 2500 (m, carboxylic acid), 1680 (s, aromatic carbonyl), 1600 (w), 1580 (m) (aromatic nucleus), 920 broad (m, carboxylic acid), 834 (m), 809 (w), 800 (w), 773 (m), 737 (s), 718 (w).

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[43] W. Bradley and L.J. Watkins, J. Chem. Soc., 319 (1956).

[44] E. De Barnett and J.L. Wiltshire, J. Chem. Soc., 1822 (1926).

### (b') Preparation of 2-Chloroanthrone, Intramolecular Acylation of o-(p-Chlorobenzyl) benzoic Acid[44]

o-(p-Chlorobenzyl) benzoic acid (74.7 g, 0.302 mole) (p 48) was cooled in a dry-ice acetone bath to approximately -30°. Concentrated sulfuric acid (225 ml d 1.84) was precooled to about -15° and added to the o-(p-chlorobenzyl)benzoic acid. The mixture was allowed to warm to room temperature overnight.

The resulting dark solution was poured onto crushed ice. A yellow solid precipitated which was collected by suction filtration. After washing the solid with water, it was recrystallized twice from denatured ethanol (5% methanol) to yield 52.3 g (75.5%) of the pale yellow solid, 2-chloroanthrone: mp 153.6 - 154.8° (lit [44,43] mp 155°, 154 - 155°); IR (KBr): 3060 (w, aromatic C-H), 2900 (w, aliphatic C-H), 1670 (s, carbonyl), 1610, 1480 (m, aromatic nucleus), 1318 (m), 1295 (s) (aromatic ketone, due to -C-(CO)-C- bending and stretching), 853, 818 (m, 1,2,4-trisubstituted aromatic), 720 (s, 1,2-disubstituted aromatic).

### (c') Preparation of 2,2'-Dichloro-9,9'-anthrapinacol. Bimolecular Reduction of 2-Chloroanthrone.[37]

In a 1-liter three-necked flask, equipped with two reflux condensers and a mechanical stirrer, were placed 47.4 g (0.207 mole) of 2-chloroanthrone (p 49), 240 ml of absolute alcohol and 160 ml of dry benzene. To the refluxing reaction solution, 20.7 g (0.770 g-atom) of aluminum foil (freshly scratched, cut into ½ inch squares and ground with approximately 5 g of mercuric chloride) was added over a period of 3 hr. After 1.5 hr, 100 ml of absolute ethanol was added. An additional 100 ml was added when the addition of aluminum foil was completed. The resulting green, viscous, reaction mixture was refluxed for an additional 3½ hr.

The reaction flask was cooled in an ice bath, and 450 ml of 1:1 hydrochloric acid was slowly added with stirring.

The organic layer was separated, and the aqueous layer was extracted with 2 liters of benzene. The combined yellow organic layer was dried over $MgSO_4$ and evaporated to yield a yellow solid. This solid was dissolved in 2 liters of hot methanol. Upon cooling, a yellow-tan solid precipitated. After filtration to remove this solid, the filtrate was concentrated to 800 ml. More of the same solid was obtained, which had a strong band in the IR region at 892 $cm^{-1}$ (probably 2-chloroanthracene). Filtration and evaporation of the filtrate gave a yellow solid. Recrystallization from methanol yielded 15.7 g of the white solid, 2,2'-dichloro-9,9'-anthrapinacol which did not have an IR band at 892 cm$^{-1}$. IR (KBr): 3040 (w, aromatic C-H), 2900 (w, aliphatic C-H), 1600 (m), 1480 (s) (aromatic nucleus), 1035 (s, broad, characteristic of all the 9,9'-anthrapinacols prepared), 740 (s); IR (Nujol mull): 3500 (m, OH).

### (d') Preparation of 2,2'-Dichloro-9,9'-bianthryl. Dehydration of 2,2'-Dichloro-9,9'-anthrapinacol.[37]

In a 500-ml flask, equipped with a magnetic stirrer and a reflux condenser, were placed 15.7 g (0.0342 mole) of 2,2'-dichloro-9,9'-anthrapinacol (p 50), 175 ml of acetic acid and 160 ml of 70% (v/v) sulfuric acid. The reaction flask was heated at 98 - 99° for 5 hr. A yellow precipitate formed after $\frac{1}{2}$ hr.

After cooling, the reaction mixture was diluted with water. The yellow precipitate was collected by suction filtration and washed with water. Recrystallization from benzene/ethanol yielded 6.88 g (16% based on 2-chloroanthrone) of the yellow solid, 2,2'-dichloro-9,9'-bianthryl: mp 290.6 - 292.3°. The infrared spectrum of this product is identical to 2,2'-dichloro-9,9'-bianthryl, obtained by the direct bimolecular reduction of 2-chloroanthrone (p 53).

### (b) By the Direct Bimolecular Reduction of 2-Chloroanthrone

#### (a') Bimolecular Reduction of 2-Chloroanthrone. Impure 2,2'-Dichloro-9,9'-bianthryl[42]

Into a 12-liter three-necked flask, equipped with a reflux condenser, a mechanical stirrer and an addition funnel, were placed 252 g (0.596 mole) of 2-chloroanthrone (p 49), 4,875 ml of glacial acetic acid and 491.5 g (7.52 g-atoms) of zinc dust. The mixture was heated to reflux. While stirring, 1,100 ml of concentrated hydrochloric acid (d 1.19) was added over a period of 4¾ hr. A yellow solid began to precipitate after approximately ⅓ of the hydrochloric acid had been added. The mixture was refluxed, with stirring, for an additional 3 hr and was left to cool overnight.

The precipitated yellow solid was collected by filtration, washed with water and methanol, and dried to yield 132 g of impure 2,2'-dichloro-9,9'-bianthryl: mp 189 - 234°. This solid was treated with maleic anhydride (p 54) to remove 2-chloroanthracene.

### (b') Treatment of Impure 2,2'-Dichloro-9,9'-bianthryl with Maleic Anhydride

Into a 2-liter flask, equipped with a reflux condenser, were placed 265 g of impure 2,2'-dichloro-9,9'-bianthryl (p 53), 370 g of maleic anhydride and 1,260 ml of 1,2-bis-(2-methoxyethoxy)ethane (triglyme).

The solution was heated at reflux for 2.0 hr. A dark solution was obtained which was cooled to 100°, and 400 ml of ethanol and 1,400 ml of 10% aqueous NaOH were added. The solution was stirred for 45 minutes while being cooled to room temperature. A yellow solid precipitated which was collected by suction filtration, washed with water and with ethanol to yield 140 g of a yellow solid: mp 261 - 275°. Recrystallization from chloroform/cyclohexane yielded a yellow solid: mp 285 - 289°. The mother liquor was concentrated by boiling until precipitation was observed. Upon cooling, more of the same solid was obtained: mp 284 - 289°.

The two crops were combined and recrystallized from chloroform/cyclohexane to yield 53.7 g of the yellow solid, 2,2'-dichloro-9,9'-bianthryl: mp 290.0 - 292.0° (lit[42a, 45] mp 288°, 289°). The mother liquor was concentrated as above. Upon cooling two types of solids were deposited, first a yellow solid, followed by a white solid.

[45] E.D. Bergmann and H. Hirschfeld, Tetrahedron Letters, 4129 (1965).

The white solid was easily separated by swirling the flask and decanting the mother liquor with the suspended white solid. After filtration to remove the white solid, this mother liquor was concentrated again in the same manner. Upon cooling, again yellow solid precipitated first, followed by white solid. The white material was again removed in the same manner.

The yellow solids so obtained from the mother liquors were combined with the mother liquor of the recrystallized material melting at 290.0 - 292.2$^{o}$ and concentrated by boiling. Upon cooling, a yellow solid was obtained (no white solid) which melted at 275 - 289$^{o}$. This solid was recrystallized to constant mp (four times) from chloroform/cyclohexane to yield 21.3 g of the yellow solid, 2,2'-dichloro-9,9'-bianthryl: mp 289.6$^{o}$ - 292.0$^{o}$. The IR spectra of both materials, melting at 290.0 - 292.0$^{o}$ and at 289.6 - 292.0$^{o}$, were identical and showed no evidence of either 2-chloroanthracene or the white solid. IR (KBr): 3050 (w, aromatic C-H), 1635 (s), 1560 (m), 1525 (w), 1475 (w), 1445 (s), 1413 (m), 1085 (s), 1075 (s), 1015 (w), 952 (s), 913 (s), 888 (s), 872 (m), 860 (w), 854 (w), 843 (w), 800 (w), 780 (s), 740 (s).

### (4) Preparation of 2,2'-Dibromo-9,9'-bianthryl

#### (a) Preparation of o-(p-Bromobenzoyl)benzoic Acid. Friedel-Crafts Reaction of p-Bromobenzene with Phthalic Anhydride[46]

In a 1-liter three-necked flask, equipped with a condenser, an efficient mechanical stirrer and a thermometer, were placed 500 g of bromobenzene and 200 g (1.35 moles) of phthalic anhydride. The reaction flask was heated in an oil bath until the phthalic anhydride dissolved. After cooling to room temperature, 400 g (3.00 moles) of aluminum chloride was added at such a rate as to maintain the temperature of the reaction at 50°. The reaction solution first turned orange, and then became red and viscous. When the evolution of hydrogen chloride subsided (approximately ½ hr), the reaction flask was heated to 85°. The reaction mixture became extremely viscous and 100 g of bromobenzene was added to facilitate stirring. After 2 hr an additional 100 g of bromobenzene was added in order to keep the stirrer turning. The reaction mixture was heated at 85° for a total of 7.0 hr.

After cooling to room temperature, crushed ice was added, and the reaction mixture was steam-distilled to remove the excess bromobenzene.

The residual solid was extracted several times with hot 10% aqueous sodium carbonate. The alkaline extracts were combined and acidified with concentrated hydrochloric acid. The precipitated white

[46] F. Ullman and M. Sonne, Ann., 380, 336 (1911).

solid was collected by suction filtration and washed with water.

Two recrystallizations from ethanol/water and three recrystallizations from benzene yielded 275 g (67%) of the white solid, o-(p-bromobenzoyl)benzoic acid: mp 172.2 - 173.0° (lit[46,39] 173°, 170 - 172°); IR (KBr): 3100 - 2500 (w, carboxylic acid), 1680 (s, carbonyl), 1600 (m), 1580 (m), 1480 (w) (aromatic nucleus) 772 (m), 742 (m), 703 (w) (aromatic C-H, out of plane bending).

### (b) Preparation of 3-(p-Bromophenyl)phthalide.[39]

### Clemmensen Reduction of o-(p-Bromobenzoyl)benzoic Acid

In a 1-liter three-necked flask were placed 111 g (1.71 moles) of mossy zinc, 75 ml of water and 8.0 g (0.03 mole) of mercuric chloride. The flask was shaken occasionally over a period of $\frac{1}{2}$ hr. The water was decanted, and the amalgamated zinc was washed with 100 ml of water.

The flask was equipped with a mechanical stirrer and a condenser, and the following reagents were placed in the flask in the given order: 80 ml of water, 230 ml of concentrated hydrochloric acid, 120 ml of toluene and 80.0 g (0.262 mole) of o-(p-bromobenzoyl)benzoic acid (p 56). The reaction mixture was heated to reflux and vigorously stirred for 26 hr.

The cooled reaction mixture was filtered to remove excess zinc. Water was added to the filtrate and the toluene was removed using a rotary evaporator. A white solid was obtained which was collected by suction filtration. This solid was dissolved in benzene and the benzene solution was extracted with 10% aqueous $Na_2CO_3$ until the alkaline extracts, when acidified with concentrated hydrochloric acid, did not give a precipitate. The white precipitates obtained were combined and recrystallized to constant mp from benzene/heptane to yield 11.9 g (16%) of the white solid, o-(p-bromobenzyl)benzoic acid: mp 135.0 - 137.0$^{\circ}$; IR: identical to o-(p-bromobenzyl) benzoic acid (p 60).

The benzene solution was dried over $Na_2SO_4$, filtered and evaporated to dryness. The white solid obtained was recrystallized to constant mp from benzene/heptane to yield 41.5 g (55%) of the white solid, 3-(p-bromophenyl)phthalide: mp 136.0 - 137.5° (lit[39] 139 - 140°); IR (KBr): 3040 (w, aromatic C-H), 2930 (w, aliphatic C-H), 1765 (s, phthalide carbonyl), 1620 (w), 1600 (w), 1490 (m), 1465 (m), (aromatic nucleus), 1210, 1065 (s, asymmetric and symmetric stretching of =C-O-C), 818, 803 (m, 1,4-disubstituted aromatic), 743 (s, 1,2-disubstituted aromatic).

### (c) Preparation of o-(p-Bromobenzyl)benzoic Acid, Reduction of 3-(p-Bromophenyl)phthalide[39]

In a 250-ml flask, equipped with a magnetic stirrer and reflux condenser, were placed 42.0 g (0.145 mole) of 3-(p-bromophenyl)phthalide (p 56 ), 11.1 g (0.044 mole) of iodine, 3.5 g (0.113 g-atom) of red phosphorus, 100 ml of glacial acetic acid and 3.5 ml of water. The reaction mixture was refluxed with stirring for 27 hr.

After cooling to room temperature, 450 ml of 5% aqueous $NaHSO_3$ was added, and the reaction mixture was stirred for 30 minutes. The precipitated light brown solid was collected by suction filtration and washed with water. The solid was extracted with 10% aqueous $Na_2CO_3$ several times. The alkaline extracts were combined and acidified with concentrated nydrochloric acid. A white precipitate was obtained which was collected by suction filtration. Crystallization from benzene/heptane yielded 15.6 g (37%) of the white solid, o-(p-bromobenzyl)benzoic acid: mp 136.5$^{\circ}$ - 137.5$^{\circ}$ (lit[39] 137$^{\circ}$); IR (KBr): 3200 - 2500 (m, carboxylic acid), 1680 (s, carbonyl), 1600 (w), 1580 (m), 1490 (m), (aromatic nucleus), 920 broad (m, carboxylic acid), 832 (m), 808 (w), 798 (w), 770 (m), 737 (s), 712 (w).

### (d) Preparation of 2-Bromoanthrone. Intramolecular Acylation of o-(p-Bromobenzyl)benzoic Acid[39]

To 6.85 g (0.0235 mole) of o-(p-bromobenzyl)benzoic acid (p 60), precooled to approximately -30° in a dry-ice acetone bath, 20.5 of concentrated sulfuric acid (d 1.84), precooled to -15°, was added. The mixture was allowed to warm to room temperature. The resulting brown solution was kept at room temperature for 7 hr.

The brown solution was poured onto crushed ice. A yellow solid precipitated which was collected by suction filtration and washed thoroughly with water. Two recrystallizations from ethanol (denatured with 5% methanol) yielded 4.90 g (76%) of the light yellow solid, 2-bromoanthrone: mp 160.0-162.0° (lit[39] mp 160.5°); IR (KBr): 3040 (w, aromatic C-H), 2900 (w, aliphatic C-H), 1670 (s, carbonyl), 1615, 1490 (m, aromatic nucleus), 1310, 1295 (s, aromatic ketone, due to -C-(CO)-C- bending and stretching), 848, 814 (m, 1,2,4-trisubstituted aromatic), 719 (s, 1,2-disubstituted aromatic).

### (e) Preparation of 2,2'-Dibromo-9,9'-anthrapinacol. Bimolecular Reduction of 2-Bromoanthrone[37]

In a 500-ml three-necked flask, equipped with an efficient stirrer and two reflux condensers, were placed 15.2 g (0.0557 mole) of 2-bromoanthrone (p 61 ), 90 ml of absolute ethanol and 80 ml of dry benzene. The solution was heated to reflux. Aluminum foil (6.84 g, 0.25 g-atom), freshly scratched, cut into ½ inch squares, and ground with approximately 1.5 g $HgCl_2$ was added to the reaction solution over a period of 1.5 hr. The addition of a portion of aluminum amalgam caused the reaction to become very vigorous, and periodically the heating bath had to be removed in order to avoid excessive foaming. The reaction mixture became green and extremely viscous. After the addition of the aluminum amalgam, 40 ml of absolute ethanol was added and the reaction mixture was refluxed for an additional 3 hr.

The reaction flask was placed in an ice bath, and 250 ml of 1:3 hydrochloric acid was slowly added with stirring. The green color disappeared, and the reaction solution separated into two layers. The organic layer was separated and the water layer was extracted with benzene (800 ml) and ether (200 ml).

All the organic solutions were combined and dried over $Na_2SO_4$. After filtration, the solvent was evaporated to yield 14.6 g of a slightly yellow solid. This solid was chromatographed on 400 g of silica gel

(100 - 200 mesh) as described below.

| FRACTION | SOLVENT | VOLUME (ml) | WEIGHT (g) | DESCRIPTION |
|---|---|---|---|---|
| 1 | Benzene | 475 | 3.08 | White solid |
| 2 | Benzene | 70 | 0.91 | White solid |
| 3 | Benzene | 130 | 0.95 | Slightly yellow solid |
| 4 | Benzene | 195 | 2.41 | Pale yellow, |
| 5 | Benzene | 345 | 3.63 | almost white |
| 6 | 30% Acetone/benzene | 320 | 2.26 | solids |
| 7 | 30% Acetone/benzene | 200 | 0.11 | Brown oil |

Fractions 1,2 and 3 were not identified. From their infrared spectra, they probably contain mainly 2-bromoanthracene. Fractions 4, 5, and 6 were 2,2'-dibromo-9,9'-anthrapinacol: IR (KBr): 3040 (w, aromatic C-H), 2900 (w, aliphatic C-H), 1610 (m, aromatic necleus), 1040 (s, broad, characteristic of all 9,9'-anthrapinacols prepared), 742 (s, aromatic out of plane bending). This preparation was dehydrated to produce 2,2'-dibromo-9,9'-bianthryl (p 64 ) without further purification.

### (f) Preparation of 2,2'-Dibromo-9,9'-bianthryl. Dehydration of 2,2'-Dibromo-9,9'-anthrapinacol [41]

In a 250-ml three-necked flask, equipped with a magnetic stirrer and reflux condenser, were placed 7.71 g (0.0141 mole) of 2,2'-dibromo-9,9'-anthrapinacol (p 62), 100 ml of glacial acetic acid and 85 ml of 70% (v/v) sulfuric acid.

The reaction flask was heated at 98 - 99° for 5 hr. Within ½ hr, the reaction solution became yellow and viscous.

Upon dilution with water, a yellow solid precipitated which was collected by suction filtration. This solid was chromatographed on 250 g of silica gel (100 - 200 mesh), using benzene as the eluent. Two yellow bands were obtained, the second being much more intense in color than the first.

The first eluted band gave a yellow solid which upon recrystallization from benzene/ethanol yielded 5.12 g (71%) of the yellow solid 2,2'-dibromo-9,9'-bianthryl: mp 310.1 - 311.0° (lit[45] 310 - 312°); IR (KBr): 3050 (w, aromatic C-H), 1620(s), 1570 (m), 1515 (w), 1470 (w), 1443 (s), 1412 (w), 1012 (w), 940 (m), 910 (s), 885 (s), 870 (m), 850 (w), 840 (w), 798 (w), 778 (s), 740 (s),

### (5) Preparation of 2,2'-Dicyano-9,9'-bianthryl

#### (a) Reaction of 2,2'-Dichloro-9,9'-bianthryl with CuCN[47,48]

In a 3-liter flask, equipped with a reflux condenser, were placed 80.0 g (0.189 mole) of 2,2'-dichloro-9,9'-bianthryl (p 54), 189.5 g (1.89 moles) of CuCN and 1,600 ml of 1-methyl-2-pyrrolidinone. The resulting yellow solution, which contained some dark precipitate (probably copper metal[47]), was refluxed for 96.5 hr. After cooling to room temperature, 1,500 ml of water was added. A yellow solid precipitated (a complex of the organic nitrile with $Cu^+$) which was collected by suction filtration. The complex was decomposed by stirring it in a solution of 995 g of ferric chloride and 250 ml of concentrated hydrochloric acid in 1,350 ml water for 2.0 hr at 80 - 83°. The resulting suspension was extracted with chloroform and the chloroform evaporated to yield a yellow-green solid. This solid was added to 400 ml of chloroform, filtered to remove a small amount of dark insoluble material and chromatographed on 407 g of Woelm alumina (acidic, activity grade I).

The column was eluted with chloroform until no further elution of material occurred.

| FRACTION | VOLUME (ml) | WEIGHT (g) | DESCRIPTION |
|---|---|---|---|
| 1 | 75 | 2.10 | Yellow solid |
| 2 | 205 | 25.31 | Yellow solid |
| 3 | 400 | 8.62 | Dark brown solid |

Fraction 1 did not have an infrared band at 1080 $cm^{-1}$ which is present in the spectrum of 2-chloro-2'-cyano-9,9'-bianthryl (see p 69).

The above three fractions were combined and rechromatographed on 270 g of Woelm alumina (acidic, activity grade I), using 50% chloroform/benzene as the eluting solvent.

| FRACTION | WEIGHT (g) | DESCRIPTION |
|---|---|---|
| 1 | 35.57 | Yellow solid |
| 2 | 0.43 | Black solid |

The solid obtained in fraction 1 was recrystallized twice from chloroform/benzene to yield the yellow solid, 2,2'-dicyano-9,9'-bianthryl: mp 337.0 - 338.5°. The mother liquors were evaporated to dryness, yielding a yellow solid which was recrystallized three times to give more of the same material: mp 337.0 - 338.4°.

The combined yield of 2,2'-dicyano-9,9'-bianthryl was 33.4 g (43.8%). IR (KBr) (p 124): 3070 (w, aromatic C-H), 2250 (s, nitrile), 1640 (m), 1530 (w), 1483 (w), 1458 (w), 1435 (m), 1410 (m), 1015 (w), 978 (w), 955 (w), 913 (m), 890 (s), 864 (w), 856 (w), 852 (w), 779 (m), 740 (s).

*Anal.* Calcd for $C_{30}H_{16}N_2$: C, 89.08; H, 3.99; N, 6.93. Found: C, 89.38; H, 3.94; N, 7.04

[47] Patterned after L. Friedman and H. Schechter, *J. Org. Chem.*, 26, 2522(1961).

[48] The use of 1-methyl-2-pyrrolidinone has been recommended for the conversion of aromatic chlorides to the corresponding nitriles by M.S. Newman and H. Boden, *J. Org. Chem.*, 26, 2525 (1961).

### (b) Reaction of 2,2'-Dibromo-9,9'-bianthryl with CuCN[47]

In a 100-ml flask, equipped with a magnetic stirrer and a reflux condenser, were placed 5.59 g (10.9 moles) of 2,2'-dibromo-9,9'-bianthryl (p 64), 2.39 g (26.4 mmoles) of cuprous cyanide and 50 ml of N,N-dimethylformamide. The yellow solution was refluxed for 6½ hr. Within minutes of refluxing, a small amount of dark precipitate was formed which is believed to be copper metal.

The reaction mixture was cooled and diluted with water. A yellow solid precipitated which was collected by suction filtration. This solid was treated with a solution of 40 g ferric chloride and 10 ml of concentrated hydrochloric acid in 60 ml of water at 60 - 70° for ¾ hr. The resulting suspension was extracted with benzene. The yellow benzene solution, which fluoresced strongly, was washed two times with 25 ml portions of dilute hydrochloric acid (1:1), two times with 25 ml portions of 10% aqueous sodium hydroxide, and dried over $Na_2SO_4$. After filtration, the benzene was evaporated to yield a yellow solid. Recrystallization from ethanol yielded 4.86 g of a yellow solid, melting at 316 - 320°, which could not be purified to a constant mp by further recrystallization.

A portion of this solid (0.876 g) was chromatographed on 250 g of Woelm alumina (acidic, activity grade I), using 50% chloroform/benzene as the eluent. The progress of chromatography was followed by the change of color as described below.

| FRACTION | VOLUME (ml) | WEIGHT (g) | DESCRIPTION |
|---|---|---|---|
| 1 | 610 | 0.033 | Green |
| 2 | 260 | 0.015 | Light green |
| 3 | 100 | 0.016 | Yellow with blue fluorescence |
| 4 | 100 | 0.055 | " |
| 5 | 350 | 0.765 | " |

All solids obtained were yellow. Fractions 1 and 2 were not identified. They were probably 2-bromo-2'-cyano-9,9'-bianthryl. Fraction 5 was 2,2'-dicyano-9,9'-bianthryl as evidenced by comparison of its thin layer chromatographic behavior and its infrared spectrum with that of an authentic sampe (p 65).

### (6) Preparation of 2-Chloro-2'-cyano-9,9'-bianthryl. Reaction of 2,2'-Dichloro-9,9'-bianthryl with CuCN[49]

In a 500-ml flask, equipped with a reflux condenser, were placed 24.3 g (0.0578 mole) of 2,2'-dichloro-9,9'-bianthryl (p 54), 16.5 g (0.183 mole) of CuCN and 250 ml of 1-methyl-2-pyrrolidinone. The resulting yellow solution, which contained some dark precipitate, was refluxed for 26 hr. After cooling to room temperature and diluting with water, a yellow solid precipitated (a complex of the organic nitrile with $Cu^+$) which was collected by suction filtration. The complex was decomposed by stirring it with a solution of 300 g $FeCl_3$ and 75 ml of concentrated hydrochloric acid in 450 ml of water for 1½ hr at 65 - 70°. The resulting suspension was extracted with 2.5 liters of benzene. The yellow benzene solution was washed with hydrochloric acid (1:1), 10% aqueous NaOH, dried over $Na_2SO_4$, and after filtration, evaporated to yield a yellow solid. This solid was recrystallized twice from benzene to yield 18.5 g of a yellow solid melting at 309 - 316° which could not be purified to a constant melting point by further recrystallization.

Part of this solid (16.3 g) was dissolved in chloroform and chromatographed on 98 g of Woelm alumina (acidic, activity grade I). Two yellow bands were obtained. One band was eluted with chloroform while the other remained at the origin.

[49] Patterned after the procedures given in references (47, 48), p 66.

The eluted band consisted of 15.6 g of a yellow solid melting at 309 - 318°. Part of this solid (4.00 g) was dissolved in chloroform and rechromatographed on 480 g of Woelm alumina (acidic, activity grade I, packed with benzene). The column was eluted with 1:1 chloroform: benzene solution. The chromatography was followed by the change of color of the eluent and the melting point of the solids obtained after evaporation of the eluent as described below. All solids obtained were yellow.

| Fraction | Volume (ml) | Weight (g) | Color of eluent | mp of solid |
|---|---|---|---|---|
| 1 | 450 | 0.96 | green | 306 - 318° |
| 2 | 500 | | " | 309 - 316° |
| 3 | 350 | 0.15 | light green | 310 - 313° |
| 4 | 475 | 0.36 | yellow with intense blue fluorescence | 316 - 323° |
| 5 | 400 | | | 333 - 336.5° |
| 6 | 283 | 2.48 | " " | 337 - 339° |
| 7 | 200 | | " " | 337.6-339.2° |
| 8 | 400 | | " " | 336.5-338.2° |

Fractions 1 and 2 were combined and recrystallized from benzene to yield the yellow solid, 2-chloro-2'-cyano-9,9'-bianthryl: mp 313.5-314.6°; IR (KBr) (p 125): 3040 (w, aromatic C-H), 2220 (m, nitrile), 1625 (m), 1580 (w), 1520 (w), 1478 (w), 1445 (m), 1080 (s), 1015 (w), 953 (m), 913 (s), 890 (s), 785 (s), 746 (s).

Anal. Calcd for $C_{29}H_{16}ClN$: C, 84.15; H, 3.90; Cl, 8.57; N, 3.38. Found: C, 84.12; H, 3.79; Cl, 8.98; N, 3.52.

Fractions 6, 7 and 8 consisted of 2,2'-dicyano-9,9'-bianthryl as evidenced by a comparison of melting points, thin layer chromatographic behavior and infrared spectra with those of an authentic sample.

### (7) Preparation of 2,2'-Dicarboxy-9,9'-bianthryl. Hydrolysis of 2,2'-Dicyano-9,9'-bianthryl

In a 5-liter flask, equipped with a reflux condenser, were placed 33.40 g (0.0826 mole) of 2,2'-dicyano-9,9'-bianthryl (p 65), and 3,350 ml of 28% methanolic potassium hydroxide. After refluxing for 4 hr a clear yellow solution was obtained which was refluxed for an addition 24 hr.

An equal volume of water was added, and the resulting solution was acidified with concentrated hydrochloric acid. A yellow flocculent precipitate was obtained which was collected by filtration and washed with water. Crystallization from glacial acetic acid yielded 26.4 g of yellow solid. Concentration of the mother liquor to one-sixth of the original volume precipitated 2.81 g of the same yellow solid (80% combined yield): mp 419.5-420.5$^{\circ}$ dec; IR (KBr) (p 126): 3300-2500 (carboxylic acid), 1700 (s, carbonyl), 1630 (m), 1525 (w), 1485 (w), 1460 (w), 1430 (w), 1410 (m), 1015 (w), 913 (m), 886 (m), ~ 770 (m, broad), 740 (s).

Anal. Calcd for $C_{30}H_{18}O_4$: C, 81.45; H, 4.10. Found: C, 81.32; H, 4.53.

## (8) Resolution of 2,2'-Dicarboxy-9,9'-bianthryl

Quinidine was obtained by treating quinidine sulfate with ammonia and extracting the resulting suspension with ether. The ether solution was dried over $MgSO_4$, filtered, and evaporated.

A suspension of 9.52 g (0.0215 mole) of 2,2'-dicarboxy-9,9'-bianthryl (p 71 ) in 750 ml of hot acetone was slowly added to a boiling solution of 16.4 g (0.0444 mole, based on $C_{20}H_{24}N_2O_2 \cdot 2\frac{1}{2}H_2O$) of quinidine in 1,100 ml of acetone. Approximately 75 ml of the solvent was evaporated by boiling when yellow crystals began to precipitate. The solution was allowed to cool overnight. The precipitated yellow solid was collected by suction filtration, and dried under vacuum at 95-100° to yield 12.0 g of quinidine salt: mp 236.2-237.1°; $[\alpha]_D^{23}$ +35° ( c 0.58, acetone). The rotation of this salt did not change upon further recrystallization from acetone.

The mother liquor was concentrated to 150 ml. Upon cooling a semi-solid was deposited. The mixture was filtered, and the filtrate was evaporated to dryness to yield 10.3 g of a yellow solid. This solid was dissolved in 65 ml of denatured ethanol (5% methanol). The solution was cooled in an ice bath, and 50 ml of concentrated hydrochloric acid was added over a period of 30 min with stirring. A yellow solid precipitated. The mixture was stirred for an additional 30 minutes. Water (70 ml) was added, and the precipitated yellow solid was collected by suction filtration. The washing process was repeated by suspending the yellow solid in 25 ml of denatured ethanol (5% methanol) and treating it with 20 ml of concentrated hydrochloric acid. The yellow solid so obtained was thoroughly washed with water and dried under vacuum at 95 - 100° to yield 3.71 g of (+)-2,2'-dicarboxy-9,9'-bianthryl: mp > 360°; $[\alpha]_D^{23.5}$ + 101° (c 0.64, acetone); IR (KBr): essentially identical to that of racemic 2,2'-dicarboxy-9,9'-bianthryl.

The dextrorotatory quinidine salt (precipitated from the acetone solution) was similarly decomposed except that it was not completely soluble in 100 ml of denatured alcohol (5% methanol). To the cooled (ice bath) suspension, 50 ml of concentrated hydrochloric acid was slowly added with stirring. When approximately 5 ml of the hydrochloric acid had been added, a clear yellow solution was obtained. The addition of the rest of the hydrochloric acid precipitated a yellow solid. The mixture was stirred for an additional 30 min, 100 ml of water was added and the yellow precipitated solid was collected by suction filtration. This washing process with HCl was repeated. The yellow solid obtained was washed thoroughly with water and dried under vacuum at 95 - 100° to yield 4.54 g of (-)-2,2'-dicarboxy-9,9'-bianthryl: mp > 360°; $[\alpha]_D^{22}$ - 114°; IR (KBr): (p 127) essentially identical to that of racemic 2,2'-dicarboxy-9,9'-bianthryl.

In similar experiments it was found that recrystallization of (-)-2,2'-dicarboxy-9,9'-bianthryl from acetic acid increased the specific rotation by only 1°, and this was accompanied by a large loss of material. The enantiomers were therefore not further recrystallized at this point.

### (9) Preparation of 2,2'-Dicarbomethoxy-9,9'-bianthryl. Esterification of 2,2'-Dicarboxy-9,9'-bianthryl with Diazomethane

Ethanol (95%, 25 ml) was added to a solution of potassium hydroxide (5.2 g) in 8.0 ml of water in a 100-ml flask fitted with a Claisen head to which a pressure equalizing funnel and a water condenser set downward for distillation were connected. The condenser was connected to two receiving flasks in series, the second of which contained 50 ml of ether. The inlet tube of the second receiver dipped below the surface of the ether. Both receivers were cooled in an ice-salt bath.

The flask containing the potassium hydroxide solution was heated in an oil bath at 65-66°, and a solution of 21.6 g (0.1 mole) of "Diazald" (N-Methyl-N-nitroso-p-toluenesulfonamide) (Aldrich Chem Co., Milwaukee, Wisconsin) in 132 ml of ether was added over a period of 2.0 hr. The rate of addition was approximately equal to the rate of distillation. Another 20 ml of ether was slowly added through the addition funnel, and distillation was continued until the distillate was colorless.

The cold diazomethane solution from both receivers was added to a yellow solution of 6.50 g (14.7 mmoles) of 2,2'-dicarboxy-9,9'-bianthryl (p 71) dissolved in 1,100 ml of dioxane. When all of the diazomethane solution was added the resulting solution became deep yellow. A solution of 50% HOAc in ether was added until the deep yellow color changed to pale yellow. This solution was combined with another solution prepared similarly from 1.59 g (3.60 mmoles) of 2,2'-dicarboxy-9,9'-bianthryl.

The combined solutions were evaporated to 200 ml, and an equal volume of water was added. A yellow solid precipitated which was collected by suction filtration, washed with water and 1:1 water-methanol, to yield 8.59 g of a yellow solid: mp 271-276°.

This solid was chromatographed on 200 g of silica gel (100-200 mesh). The column was eluted with 50% $CHCl_3$/Benzene. A yellow band, moving with the solvent front, was collected, while a red band remained at the origin.

The resulting solid was recrystallized from chloroform/methanol to yield 5.60 g (87%) of the yellow solid, 2,2'-dicarbomethoxy-9,9'-bianthryl: mp 281.5-282.3°; IR (KBr) (p 128): 3040 (w, aromatic C-H), 2950 (w, aliphatic C-H), 1725 (s, carbonyl), 1630 (m), 1520 (w), 1490 (w), 1455 (w), 1435 (s), 1405 (w), (1310, 1272, 1233) (s, aromatic ester), 1010 (w), 911 (m), 888 (m), 784 (m), 760 (m), 743 (s).

Anal. Calcd for $C_{32}H_{22}O_4$: C, 81.68; H, 4.71. Found: C, 81.48; H, 4.69.

### (10) Preparation of (+) and (-)-2,2'-Dicarbomethoxy-9,9'-bianthryl. Esterification of the Corresponding Acids with Diazomethane

Diazomethane was generated by the procedure on p 74 , using 29.7 g (0.14 mole) of "Diazald" dissolved in 180 ml of ether and a solution of 7.06 g of potassium hydroxide in 35 ml of 95% ethanol and 11 ml of water. The total volume of diazomethane solution obtained was 230 ml.

A 105 ml portion of this diazomethane solution was added to a solution of 3.71 g ( 8.39 mmoles) of (+)-2,2'-dicarboxy-9,9'-bianthryl (p 72) in one liter of dioxane; the remainder ( 125 ml) was added to a solution of 4.55 g (10.3 mmoles) of (-)-2,2'-dicarboxy-9,9'-bianthryl (p 72) in 1,300 ml of dioxane. The excess diazomethane was destroyed by the addition of 2 ml of acetic acid to each solution. Upon standing for 45 hr, the yellow solutions acquired a red color. Each of the solutions was evaporated to a small volume (approximately 5 ml), and water was added to precipitate the esters. The solid esters were collected by suction filtration and dried under vacuum at 95-100$^{\circ}$ for 3 hr.

(+)-2,2'-Dicarboxy-9,9'-bianthryl gave (+)-2,2'-dicarbomethoxy-9,9'-bianthryl: $[\alpha]_{D}^{26}$ + 102$^{\circ}$ (c 0.53, acetone). (-)-2,2'-Dicarboxy-9,9'-bianthryl gave (-)-2,2'-dicarbomethoxy-9,9'-bianthryl: $[\alpha]_{D}^{26}$ - 130$^{\circ}$ (c 0.57, acetone). Two recrystallizations of each ester from chloroform-benzene yielded 2.73 g (69%) of (+)-2,2'-dicarbomethoxy-9,9'-bianthryl: mp 229.5-231.5$^{\circ}$; $[\alpha]_{D}^{22}$ + 114$^{\circ}$ (c 0.58, acetone) and 3.01 g (66%) of (-)-2,2'-dicarbomethoxy-9,9'-bianthryl: mp 232.7-233.5$^{\circ}$;

$[\alpha]_D^{22}$ -133° (c 0.57, acetone). The infrared spectra of the enantiomeric 2,2'-dicarbomethoxy-9,9'-bianthryls are essentially identical to that of the racemic form (p 129).

In similar experiments, the specific rotations of the enantiomeric esters were not enhanced to any significant extent by further recrystallization.

### (11) Attempted Preparation of 3,3'-Dicarboxy-9,9'-bianthryl. Oxidation of 3,3'-Dimethyl-9,9'-bianthryl with Chromic Acid[36]

In a 50-ml flask, equipped with a reflux condenser and a magnetic stirrer, were placed 0.61 g (1.5 mmoles) of 3,3'-dimethyl-9,9'-bianthryl (p 37) and 20 ml of glacial acetic acid.

To this solution, 1.10 g (11.0 mmoles) of chromic acid was gradually added and the mixture was stirred overnight at room temperature. It was then refluxed for an additional 4 hr. The solution became dark red.

The solution was poured into 100 ml of water. Upon filtration, a dark tar was obtained which was extracted with two 50-ml portions of 10% aqueous sodium carbonate solution.

The combined alkaline extracts were filtered and acidified to yield 0.051 g of a dark amorphous solid. This solid was extracted with 30 ml of benzene. The benzene was evaporated to yield a dark solid (~ 1 mg), the infrared spectrum of which indicated that it could be 3,3'-dicarboxy-9,9'-bianthryl.

Attempts to crystallize the remaining amorphous solid from acetic acid failed.

## (12) Attempted Preparation of 2,2'-Dicarboxy-9,9'-bianthryl.

### (a) Oxidation of 2,2'-Dimethyl-9,9'-bianthryl with Chromic Acid[50]

To a solution of 0.60 g (1.5 mmoles) of 2,2'-dimethyl-9,9'-bianthryl (p 44 ) in 20 ml of glacial acetic acid, 1.07 g (10.7 mmoles) of chromic acid was gradually added, with stirring, over a period of 1 hr. The mixture was refluxed for 5 hr.

The resulting deep red solution was cooled and poured into water. A black tar precipitated which was collected by filtration. This tar was extracted with 10% aqueous $Na_2CO_3$, and the alkaline extracts were filtered and acidified with concentrated hydrochloric acid to yield approximately 15 mg of a black-red amorphous solid which could not be further purified.

The base-insoluble material contained 2-methylanthraquinone, as evidenced by its infrared spectrum.

[50] Patterned after the procedure on p 78 (ref 36).

### (b) Oxidation of 2,2'-Dimethyl-9,9'-bianthryl with Sodium Dichromate[51]

A 200 ml steel autoclave, heated by an electrical heating jacket, was charged with 0.51 g (1.3 mmoles) of 2,2'-dimethyl-9,9'-bianthryl (p 44), 0.96 g (3.2 mmoles) of sodium dichromate dihydrate and 107 ml of water. The autoclave was sealed and heated at 208° for 19 hr.

When the autoclave was opened, the water solution was found to be acidic. The organic solid was collected by filtration and extracted with 10% aqueous NaOH. Upon acidification of the alkaline extracts with concentrated hydrochloric acid, 10 mg of an amorphous brown solid was obtained. This solid was shown to be mostly 2-carboxyanthraquinone by comparison of its infrared spectrum with an authentic sample. The base-insoluble residue was shown to be, the starting material, 2,2'-dimethyl-9,9'-bianthryl.

Similar results were obtained with reactions at 220° and 230°. At 250° the base-insoluble material was neither starting material nor 2-methylanthraquinone. It was not identified.

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[51] Patterned after L. Friedman, Ph.D. Thesis, Ohio State University, 1959.

## (B) Preparation of Triptycene and 9,9'-Bitriptycyl Derivatives. General Procedure Using Anthranilic Acid as the Benzyne Source[52]

Unless otherwise stated, a three-necked flask equipped with three reflux condensers and a magnetic stirrer was used. On two of the condensers, pressure equalizing addition funnels were mounted. The other condenser was connected to a capillary tube immersed in mineral oil.

The 9,9'-bianthryl or anthracene derivative was dissolved in 2-butanone (dried over $CaSO_4$) and placed in the reaction flask. The anthranilic acid and n-butyl nitrite were each dissolved in 2-butanone and placed in separate addition funnels. A positive pressure of nitrogen was applied on the funnel containing the anthranilic acid. The 9,9'-bianthryl or anthracene solution was heated to reflux and a few drops of the n-butyl nitrite solution was added. While stirring the reaction mixture, the anthranilic acid and n-butyl nitrite solutions were simultaneously added, dropwise, over the specified period of time.

The anthranilic acid (Metro Scientific, Inc., Long Island, N.Y.) used was recrystallized once from water, twice from denatured ethanol (5% methanol), and finally thoroughly washed with absolute ethanol.

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[52] Patterned after the procedure of L. Friedman and F.M. Logullo, J. Am. Chem. Soc., 85, 1549 (1963).

The resulting crystalline white solid was dried at 60° under vacuum to constant weight: mp 144.5 - 146.0° (lit[53] 146.1°).

The n-butyl nitrite was prepared by the procedure of W.A. Noyce.[54] It was stored over $CaSO_4$ in a refrigerator at 4°.

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[53] C.L. Lazell and J. Johnston, *J. Phys. Chem.*, **32**, 1331 (1928).

[54] W.A. Noyes, "Organic Syntheses," Coll. Vol. II, A.H. Blatt, ed., John Wiley and Sons, Inc., New York, N.Y. 1943, p 108.

## (C) Preparation of Triptycene Derivatives

### (1) Preparation of 2-Methyltriptycene. Addition of 4-Methylbenzyne to Anthracene

The procedure given on p 81 was used. 5-Methylanthranilic acid (K and K Laboratories, Inc., Plainview, New York) was recrystallized twice from absolute alcohol and dried under vacuum at 95° to yield a yellow solid, mp 174.0-175.1 (lit[55] 173.8-174.8°).

In the reaction flask were placed 0.965 g (5.42 mmoles) of anthracene and 60 ml of 2-butanone. 5-Methylanthranilic acid (3.56 g, 23.6 mmoles) and n-butyl nitrite (2.68 g, 26.0 mmoles) were each dissolved in 45 ml of 2-butanone and added to the refluxing reaction, with stirring, over a period of $2\frac{1}{2}$ hr. The resulting dark reaction solution was refluxed for an additional 2 hr. The solvent and excess n-butyl nitrite were evaporated to yield a dark tar. Xylene (bp 137-140°) (30 ml) and maleic anhydride (1.19 g 12.1 mmoles) were added to the dark tar, and the resulting dark solution was refluxed for 40 min.

The xylene was evaporated and 20 ml of 10% aqueous potassium hydroxide solution was added. The resulting mixture was stirred for 15 min at 80°. After cooling, 100 ml of water was added, and the mixture was extracted with 250 ml of methylene chloride. The dark methylene chloride solution was washed six times with 50-ml portions of 5% aqueous potassium hydroxide, and dried over $MgSO_4$. After filtration, the methylene chloride was evaporated to yield a dark tar which was chromatographed on 150 g of silica gel (100 - 200 mesh), using benzene as the eluent. The first light yellow band was collected giving a light yellow solid plus some sweet smelling oil. Recrystallization from chloroform/ethanol yielded 0.496 g (34%) of the white solid, 2-methyltriptycene: mp 163.3 - 164.0° (lit[56] 173.5 - 174°); IR (KBr) (p 130): 3010 (w, aromatic C-H), 2970 (w, aliphatic C-H), 1615 (w), 1602 (w), 1492 (w), 1460 (s), 790 (w), 779 (w), 748 (s), 739 (s); UV: $\lambda_{max}^{CHCl_3}$ 283 mμ (log ε 3.63), 280 (3.64), 273 (3.56), 266 (sh) (3.28); Mass spectrum: see p 142.

<u>Anal.</u> Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 94.43; H, 5.88.

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[55] N.S. Dokunikhin and L.A. Gaeva, <u>Zhur. Obshchei Khim.</u>, **23**, 606 (1953); CA 52: 7018 f

[56] L. Friedman and F.M. Logullo, <u>J. Am. Chem. Soc.</u>, **85**, 1549 (1963).

### (2) Preparation of 2-Chlorotriptycene. Addition of 4-Chlorobenzyne to Anthracene

The procedure given on p 81 was used. In the reaction flask were placed 2.046 g (11.5 mmoles) of anthracene and 100 ml of 2-butanone. 5-Chloroanthranilic acid (8.12 g, 47.3 mmoles) and n-butyl nitrite (5.44 g, 52.8 mmoles) were each dissolved in 90 ml of 2-butanone and added to the refluxing reaction solution, with stirring, over a period of 4.0 hr. The resulting dark reaction solution which contained some precipitate was refluxed for an additional $1\frac{1}{2}$ hr. After cooling, the reaction solution was filtered to remove the yellow precipitate. This solid was washed with acetone and the acetone washings were combined with the filtrate and evaporated to give a dark tar. This tar was dissolved in 35 ml of xylene, 2.32 g (23.7 mmoles) of maleic anhydride was added, and the mixture was heated at reflux for 45 min. The xylene was evaporated to give a dark tar which was chromatographed on 246 g of Woelm alumina (acidic, activity grade I) using benzene as the eluent.

The first eluted fraction consisted of a white solid plus a little sweet smelling oil. Recrystallization from chloroform/ethanol yielded 1.20 g (36%) of the white solid, 2-chlorotriptycene: mp 166.3 - 167.1°; IR (KBr) (p 131): 3050 (w, aromatic C-H), 2980 (w, aliphatic C-H), 1620 (w), 1605 (w), 1460 (s), 1415 (w), 802 (w), 780 (w), 743 (s, broad)

713 (w); UV: $\lambda_{max}^{CHCl_3}$ 285 mμ (log ε 3.50), 278 (3.61), 271 (3.49); Mass spectrum: see p 144

*Anal*. Calcd for $C_{20}H_{13}Cl$: C, 83.18; H, 4.54; Cl, 12.28. Found: C, 82.96; H, 4.51; Cl, 12.44.

### (3) Preparation of 2-Carbomethoxytriptycene

#### (a) Preparation of 2-Carbomethoxyanthracene. Esterification of 2-Anthroic Acid with Diazomethane

2-Anthroic acid (Aldrich Chem. Co., Milwaukee, Wisconsin) was recrystallized from acetic acid to constant melting point: mp 280.5 - 181.8° (lit[57, 58] 277 - 278°, 280°); IR (KBr): 3200 - 2500 (m, carboxylic acid), 1695 (s, carbonyl), 1640 (m), 1580 (w), 1540 (w), 1485 (w), 1460 (w), 1410 (m), 880 (s), 775 (w, broad), 760 (w), 730 (s).

Diazomethane was generated using the procedure on p 74, from 6.70 g (0.03 mole) of "Diazald" dissolved in 41 ml of ether and a solution of 1.7 g of potassium hydroxide in 8 ml of 95% ethanol and 2.5 ml of water.

The diazomethane solution was added to a solution of 2.07 g (9.32 mmoles) of 2-anthroic acid in 350 ml of dioxane. The resulting deep yellow solution was left standing for 2 hr. Acetic acid (approximately 1.5 ml) was added until the intensity of the yellow color decreased sharply to pale yellow. This solution was concentrated to 4 - 5 ml, and 20 ml of water was added. A yellow solid precipitated which was collected by suction filtration and dried under vacuum at

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[57] A. Sonoda, F. Ogura and M. Nakagawa, Bull. Chem. Soc. Japan, 35, 853 (1962).

[58] E. Bornstein, Chem. Ber., 16, 2609 (1883).

95 - 100°. Three recrystallizations from chloroform/benzene yielded 1.80 g (82%) of the yellow solid, 2-carbomethoxyanthracene: mp 187.2 - 189.0° (lit[59] 128° dec); IR (KBr): 3050 (w, aromatic C-H), 2980 (w, aliphatic C-H), 1725 (s, carbonyl), 1640 (w), 1485 (w), 1460 (w), 1445 (m), 1410 (w), (1317, 1280, 1240) (s, aromatic ester), 860 (s), 802 (w), 745 (s), 735 (s); Mass spectrum: see p 140.

*Anal*. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 80.93; H, 4.90.

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[59] K. Lauer, *Chem. Ber.*, **70B**, 1288 (1937).

### (b) Preparation of 2-Carbomethoxytriptycene. Addition of Benzyne to 2-Carbomethoxyanthracene

The procedure given on p 81 was used. In the reaction flask were placed 0.751 g (3.18 mmoles) of 2-carbomethoxyanthracene (p 87) and 65 ml of 2-butanone. Anthranilic acid (3.47 g, 25.4 mmoles) and n-butyl nitrite (3.17 g, 30.8 mmoles) were each dissolved in 44 ml of 2-butanone and added to the refluxing reaction solution, with stirring, over a period of $4\frac{1}{2}$ hr. The resulting dark reaction solution was refluxed for an additional 50 min. The 2-butanone was evaporated using a rotary evaporator, and 150 ml of methylene chloride was added to the residue. The resulting dark solution was washed six times with 60 ml portions of 2% aqueous potassium hydroxide, washed with water, and then dried over $MgSO_4$. After filtration, the solvent was evaporated yielding a dark tar. Methanol (10 ml) was added, and the mixture was thoroughly mixed and placed in a refrigerator overnight. Upon suction filtration, 0.626 g of a tan solid was obtained.

This solid was dissolved in 20 ml of xylene (bp 137 - 140$^{\circ}$), and 0.792 g (8.09 mmoles) of maleic anhydride was added. The resulting dark red solution was refluxed for 45 min. The xylene was evaporated to give a dark tar which was chromatographed on 40 g of silica gel (100 - 200 mesh), using benzene as the eluent. The first colorless fraction was collected giving 0.637 g of a white solid and a colorless sweet smelling oil. Recrystallization from chloroform/methanol yielded 0.445 g (45%) of the white solid, 2-carbomethoxytriptycene: mp 213.5 - 215.0°; IR (KBr) (p 132): 3040 (w, aromatic C-H), 2980 (w, aliphatic C-H), 1730 (carbonyl), 1620 (w), 1580 (w), 1460 (s), 1435 (s), 798 (m), 790 (m), 740 (s, broad); UV: $\lambda_{max}^{CHCl_3}$ 293 mμ (log ε 3.46), 283 (3.52), 265 (3.86); Mass spectrum: see p 146.

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.46; H, 4.78.

## (4) Preparation of 2-Carboxytriptycene. Hydrolysis of 2-Carbomethoxytriptycene

In a 25-ml flask, equipped with a reflux condenser and a magnetic stirrer , were placed 0.439 g (1.38 mmoles) of 2-carbomethoxytriptycene (p 89 ) and a solution of 1.26 g of potassium hydroxide in 15 ml diethylene glycol and 2 ml of water. The mixture was heated at 120° for 1¼ hr. The resulting orange solution was diluted with 40 ml of water, filtered, and acidified with concentrated hydrochloric acid. A white solid precipitated which was collected by filtration, dissolved in acetone and the acetone solution dried over $Na_2SO_4$. After filtration, the acetone was evaporated to yield a white solid, mp 270.4 - 274.0° with dec. Recrystallization from dioxane/hexane yielded 0.323 g (78%) of the white solid, 2-carboxytriptycene: mp 273.5 - 275.0° with dec; IR (KBr) (p 133): 3200 - 2500 (m, carboxylic acid), 1685 (s, carbonyl), 1623 (w), 1580 (w), 1490 (w), 1460 (m), 1430 (m), 783 (m), 740 (s, broad); UV: $\lambda_{\max}^{\text{dioxane}}$ 291 mμ (log ε 3.42), 275 (sh) (3.63), 263 (3.86); Mass spectrum: see p 148.

Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.55; H, 4.73. Found: C, 84.48; H, 4.67.

### (5) Preparation of 2,3-Benzotriptycene. Addition of Naphthyne to Anthracene

The procedure given on p 81 was used. In the reaction flask were placed 3.667 g (20.6 mmoles) of anthracene and 100 ml of 2-butanone. 3-Amino-2-naphthoic acid (1.012 g, 5.41 mmoles) and n-butyl nitrite (0.855 g, 8.30 mmoles) were each dissolved in 90 ml of 2-butanone and added to the refluxing reaction solution, with stirring, over a period of 3 hr and 40 min.

The 2-butanone was removed using a rotary evaporator to give a red amorphous solid. To this solid, 5.04 g (51.4 mmoles) of maleic anhydride and 35 ml of xylene were added, and the mixture was heated at reflux for 45 min. The resulting dark solution was evaporated using a rotary evaporator to give a dark red amorphous solid. A solution of 10% aqueous potassium hydroxide (30 ml) was added, and the mixture was heated at 80°, with stirring, for 20 min.

To the cooled mixture, 150 ml of chloroform was added, and after stirring the mixture, the chloroform layer was separated and washed several times with 10% aqueous potassium hydroxide solution until the red alkaline washings became pale yellow. The light red chloroform solution was dried over $MgSO_4$, filtered, and evaporated to dryness to yield a red amorphous solid. This solid was chromatographed on 150 g of silica gel (100 - 200 mesh) using benzene as the eluent. The first fraction was collected giving 0.851 g of a white solid. Two recrystallizations from chloroform/ethanol yielded 0.740 g (45%) of the white solid, 2,3-benzotriptycene : mp 257.5 - 258.2° (lit[60] 257 - 258°); IR (KBr): 3030 (w, aromatic C-H), 2940 (w, aliphatic C-H), 1620 (w), 1500 (w), 1480 (w), 1460 (s), 889 (s), 879 (m), 787 (w), 767 (s), 749 (s), 738 (s, broad); UV: $\lambda_{max}^{CHCl_3}$ 323 m$\mu$ (log $\epsilon$ 3.20), 309 (3.09), 302 (2.80), 289 (3.66), 277 (4.10), 268 (4.17).

Anal. Calcd for $C_{24}H_{16}$ : C, 94.71; H, 5.30. Found: C, 94.89; H, 5.19.

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[60] G. Wittig, H. Harle, E. Knauss and K. Niethammer, Chem. Ber., 93, 951 (1960).

## (D) Preparation of 9,9'-Bitriptycyl and Derivatives

### (1) Preparation of 9,9'-Bitriptycyl. Addition of Benzyne to 9,9'-Bianthryl

### (a) Benzyne Generated from Anthranilic Acid

In a 100-ml three-necked resin flask, equipped with a magnetic stirrer and three reflux condensers, were placed 0.515 g (1.46 mmoles) of 9,9'-bianthryl[61] and 30 ml of acetone. Two pressure equalizing addition funnels were mounted on the condensers. Anthranilic acid (1.91 g, 13.9 mmoles) and n-butyl nitrite 1.521 g (14.8 mmoles) were each dissolved in 25 ml of acetone and placed in separate addition funnels. Under a nitrogen atmosphere, the anthranilic acid and n-butyl nitrite solutions were simultaneously added over a period of 3¼ hr. The n-butyl nitrite solution was always in slight excess over the anthranilic acid solution. Within 15 minutes a solid began to precipitate. The resulting red solution was refluxed for an additional 1 hr, and was left standing over night to ensure complete precipitation of the product.

The precipitated solid was collected by suction filtration and was thoroughly washed with acetone to yield 96.5 mg (15%) of an almost colorless solid.

Samples from similar preparations were combined and recrystallized twice from nitrobenzene to yield the white solid, 9,9'-bitriptycyl: mp[62] 575 ± 5° with dec; IR (Nujol) (p 134): 1284 (w), 1151 (m), 1133 (w), 1036 (m), 915 (m), 808 (m), 771 (m), 753 (m), 745 (s), 738 (s); this compares favorably with the published spectrum of Bartlett and Green[63] for "compound x" obtained in the thermal decomposition of ditriptoyl peroxide. IR (KBr) (p 135): 3050 (w, aromatic C-H), 2960 (w, aliphatic C-H), 1464 (s), 1319 (w), 1284 (w), 1153 (m), 1131 (w), 1036 (m), 914 (m), 808 (m), 772 (m), 740 (s); UV: $\lambda_{max}^{dioxane}$ (10-cm cell) 280 m$\mu$ (log $\epsilon$ 3.69), 272 (3.63), 266 (sh) (3.38). For comparison, triptycene has $\lambda_{max}^{dioxane}$ 279 m$\mu$ (log $\epsilon$ 3.67), 271 (3.55) and 265 (sh) 3.32. Mass spectrum: see p 150.

*Anal.* Calcd for $C_{40}H_{28}$: C, 94.83; H, 5.17. Found: C, 94.96; H, 5.15.

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[61] F. Bell and D.H. Waring, *J. Chem. Soc.*, 1579 (1949).

[62] Melting point determined in a sealed tube, under nitrogen, using a zinc chloride bath and a 100 - 620° partial-immersion thermometer.

[63] P.D. Bartlett and F.D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954).

### (b) Benzyne Generated from o-Bromofluorobenzene and Magnesium[64]

In a three-necked resin flask, equipped with a mechanical stirrer, a condenser and a pressure equalizing addition funnel, were placed 0.741 g (2.09 mmoles) of 9,9'-bianthryl[61], 3.58 g (0.147 g-atom) of magnesium turnings (Grignard Grade) and 50 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride). Nitrogen was slowly passed through the system. To the refluxing solution 16.6 g (94.9 mmoles) of o-bromofluorobenzene was added, with stirring, over a period of 2½ hr. After 70 min an additional 0.76 g (0.032 g-atoms) of magnesium turnings was added.

A dark solution was obtained which contained unreacted magnesium and insoluble salts. The reaction mixture was left standing overnight. The insoluble material was collected by centrifugation, treated with 3 M hydrochloric acid, and washed with water and acetone. The remaining white solid (0.11 g, 11%) was shown to be 9,9'-bitriptycyl, contaminated with some unidentified side product from o-bromofluorobenzene. This side product was obtained in a control experiment under identical conditions, except that 9,9'-bianthryl was omitted from the reaction.

[64] Patterned after (a) G. Wittig and E. Knauss, Chem. Ber., **91**, 895 (1958); (b) G. Wittig and L. Pohmer, ibid., **89**, 1335 (1956).

### (c) Benzyne Generated from 1,1-Dioxo-1,2,3-benzothiadiazole

#### (a') Preparation of o-Nitrosulfinic Acid from o-Aminonitrobenzene[65]

2-Nitroaniline (20.7 g, 0.150 mole) was dissolved in a hot mixture of 103 ml of concentrated sulfuric acid (d = 1.84), 150 ml of 85% phosphoric acid and 75 ml of water. The resulting solution was cooled and diazotized at 10 - 15° by the dropwise addition of a solution of 12.4 g (0.180 mole) of sodium nitrite in 38 ml of water. The excess nitrite was destroyed by the addition of urea.

The reaction mixture was cooled in an ice bath, and $SO_2$ was bubbled through until the weight of the reaction solution was increased by 27 g (0.42 mole). It was then poured into a mixture of 83 g of $FeSO_4 \cdot 7H_2O$ and 1.5 g of copper powder. The temperature of the reaction rose to 22°. After 45 minutes, evolution of nitrogen had essentially ceased. The resulting mixture was filtered, and the filtrate was extracted with 300 ml of 1:1 ether/methylene chloride. The solvent was evaporated at 0 - 15° to give a yellow solid. This solid was dissolved in dilute aqueous ammonia and reprecipitated with concentrated hydrochloric acid to yield 18.5 g (66%) of the yellow solid, o-nitrosulfinic acid: mp 122 - 123° (lit[65] 125°).

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[65] G. Wittig and R.W. Hoffman, Chem. Ber. 95, 2723 (1962).

### (b') Preparation of Sodium o-Aminosulfinate. Hydrogenation of Sodium o-Nitrosulfinate

o-Nitrosulfinic acid (5.27 g, 30.0 mmoles) (p 97) was suspended in 20 ml of water, and 1 M aqueous sodium hydroxide solution was added until a clear solution was obtain (pH 9). To this solution, 2.0 g of 10% palladium on charcoal suspended in 30 ml of water was added, and the mixture was hydrogenated at atmospheric pressure. The volume of hydrogen taken up was 98% of the theoretical amount.

After filtration to remove the catalyst, the water solution was evaporated at $25^{\circ}$ to yield 4.06 (81%) of the colorless solid, sodium o-aminosulfinate, which was dried over $P_2O_5$ in a desiccator.

This salt was diazotized to form 1,1-dioxo-1,2,3-benzothiadiazole (p 99 ) without further purification.

### (c') Preparation of 1,1 -Dioxo-1,2,3-benzothiadiazole. Diazotization of Sodium o-Aminosulfinate[65]

Sodium o-aminosulfinate (2.52 g, 14.1 mmoles) (p 98) and 0.970 g (14.1 mmoles) of $NaNO_2$ were dissolved in a minimum amount of water. The resulting solution was added, dropwise with stirring at -15°, to a mixture of 22 ml of 2 N sulfuric acid and 39 ml of glycerol. Stirring was continued for an additional two hr. Methylene chloride (25 ml), precooled to -15°, was added, and the mixture was further stirred. The organic layer was separated without allowing the temperature to rise above -6°.

The extraction process was repeated seven times. The yellow methylene chloride extractions were combined, and dried at -15°, first over $CaCl_2$ and finally over $P_2O_5$. The drying agents were removed by filtration through a funnel containing a dry ice-acetone cooled jacket. Evaporation of the solvent at 0° yielded 1.68 g (70%) of the yellow solid, 1,1-dioxo-1,2,3-benzothiadiazole, contaminated with a little dark material.

### (d') Preparation of 9,9'-Bitriptycyl from 9,9'-Bianthryl and 1,1-Dioxo-1,2,3-benzothiadiazole

9,9'-Bianthryl (0.450 g, 1.28 mmoles), dissolved in 30 ml of methylene chloride, was added to 1.68 g (10 mmoles) of freshly prepared 1,1-dioxo-1,2,3-benzothiadiazole (p 99) precooled to -15° C. The temperature of the reaction solution was raised slowly. At approximately 14° C evolution of a gas was noticed. The reaction was left standing overnight at room temperature and was then refluxed for 1¾ hr. A white solid which had precipiated was collected by suction filtration and washed repeatedly with acetone. The methylene chloride filtrate was evaporated, and 30 ml of acetone was added to the residue. More of the same white solid, 9,9'-bitriptycyl, remained undissolved to give a combined yield of 41 mg (6%).

### (2) Preparation of 2,2'-Dimethyl-9,9'-bitriptycyl. Addition of Benzyne to 2,2'-Dimethyl-9,9'-bianthryl

#### a. Benzyne Generated from Anthranilic Acid

The procedure given on p 81 was used. In the reaction flask were placed 1.185 g (3.09 mmoles) of 2,2'-dimethyl-9,9'-bianthryl (p 44 ) and 50 ml of 2-butanone. Anthranilic acid (6.397 g, 46.7 mmoles) and n-butyl nitrite (5.267 g, 51.1 mmoles) were each dissolved in 100 ml of 2-butanone and added to the refluxing reaction solution, with stirring, over a period of $4\frac{1}{4}$ hr. The resulting dark reaction solution was refluxed for an additional $\frac{1}{2}$ hr.

The solvent was removed, using a rotary evaporator, to yield a dark tar. This tar was dissolved in chloroform and chromatographed on 170 g of Woelm alumina (acidic, activity grade I) using benzene as the eluent. The first eluted band gave 2.04 g of a pale yellow solid plus a sweet smelling oil. To this mixture 35 ml of a 70% acetone/benzene mixture was added. After stirring, a white powder remained undissolved. The mixture was left standing for two days to ensure complete precipitation of the white powder. This powder was collected by centrifugation, washed thoroughly with acetone and dried under vacuum to yield 0.148 g (12%) of the almost white solid, 2,2'-dimethyl-9,9'-bitriptycyl. Two recrystallization from chloroform/acetone yielded the white solid, 2,2'-dimethyl-9,9'-bianthryl: mp 490 - 492.5$^{\circ}$ with dec; IR (KBr) (p 136): 3030 (w, aromatic C-H), 2940 (w, aliphatic C-H), 1620 (w), 1460 (s), 1278 (w), 1205 (w), 1142 (m), 1035 (w), 918 (w), 908 (w), 823 (m), 802 (w), 793 (w), 741 (s), 734 (s); UV: $\lambda_{\text{max}}^{\text{CHCl}_3}$ 284 mμ (log ε 3.57), 280 (3.65), 273 (3.62), 266 (sh) (3.39); Mass spectrum: see p 153.

Anal. Calcd for $C_{42}H_{30}O$: C, 94.35; H, 5.66. Found: C, 94.03; H, 5.68.

### (b) Benzyne Generated from o-Diphenyliodonium Carboxylate

#### (a') Preparation of Diphenyliodonium 2-Carboxylate Monohydrate[66]

o-Iodobenzoic acid (10.0 g, 40.5 mmoles), and potassium peroxydisulfate (13.1 g, 50.4 mmoles) were mixed and cooled in an ice-bath. To the mixture, 40 ml of precooled concentrated sulfuric acid (d = 1.84) was added, and the mixture was shaken in an ice bath for 5 minutes. The reaction mixture foamed a little, and changed color from yellow to green to black. The black reaction solution was left standing at room temperature for 20 minutes. It was again cooled in an ice bath and 10.5 ml of precooled benzene was added. The reaction flask was shaken in the ice bath until the benzene froze. It was then shaken at room temperature for ½ hr.

The reaction solution was cooled in an ice bath, and 95 ml of precooled distilled water was slowly added. A solid precipitated. Methylene chloride (200 ml) was added, and 115 ml of precooled concentrated ammonia (29%) was added dropwise. The methylene chloride layer was separated, and the aqueous layer was extracted with two 50 ml portions of methylene chloride. The yellow-red methylene chloride solutions were combined, and dried over $Na_2SO_4$. After filtration, the solvent was evaporated to yield 12.7 g of a tan solid. Two recrystallization from distilled water, with Norit, yielded 10.9 g (79%) (dried under vacuum at 80°) of the white crystalline solid, diphenyliodonium-2-carboxylate monohydrate: mp 217 - 220° with dec (lit[66] 219 - 220°).

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[66] L. F. Fieser, "Organic Experiments," D.C. Heath and Co., Boston, 1964, p 311.

### (b') Preparation of 2,2'-Dimethyl-9,9'-bitriptycyl from 2,2'-Dimethyl-9,9'-bianthryl and Diphenyliodonium-2-carboxylate Monohydrate

In a 50-ml flask, equipped with an air condenser and a magnetic stirrer, were placed 0.406 g (1.06 mmoles) of 2,2'-dimethyl-9,9'-bianthryl (p 44), 1.50 g (4.61 mmoles) of diphenyliodonium-2-carboxylate monohydrate (p 103) and 25 ml of 1,2-bis(2-methoxyethoxy)-ethane (triglyme). The resulting yellow solution was heated at 220° for 3 hr and refluxed for an additional ½ hr. The reaction solution was left standing for 30 hr at room temperature. No precipitate was observed. Addition of 20 ml of ethanol gave no precipitate. Water was added dropwise. A yellow solid precipitated (probably starting material) which was soluble in acetone. The remaining solution was left standing. After six months, a white solid had precipitated which was collected by centrifugation and washed with acetone. Its infrared spectrum was identical to that of 2,2'-dimethyl-9,9'-bitriptycyl prepared by the addition of benzyne, generated from anthranilic acid, to 2,2'-dimethyl-9,9'-bianthryl (p 101).

### (3) Preparation of 2,2'-Dichloro-9,9'-bitriptycyl. Addition of Benzyne to 2,2'-Dichloro-9,9'-bianthryl

The procedure given on p 81 was used. In the reaction flask were placed 3.028 g (7.18 mmoles) of 2,2'-dichloro-9,9'-bianthryl (p 54 ) and 150 ml of 2-butanone. Anthranilic acid (14.80 g, 108 mmoles) and n-butyl nitrite (12.90 g, 125 mmoles) were each dissolved in 200 ml of 2-butanone and added to the refluxing reaction solution, with stirring, over a period of 5 hr. The resulting dark reaction solution was refluxed for another 1½ hr.

The solvent was removed, using a rotary evaporator, to give a dark tar. Methanol (80 ml) was added, and the mixture was shaken and left standing in a refrigerator for one day. An orange solid which did not dissolve was collected by suction filtration. Acetone was added to the solid and the mixture was thoroughly mixed; white and red solids remained undissolved. This mixture was repeatedly washed with acetone until the acetone washings were colorless. It was then washed with a 3% potassium hydroxide in a 1:1 water/acetone solution until the solid became white. Further washing with water and acetone followed by vacuum drying at 80° yielded 0.425 g of almost pure 2,2'-dichloro-9,9'-bitriptycyl.

The acetone washings were combined with the methanol solution and evaporated to yield a dark tar. This tar was dissolved in chloroform and chromatographed on a column of 2.66 g of Woelm alumina (neutral, activity grade I) prepared in benzene. The column was eluted with benzene. The first eluted fraction, which fluoresced strongly, yielded a mixture of a yellow solid plus a sweet smelling oil. This mixture was washed with 10 ml of cold methanol to yield 3.013 g of a yellow solid which was mainly the starting material, 2,2'-dichloro-9,9'-bianthryl, as evidenced by the comparison of its infrared spectrum with that of an authentic sample. To this solid 60 ml of 1:1 acetone/benzene was added. The yellow solid dissolved, while a white powder remained undissolved. This mixture was left standing overnight in a refrigerator. The white powder was collected by centrifugation and washed with acetone to yield 0.125 g (12% combined yield) of material. Recrystallization from nitrobenzene gave pure 2,2'-dichloro-9,9'-bitriptycyl: mp 514 - 517$^{\circ}$ with dec; IR (KBr) (p 137): 3030 (w, aromatic C-H), 2970 (w, aliphatic C-H), 1600 (w), 1540 (w), 1460 (s), 1400 (w), 1265 (w), 1155 (w), 1098 (m), 1035 (w), 917 (m), 905 (w), 885 (w), 862 (w), 819 (m), 788 (w), 743 (s), 717 (w), 708 (w); UV: $\lambda_{max}^{dioxane}$ 287 m$\mu$ (log $\epsilon$ 3.45), 280 (3.63), 272 (3.55); Mass spectrum: see p 156.

<u>Anal.</u> Calcd for $C_{40}H_{24}Cl_2$: C, 83.49; H, 4.10; Cl, 12.31. Found: C, 83.15; H, 4.15; Cl, 12.65.

### (4) Preparation of 2,2'-Dicarbomethoxy-9,9'-bitripticyl. Addition of Benzyne to 2,2'-Dicarbomethoxy-9,9'-bianthryl

The procedure given on p 81 was followed. In the reaction flask were placed 0.370 g (0.848 mmole) of 2,2'-dicarbomethoxy-9,9'-bianthryl (p 74 ) and 35 ml of 2-butanone. Anthranilic acid (1.92 g, 14.1 mmoles) and n-butyl nitrite (1.70 g, 16.6 mmoles) were each dissolved in 25 ml of 2-butanone and added to the refluxing reaction solution, with stirring, over a period of $2\frac{1}{2}$ hr. The resulting dark reaction solution was heated at reflux for an additional $\frac{1}{2}$ hr.

The solvent was evaporated to yield a dark tar. Methanol (30 ml) was added, and the mixture was left overnight. Centrifugation yielded an orange solid which was repeatedly washed with acetone until the acetone washings became colorless, to yield 8.0 mg of white solid. The acetone washings were combined with the methanol solution. After 3 days, 3.5 mg of the same white solid precipitated (2.2% combined yield).

Several such preparations were combined and recrystallized from nitrobenzene to yield the white solid, 2,2'-dicarbomethoxy-9,9'-bitriptycyl: mp 484 - 487° ; IR (KBr) (p 138): 3030 (w, aromatic C-H), 2970 (w, aliphatic C-H), 1730 (s, carbonyl), 1620 (w), 1445 (m), 1435 (m), 1295 (m), 1262 (s), 1152 (w), 1127 (w), 1108 (m), 779 (w), 772 (w), 744 (s); UV: $\lambda_{\text{max}}^{\text{CHCl}_3}$ 292 mμ (log ϵ 3.46), ca 280 (sh), 264 (4.14); Mass spectrum: see p 159 .

### (5) Preparation of 2,2'-Dicarboxy-9,9'-bitriptycyl

2,2'-Dicarbomethoxy-9,9'-bitriptycyl (27.5 mg) (p 108) was added to a solution of 1.9 g of potassium hydroxide in 11.5 ml of diethylene glycol and 2 ml of water. The mixture was heated at 137 - 140°, with stirring, for 3½ hr.

The resulting yellow solution was diluted with 30 ml of water, filtered and acidified with concentrated hydrochloric acid. An almost colorless solid precipitated which was collected by centrifugation, washed with two 7-ml portions of water and two 2½-ml portions of acetone, and dried under vacuum at 120° to yield an almost colorless solid. This crude product was contaminated with silicates, as evidenced by its infrared spectrum. Recrystallization from quinoline, with hot filtration in order to remove the silicates, yielded a white solid which was washed three times with 5-ml portions of chloroform, three times with 3½-ml portions of acetone, and dried under vacuum at 185 - 188° to yield 21.5 mg of the white solid, 2,2'-dicarboxy-9,9'-bitriptycyl: mp 532 - 536°; IR (KBr) (p 139): 3200 - 2500 (w, carboxylic acid), 1680 (s, carbonyl), 1620 (w), 1450 (m), 1418 (m), 1378 (w), 1295 (w), 1262 (s), 1210 (w), 1158 (w), 1123 (w), 1108 (w), 1016 (w), 928 (w), 908 (w), 893 (w), 803 (w), 779 (w), 748 (s, broad); UV: $\lambda_{max}^{dioxane}$ 290 mμ (log ε 3.47), 278 (sh) (3.78), 263 (4.13); Mass spectrum: m/e 596 (M+2), 595 (M+1), 594 (base peak, molecular ion), 550 (M - $CO_2$), 549 (M - COOH).

Because of the extremely low volatility of the compound, the rest of the spectrum could not be determined.

*Anal.* Calcd for $C_{42}H_{28}O_4$: C, 84.33; H, 4.41. Found: C, 84.66; H, 4.36.

### (6) Preparation of 2,3,2',3'-Dibenzo-9,9'-bitriptycl and 9-(2,3-Benzotriptycyl)-9'-anthracene. Addition of 2,3-Naphthyne to 9,9'-Bianthryl

The procedure described on p 81 was used. In the reaction flask were placed 0.890 (2.52 mmoles) of 9,9'-bianthryl and 50 ml of 2-butanone. 3-Amino-2-naphthoic acid (7.63 g, 37.6 mmoles) and n-butyl nitrite (4.56 g, 44.2 mmoles) were each dissolved in 450 ml of 2-butanone, and added to the refluxing solution over a period of 4½ hr. The resulting dark red solution was heated at reflux for an additional ½ hr.

The solvent was removed using a rotary evaporator to give a dark red tar. This tar was dissolved in chloroform and chromatographed on 248 g of Woelm alumina (acidic, activity grade I) using benzene as the eluent until no further elution occurred. Four fractions were arbitrarily taken. Each of the fractions gave a yellow solid upon evaporation of the eluent.

| Fraction | Weight (g) | Volume (ml) |
|---|---|---|
| 1 | 0.375 | 215 |
| 2 | 0.520 | 50 |
| 3 | 0.365 | 150 |
| 4 | 0.112 | 350 |

Each fraction was dissolved in acetone. Slow addition of either benzene or methanol precipitated a yellow, low melting (250 - 300$^{\circ}$) solid (impure 9,9'-bianthryl).

In order to increase the concentration of the corresponding 9,9'-bitriptycyl in the crude product, it was decided to attempt the addition of naphthyne to the chromatographed material.

The same procedure was followed, using 1.114 g of the combined fractions from the chromatography, 6.70 g (35.8 mmoles) of 3-amino-2-naphthoic acid and 4.20 (40.8 mmoles) of n-butyl nitrite.

The dark tar obtained after evaporation of the solvent was chromatographed on 242 g of Woelm alumina (acidic, activity grade I), using benzene as the eluent. The fraction eluted with benzene was collected and evaporated to dryness to yield a yellow solid.

Naphthyne addition to this yellow solid was repeated, using 6.85 g (38.7 mmoles) of 3-amino-2-naphthoic acid, and 4.86 g (47.1 mmoles) of n-butyl nitrite.

The resulting dark reaction solution was evaporated to give a dark tar which was chromatographed on 245 g of Woelm alumina (acidic, activity grade I) using benzene as the eluent until no further elution occurred. **Three** arbitrary fractions were collected.

| Fraction | Weight (g) | Volume (ml) |
|---|---|---|
| 1 | 0.994 | 250 |
| 2 | 0.283 | 150 |
| 3 | 0.171 | 420 |

All fractions gave yellow solids upon evaporation of the eluent. To fraction 1, 35 ml of 1:1 acetone/benzene was added. A yellow solution was obtained which upon standing slowly precipitated a white solid. This solid was washed 3 times with 4-ml portions of acetone to give 50 mg of a solid which melted at 300 - 360° (some solid still present).

Two recrystallizations from chloroform/ethanol gave the white solid, 2,3,2',3'-dibenzo-9,9'-bianthryl, contaminated with a little tri-naphthyne adduct as evidenced by its mass spectrum: mp > 360°; IR (KBr): 3060 (m), 2980 (w), 1620 (w), 1500 (w), 1480 (w), 1457 (m), 894 (m), 870 (w), 773 (m), 740 (s); UV: $\lambda_{max}^{dioxane}$ 325, 312 (naphthalene nucleus), 294, 276, 270, 253. Mass spectrum (a low intensity ion (tri-naphthyne adduct) appears at m/e 732): m/e 608 (14%, M+2), 607 (53%, M+1), 606 (base peak, molecular ion), 303 (56%, $\frac{M^+}{2}$ plus $M^{+2}$).

<u>Anal.</u> Calcd for $C_{48}H_{30}$: C, 95.01; H, 4.99. Found: C, 95.38; H, 4.87.

The second fraction was washed with 10 ml of 1:1 acetone/benzene and with 4 ml of acetone. Three recrystallizations from chloroform/acetone gave the white solid, 9-(2,3-benzotriptycyl)-9'-anthracene, contaminated with some 2,3,2',3'-dibenzo-9,9'-bitriptycyl as evidenced by its mass spectrum (a low intensity ion appears at m/e 606): mp 320°; IR (KBr) (p 139): 3060 (w), 2980 (w), 1630 (w), 1500 (w), 1440 (w), 880 (m), 840 (w), 805 (w), 783 (w), 740 (s, broad); UV: $\lambda_{max}^{dioxane}$ 388, 367, 348, 328, 313, 280, 255; Mass spectrum: m/e 482 (9.5% M+2), 481 (46%, M+1), 480 (base peak, molecular ion), 303 (14%, 2,3-benzotriptycyl ion), 240 (19%, $M^{+2}$ ).

## (E) Addition of Benzyne Generated from Anthranilic Acid to Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl

### (1) Benzyne Generated in Boiling 2-Butanone

### (a) Preparation of 2,2'-Dicarbomethoxy-9,9'-bitriptycyl

The procedure described on p 81 was used. In the reaction flask were placed 1.48 g (3.13 mmoles) of (-)-2,2'-dicarbomethoxy-9,9'-bianthryl (p 76 ), $[\alpha]_D^{22}$ -139° (c 0.76, acetone), and 100 ml of 2-butanone. Anthranilic acid (6.00 g, 43.8 mmoles) and n-butyl nitrite (6.13 g, 59.6 mmoles) were each dissolved in 95 ml of 2-butanone and added to the refluxing reaction solution, with stirring, over a period of 5 hr and 10 min. The resulting dark reaction solution was heated under reflux for an additional 20 min.

The solvent was removed at 41°, using a rotary evaporator, to yield a dark tar. Methanol (22 ml) was added, and the mixture left overnight. An insoluble orange solid was collected by centrifugation.

This solid was combined with the corresponding product of a second similar experiment from 1.52 (3.43 mmoles) of (-)-2,2'-dicarbomethoxy-9,9'-bianthryl. The combined solids were repeatedly washed with acetone until colorless.

Two recrystallizations from chloroform/acetone yielded 84.7 mg (2.1%) of 2,2'-dicarbomethoxy-9,9'-bitriptycyl. IR (KBr): identical to 2,2'-dicarbomethoxy-9,9'-bitriptycyl obtained from racemic 2,2'-dicarbomethoxy-9,9'-bianthryl.

### (b) Preparation of 2,2'-Dicarboxy-9,9'-bitriptycyl

To a solution of 6.09 g of potassium hydroxide in 40 ml of diethylene glycol and 7.0 ml of water, 77.2 mg of 2,2'-dicarbomethoxy-9,9'-bitriptycyl (p 114) was added. The mixture was heated at 130-135°, with stirring, for 2½ hr.

The resulting orange solution was diluted with 100 ml of water, filtered and acidified with concentrated hydrochloric acid. A white flocculent precipitate was obtained which was collected by centrifugation. This solid was added to approximately 1,500 ml of acetone; the mixture was stirred, and filtered to remove silicates. The filtrate was evaporated, to yield a tan solid which was washed 4 times with 3½-ml portions of chloroform, two times with 2½-ml portions of acetone, and dried under vacuum to yield 69.5 mg (94%) of 2,2'-dicarboxy-9,9'-bitriptycyl.

The optical rotation of this solid was determined with a Perkin-Elmer Model 141 polarimeter having a precision of ± 0.002°. The solvent used was 5.5% tetramethylammonium hydroxide in 48% DMSO/water. A 1.1% solution in a 10 cm cell showed no rotation at 589, 579, 546 and 436 mμ.

## (2) Benzyne Generated in Boiling Methylene Chloride

### (a) Preparation of 2,2'-Dicarbomethoxy-9,9'-bitriptycyl

A modification of the procedure described on p 81 was used. In the reaction flask were placed 0.489 g (1.04 mmoles) of (+)-2,2'-dicarbomethoxy-9,9'-bianthryl (p 76), $[\alpha]_D$ +114° (C 0.55, acetone), 0.891 g (8.65 mmoles) of n-butyl nitrite and 75 ml of methylene chloride. Anthranilic acid (0.983 g, 7.24 mmoles) was dissolved in 31 ml of acetone and added to the refluxing reaction solution, with stirring, over a period of 3½ hr. The resulting dark reaction solution was evaporated at 34°, using a rotary evaporator, to yield a dark tar. Methanol (10 ml) was added, and the mixture was left overnight in a refrigerator. An insoluble yellow solid was collected by centrifugation. This solid was washed with acetone and a solution of one drop of 10% aqueous potassium hydroxide in 3 ml of acetone, to yield 10.1 mg (1.6%) of 2,2'-dicarbomethoxy-9,9'-bitriptycyl. Four such preparations were combined and recrystallized twice from chloroform/acetone.

### (b) Preparation of 2,2'-Dicarboxy-9,9'-bitriptycyl

In a 100-ml flask equipped with a reflux condenser and a magnetic stirrer were placed 32.2 mg (0.0519 mmoles) of 2,2'-dicarbomethoxy-9,9'-bitriptycyl (p 116), and a solution of 10.0 g of potassium hydroxide in 40 ml of diethylene glycol and 5 ml of water. The mixture was heated at 70°, with stirring, under a nitrogen atmosphere, until complete solution occurred. After 43 hr, a light red, very slightly turbid solution was obtained which was diluted with 40 ml of water and filtered. Acidification with concentrated hydrochloric acid gave a flocculent tan solid which was collected by centrifugation. This solid was washed three times with 3-ml portions of acetone to give a white solid which was added to approximately one liter of acetone, mixed, and filtered to remove silicates formed during the hydrolysis step. The acetone was removed at 30° using a rotary evaporator to yield 24.3 mg (79%) of 2,2'-dicarboxy-9,9'-bitriptycyl.

A 1.2% solution of this solid gave no rotation (using a Perkin-Elmer Model 141 polarimeter see p 116) at 589, 578, 546, 436 and 365 mμ using a 10 cm cell.

## (F) Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl[67]

### (1) Racemization of (-)-2,2'-Dicarbomethoxy-9,9'-bianthryl in Dimethyl Phthalate

Nitrogen was passed through a solution of (-)-2,2'-dicarbomethoxy-9,9'-bianthryl ($\alpha_D = -0.596 \pm 0.002^{\circ}$) (see p 76) in dimethyl phthalate, in an ampoule, in order to remove dissolved oxygen. The ampoule was sealed and placed in a constant temperature bath at $220.2 \pm 0.1^{\circ}$.

After 6.00 hr the ampoule was removed from the bath. The optical rotation of this solution was found to be $-0.593 \pm 0.002^{\circ}$. Thus no racemization had occurred.

The experiment was repeated with a solution of $\alpha_D = -0.511 \pm 0.002^{\circ}$, except that oxygen was passed through the solution instead of nitrogen. After 2.00 hr of heating the solution had become very slightly red and had a rotation of $\alpha_D = -0.449 \pm 0.01$ (12% racemization).

In these and the following racemization experiments no special precautions were taken to exclude light. However, the amount of light reaching the sample would have to be very small since the sides of the bath except for the top were thoroughly covered with asbestos paper and cotton. The bath was placed in a hood without internal lights.

[67] A Perkin-Elmer Model 141 polarimeter was used to measure optical rotations using a 10-cm cell.

### (2) Racemization of (-)-2,2'-Dicarbomethoxy-9,9'-bianthryl in Triglyme

A solution of 0.101 g of (-)-2,2'-dicarbomethoxy-9,9'-bianthryl (p 76 ) was dissolved in approximately 14 ml of 1,2-bis-(2-methoxyethoxy)ethane (triglyme), freshly distilled from lithium aluminum hydride. Nitrogen was bubbled through the solution for 20 - 25 min in order to remove dissolved oxygen. The rotation of the solution was measured, $\alpha_D = -0.762^\circ$, and the solution was divided between two ampoules. Nitrogen was bubbles through one of the solutions for 10 min while oxygen was bubbled through the other for 20 min. The ampoules were sealed and placed in a constant temperature bath (see p.119) at $220.2 \pm 0.1^\circ$.

The ampoules were removed from the bath after 1.50 hr, and immediately immersed in cold water. The optical rotation of the solution through which nitrogen had been bubbled was $\alpha_D = -0.732 \pm 0.002^\circ$ (3.9% racemization) while the rotation of the solution through which oxygen had been bubbled was $\alpha_D = -0.216 \pm 0.002^\circ$ (72% racemization).

Each solution was distilled at 0.3 mm and $70^\circ$ in order to remove the solvent. The residues, consisting of a yellow solid and a little solvent, were washed with pentane and dried under vacuum. The pentane washings were evaporated under vacuum to yield pale yellow liquids which were shown by nmr to consist of the solvent, triglyme, contaminated only by small amounts of 2,2'-dicarbomethoxy-

9,9'-bianthryl. The nmr and ir spectra of the solid residues were identical with authentic 2,2'-dicarbomethoxy-9,9'-bianthryl.

## Spectra*

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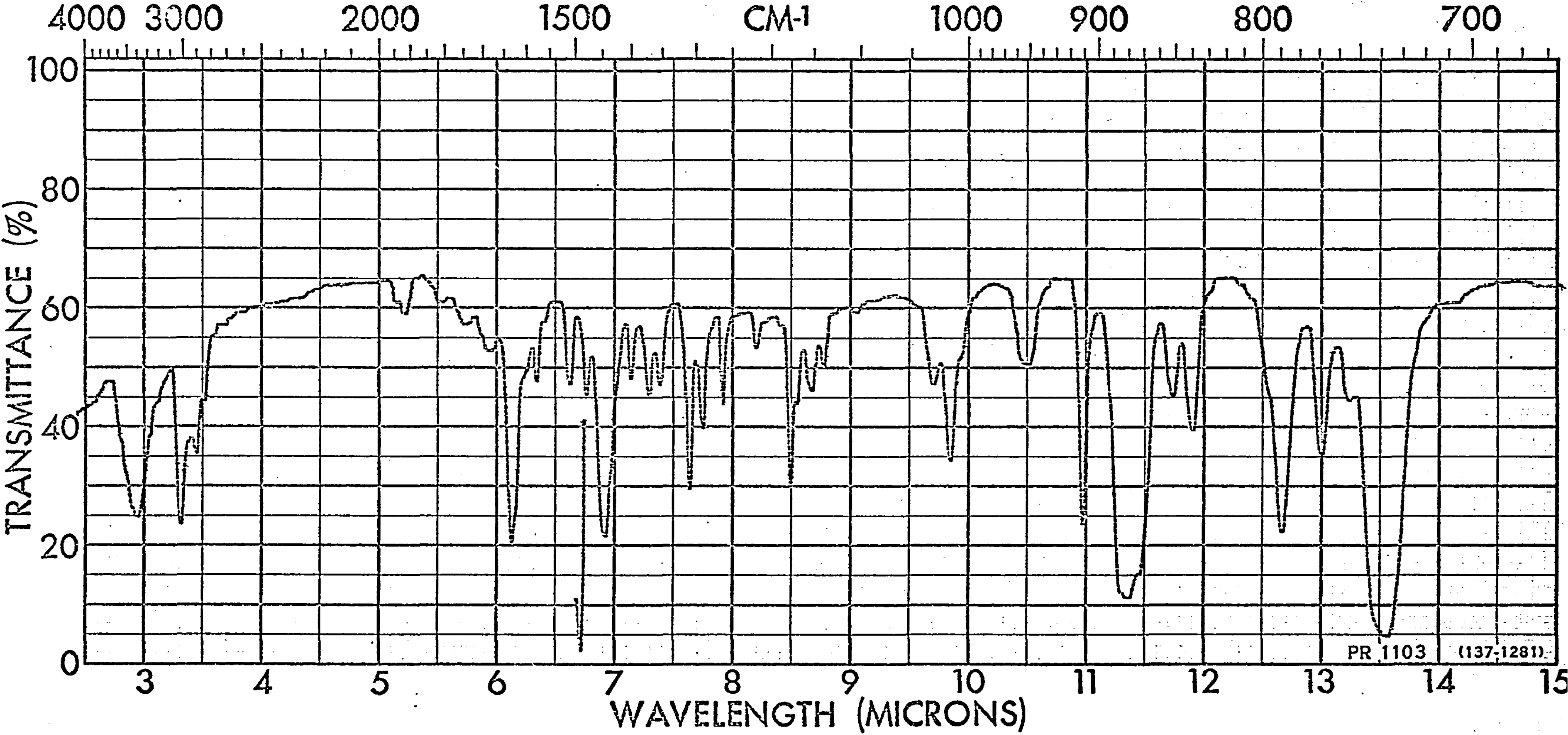
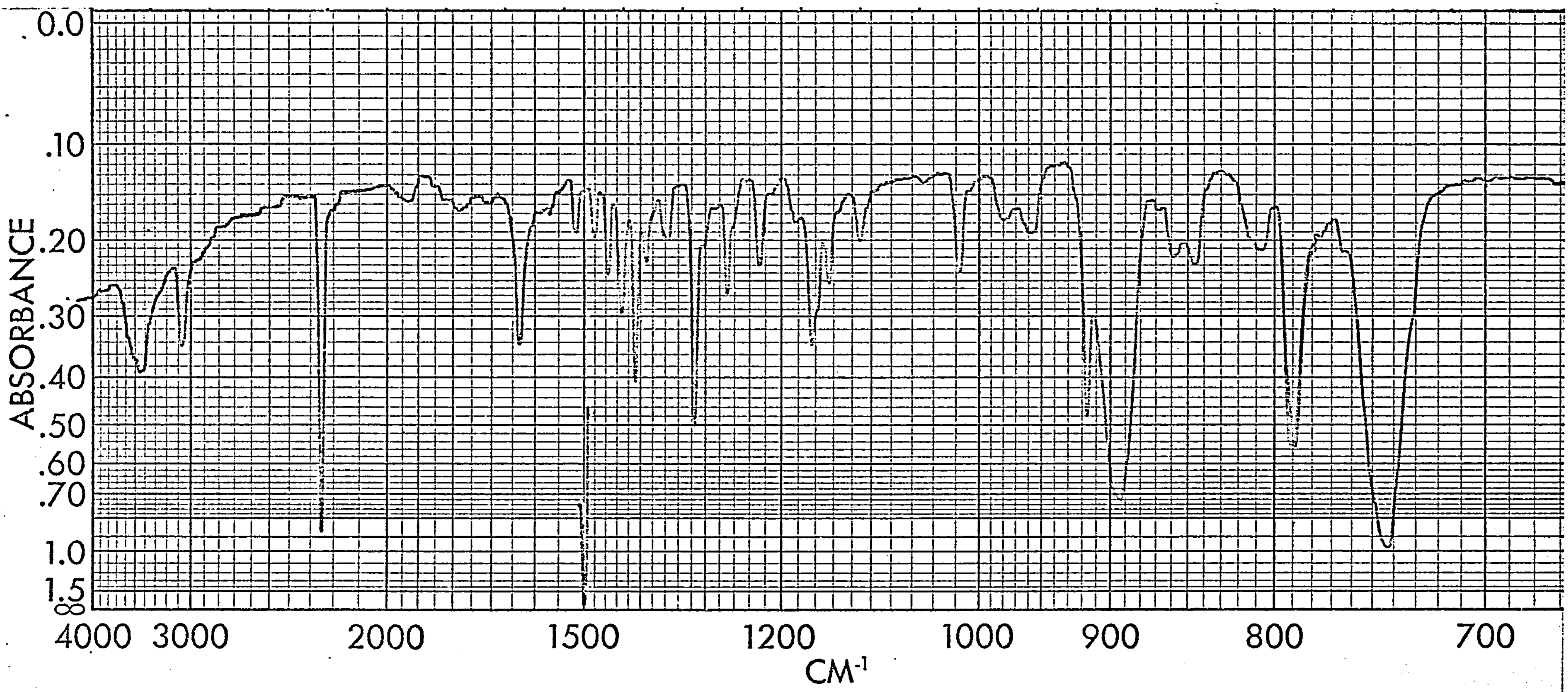
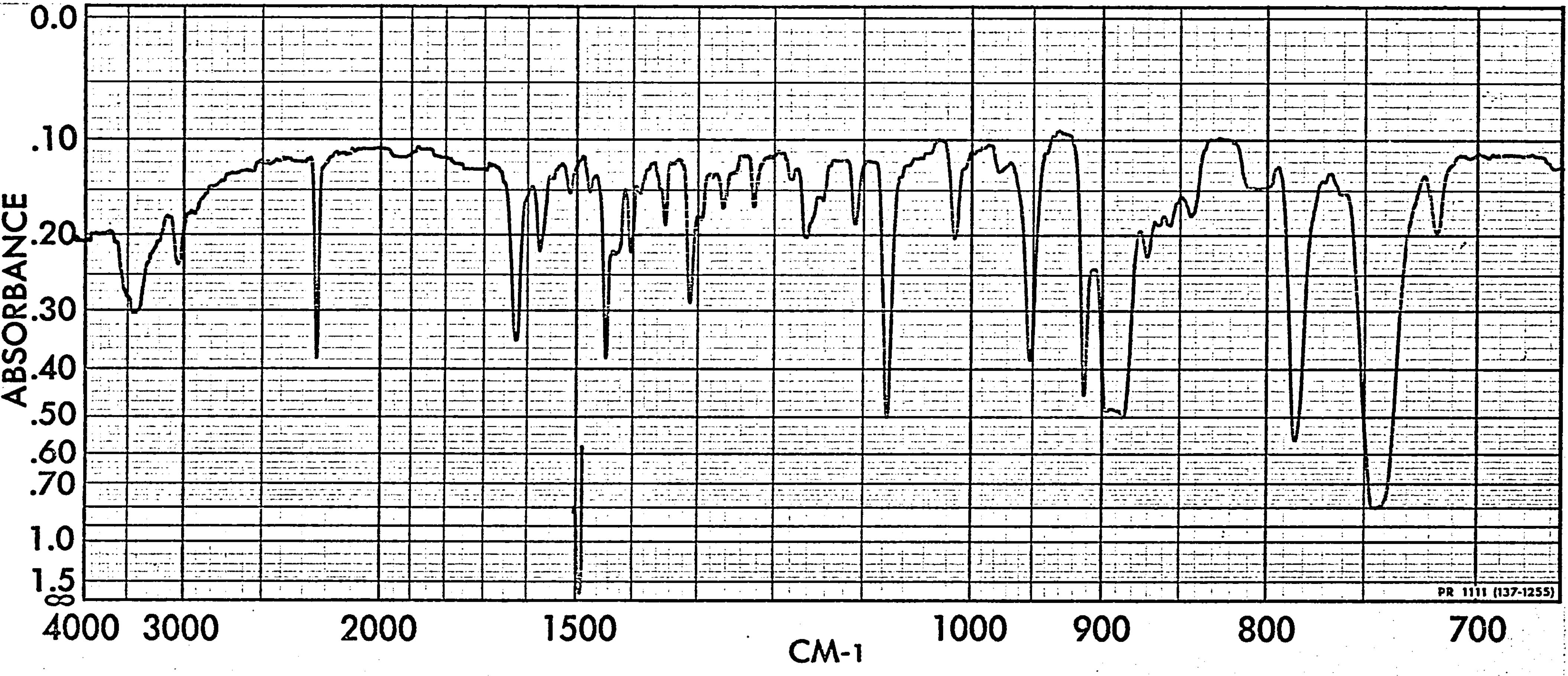
* Infrared spectra were calibrated with the 1449 $cm^{-1}$ (6.69 $\mu$) line of polystyrene.



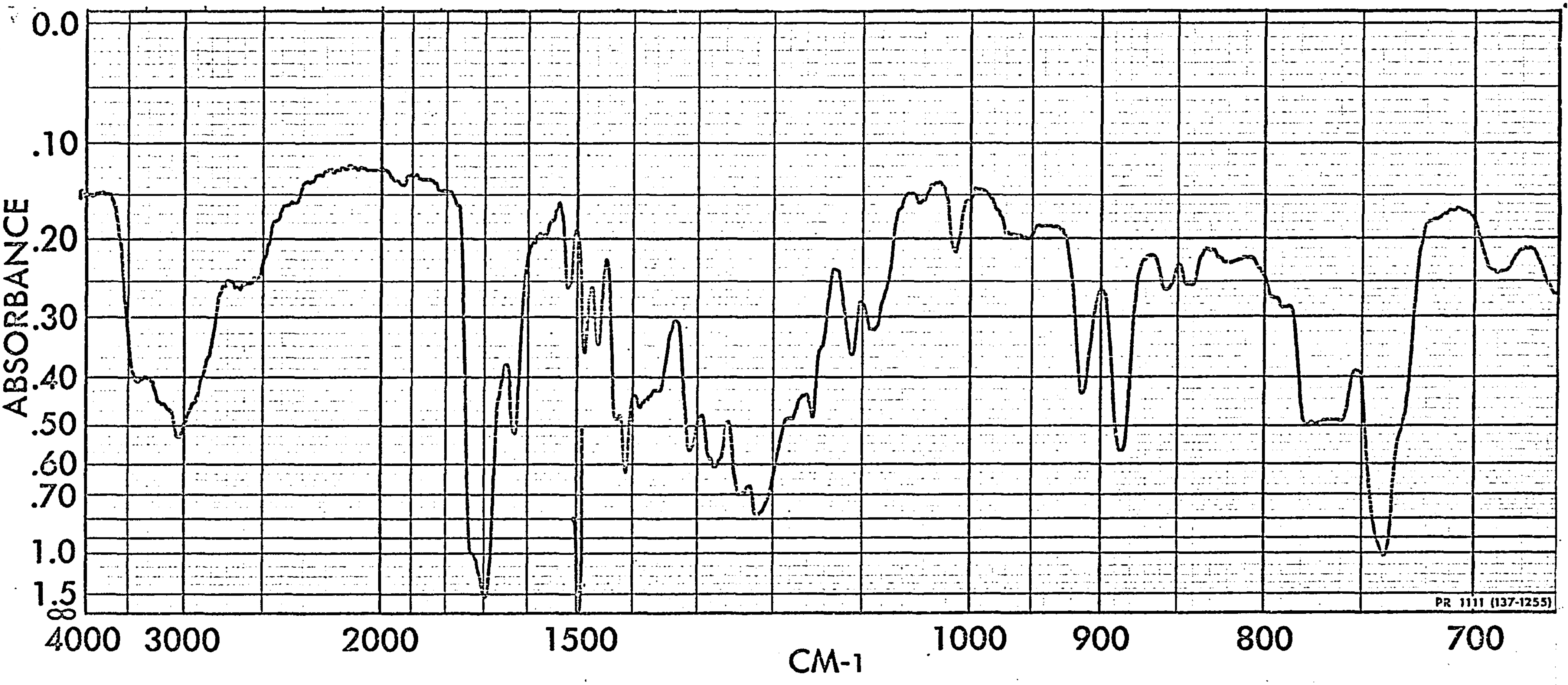
The Infrared Spectrum of 2,2'-Dimethyl-9,9'-bianthryl in KBr



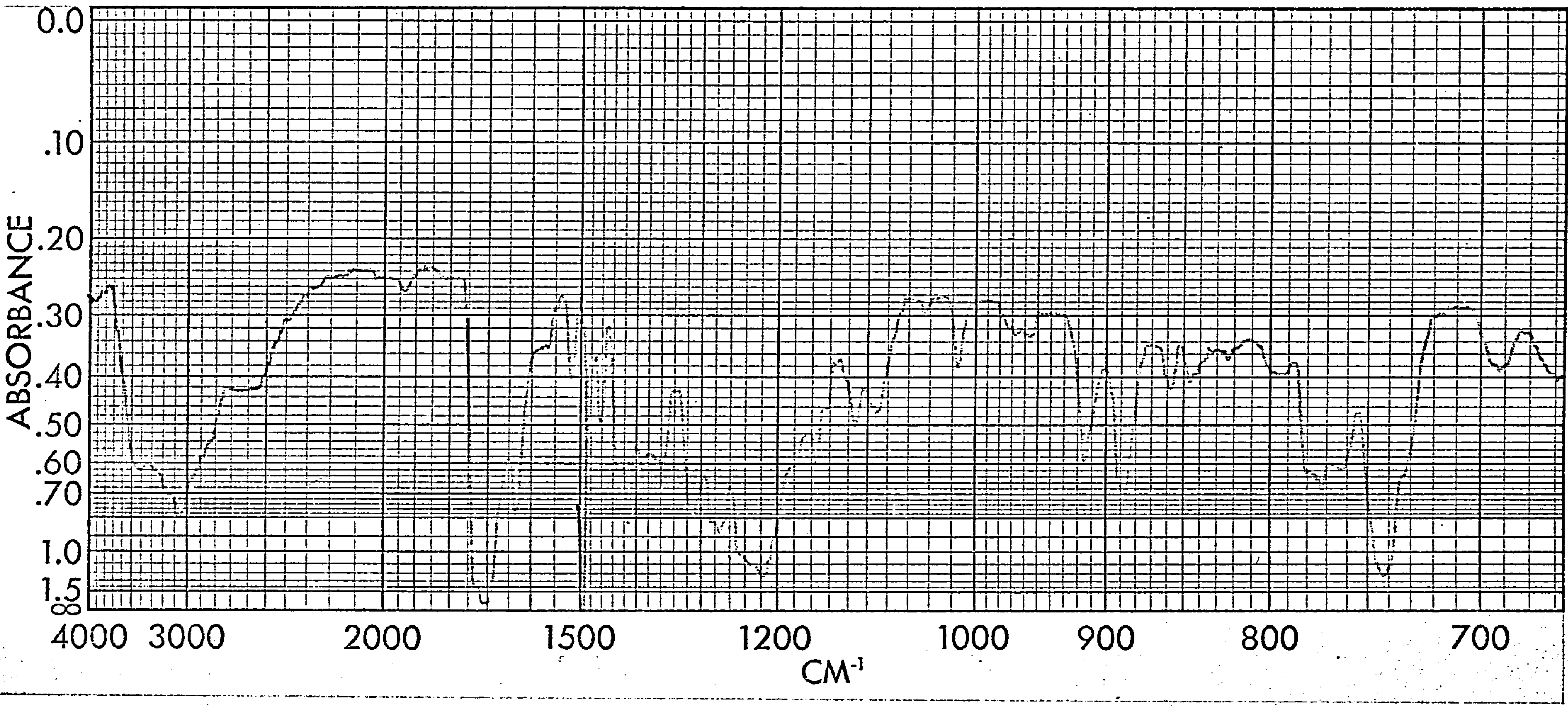
The Infrared Spectrum of 2,2'-Dicyano-9,9'-bianthryl in KBr.



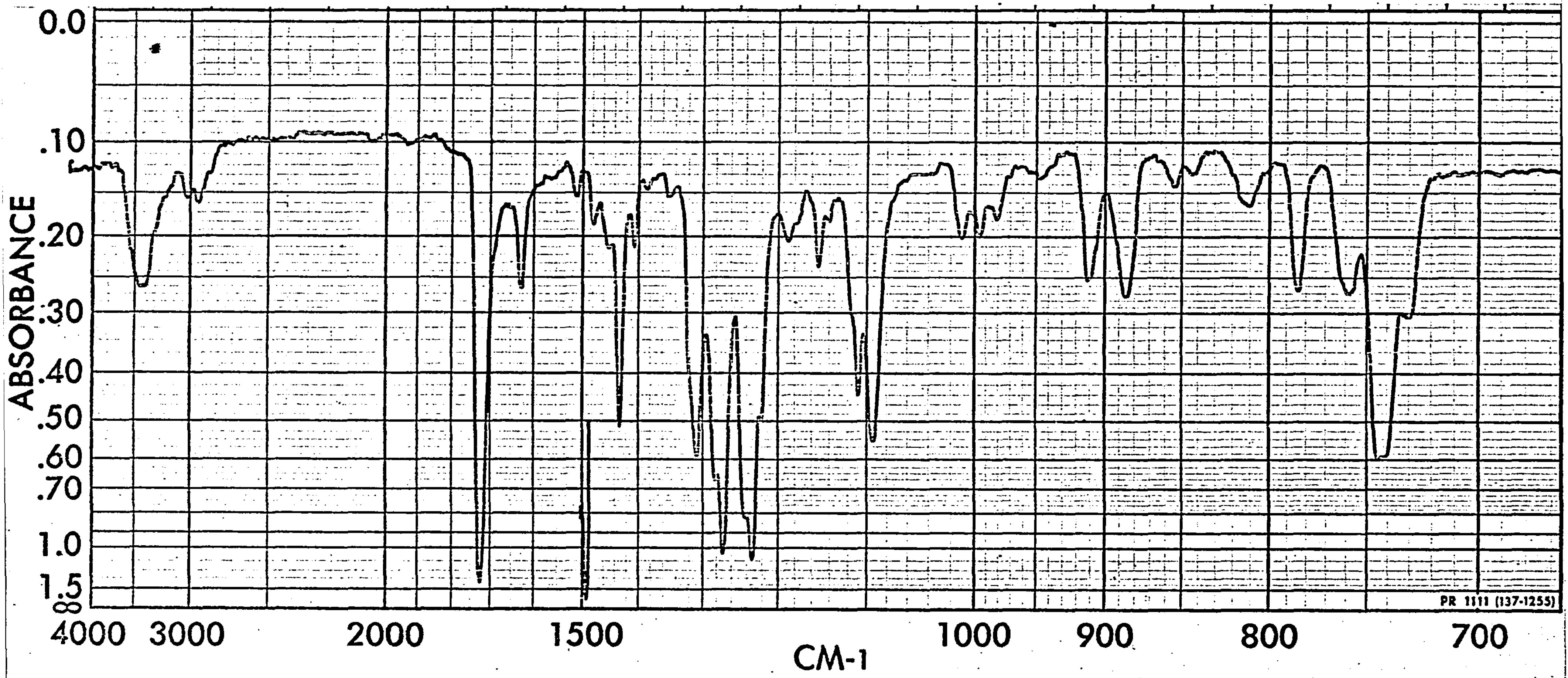
The Infrared Spectrum of 2-Chloro-2'-cyano-9,9'-bianthryl in KBr.



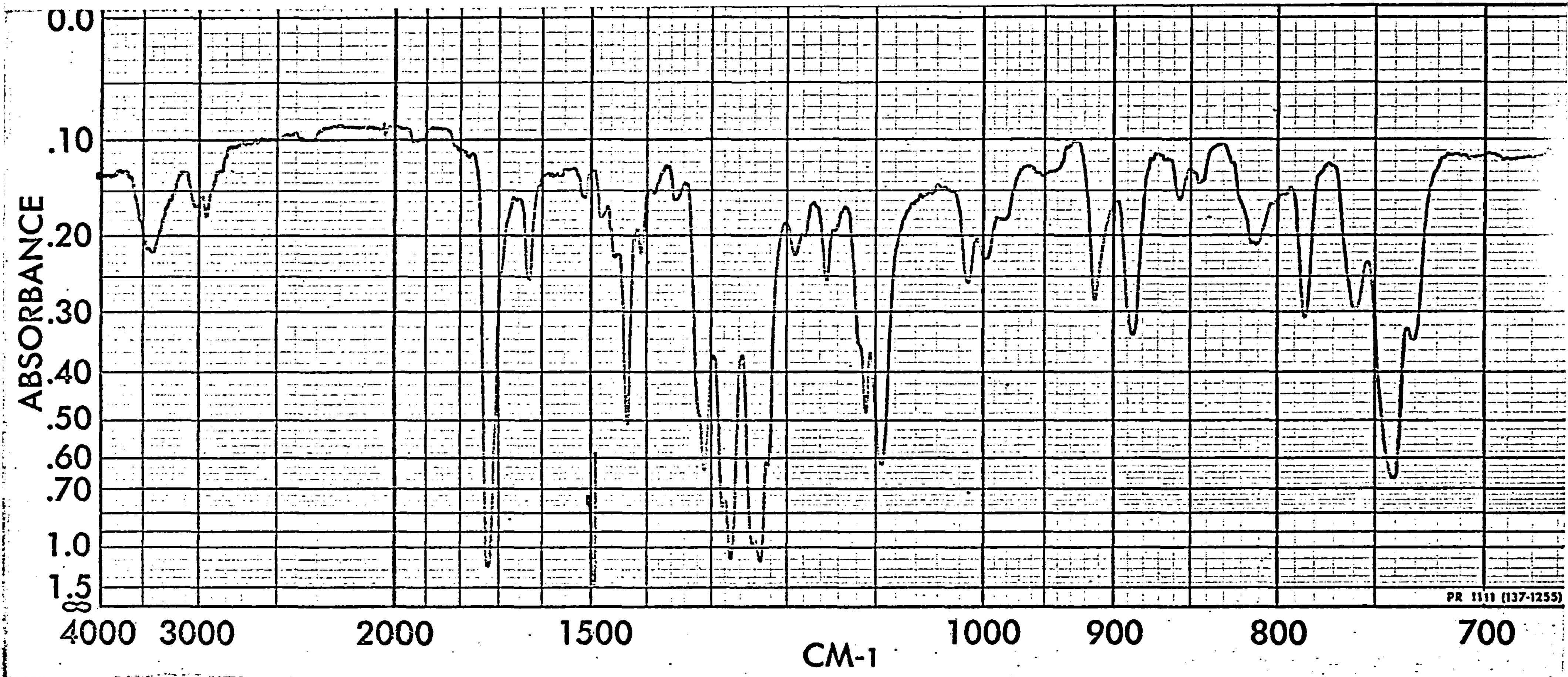
The Infrared Spectrum of 2,2'-Dicarboxy-9,9'-bianthryl in KBr



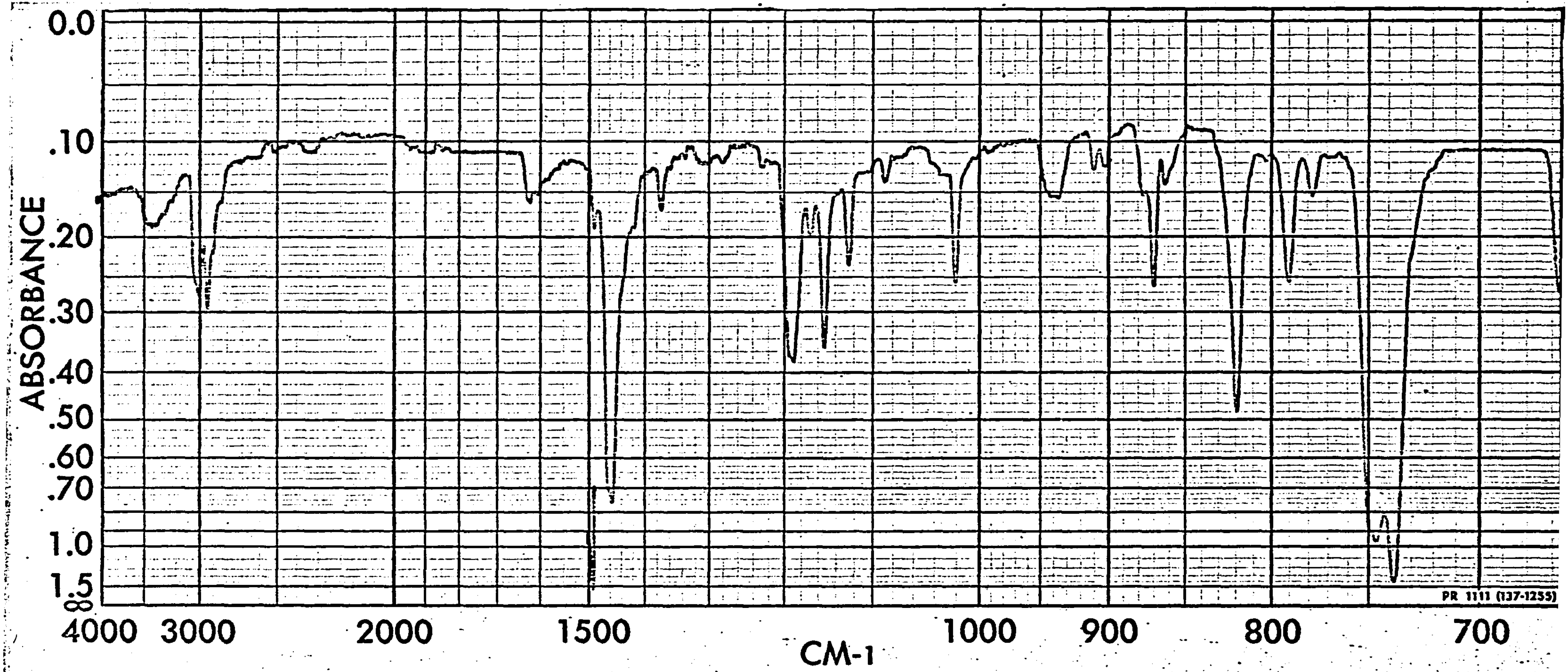
The Infrared Spectrum of (-)-2,2'-Dicarboxy-9,9'-bianthryl in KBr



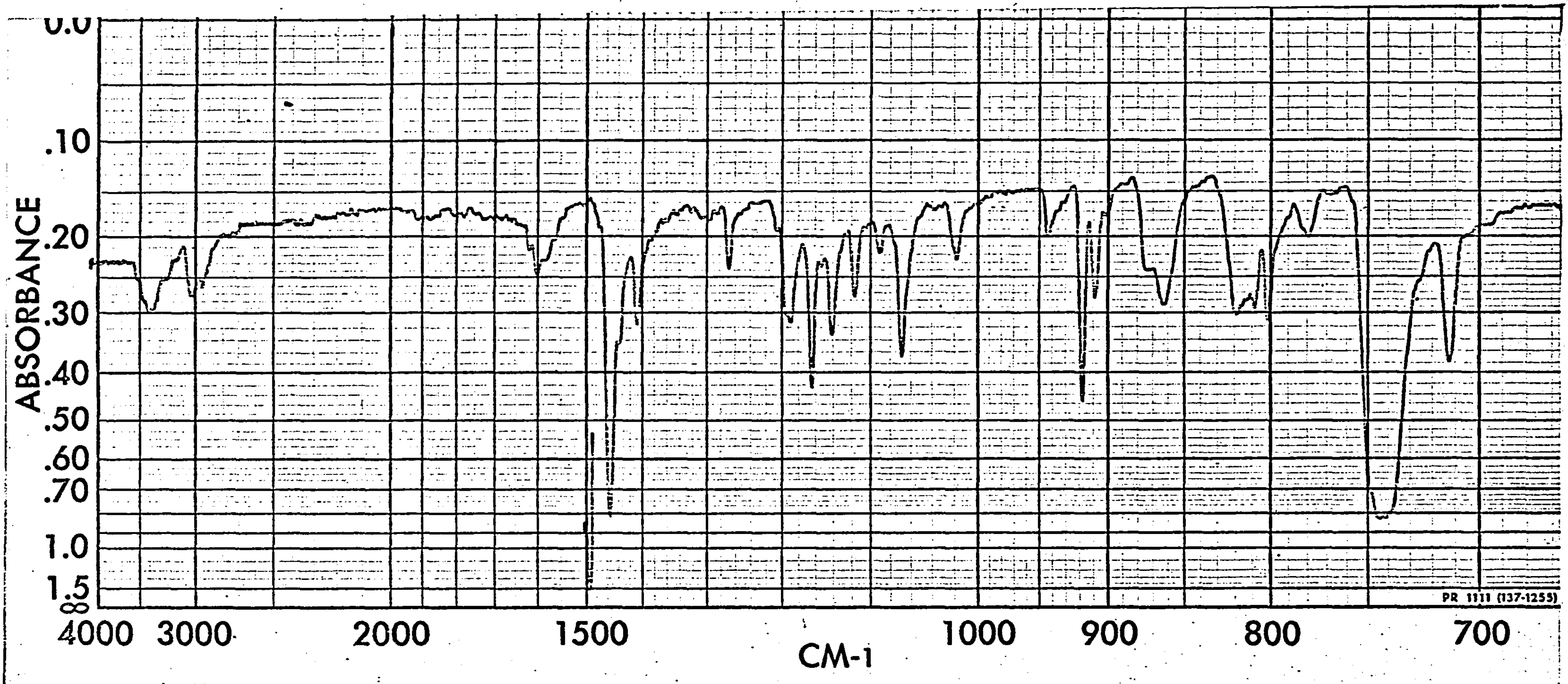
The Infrared Spectrum of 2,2'-Dicarbomethoxy-9,9'-bianthryl in KBr.



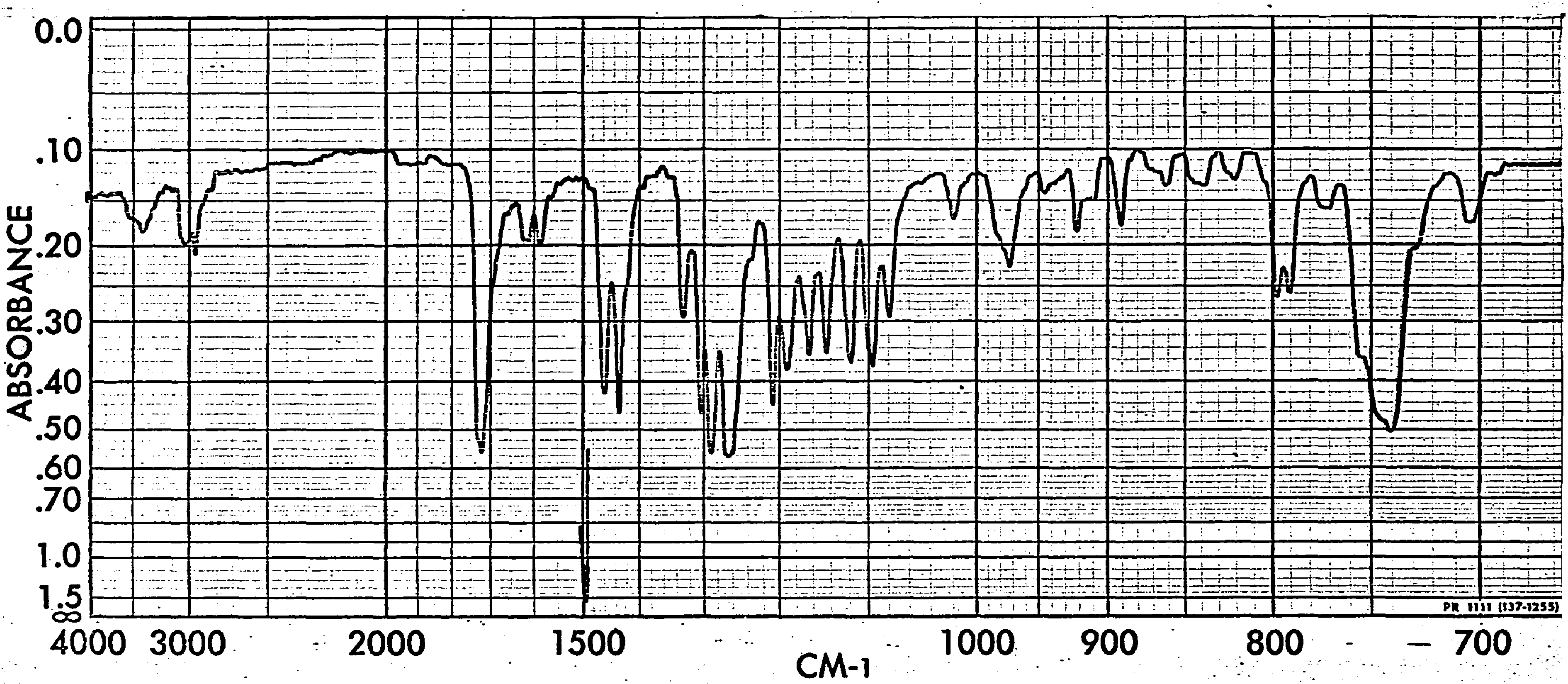
The Infrared Spectrum of (-)-2,2'-Dicarbomethoxy-9,9'-bianthryl in KBr.



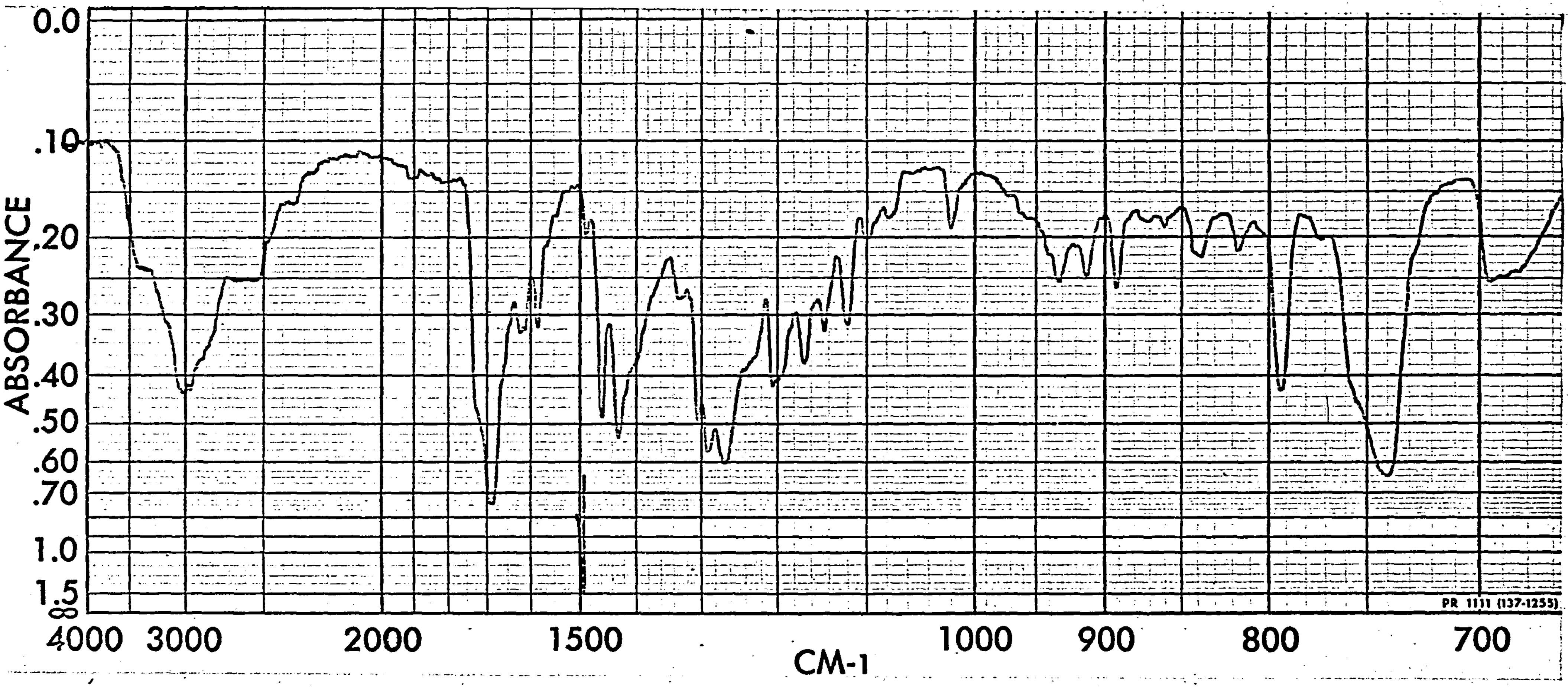
The Infrared Spectrum of 2-Methyltriptycene in KBr



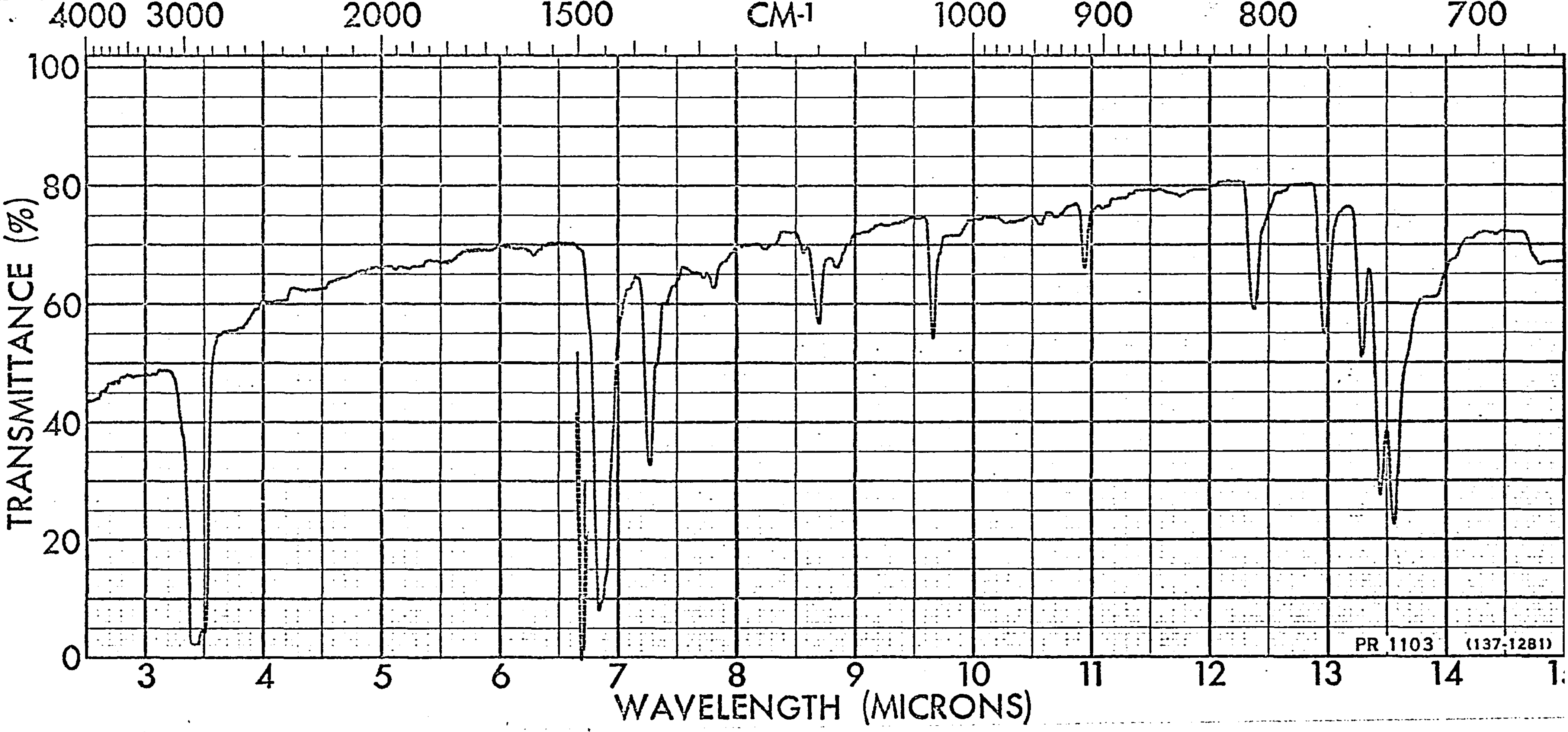
The Infrared Spectrum of 2-Chlorotriptycene in KBr.



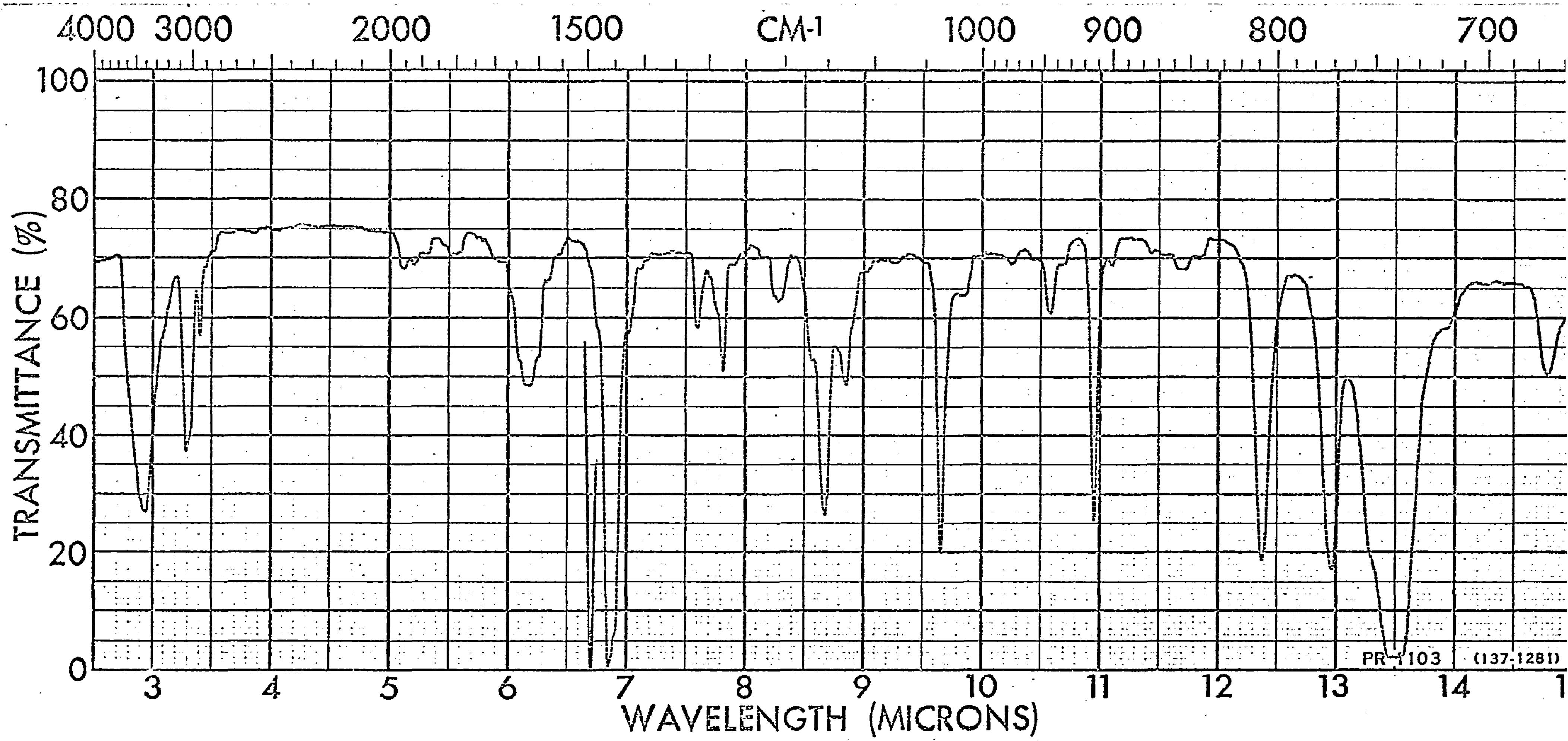
The Infrared Spectrum of 2-Carbomethoxytriptycene in KBr.



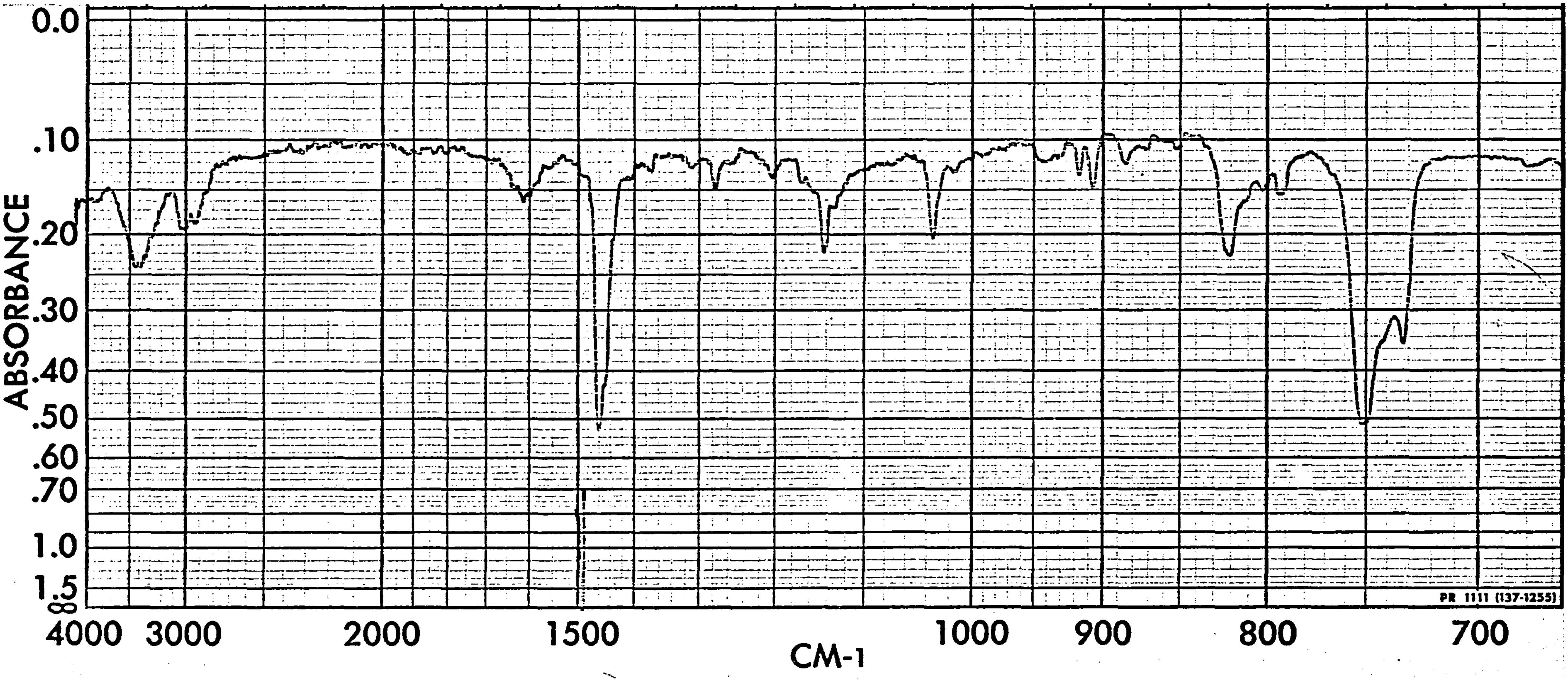
The Infrared Spectrum of 2-Carboxytriptycene in KBr.



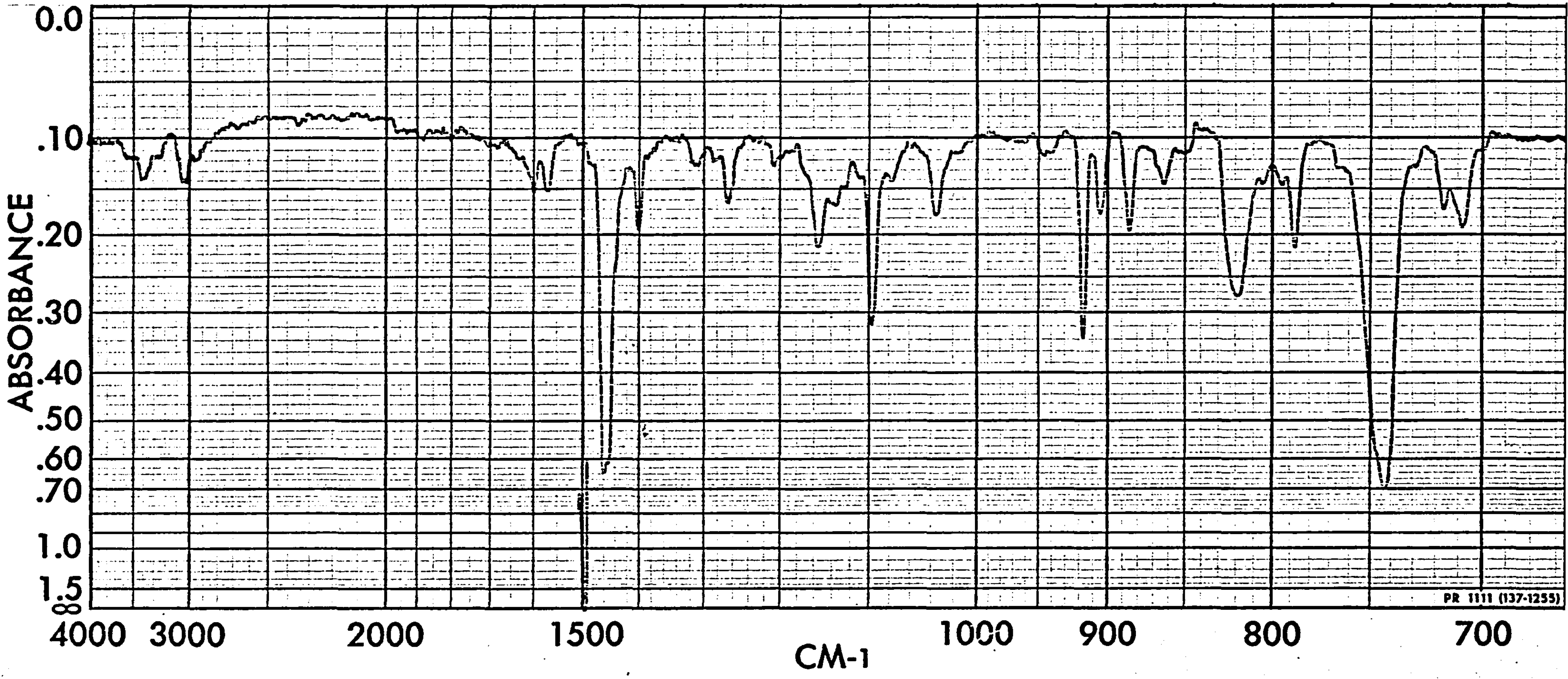
The Infrared Spectrum of 9,9'-Bitriptycyl in Nujol.



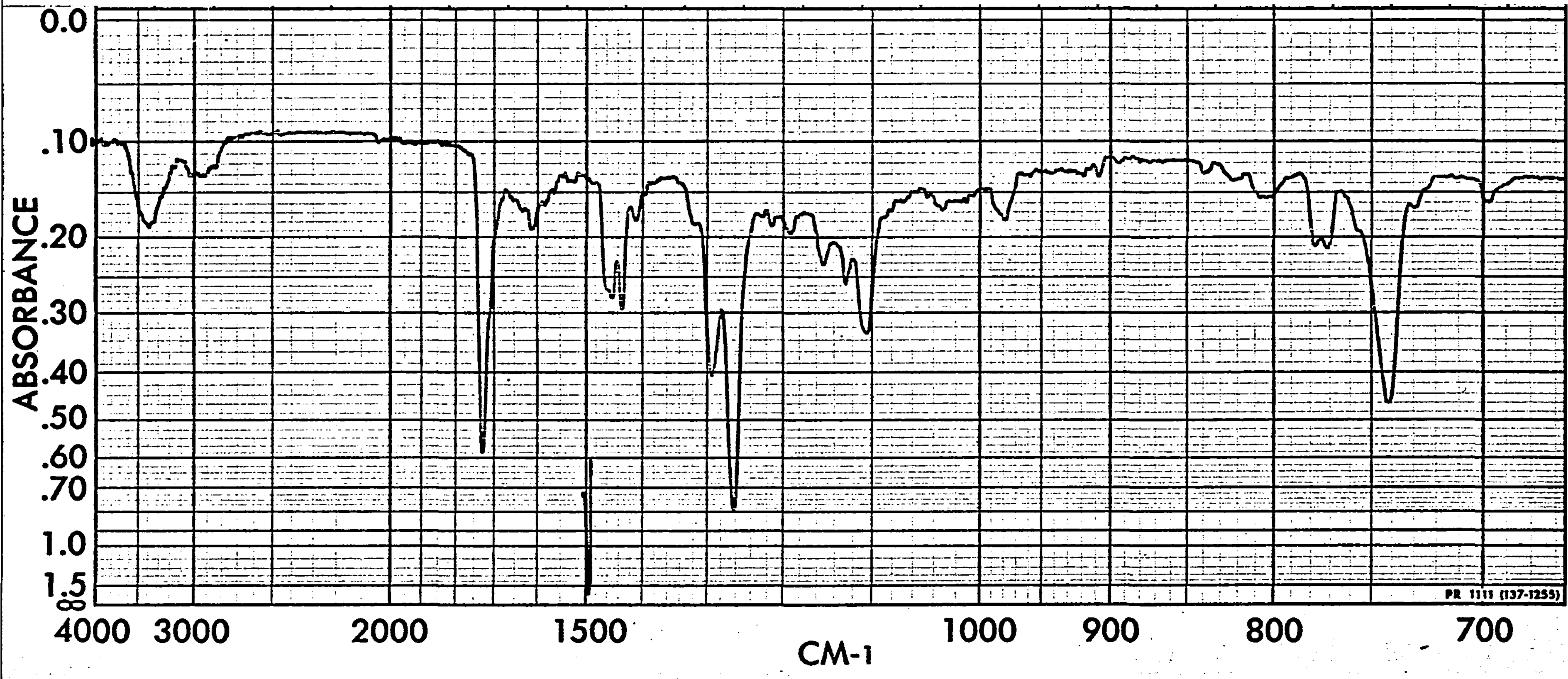
The Infrared Spectrum of 9,9'-Bitriptycyl in KBr.



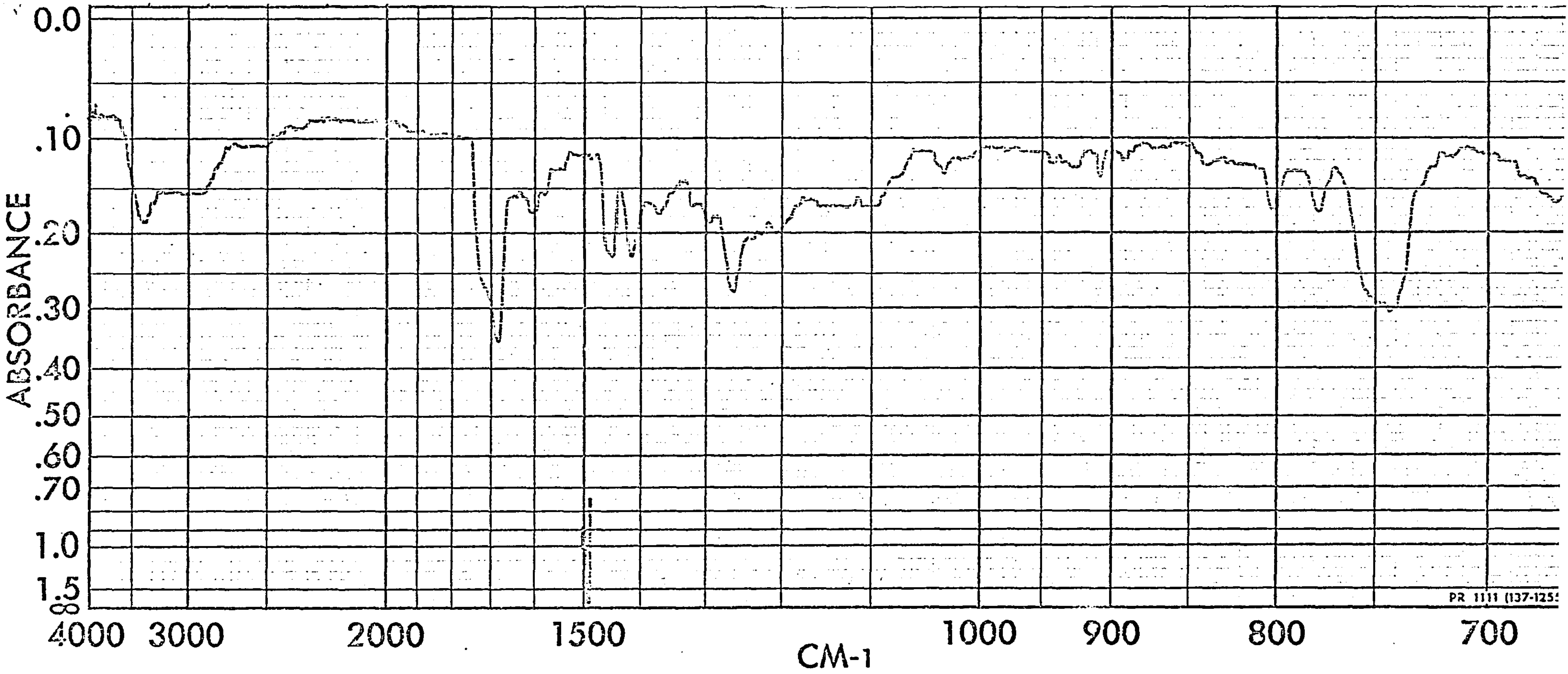
The Infrared Spectrum of 2,2'-Dimethyl-9,9'-bitriptycyl in KBr



The Infrared Spectrum of 2,2'-Dichloro-9,9'-bitriptycyl in KBr



The Infrared Spectrum of 2,2'-Dicarbomethoxy-9,9'-bitriptycyl in KBr



The Infrared Spectrum of 2,2'-Dicarboxy-9,9'-bitriptycyl in KBr.

## The Mass Spectrum of 2-Carbomethoxyanthracene

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 15 | 2.1 | 88½ | 16.7 | 152 | 3.3 |
| 29 | 0.9 | 89 | 3.5 | 153 | 0.6 |
| 31 | 0.6 | 98 | 2.7 | 163 | 2.1 |
| 39 | 1.7 | 99 | 2.6 | 164 | 2.0 |
| 43 | 0.5 | 100 | 1.5 | 165 | 2.3 |
| 50 | 3.4 | 101 | 1.3 | 173 | 0.5 |
| 51 | 2.7 | 102 | 1.2 | 174 | 5.4 |
| 59 | 0.5 | 102½ | 8.2 | 175 | 8.4 |
| 62 | 2.2 | 103 | 1.7 | 176 | 45.3 |
| 63 | 3.5 | 110 | 1.0 | 177 | 80.8 |
| 64 | 0.5 | 110½ | 0.4 | 178 | 16.6 |
| 74 | 4.1 | 111 | 1.4 | 179 | 2.3 |
| 74½ | 0.4 | 113 | 0.8 | 189 | 0.6 |
| 75 | 9.2 | 118 | 2.8 | 190 | 0.7 |
| 75½ | 1.4 | 118½ | 0.5 | 191 | 1.9 |
| 76 | 2.8 | 122 | 1.0 | 192 | 0.7 |
| 77 | 2.3 | 123 | 0.8 | 204 | 0.8 |
| 81½ | 0.3 | 124 | 0.6 | 205 | 51.0 |
| 82 | 0.3 | 125 | 1.5 | 206 | 8.5 |
| 82½ | 0.3 | 126 | 3.3 | 207 | 0.9 |
| 83 | 1.1 | 127 | 3.2 | 220 | 0.5 |
| 85 | 0.9 | 137 | 0.8 | 235 | 1.2 |
| 86 | 2.0 | 139 | 0.9 | 236 | 100 |
| 87 | 5.0 | 149 | 2.8 | 237 | 18.0 |
| 87½ | 2.8 | 150 | 12.6 | 238 | 2.0 |
| 88 | 26.9 | 151 | 18.0 | | |

## The Mass Spectrum of Triptycene[68]

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 31 | 1.1 | 111 | 0.6 | 127½ | 1.3 |
| 63 | 1.2 | 111½ | 0.8 | 128 | 0.5 |
| 75 | 1.2 | 112 | 4.5 | 150 | 1.8 |
| 83 | 0.2 | 112½ | 2.2 | 151 | 2.1 |
| 83⅓ | 0.5 | 113 | 13 | 152 | 2.1 |
| 83⅔ | 0.2 | 113½ | 2.9 | 176 | 4.1 |
| 84 | 0.5 | 114 | 3.0 | 177 | 1.9 |
| 87 | 1.3 | 114½ | 0.5 | 178 | 4.1 |
| 87½ | 0.2 | 115 | 0.6 | 179 | 0.9 |
| 88 | 1.2 | 117½ | 0.2 | 200 | 1.4 |
| 88½ | 0.2 | 118 | 0.4 | 213 | 1.2 |
| 89 | 1.1 | 118½ | 1.2 | 224 | 3.0 |
| 93½ | 0.4 | 119 | 1.2 | 225 | 2.1 |
| 94 | 0.2 | 119½ | 7.9 | 226 | 4.2 |
| 94½ | 0.3 | 120 | 1.8 | 227 | 1.3 |
| 99 | 0.8 | 123 | 0.5 | 239 | 5.0 |
| 99½ | 0.6 | 123½ | 0.2 | 240 | 1.1 |
| 100 | 2.7 | 124 | 2.2 | 248 | 2.1 |
| 100½ | 0.7 | 124½ | 1.8 | 249 | 2.1 |
| 101 | 2.4 | 125 | 9.7 | 250 | 15 |
| 101½ | 0.6 | 125½ | 4.1 | 251 | 7.3 |
| 105½ | 0.3 | 126 | 29 | 252 | 49 |
| 106 | 0.2 | 126½ | 11 | 253 | 100 |
| 106½ | 0.8 | 127 | 6.9 | 254 | 93 |
|  |  |  |  | 255 | 18 |
|  |  |  |  | 256 | 2.1 |

[68] Singly charged ions of less than 1% of base peak intensity have been omitted.

## The Mass Spectrum of 2-Methyltriptycene

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 39 | 1.2 | 101 | 1.3 | 120½ | 1.0 |
| 51 | 1.0 | 101½ | 0.4 | 121 | 0.8 |
| 63 | 1.5 | 102 | 0.4 | 124 | 1.2 |
| 69 | 0.4 | 105 | 0.2 | 124½ | 1.4 |
| 69½ | 0.3 | 105½ | 0.8 | 125 | 8.5 |
| 75 | 1.0 | 106 | 0.7 | 125½ | 4.3 |
| 79⅔ | 0.2 | 106½ | 2.5 | 126 | 32 |
| 81 | 0.3 | 107 | 0.8 | 126½ | 19 |
| 81½ | 0.4 | 107½ | 0.9 | 127 | 3.7 |
| 82 | 0.2 | 108 | 0.4 | 127½ | 0.5 |
| 82½ | 0.3 | 111 | 0.5 | 128 | 0.3 |
| 87 | 1.0 | 111½ | 0.5 | 130 | 0.5 |
| 87⅓ | 0.2 | 112 | 2.2 | 130½ | 2.1 |
| 87⅔ | 0.5 | 112½ | 1.4 | 131 | 2.5 |
| 88 | 1.0 | 113 | 10 | 131½ | 9.0 |
| 88⅓ | 0.4 | 113½ | 2.3 | 132 | 5.2 |
| 88⅔ | 0.4 | 114 | 1.0 | 132½ | 6.1 |
| 89 | 0.8 | 114½ | 0.2 | 133 | 9.0 |
| 93 | 0.2 | 115 | 0.6 | 133½ | 3.3 |
| 93½ | 0.9 | 117 | 0.2 | 134 | 6.0 |
| 94 | 0.5 | 117½ | 0.8 | 134½ | 1.5 |
| 94½ | 1.2 | 118 | 1.1 | 135 | 0.4 |
| 95 | 0.5 | 118½ | 3.7 | 150 | 1.2 |
| 99½ | 0.3 | 119 | 3.0 | 151 | 1.3 |
| 100 | 1.4 | 119½ | 7.4 | 152 | 1.5 |
| 100½ | 1.3 | 120 | 1.0 | 163 | 1.3 |

| m/e | % of base peak |
|---|---|
| 165 | 1.9 |
| 176 | 2.2 |
| 178 | 1.7 |
| 187 | 1.4 |
| 189 | 3.9 |
| 190 | 1.6 |
| 191 | 2.9 |
| 192 | 1.3 |
| 200 | 1.1 |
| 213 | 1.5 |
| 224 | 1.7 |
| 225 | 1.2 |
| 226 | 3.4 |
| 227 | 1.0 |
| 237 | 2.4 |
| 238 | 1.7 |
| 239 | 5.6 |
| 240 | 1.8 |
| 248 | 1.0 |
| 249 | 1.4 |
| 250 | 8.8 |
| 251 | 5.0 |
| 252 | 49 |
| 253 | 100 |
| 254 | 20 |
| 255 | 2.0 |
| 261 | 1.6 |
| 262 | 1.2 |
| 263 | 8.9 |
| 264 | 3.3 |
| 265 | 10 |
| 266 | 7.2 |
| 267 | 30 |
| 268 | 65 |
| 269 | 15 |
| 270 | 1.6 |

## The Mass Spectrum of 2-Chlorotriptycene[69]

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 39 | 1.1 | 111 | 1.5 | 130 | 0.9 |
| 50 | 1.1 | 111½ | 1.6 | 130½ | 0.4 |
| 51 | 1.1 | 112 | 7.1 | 131 | 0.8 |
| 63 | 1.5 | 112½ | 3.4 | 131½ | 0.4 |
| 74 | 1.3 | 113 | 15 | 132 | 0.4 |
| 75 | 1.7 | 113½ | 3.4 | 136½ | 0.9 |
| 83 | 0.7 | 114 | 0.6 | 137 | 0.6 |
| 83⅓ | 1.0 | 117 | 0.3 | 137½ | 0.5 |
| 83⅔ | 0.6 | 117½ | 0.4 | 138 | 0.5 |
| 84 | 0.9 | 118 | 0.9 | 139 | 0.5 |
| 84⅓ | 0.4 | 118½ | 1.2 | 143 | 1.4 |
| 87 | 1.5 | 119 | 0.8 | 143½ | 0.5 |
| 87½ | 0.3 | 119½ | 0.5 | 144 | 2.4 |
| 88 | 1.1 | 122 | 0.4 | 144½ | 0.7 |
| 99 | 1.7 | 123 | 0.9 | 145 | 1.0 |
| 99½ | 0.8 | 123½ | 1.0 | 145½ | 0.3 |
| 100 | 2.8 | 124 | 5.0 | 150 | 2.1 |
| 100½ | 0.8 | 124½ | 4.3 | 151 | 2.6 |
| 101 | 1.3 | 125 | 19 | 152 | 1.3 |
| 101½ | 0.5 | 125½ | 9.7 | 174 | 1.4 |
| 102 | 0.5 | 126 | 36 | 175 | 1.6 |
| 105 | 0.4 | 126½ | 25 | 176 | 5.6 |
| 105½ | 0.5 | 127 | 3.9 | 177 | 2.4 |
| 106 | 0.5 | 127½ | 0.5 | 178 | 1.7 |
| 106½ | 0.6 | 128 | 0.3 | 200 | 1.5 |

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[69] Singly charged ions of less than 0.5% of base peak intensity have been omitted.

| m/e | % of base peak |
|---|---|
| 212 | 2.1 |
| 213 | 1.2 |
| 222[70] | 1.2 |
| 223 | 1.4 |
| 224 | 3.4 |
| 225 | 2.2 |
| 226 | 3.1 |
| 248 | 2.2 |
| 249 | 2.8 |
| 250 | 18 |
| 251 | 8.5 |
| 252 | 55 |
| 253 | 100 |
| 254 | 22 |
| 255 | 2.5 |
| 286 | 3.4 |
| 287 | 5.6 |
| 288 | 36 |
| 289 | 9.3 |
| 290 | 12 |
| 291 | 3.7 |

[70] Metastable ion

## The Mass Spectrum of 2-Carbomethoxytriptycene

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 15 | 3.5 | 113 | 10.7 | 163 | 0.6 |
| 17 | 0.5 | $113\frac{1}{2}$ | 2.6 | 174 | 0.9 |
| 18 | 1.8 | 114 | 0.4 | 175 | 1.1 |
| 28 | 1.6 | 118 | 0.3 | 176 | 4.3 |
| 39 | 0.7 | $118\frac{1}{2}$ | 0.77 | 177 | 3.9 |
| 50 | 0.7 | 119 | 1.2 | 178 | 3.1 |
| 51 | 0.7 | $119\frac{1}{2}$ | 0.71 | 179 | 0.5 |
| 59 | 1.6 | 120 | 0.5 | 187 | 0.6 |
| 63 | 0.84 | 124 | 2.3 | 198 | 0.5 |
| 74 | 0.84 | $124\frac{1}{2}$ | 2.1 | 199 | 0.5 |
| 75 | 1.7 | 125 | 11.0 | 200 | 1.5 |
| 76 | 0.7 | $125\frac{1}{2}$ | 4.9 | 201 | 0.6 |
| 77 | 0.4 | 126 | 18.4 | 202 | 0.8 |
| 86 | 0.3 | $126\frac{1}{2}$ | 6.13 | 205[70] | 1.2 |
| 87 | 1.0 | 127 | 1.2 | 211 | 0.6 |
| 88 | 1.5 | 133 | 1.7 | 213 | 0.8 |
| $88\frac{1}{2}$ | 0.4 | $133\frac{1}{2}$ | 0.4 | 214 | 0.3 |
| 89 | 0.7 | 134 | 0.3 | 215 | 0.3 |
| 98 | 0.4 | 139 | 0.5 | 222 | 0.5 |
| 99 | 0.6 | $139\frac{1}{2}$ | 1.2 | 223 | 0.6 |
| 100 | 1.8 | 140 | 6.84 | 224 | 2.9 |
| $100\frac{1}{2}$ | 0.5 | $140\frac{1}{2}$ | 6.55 | 225 | 2.1 |
| 101 | 0.95 | 141 | 1.5 | 226 | 3.9 |
| 111 | 0.6 | 149 | 0.5 | 227 | 0.8 |
| $111\frac{1}{2}$ | 0.6 | 150 | 1.7 | 237 | 1.0 |
| 112 | 3.6 | 151 | 2.2 | 238 | 0.5 |
| $112\frac{1}{2}$ | 1.9 | 152 | 1.2 | 239 | 1.2 |

| m/e | % of base peak |
|---|---|
| 240 | 0.6 |
| 248 | 2.6 |
| 249 | 3.0 |
| 250 | 15.9 |
| 251 | 11.2 |
| 252 | 50.5 |
| 253 | 100 |
| 254 | 20.4 |
| 255 | 2.4 |
| 265 | 0.3 |
| 266 | 0.5 |
| 267 | 1.1 |
| 268 | 0.5 |
| 279 | 3.0 |
| 280 | 1.4 |
| 281 | 5.9 |
| 282 | 1.7 |
| 296 | 1.3 |
| 297 | 4.7 |
| 298 | 1.1 |
| 310 | 0.7 |
| 311 | 3.3 |
| 312 | 44.4 |
| 313 | 4.76 |
| 314 | 1.4 |

## The Mass Spectrum of 2-Carboxytriptycene[68]

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 39 | 3.1 | 88 | 2.6 | 113 | 17.5 |
| 41 | 3.0 | 88½ | 0.7 | 113½ | 4.1 |
| 42 | 1.3 | 89 | 1.2 | 114 | 2.0 |
| 43 | 1.9 | 93 | 0.4 | 114½ | 0.5 |
| 44 | 1.1 | 93½ | 0.5 | 115 | 1.1 |
| 45 | 6.7 | 94 | 0.7 | 117 | 0.4 |
| 46 | 1.0 | 94½ | 0.5 | 117½ | 0.5 |
| 50 | 2.7 | 98 | 1.2 | 118 | 0.6 |
| 51 | 2.2 | 99 | 2.4 | 118½ | 1.5 |
| 55 | 1.0 | 99½ | 0.7 | 119 | 1.7 |
| 56 | 1.1 | 100 | 4.0 | 119½ | 3.8 |
| 57 | 1.1 | 100½ | 0.8 | 120 | 1.4 |
| 58 | 1.0 | 101 | 2.7 | 122 | 0.8 |
| 62 | 1.1 | 101½ | 0.6 | 123 | 1.1 |
| 63 | 3.6 | 102 | 1.1 | 123½ | 0.7 |
| 73 | 1.1 | 102½ | 0.5 | 124 | 4.2 |
| 74 | 2.6 | 105 | 0.4 | 124½ | 3.2 |
| 75 | 3.6 | 105½ | 0.7 | 125 | 8.5 |
| 76 | 1.6 | 106 | 0.6 | 125½ | 7.9 |
| 77 | 1.6 | 106½ | 1.3 | 126 | 23.6 |
| 83 | 0.4 | 107 | 0.7 | 126½ | 7.9 |
| 83⅓ | 0.3 | 107½ | 0.4 | 127 | 4.1 |
| 83⅔ | 0.3 | 110 | 1.0 | 127½ | 0.8 |
| 84 | 0.3 | 111 | 1.6 | 128 | 0.9 |
| 86 | 0.5 | 111½ | 1.2 | 133 | 0.9 |
| 87 | 1.7 | 112 | 6.6 | 133½ | 0.3 |
| 87½ | 2.8 | 112½ | 3.1 | 139 | 1.6 |

| m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|
| 139½ | 1.2 | 215[70] | 1.7 |
| 140 | 2.7 | 222 | 2.5 |
| 140½ | 1.2 | 223 | 2.6 |
| 149 | 2.5 | 224 | 10.0 |
| 149½ | 0.4 | 225 | 5.5 |
| 150 | 5.8 | 226 | 8.7 |
| 151 | 6.6 | 227 | 2.6 |
| 152 | 3.5 | 236 | 2.3 |
| 163 | 3.0 | 237 | 3.2 |
| 164 | 1.3 | 238 | 1.4 |
| 165 | 2.6 | 239 | 5.0 |
| 174 | 3.2 | 240 | 1.8 |
| 175 | 3.5 | 247 | 1.1 |
| 176 | 14.1 | 248 | 6.8 |
| 177 | 11.1 | 249 | 6.5 |
| 178 | 7.2 | 250 | 41.3 |
| 179 | 1.3 | 251 | 24.0 |
| 187 | 2.3 | 252 | 100 |
| 189 | 1.1 | 253 | 55.4 |
| 198 | 1.6 | 254 | 52.6 |
| 199 | 1.6 | 255 | 6.4 |
| 200 | 4.1 | 279 | 2.7 |
| 201 | 2.0 | 280 | 0.9 |
| 202 | 2.1 | 281 | 1.7 |
| 205 | 1.6 | 283 | 0.8 |
| 211 | 2.0 | 296 | 2.6 |
| 212 | 1.0 | 297 | 7.8 |
| 213 | 4.2 | 298 | 80.2 |
| 214 | 1.5 | 299 | 20.4 |
|  |  | 300 | 2.8 |

The Mass Spectrum of 9,9'-Bitriptycyl

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 31 | 1.3 | 78 | 1.2 | 199 | 2.2 |
| 32 | 1.2 | 79 | 1.1 | 199½ | 1.4 |
| 36 | 2.3 | 81 | 1.1 | 200 | 3.2 |
| 37 | 0.7 | 82 | 1.6 | 200½ | 1.1 |
| 38 | 1.1 | 83 | 1.6 | 201 | 0.9 |
| 39 | 1.9 | 84 | 1.2 | 204½ | 0.7 |
| 41 | 4.6 | 85 | 1.9 | 205 | 1.6 |
| 42 | 1.2 | 91 | 1.4 | 205½ | 5.1 |
| 43 | 4.3 | 92 | 0.7 | 206 | 3.7 |
| 45 | 2.1 | 93 | 1.3 | 206½ | 3.1 |
| 51 | 1.9 | 97 | 1.7 | 207 | 1.9 |
| 53 | 1.1 | 98 | 1.1 | 211 | 3.5 |
| 55 | 3.1 | 99 | 1.3 | 211½ | 2.0 |
| 56 | 2.3 | 103 | 0.8 | 212 | 9.2 |
| 57 | 5.1 | 113 | 1.3 | 212½ | 5.2 |
| 58 | 0.7 | 126 $^{7\overline{0}}$ | 1.3 | 213 | 8.4 |
| 59 | 0.7 | 165 | 2.9 | 213½ | 4.4 |
| 60 | 0.9 | 175 | 2.4 | 214 | 4.8 |
| 67 | 1.2 | 175½ | 1.2 | 214½ | 1.1 |
| 68 | 1.6 | 176 | 1.2 | 215 | 1.1 |
| 69 | 2.4 | 177 | 0.7 | 217½ | 0.8 |
| 70 | 1.2 | 178 | 2.0 | 218 | 0.5 |
| 71 | 2.5 | 179 | 2.0 | 218½ | 0.8 |
| 72 | 0.7 | 187 | 1.1 | 219 | 0.5 |
| 73 | 1.1 | 193½ | 1.8 | 223 | 0.8 |
| 77 | 1.7 | 194 | 0.9 | 223½ | 0.8 |

| m/e | % of base peak |
|---|---|
| 224 | 2.9 |
| 224½ | 0.9 |
| 225 | 2.2 |
| 225½ | 0.8 |
| 226 | 1.2 |
| 228 | 0.8 |
| 229½ | 1.3 |
| 230 | 1.1 |
| 230½ | 4.7 |
| 231 | 2.8 |
| 231½ | 2.7 |
| 232 | 1.5 |
| 236 | 2.6 |
| 236½ | 2.5 |
| 237 | 5.0 |
| 237½ | 3.7 |
| 238 | 3.7 |
| 238½ | 1.7 |
| 239 | 4.7 |
| 240 | 1.7 |
| 241 | 1.1 |
| 242 | 1.3 |
| 242½ | 3.2 |
| 243 | 2.9 |
| 243½ | 4.2 |
| 244 | 3.7 |
| 244½ | 3.2 |
| 245 | 2.9 |
| 245½ | 1.7 |
| 246 | 0.8 |
| 248 | 1.3 |
| 249 | 2.9 |
| 249½ | 1.9 |
| 250 | 11.1 |
| 250½ | 3.2 |
| 251 | 6.6 |
| 251½ | 4.3 |
| 252 | 45.7 |
| 252½ | 6.8 |
| 253 | 78.7 |
| 253½ | 11.4 |
| 254 | 23.6 |
| 255 | 5.3 |
| 256 | 0.7 |
| 263 | 1.9 |
| 264 | 0.6 |
| 265 | 7.2 |
| 266 | 2.1 |
| 274 | 0.7 |
| 276 | 0.7 |
| 277 | 0.7 |
| 278 | 0.7 |
| 289 | 1.4 |
| 290 | 0.6 |
| 300 | 0.8 |
| 302 | 0.9 |
| 303 | 0.9 |
| 311 | 0.8 |
| 312 | 2.1 |
| 313 | 1.6 |
| 314 | 0.6 |
| 315 | 0.6 |
| 326 | 3.4 |
| 327 | 3.4 |
| 328 | 2.6 |
| 329 | 0.7 |
| 337 | 1.9 |
| 338 | 0.8 |
| 339 | 5.6 |
| 340 | 2.1 |
| 341 | 2.1 |
| 342 | 0.8 |
| 350 | 3.2 |
| 351 | 2.3 |
| 352 | 2.1 |
| 353 | 0.8 |
| 387 | 1.2 |
| 388 | 0.8 |
| 389 | 0.6 |
| 398 | 1.4 |
| 399 | 0.6 |
| 400 | 1.6 |
| 401 | 1.1 |
| 402 | 0.6 |

| m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|
| 409 | 1.1 | 485 | 1.3 |
| 411 | 4.9 | 486 | 1.3 |
| 412 | 3.1 | 487 | 3.1 |
| 413 | 9.3 | 488 | 2.1 |
| 414 | 4.5 | 489 | 3.7 |
| 415 | 3.2 | 490 | 2.4 |
| 416 | 0.9 | 491 | 2.3 |
| 424 | 4.2 | 492 | 1.4 |
| 425 | 3.2 | 498 | 1.9 |
| 426 | 4.6 | 499 | 1.9 |
| 427 | 7.4 | 500 | 2.0 |
| 428 | 5.3 | 501 | 2.3 |
| 429 | 7.2 | 502 | 2.1 |
| 430 | 2.9 | 503 | 2.8 |
| 450 | 1.1 | 504 | 3.2 |
| 451 | 0.8 | 505 | 7.5 |
| 461 | 1.3 | 506 | 100 |
| 462 | 1.2 | 507 | 44.2 |
| 463 | 2.9 | 508 | 10.5 |
| 464 | 1.9 | | |
| 465 | 2.0 | | |
| 466 | 1.1 | | |
| 474 | 2.1 | | |
| 475 | 2.1 | | |
| 476 | 2.9 | | |
| 477 | 2.9 | | |
| 478 | 2.3 | | |
| 479 | 1.4 | | |

## The Mass Spectrum of 2,2'-Dimethyl-9,9'-Bitriptycyl[71]

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 43 | 2.2 | 206 | 3.5 | 224½ | 1.2 |
| 83 | 1.4 | 206½ | 2.0 | 225 | 1.4 |
| 126½ | 0.3 | 207 | 1.2 | 225½ | 0.7 |
| 161½ | 0.7 | 207½ | 0.6 | 226[70] | 1.1 |
| 162½ | 0.6 | 211 | 1.5 | 226½ | 0.3 |
| 165 | 1.3 | 211½ | 1.4 | 228 | 1.2 |
| 175 | 1.5 | 212 | 6.8 | 228½ | 0.6 |
| 175½ | 0.6 | 212½ | 4.5 | 229½ | 1.2 |
| 178 | 2.2 | 213 | 7.6 | 230 | 1.3 |
| 179 | 2.3 | 213½ | 3.9 | 230½ | 3.2 |
| 180½ | 0.5 | 214 | 1.5 | 231 | 2.8 |
| 181½ | 0.4 | 214½ | 0.6 | 231½ | 2.0 |
| 182½ | 0.6 | 216 | 1.1 | 232 | 1.1 |
| 187½ | 0.5 | 217½ | 1.5 | 232½ | 0.8 |
| 192½ | 0.6 | 218 | 1.4 | 236 | 2.7 |
| 193 | 1.2 | 218½ | 1.8 | 236½ | 2.7 |
| 193½ | 1.4 | 219 | 1.9 | 237 | 6.0 |
| 194½ | 0.3 | 219½ | 1.4 | 237½ | 4.3 |
| 199 | 1.5 | 220 | 2.3 | 238 | 3.8 |
| 199½ | 1.0 | 220½ | 2.0 | 238½ | 2.3 |
| 200 | 2.3 | 221 | 1.8 | 239 | 3.3 |
| 200½ | 1.1 | 221½ | 0.8 | 240 | 1.3 |
| 204½ | 0.6 | 223½ | 0.5 | 241½ | 0.6 |
| 205½ | 4.6 | 224 | 2.3 | 242 | 1.2 |

[71] Peaks at integral m/e values of intensity less than 1% of the base peak have been omitted.

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 242½ | 5.0 | 260 | 6.2 | 366 | 1.4 |
| 243 | 6.1 | 260½ | 1.4 | 367 | 1.3 |
| 243½ | 6.8 | 263 | 3.8 | 400 | 1.0 |
| 244 | 6.9 | 264 | 1.8 | 401 | 0.9 |
| 244½ | 5.0 | 265 | 8.2 | 411 | 1.5 |
| 245 | 2.8 | 266 | 19 | 413 | 2.1 |
| 245½ | 1.5 | 267 | 47 | 414 | 1.2 |
| 248 | 1.2 | 267½ | 9.2 | 424 | 2.9 |
| 248½ | 1.1 | 268 | 17 | 425 | 3.3 |
| 249 | 5.2 | 269 | 3.4 | 426 | 3.6 |
| 249½ | 4.1 | 276 | 1.3 | 427 | 5.2 |
| 250 | 7.9 | 277 | 1.3 | 428 | 2.5 |
| 250½ | 5.1 | 278 | 1.2 | 429 | 1.2 |
| 251 | 7.3 | 279 | 5.2 | 437 | 1.2 |
| 251½ | 5.9 | 280 | 1.5 | 438 | 1.2 |
| 252 | 30 | 303 | 1.1 | 439 | 1.5 |
| 252½ | 3.8 | 326 | 2.8 | 440 | 2.2 |
| 253 | 24 | 327 | 2.1 | 441 | 4.2 |
| 254 | 6.0 | 337 | 1.5 | 442 | 3.1 |
| 255 | 2.9 | 339 | 4.2 | 443 | 2.9 |
| 255½ | 1.6 | 340 | 2.7 | 444 | 1.0 |
| 256 | 1.7 | 341 | 1.8 | 455 | 1.1 |
| 256½ | 1.4 | 342 | 1.5 | 456 | 1.1 |
| 257 | 1.6 | 350 | 2.3 | 457 | 2.1 |
| 257½ | 1.3 | 351 | 2.0 | 463 | 1.0 |
| 258 | 1.7 | 352 | 1.6 | 474 | 1.1 |
| 258½ | 2.0 | 353 | 3.5 | 475 | 1.3 |
| 259 | 4.7 | 354 | 1.7 | 476 | 1.2 |
| 259½ | 15 | 355 | 1.6 | 477 | 1.5 |

| m/e | % of base peak |
|---|---|
| 478 | 1.1 |
| 479 | 1.0 |
| 487 | 1.4 |
| 488 | 1.2 |
| 489 | 1.6 |
| 490 | 1.2 |
| 491 | 1.4 |
| 498 | 1.0 |
| 499 | 1.2 |
| 500 | 1.6 |
| 501 | 2.3 |
| 502 | 2.0 |
| 503 | 2.9 |
| 504 | 2.6 |
| 505 | 1.6 |
| 515 | 1.0 |
| 516 | 1.1 |
| 517 | 2.3 |
| 518 | 2.3 |
| 519 | 6.5 |
| 520 | 2.8 |
| 532 | 1.2 |
| 533 | 4.4 |
| 534 | 100 |
| 535 | 47 |
| 536 | 10 |
| 537 | 1.8 |

## The Mass Spectrum of 2,2'-Dichloro-9,9'-bitriptycyl[72,73]

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 36 | 1.4 | 193½ | 0.5 | 217½ | 0.5 |
| 38 | 0.5 | 198 | 0.4 | 218 | 0.4 |
| 39 | 0.5 | 198½ | 0.4 | 218½ | 0.4 |
| 41 | 1.2 | 199 | 1.8 | 223 | 0.8 |
| 43 | 1.4 | 199½ | 0.5 | 223½ | 0.6 |
| 44 | 0.8 | 200 | 1.1 | 224 | 1.8 |
| 47 | 0.8 | 200½ | 0.4 | 224½ | 0.7 |
| 48 | 0.5 | 201 | 0.5 | 225 | 0.9 |
| 55 | 0.9 | 204½ | 0.4 | 225½ | 0.3 |
| 57 | 0.9 | 205 | 0.4 | 226 | 0.7 |
| 69 | 0.5 | 205½ | 3.0 | 229 | 0.5 |
| 71 | 0.5 | 206 | 1.7 | 229½ | 1.2 |
| 149 | 0.5 | 206½ | 0.8 | 230 | 1.3 |
| 161⅔ | 0.2 | 211 | 1.8 | 230½ | 2.6 |
| 162 | 0.4 | 211½ | 1.1 | 231 | 1.7 |
| 162⅓ | 0.3 | 212 | 5.5 | 231½ | 0.9 |
| 166 | 1.1 | 212½ | 2.9 | 232 | 0.5 |
| 175 | 1.0 | 213 | 4.2 | 235 | 0.9 |
| 175½ | 0.3 | 213½ | 1.5 | 235½ | 0.9 |
| 178 | 0.7 | 214 | 0.5 | 236 | 3.1 |
| 187 | 0.3 | 214½ | 0.2 | 236½ | 2.3 |
| 187½ | 0.2 | 216 | 0.2 | 237 | 4.1 |
| 192½ | 0.3 | 216½ | 0.2 | 237½ | 2.3 |
| 193 | 0.3 | 217 | 0.2 | 238 | 1.8 |

[72] Masses of integral value of less than 0.5% of base peak intensity have been omitted.

[73] Triply charged ions of low intensity (< 0.2%) appear at m/e 150-160.

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 238½ | 0.7 | 264 | 0.5 | 337 | 1.5 |
| 239 | 2.1 | 265 | 0.8 | 339 | 1.0 |
| 240 | 0.8 | 267 | 0.3 | 340 | 1.4 |
| 241½ | 0.8 | 267½ | 0.2 | 348 | 0.8 |
| 242 | 0.8 | 268 | 0.3 | 350 | 1.4 |
| 242½ | 4.5 | 268½ | 0.3 | 351 | 0.8 |
| 243 | 4.5 | 269 | 1.1 | 352 | 0.5 |
| 243½ | 4.0 | 269½ | 10.9 | 360 | 0.5 |
| 244 | 3.7 | 270 | 5.2 | 362 | 0.7 |
| 244½ | 3.6 | 270½ | 4.6 | 363 | 0.5 |
| 245 | 0.7 | 271 | 1.9 | 373 | 1.4 |
| 248 | 1.9 | 271½ | 0.4 | 374 | 0.9 |
| 248½ | 1.2 | 275 | 0.6 | 375 | 1.0 |
| 249 | 5.2 | 276 | 0.6 | 376 | 0.8 |
| 250 | 10.0 | 286 | 7.2 | 377 | 0.5 |
| 250½ | 3.6 | 287 | 7.6 | 384 | 0.5 |
| 251 | 6.3 | 287½ | 0.8 | 385 | 0.6 |
| 251½ | 4.3 | 288 | 6.6 | 386 | 0.7 |
| 252 | 30.4 | 288½ | 0.8 | 387 | 0.8 |
| 252½ | 3.0 | 289 | 3.7 | 398 | 0.6 |
| 253 | 18.1 | 290 | 1.2 | 400 | 0.6 |
| 254 | 2.4 | 299 | 2.4 | 411 | 1.3 |
| 260 | 0.2 | 300 | 0.9 | 412 | 0.8 |
| 260½ | 0.2 | 301 | 1.0 | 413 | 1.2 |
| 261 | 0.5 | 324 | 0.9 | 414 | 0.5 |
| 261½ | 0.3 | 325 | 0.5 | 422 | 1.3 |
| 262 | 0.5 | 326 | 2.3 | 423 | 0.9 |
| 262½ | 0.2 | 327 | 1.4 | 424 | 4.3 |
| 263 | 1.3 | 335 | 0.5 | 425 | 3.7 |

| m/e | % of base peak |
|---|---|
| 426 | 3.9 |
| 427 | 3.1 |
| 428 | 1.3 |
| 447 | 1.0 |
| 448 | 0.7 |
| 449 | 0.7 |
| 458 | 0.6 |
| 459 | 0.6 |
| 460 | 1.2 |
| 461 | 2.3 |
| 462 | 1.8 |
| 463 | 1.5 |
| 464 | 0.8 |
| 472 | 0.6 |
| 474 | 0.9 |
| 475 | 1.0 |
| 476 | 0.8 |
| 485 | 0.7 |
| 487 | 1.5 |
| 488 | 1.0 |
| 489 | 0.8 |
| 495 | 0.5 |
| 496 | 1.0 |
| 497 | 1.3 |
| 498 | 2.3 |
| 499 | 2.3 |
| 500 | 2.8 |
| 501 | 2.8 |
| 502 | 3.4 |
| 503 | 7.2 |
| 504 | 10.0 |
| 505 | 3.9 |
| 506 | 1.1 |
| 507 | 0.5 |
| 508 | 0.5 |
| 510 | 0.5 |
| 523 | 0.7 |
| 524 | 0.5 |
| 537 | 1.3 |
| 538 | 2.5 |
| 539 | 5.6 |
| 540 | 3.7 |
| 541 | 2.1 |
| 542 | 0.9 |
| 572 | 0.5 |
| 573 | 1.9 |
| 574 | 100.0 |
| 575 | 42.7 |
| 576 | 64.2 |
| 577 | 23.8 |
| 578 | 13.0 |
| 579 | 4.1 |
| 580 | 0.8 |

## The Mass Spectrum of 2,2'-Dicarbomethoxy-9,9'-Bitriptycyl[71]

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 12 | 1.8 | 56 | 5.5 | 91 | 3.8 |
| 14 | 2.4 | 57 | 7.6 | 92 | 2.4 |
| 15 | 7.7 | 58 | 4.6 | 93 | 3.2 |
| 16 | 7.6 | 59 | 9.4 | 94 | 1.4 |
| 26 | 8.0 | 60 | 3.5 | 95 | 1.6 |
| 27 | 36.1 | 63 | 1.5 | 96 | 1.6 |
| 29 | 15.8 | 64 | 47.9 | 97 | 1.8 |
| 30 | 4.0 | 65 | 3.2 | 98 | 2.2 |
| 31 | 5.2 | 66 | 23.6 | 100 | 1.7 |
| 33½ | 0.1 | 67 | 3.9 | 103 | 1.4 |
| 34 | 3.0 | 68 | 13.6 | 104 | 1.3 |
| 35 | 2.5 | 69 | 26.8 | 105 | 1.7 |
| 36 | 19.3 | 70 | 3.4 | 107 | 1.2 |
| 37 | 1.5 | 71 | 2.8 | 111 | 1.2 |
| 38 | 7.6 | 72 | 2.2 | 112 | 1.2 |
| 39 | 8.5 | 73 | 1.6 | 113 | 1.2 |
| 40 | 3.2 | 74 | 1.4 | 115 | 1.2 |
| 41 | 19.6 | 76 | 1.6 | 119 | 5.1 |
| 42 | 12.0 | 77 | 4.6 | 123 | 1.3 |
| 43 | 31.5 | 78 | 3.5 | 123½ | < 0.5 |
| 48 | 1.6 | 79 | 3.2 | 124 | 1.4 |
| 50 | 3.0 | 80 | 1.9 | 124½ | < 0.5 |
| 51 | 5.4 | 81 | 3.8 | 125 | 1.8 |
| 52 | 3.2 | 82 | 2.4 | 125½ | 0.6 |
| 53 | 2.4 | 83 | 2.8 | 126 | 2.0 |
| 54 | 2.8 | 84 | 1.3 | 126½ | < 0.5 |
| 55 | 12.0 | 85 | 1.4 | 129 | 1.2 |

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 131 | 5.7 | 187 | 1.1 | 224 | 3.0 |
| 141 | 3.5 | $192\frac{1}{2}$ | 0.8 | $224\frac{1}{2}$ | 1.2 |
| 150 | 6.4 | 193 | 1.8 | 225 | 1.4 |
| $151\frac{2}{3}$ | < 0.3 | $193\frac{1}{2}$ | 0.8 | $225\frac{1}{2}$ | 0.5 |
| $153\frac{1}{3}$ | < 0.3 | 198 | 1.0 | 226 | 2.5 |
| $153\frac{2}{3}$ | < 0.3 | $198\frac{1}{2}$ | 0.7 | $226\frac{1}{2}$ | 0.8 |
| 155 | 1.4 | 199 | 2.5 | 227 | 1.6 |
| $156\frac{2}{3}$ | < 0.3 | $199\frac{1}{2}$ | 0.9 | $227\frac{1}{2}$ | 0.7 |
| $157\frac{1}{3}$ | < 0.3 | 200 | 2.0 | $228\frac{1}{2}$ | 0.6 |
| $157\frac{2}{3}$ | < 0.3 | $204\frac{1}{2}$ | 1.3 | $229\frac{1}{2}$ | 2.4 |
| 161 | 1.2 | 205 | 2.0 | 230 | 2.2 |
| $161\frac{1}{3}$ | < 0.3 | $205\frac{1}{2}$ | 5.7 | $230\frac{1}{2}$ | 5.7 |
| $161\frac{2}{3}$ | 0.6 | 206 | 3.5 | 231 | 3.9 |
| 162 | 1.4 | $206\frac{1}{2}$ | 1.2 | $231\frac{1}{2}$ | 1.4 |
| $162\frac{1}{3}$ | 0.5 | 207 | 1.0 | 234 | 1.3 |
| $162\frac{2}{3}$ | 0.5 | $210\frac{1}{2}$ | < 0.3 | $234\frac{1}{2}$ | 0.7 |
| $164\frac{1}{3}$ | < 0.3 | 211 | 3.2 | 235 | 1.7 |
| $164\frac{2}{3}$ | < 0.3 | $211\frac{1}{2}$ | 2.2 | $235\frac{1}{2}$ | 0.8 |
| 165 | 2.4 | 212 | 11.7 | 236 | 6.7 |
| $165\frac{1}{3}$ | 0.5 | $212\frac{1}{2}$ | 14.8 | $236\frac{1}{2}$ | 4.7 |
| $165\frac{2}{3}$ | < 0.3 | 213 | 5.3 | 237 | 8.7 |
| 166 | 1.2 | $213\frac{1}{2}$ | 1.7 | $237\frac{1}{2}$ | 4.7 |
| $166\frac{1}{3}$ | < 0.3 | $217\frac{1}{2}$ | 0.9 | 238 | 3.3 |
| $166\frac{2}{3}$ | < 0.3 | 218 | 1.0 | $238\frac{1}{2}$ | 1.2 |
| 167 | 1.2 | $218\frac{1}{2}$ | 0.7 | 239 | 2.8 |
| $168\frac{1}{2}$ | < 0.3 | 219 | 1.4 | 240 | 1.4 |
| 169 | 3.2 | $219\frac{1}{2}$ | < 0.3 | $240\frac{1}{2}$ | 0.7 |
| 178 | 1.3 | 223 | 1.4 | $241\frac{1}{2}$ | 2.4 |
| 181 | 3.8 | $223\frac{1}{2}$ | < 0.3 | 242 | 2.2 |

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 242½ | 12.6 | 264 | 2.0 | 326 | 4.5 |
| 243 | 12.6 | 264½ | 0.8 | 327 | 2.6 |
| 243½ | 11.4 | 265 | 4.4 | 337 | 3.2 |
| 244 | 7.6 | 265½ | 1.8 | 338 | 1.7 |
| 244½ | 2.4 | 266 | 2.2 | 339 | 5.7 |
| 245 | 1.7 | 266½ | < 0.3 | 340 | 2.2 |
| 245½ | 0.6 | 267 | 3.5 | 350 | 2.8 |
| 246½ | < 0.5 | 273 | 1.2 | 351 | 1.8 |
| 247½ | < 0.5 | 273½ | < 0.5 | 376 | 1.3 |
| 248 | 4.4 | 279 | 20.5 | 377 | 1.6 |
| 248½ | 2.8 | 279½ | 2.8 | 387 | 1.6 |
| 249 | 11.0 | 280 | 16.0 | 397 | 1.6 |
| 249½ | 7.0 | 280½ | 3.2 | 398 | 1.8 |
| 250 | 20.5 | 281 | 4.2 | 399 | 1.1 |
| 250½ | 6.9 | 281½ | < 0.5 | 400 | 1.6 |
| 251 | 16.8 | 286½ | < 0.5 | 411 | 2.3 |
| 251½ | 4.1 | 295 | 5.6 | 413 | 2.6 |
| 252 | 41.6 | 295½ | 3.8 | 414 | 1.5 |
| 252½ | 0.8 | 296 | 2.8 | 422 | 2.5 |
| 253 | 25.1 | 297 | 2.2 | 423 | 2.2 |
| 254 | 5.1 | 299 | 1.3 | 424 | 11.9 |
| 255 | 1.6 | 300 | 1.2 | 425 | 12.8 |
| 255½ | 0.8 | 310 | 11.0 | 426 | 13.8 |
| 256 | 1.5 | 311 | 8.9 | 427 | 9.7 |
| 256½ | 0.8 | 312 | 7.2 | 428 | 3.4 |
| 257½ | 0.9 | 313 | 2.4 | 436 | 1.0 |
| 258½ | < 0.5 | 323 | 2.0 | 437 | 1.0 |
| 263 | 2.4 | 324 | 1.8 | 448 | 1.3 |
| 263½ | < 0.3 | 325 | 1.4 | 450 | 1.2 |

| m/e | % of base peak | m/e | % of base peak | m/e | % of base peak |
|---|---|---|---|---|---|
| 453 | 1.7 | 502 | 15.8 | 590 | 6.5 |
| 454 | 1.2 | 503 | 19.8 | 591 | 12.8 |
| 455 | 1.3 | 504 | 15.1 | 592 | 6.0 |
| 459 | 1.2 | 505 | 5.4 | 593 | 2.0 |
| 461 | 2.8 | 506 | 1.1 | 607 | 1.3 |
| 462 | 2.6 | 513 | 1.6 | 621 | 1.4 |
| 463 | 2.2 | 514 | 1.1 | 622 | 100 |
| 464 | 1.2 | 529 | 2.6 | 623 | 48.0 |
| 470 | 1.3 | 530 | 5.4 | 624 | 12.3 |
| 471 | 2.0 | 531 | 8.8 | 625 | 2.4 |
| 472 | 2.4 | 532 | 5.4 | | |
| 473 | 1.8 | 533 | 1.5 | | |
| 474 | 4.7 | 534 | 1.2 | | |
| 475 | 4.7 | 535 | 1.1 | | |
| 476 | 3.2 | 545 | 1.7 | | |
| 477 | 1.8 | 546 | 1.6 | | |
| 484 | 2.5 | 547 | 4.2 | | |
| 485 | 7.9 | 548 | 2.8 | | |
| 486 | 4.7 | 549 | 1.2 | | |
| 487 | 5.0 | 558 | 1.6 | | |
| 488 | 5.9 | 559 | 1.3 | | |
| 489 | 3.2 | 560 | 1.3 | | |
| 490 | 1.3 | 561 | 5.1 | | |
| 496 | 1.6 | 562 | 16.4 | | |
| 497 | 1.3 | 563 | 12.1 | | |
| 498 | 6.1 | 564 | 4.7 | | |
| 499 | 7.1 | 565 | 1.4 | | |
| 500 | 10.4 | 575 | 1.4 | | |
| 501 | 15.2 | 589 | 3.0 | | |

# Discussion

## Syntheses of 9,9'-Bianthryls

Of the available routes to investigate restricted rotation in the bitriptycyl system, the addition of benzyne to an optically active 9,9'-bianthryl was chosen for investigation.

Prior to this investigation there was only one previously known optically active 9,9'-bianthryl, 3,3'-dicarboxy-9,9'-bianthryl.[36] This compound had been obtained by chromic acid oxidation of 3,3'-dimethyl-9,9'-bianthryl. In our hands, attempts to repeat this oxidation failed. Similarly, the oxidation of the previously unknown 2,2'-dimethyl-9,9'-bianthryl with chromic acid failed to give the corresponding dicarboxylic acid. Instead, 2-methylanthraquinone was obtained. The oxidation of the methylnaphthalenes and 2-methylanthracene with potassium dichromate under autogenic pressures at high temperatures to the corresponding carboxylic acids has been reported.[51] Our attempts to oxidize 2,2'-dimethyl-9,9'-bianthryl under these conditions did not give the desired 2,2'-dicarboxy-9,9'-bianthryl, but gave instead recovered starting material together with a small amount of 2-carboxyanthraquinone.

Since the oxidation of 3,3'-dimethyl- and 2,2'-dimethyl-9,9'-bianthryl did not yield the desired corresponding acids, we attempted to synthesize 2,2'-dicarboxy-9,9'-bianthryl through the corresponding halogen substituted 9,9'-bianthryls. Both 2,2'-dibromo-9,9'-bianthryl and 2,2'-dichloro-9,9'-bianthryl were converted with cuprous cyanide to 2,2'-dicyano-9,9'-bianthryl. Using a molar ratio of CuCN to 2,2'-dichloro-9,9'-bianthryl of 2:1 and a short reaction time, both

2,2'-dicyano-9,9'-bianthryl and 2-chloro-2'-cyano-9,9'-bianthryl were obtained. These were separated by column chromatography.

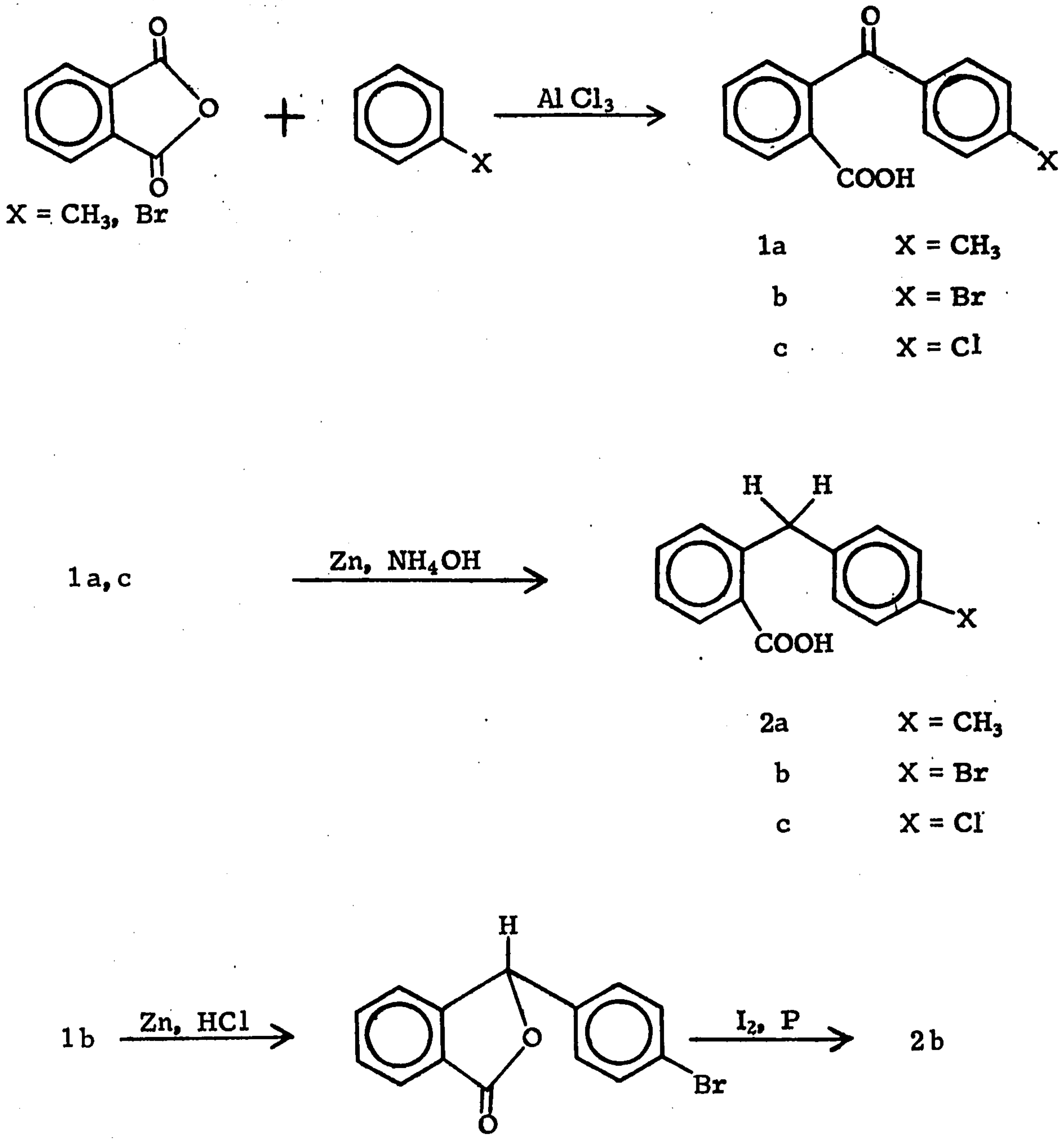
The synthesis of 2-chloro-2'-cyano-9,9'-bianthryl provides the first reported case of an unsymmetrically substituted 9,9'-bianthryl. A modification of the method, e.g., a lower ratio of CuCN to symmetrically substituted dibromo- or dichloro-9,9'-bianthryl could provide a general synthetic method for the preparation of unsymmetrically substituted 9,9'-bianthryls.

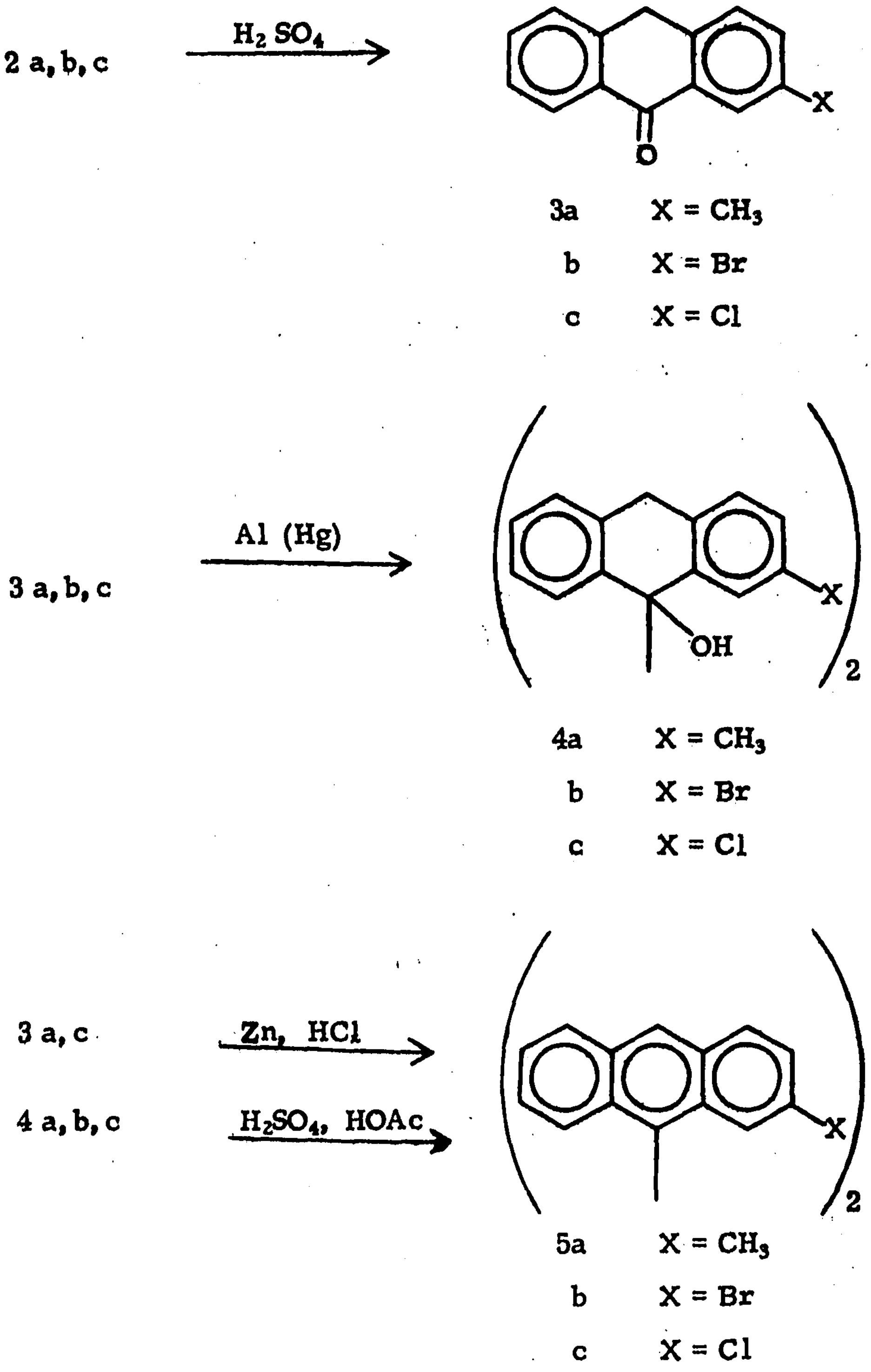
The most efficient path to the synthesis of 2,2'-dicyano-9,9'-bianthryl turned out to be through the chlorine derivatives (see scheme I on p 166) since o-(p-chlorobenzoyl)benzoic acid was commercially available and the reduction to o-(p-chlorobenzyl)benzoic acid proceeded in one step with good yield. The corresponding o-(p-bromobenzoyl)benzoic acid was not commercially available, and the reduction to o-(p-bromobenzyl)benzoic acid requires two steps and leads to a comparatively poor overall yield.[74]

Hydrolysis of 2,2'-dicyano-9,9'-bianthryl gave 2,2'-dicarboxy-9,9'-bianthryl. Resolution with quinidine gave (+) and (-)-2,2'-dicarboxy-9,9'-bianthryl. (+) and (-)-2,2'-Dicarbomethoxy-9,9'-bianthryl were obtained by esterification of the corresponding diacids with diazomethane.

[74] It has been reported (ref 39) that the reduction of o-(p-bromobenzoyl) benzoic acid with zinc in $NH_4OH$ is accompanied by debromination.

Scheme I. Syntheses of 2, 2'-Disubstituted-9-9'-bianthryls

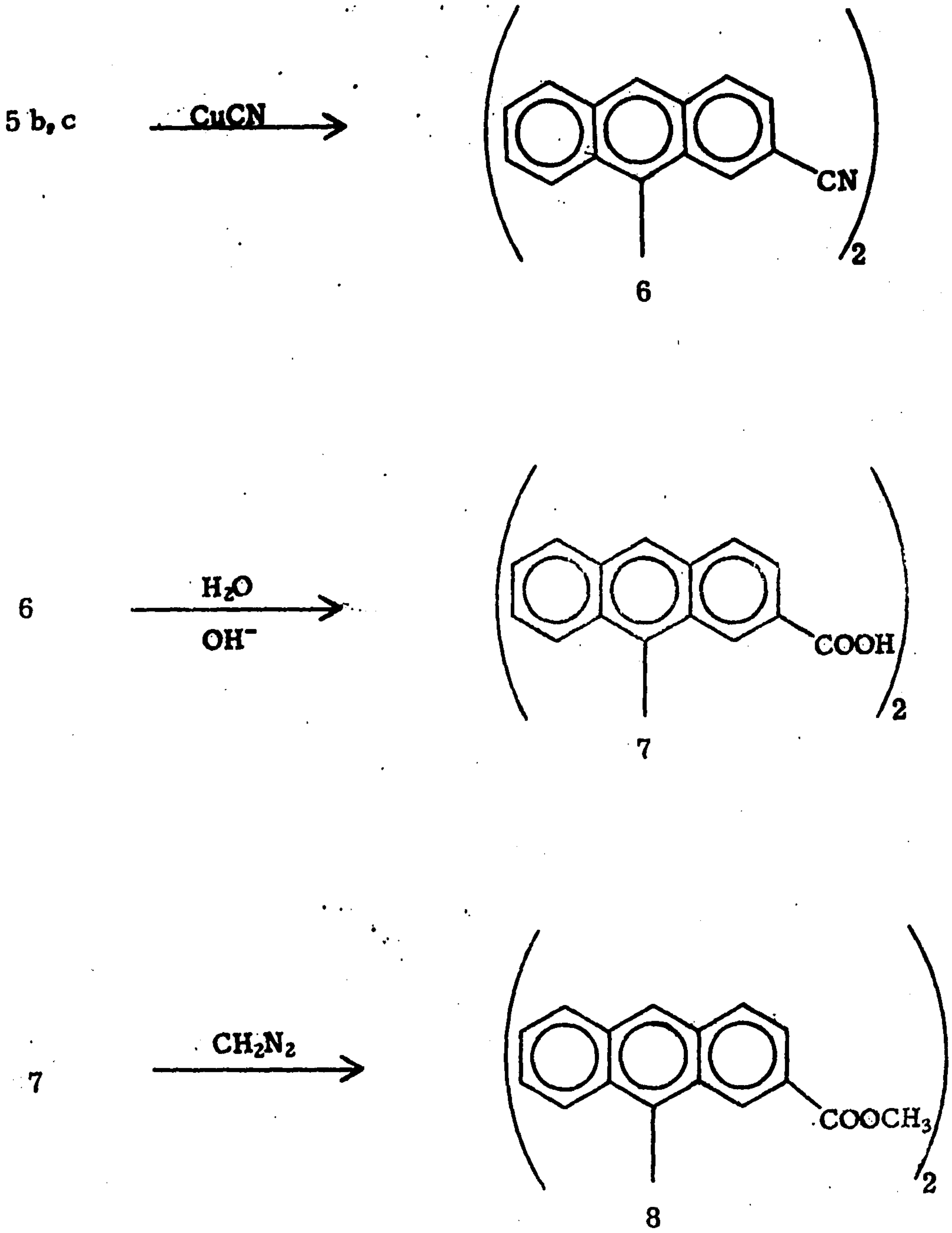




3a $X = CH_3$
b $X = Br$
c $X = Cl$

4a $X = CH_3$
b $X = Br$
c $X = Cl$

5a $X = CH_3$
b $X = Br$
c $X = Cl$


5 b, c
CuCN
CN
2
6
6
$H_2O$
$OH^-$
COOH
2
7
7
$CH_2N_2$
$COOCH_3$
2
8

### Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl

If one assumes a planar transition state, the racemization of a 9,9'-bianthryl would involve two benzo-benzo interactions. One may also envisage a non-planar transition state in which the 9,9'-bond is bent, i.e., a rehybridization of the 9-carbon atom has occurred (see p 6). This would require only one benzo-benzo interaction for racemization. Such a non-planar transition state would probably lead to a reduced steric interaction.[75] However, a bent transition state implies less conjugation across the 9,9'-bond. This would result in increasing the energy of the transition state. In addition, a bent transition state requires a change of hybridization of the pivotal carbon atom from $sp^2$ towards $sp^3$. This would reduce the $\pi$ overlap in the original anthracyl ring. Hence a loss of resonance energy and an increase of transition state energy.

Whatever the exact nature of the transition state may be, the ground state strain energy of a 9,9'-bianthryl must be considerably lower than that of the bridged 1,1'-binaphthyl (XXV) (p 16). One can therefore predict a barrier of at least 29 kcal mole$^{-1}$ based upon one benzo-benzo interaction (see pp 16-18).

In our hands, optically active 2,2'-dicarboxy-9,9'-bianthryl was stable to racemization upon recrystallization from glacial acetic acid. In addition, it is claimed that 3,3'-dicarboxy-9,9'-bianthryl does not racemize in boiling toluene for 2 hr.[36]

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[75] An examination of Dreiding models reveals that the benzo-benzo interactions in the planar and bent transition states are not the same.

We attempted to measure the racemization energy of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl. Nitrogen was bubbled through a solution of (-)-2,2'-dicarbomethoxy-9,9'-bianthryl in dimethyl phthalate, in an ampoule, in order to exclude dissolved oxygen. The ampoule was then sealed and heated at $220^{\circ}$. No racemization was observed after 6 hr. Assuming[76] a preexponential Arrhenius factor "A" of $10^{12}$ and an error in polarimetry of 1%,[77] $E_{rac}$ is estimated to be at least 42 kcal $mole^{-1}$.

When oxygen instead of nitrogen was passed through the solution, prior to sealing, 12% racemization was observed after heating for 2 hr. The effect of oxygen was more dramatic when the solvent was changed to triglyme. With preliminary nitrogen passage, 4% racemization occurred after heating for 1.5 hr. In the presence of oxygen, 72% racemization was observed after heating for the same period of time. In all cases, the nmr and ir spectra were identical before and after heating.

It thus appears that oxygen catalyzes the racemization of 2,2'-dicarbomethoxy-9,9'-bianthryl. Such an effect of oxygen in the racemization of biphenyls and binaphthyls has not been previously reported.

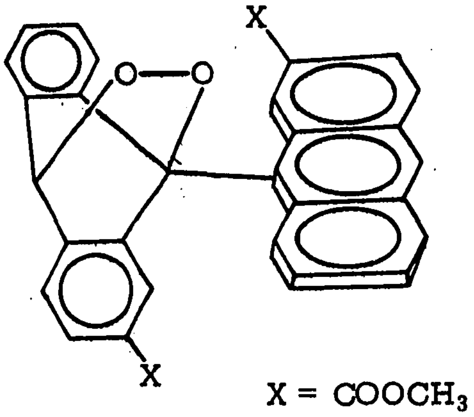
The 9,9'-bianthryl system differs from other such biaryl systems in that the 9,10-positions are much more reactive. Oxygen could

[76] See p 10, ref 23, for typical "A" values commonly encountered in the racemization of biphenyls and binaphthyls.

[77] See p 119 for errors involved in polarimetry.

interact reversibly with the 9,10-positions of a 9,9'-bianthryl changing the hybridization of the pivotal carbon and therefore reducing the barrier to racemization.

Formation of a 9,10-endoperoxide intermediate such as XLII could account for the racemization of 2,2'-dicarbomethoxy-9,9'-bianthryl. This intermediate resembles the mono-adduct (XXVIII) (p 23) formed from the addition of benzyne to a 2,2'-disubstituted-9,9'-bianthryl. The transannular peroxide (XLII), like the benzyne mono-adduct (XXVIII), would have only one benzo-benzo interaction in the transition state to rotation.



XLII

Using the estimated value for a benzo-benzo interaction of 29 kcal mole$^{-1}$ (pp 17,18) and a pre-exponential Arrhenius factor "A" of $10^{11}$ - $10^{13}$ [76] the intermediate, XLII, would be expected to racemize at 220$^{\circ}$ with a half-life of racemization of at most 35 sec.

Endoperoxides of substituted anthracenes are known. However, these are produced photochemically.[78,79,80] Recently, such endoperoxides were obtained by the addition of externally (chemically[81] or electrically[82]) produced singlet oxygen molecules. Hence, it has been suggested that even in photochemical oxidations the reacting intermediate is singlet oxygen.[83] Photochemical studies also indicate that anthracenes acting as sensitizers excite oxygen to the singlet state which then reacts with ground state anthracene to form the endoperoxide.[84] In contrast, the bianthryl system appears to be resistant to photooxidation. Thus, no endoperoxide of 9,9'-bianthryl and 10,10'-diphenyl-9,9'-bianthryl was obtained under illumination with sunlight.[85]

[78] W. Bergmann and M.J. McLean, Chem. Rev., 28, 367 (1941).

[79] K. Gollnick and G.O. Schenck in "Organic Reactions," Vol.8, J. Hammer, ed., Academic Press, New York, N.Y., 1967, chapter 10.

[80] E.J. Bowen in "Advances in Photochemistry" Vol.1, W.A. Noyes, G.S. Hammond and J.N. Pitts,Jr., ed., Interscience Publishers, Inc., New York, N.Y., 1963, p 23.

[81] C.S. Foote and S. Wexler J. Am. Chem. Soc., 86, 3879 (1964).

[82] E.J. Corey and W.C. Taylor, ibid., 86, 3881 (1964).

[83] C.S. Foote and S. Wexler, ibid., 86, 3880 (1964).

[84] T. Wilson, ibid., 88, 2898 (1966).

[85] C. Dufraisse, L. Vellus and L. Vellus, Bull. Soc. Chim. France, 5, 600 (1938).

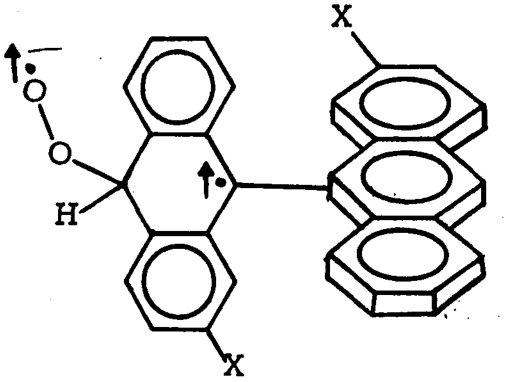
With exclusion of light, no oxygen addition to anthracene or 9,10-diphenylanthracene was observed for 6 yrs,[86] although Corey and Taylor reported formation of a trace amount of an endoperoxide by the addition of oxygen to anthracene in the dark.[82]

If indeed traces of the endoperoxide, XLII, had formed, in order to account for the extensive racemization in triglyme (72%), the formation of such an intermediate would have to be reversible. Endoperoxides of anthracenes, in varying degrees, liberate oxygen upon heating to regenerate the parent anthracene. The extent of oxygen evolution generally depends on the number and type of 9,10-substituents, aryl substituents being more effective than alkyl substituents.[78,79] In the cases where oxygen evolution with regeneration of the parent hydrocarbons is diminished, other competitive radical reactions, initiated by O - O bond cleavage, and leading to a variety of products, are observed.[87]

Alternately, addition of ground state triplet oxygen to 2,2'-dicarbomethoxy-9,9'-bianthryl could give the diradical XLIIIa (triplet, due to spin conservation). The unpaired electron on the benzylic carbon atom would be stabilized through delocalization by the two

[86] C. Dufraisse, J.L. Bras and A. Allais, Compt. Rend., 388 (1943).

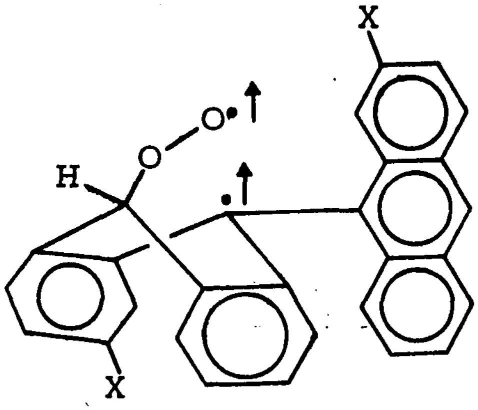
[87] P.F. Southern and W.A. Waters, J. Chem. Soc., 4340 (1960).



X = COOCH$_3$

XLIIIa

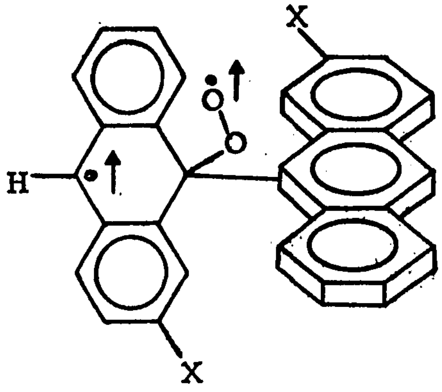
adjacent phenyl rings. Hence, that portion of the molecule would tend towards planarity. The molecule might, however, distort to effect racemization. A non-planar conformation such as XLIVb would have somewhat diminished resonance energy but also only one benzo-benzo interaction in the transition state to rotation. Therefore like XLII (p 171) it would be expected to racemize at 220°.



X = COOCH$_3$

XLIIIb

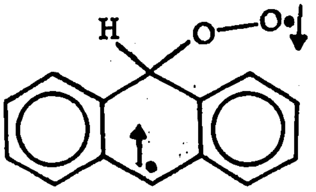
In a similar fashion the addition of triplet oxygen at the 10-carbon would give XLIV. This intermediate would also be expected to racemize at 220°.



$X = COOCH_3$

XLIV

An intermediate such as XLV, similar to XLIII, but in the singlet state, has been proposed as an alternative to the singlet oxygen mechanism for the photooxidation of polyacenes (e.g., anthracene).



XLV

It was proposed to arise from the triplet state of a polyacene and ground state oxygen. However, there is no direct evidence for the existence of such an intermediate.[84] Furthermore, contrary to what one might expect, the kinetics of photooxidation require that another polyacene molecule react with XLV to form the endoperoxide, rather than have it ring close directly.[88]

In order to form XLII from XLIII, a triplet-singlet spin conversion would be required. In view of the known instability of such transannular peroxides at high temperatures and in particular the fact that 9,9'-bianthryl and 10,10'-diphenyl-9,9'-bianthryl do not form peroxides at least under the reported conditions, the formation of the 9,10-endoperoxide, XLII is at present only conjecture.

## Syntheses and Properties of 9,9'-Bitriptycyls and Triptycenes

Bartlett and Greene,[63] in the course of styding the thermal decomposition of ditriptoyl peroxide, isolated a small amount of a high-melting highly insoluble solid, "compound X," which they suggested might be bitriptycyl. We have synthesized 9,9'-bitriptycyl by the addition of benzyne to 9,9'-bianthryl. Benzyne was generated from three different sources: (1) diazotization of anthranilic acid[56] (2) dehalogenation of o-bromofluorobenzene with magnesium[64a,b] and (3) decomposition of 1,1—dioxo-1,2,3-benzothiadiazole.[65] 9,9-Bitriptycyl was obtained most conveniently and in best yields by using the anthranilic acid method.

The proof of structure of bitriptycyl is based on the following facts. Carbon and hydrogen analysis is consistent with the formula

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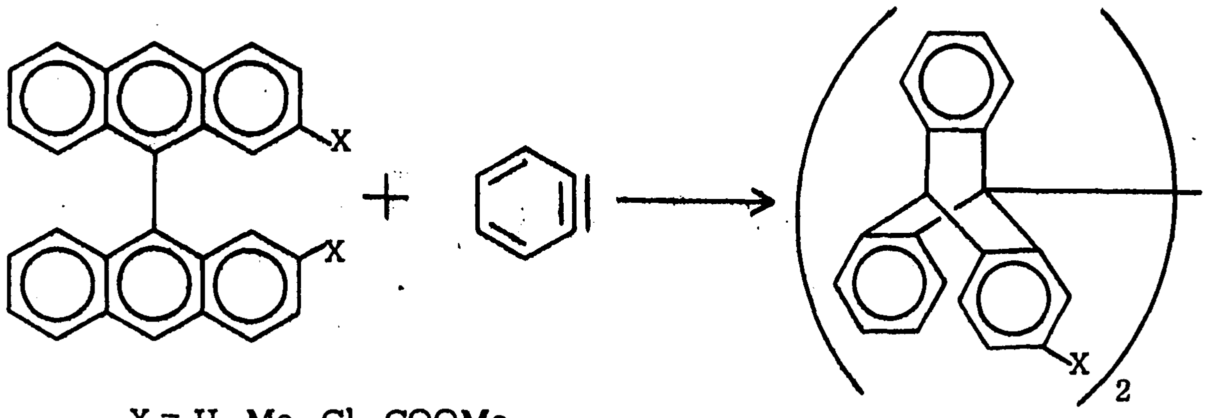
[88] For a critical discussion see ref 83.

$C_{40}H_{26}$. The mass spectrum shows a base peak at m/e 506 (molecular ion), a strong peak at m/e 253 and a metastable ion at approximately m/e 127 indicating a cleavage of the 9,9'-bond of the molecular ion to give formally a triptycyl ion. The presence of 253½ peak indicates that the 253 peak is also due in part to the doubly charged molecular ion. The infrared spectrum is relatively simple and agrees with the published spectrum of Bartlett and Greene for "compound X." The ultraviolet spectrum compares favorably with the ultraviolet spectrum of triptycene.

Each of the 2,2'-disubstituted-9,9'-bitriptycyls was synthesized by the addition of benzyne, generated from anthranilic acid, to the corresponding 2,2'-disubstituted-9,9'-bianthryl (see scheme II), except for the case of 2,2'-dicarboxy-9,9'-bitriptycyl which was obtained from the hydrolysis of the corresponding methyl ester.

Scheme II. Syntheses of 9,9'-Bitriptycyls



X = H, Me, Cl, COOMe

Although the products were obtained in low yields, their isolation was greatly facilitated by their extreme insolubilities in the common organic solvents. The structure proof of the substituted 9,9'-bitriptycyls is based on similar data and arguments presented for the structure proof of the parent hydrocarbon, 9,9'-bitriptycyl. Elemental analyses agree with their respective molecular formulas. The mass spectra establish the molecular weights and the fragmentation patterns are consistent with such structures (see p 181 for discussion of mass spectra). Intense peaks of m/e P-X and P-2X, where P is the parent ion (molecular ion) and X is the substituent, identify the substituents present. The infrared spectra are consistent with the postulated structures and serve also to identify the substituents. The ultraviolet data for 9,9'-bitriptycyl, 2,2'-disubstituted-9,9'-bitriptycyls and the corresponding triptycenes are presented for comparison in Table II. As would be anticipated, there is generally a very close correspondence in position of absorption between the bitriptycyls and the corresponding triptycenes. Unexpectedly, a number of the corresponding absorption bands of the bitriptycyls and corresponding triptycenes show very similar absorption coefficients. A priori, the absorption coefficients of bitriptycyls would be expected to be twice those of the corresponding triptycenes.

## Table II. Ultraviolet Data for 9,9'-Bitriptycyls and the Corresponding Triptycenes[89]

| Triptycene | | 9,9'-Bitriptycyl | |
|---|---|---|---|
| λ max(mμ) | log ε | λ max(mμ) | log ε |
| 279 | 3.67 | 280 | 3.69 |
| 271 | 3.55 | 272 | 3.63 |
| 265 (sh) | 3.32 | 266 (sh) | 3.38 |

| 2-Methyltriptycene | | 2,2'-Dimethyl-9,9'-bitriptycyl | |
|---|---|---|---|
| λ max (mμ) | log ε | λ max (mμ) | log ε |
| 283 | 3.63 | 284 | 3.57 |
| 280 | 3.64 | 280 | 3.65 |
| 273 | 3.56 | 273 | 3.62 |
| 266 (sh) | 3.28 | 266 (sh) | 3.39 |

| 2-Chlorotriptycene | | 2,2'-Dichloro-9,9'-bitriptycyl | |
|---|---|---|---|
| λ max (mμ) | log ε | λ max (mμ) | log ε |
| 285 | 3.50 | 287 | 3.45 |
| 278 | 3.61 | 280 | 3.63 |
| 271 | 3.49 | 272 | 3.55 |

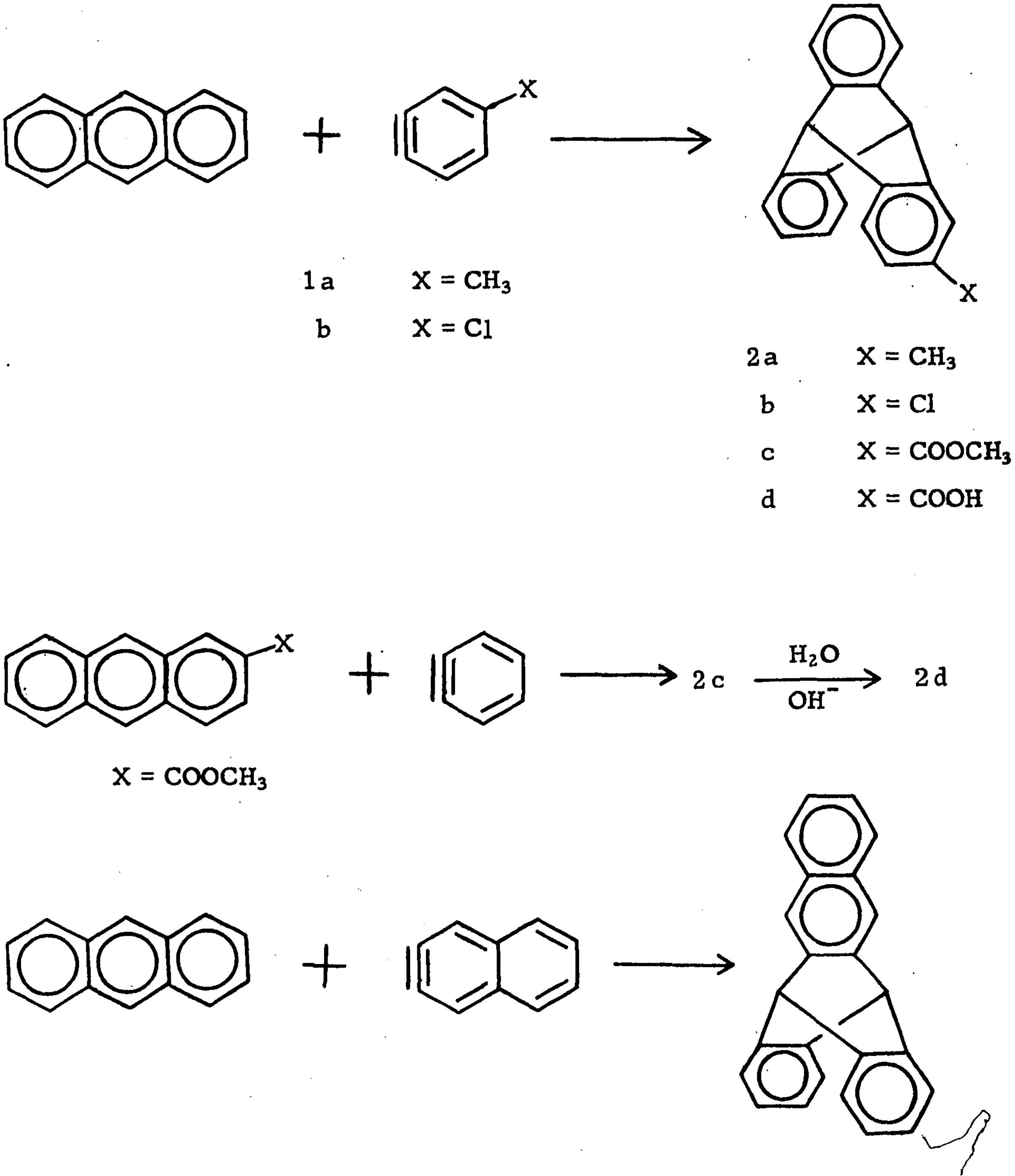
| 2-Carbomethoxytriptycene | | 2,2'-Dicarbomethoxy-9,9'-bitriptycyl | |
|---|---|---|---|
| λ max (mμ) | log ε | λ max (mμ) | log ε |
| 293 | 3.46 | 292 | 3.46 |
| 283 (sh) | | 280 (sh) | |
| 265 | 3.86 | 264 | 4.14 |

| 2-Carboxytriptycene | | 2,2'-Dicarboxy-9,9'-bitriptycyl | |
|---|---|---|---|
| λ max (mμ) | log ε | λ max (mμ) | log ε |
| 291 | 3.43 | 290 | 3.47 |
| 275 (sh) | 3.63 | 278 (sh) | 3.78 |
| 263 | 3.86 | 263 | 4.13 |

[89] The ultraviolet spectra of triptycene, 9,9'-bitriptycyl and their carboxy derivatives were taken in dioxane. All others were taken in Chloroform.

Triptycene derivatives corresponding to the 9,9'-bitriptycyl derivatives were synthesized in order to compare physical data. The synthetic routes are outlined in scheme III.

Scheme III. Syntheses of Triptycenes

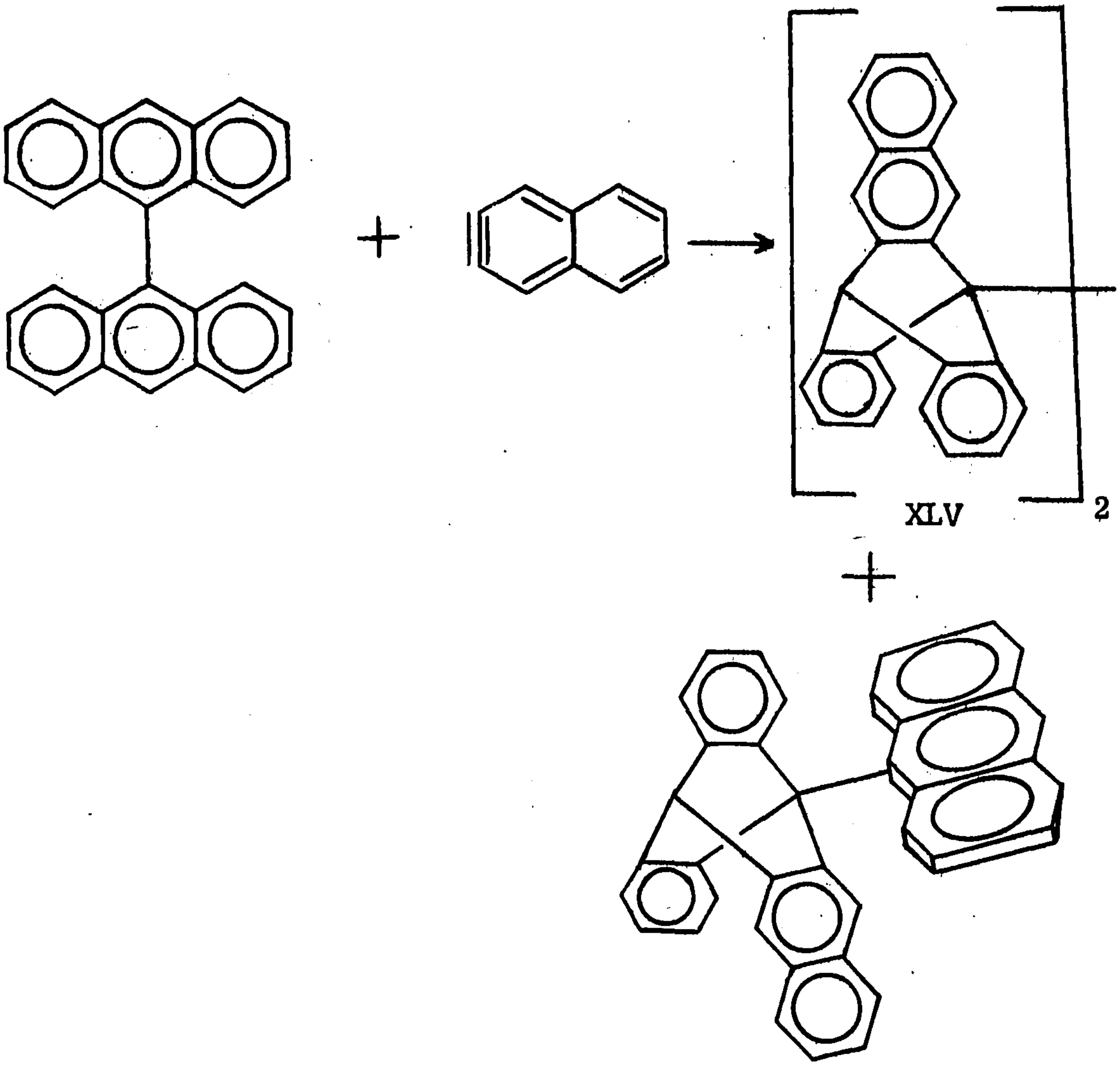


1a $X = CH_3$
b $X = Cl$

2a $X = CH_3$
b $X = Cl$
c $X = COOCH_3$
d $X = COOH$

$X = COOCH_3$

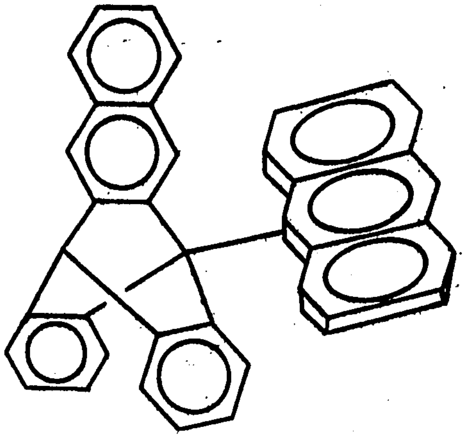
Addition of 2,3-naphthyne (from 2-amino-3-naphthoic acid and n-butyl nitrite) to 9,9'-bianthryl yielded not only the di-adduct, 2,3,2',3'-dibenzo-9,9'-bitriptycyl (XLV), but also the mono-adduct, 9-(9-anthracyl)-2,3-benzotriptycene (XLVI).



XLV

XLVI

In addition to conformation XLVI, the mono-adduct can exist in another conformation, XLVII. The initial attack of naphthyne on 9,9'-bianthryl should produce only XLVI (or its enantiomer).



XLVII

If the second molecule of naphthyne adds before rotation can occur, i.e., the interconversion of isomers XLVI and XLVII, then only one dibenzo-9,9'-bitriptycyl (syn-skew) would be obtained. The assumption here is that the second naphthyne molecule adds from the most favored direction (see p 26), i.e., in the direction which bisects the angle formed by the naphtho and benzo groups.

Whether isomer XLVII is obtained or not depends on the barrier to rotation in XLVI. This barrier is due to one benzo-benzo interaction.

The reactivity of XLVII towards a naththyne molecule should be similar to that of the benzyne mono-adduct XXVIII (p 23) as far as the least hindered direction of attack is concerned. However, XLVI would probably be less reactive since the favored direction of addition would be more crowded because a benzo group is replaced by the bulkier naphtho group. Thus, the fact that a mixture of the mono-adduct and di-adduct is obtained when naphthyne is added to 9,9'-bianthryl, but only the di-adduct, 9,9'-bitriptycyl, is obtained when benzyne is added to 9,9'-bianthryl, might be attributed to the difference in reactivities of the mono-adducts XLVI (p 181) and XXVIII (X= H) (p 23).

Addition of benzyne generated from anthranilic acid, in boiling 2-butanone, to optically active (-)-2,2'-dicarbomethoxy-9,9'-bianthryl yielded 2,2'-dicarbomethoxy-9,9'-bitriptycyl. The product was extremely insoluble in the common organic solvents. It was thus impossible to measure its optical rotation. It was therefore hydrolyzed, at 130 - 135°, to the corresponding diacid, 2,2'-dicarboxy-9,9'-bitriptycyl. A 1% solution of this acid in basic solution showed no optical activity.

Benzyne was also added to (+)-2,2'-dicarbomethoxy-9,9'-bianthryl in boiling methylene chloride, a solvent of lower boiling point than 2-butanone, above. The product 2,2'-dicarbomethoxy-9,9'-bitriptycyl was hydrolyzed at 70° (lower temperature than above) to 2,2'-dicarboxy-9,9'-bitriptycyl. A 1.2% solution of the resulting diacid showed no optical activity.

It remains now to speculate on this lack of optical activity. The first and obvious possibility is that rotation is not appreciably hindered in the 9,9'-bitriptycyl system and thus easy interconversion of enantiomers can occur. The barrier to rotation will be equal to the difference in energy between the transition state and the ground state (see p 3). Since the transition state in the 9,9'-bitriptycyl system would involve three benzo-benzo interactions, which we believe would entail some 87 kcal mole$^{-1}$ (three benzo-benzo interactions, see p 19), the lack of optical activity cannot be due to a lack of hindrance in the transition state. For the lack of optical activity to be due to increased steric compression in the ground state also seems unlikely. For example an additional 67 kcal mole$^{-1}$ of ground state compression would be necessary to give a rotational barrier of 20 kcal mole$^{-1}$. Such a situation would not be consistent with the high thermal stability of 9,9'-bitriptycyl.[26] Such a barrier, assuming a normal "A" factor would lead to easy racemization during the hydrolysis reaction of the diester to the diacid.

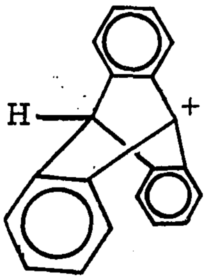
A second, more plausible, possibility for the lack of optical activity is that racemization (rotation) occurs in the mono-adduct. As previously discussed (pp 24, 25), the rotational barrier would involve only a single benzo-benzo interaction. In addition, because of the $sp^3$-$sp^2$ situation at the central carbon-carbon bond, the ground state of the mono-adduct should be of somewhat higher energy (due to steric compression) than, for example, the starting 9,9'-bianthryl. In an attempt to investigate this possibility, the addition of benzyne to (+)-2,2'-dicarbomethoxy-9,9'-bianthryl was carried out in $CH_2Cl_2$ (bp 41°) rather than the usual solvent, 2-butanone (bp 80°). However, here too no optical activity was detected.

A third possibility is that the optical rotation of the salt of syn-skew 2,2'-dicarboxy-9,9'-bitriptycyl is very small. Examples of dissymmetric molecules which show no rotation are known. Thus, (S)-2,2'-dimethyl-6,6'-bis(trideuteriomethyl)biphenyl shows no optical activity at all wavelengths from the visible to 250 mμ.[90] Similarly, both enantiomers of the asymmetric hydrocarbon butylethylhexylpropylmethane showed no optical activity at 280 - 580 mμ.[91]

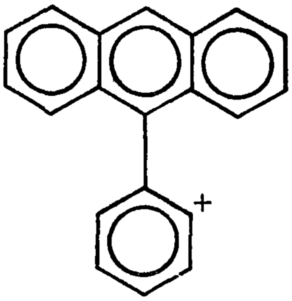
Further work is necessary before any definite conclusions can be made concerning the degree of hindrance to rotation in 9,9'-bitriptycyls.

## Discussion of the Mass Spectra of Triptycenes and 9,9'-Bitriptycyls

The singly charged ions of triptycene are found mainly at P-nH. Interestingly, the base peak is due to the P-H ion. The high resolution mass spectrum of triptycene has been reported.[92] A bridgehead carbonium ion XLVIII was proposed as the structure of the P-H ion, in analogy with the fact that triphenyl methane shows a large P-H ion which is postulated to be the triphenyl carbonium ion.



XLVIII



XLIX

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[90] K. Mislow, R. Graeve, A.J. Gordon and G.H. Wahl,Jr., J. Am. Chem. Soc., 86, 1733 (1964).

[91] H. Wynberg, G.L. Heckkert, J.P.M. Houbiers and H.W. Borsch, J. Am. Chem. Soc., 87, 2635 (1965).

[92] M.I. Bruce, Chem. Comm. 593 (1967).

In light of the known instability of bridgehead carbonium ions, in contrast to the resonance stabilized triphenylmethyl carbonium ion, this analogy is perhaps not a good one. In the absence of further evidence, structure XLVIII must be considered as highly speculative. Perhaps the loss of a bridgehead hydrogen atom from the molecular ion is accompanied by carbon-carbon bond cleavage to give a structure such as XLIX. Alternately, an open chain structure may be postulated.

It has been observed that benzene and its open-chain isomer, 1,3-hexadiene-5-yne, show very similar mass spectra. This has led to the suggestion that the benzene ion isomerizes to the ion of 1,3-hexadiene-5-yne prior to decomposition, and that the $C_6H_5^+$ and $C_6H_4^+$ ions derived from benzene are linear.[93] It has similarly been suggested that the $C_6H_5^+$ ion observed in the decomposition of toluene, ethylbenzene, 2-chloroethylbenzene and p-xylene is best represented as an open-chain ion.[94] For the case at hand one might postulate the open-chain isomer L. The rest of the singly charged ions appear to be due to P-2H-n(CH).

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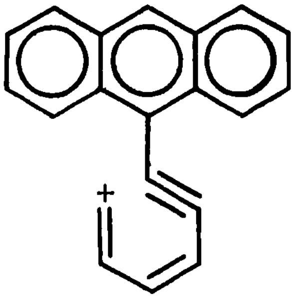
[93] J. Momigny, L. Brakier and L. d'Or, Bull. Class. Sci. Acad. Belg., **48**, 1002 (1962); CA 59: 7065 g.

[94] H. Budikiewicz, C. Djerassi and D.H. Williams, "Mass Spectroscopy of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, pp 74-76.



L

The 2-substituted triptycenes show peaks for singly charged ions due to P-X, P-X-nH and P-X-H-n(CH) where X is the substituent. The base peak of the 2-substituted triptycenes is found at P-X except for 2-carboxytriptycene which has a base peak due to the P-X-H ion. Analogously substituted benzenes also lose their substituents readily. Thus toluene[95], chlorobenzene[96], methyl benzoate[97,98,99] and benzoic acid[97] show P-X peaks. 2-Methyltriptycene, as does toluene[95], shows a relatively intense peak at P-H probably due either to the stable substituted benzyl or the substituted tropylium ion. 2-Carbomethoxytriptycene also exhibits ions due to P-$CH_3$ and P-$OCH_3$. 2-Carboxytriptycene shows ions due to P-OH and P-$CO_2$, the latter clearly due to a rearrangement.

[95] H.M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F.W. McLafferty, ed., Academic Press, New York, N.Y.,1963, Chap. 10.

[96] F.W. McLafferty, Anal. Chem., 34, 16 (1962).

[97] F.W. McLafferty and R.S. Gohlke, Anal. Chem., 31, 2076 (1959).

[98] E.M. Emery, Anal. Chem., 32, 1495 (1960).

[99] T. Aczel and H.E. Lumkin, Anal. Chem., 34, 33 (1962).

A retrograde benzyne addition appears to occur. Thus the ion of mass 178 (anthracene) is present in all the spectra studied.

An abundance of doubly charged ions is found, mostly due to the corresponding singly charged ions. Triply charged ions are also observed due to M-X-nH, the most prominent being at $83\frac{1}{3}$ $(83.3599)^{92}$ and $83\frac{2}{3}$ $(83.6948)^{92}$ for triptycene, 2-chlorotriptycene and 2-carboxytriptycene, and at $87\frac{1}{3}$, $87\frac{2}{3}$, $88\frac{1}{3}$ and $88\frac{2}{3}$ for 2-methyltriptycene.

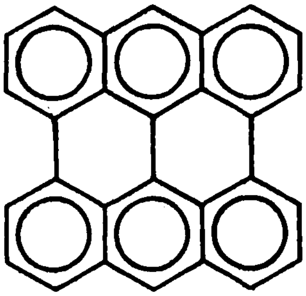
The predominant ions of 2,2'-disubstituted-9,9'-bitriptycyls are found at P-X, P-X-nH, P-2X and P-2X-nH. The mass spectrum of 9,9'-bitriptycyl shows an intense peak at one-half the parent ion due to both $\frac{1}{2}P^{+}$ and $P^{+2}$ ions. 2,2'-Dimethyl-, 2,2'-dichloro- and 2,2'-dicarbomethoxy-9,9'-bitriptycyl exhibit the corresponding peak, but the contribution of the $P^{+2}$ ion is smaller for the first two compounds and zero for 2,2'-dicarbomethoxy-9,9'-bitriptycyl.

An abundance of doubly charged ions is found. These ions are mainly due to P-X, P-X-nH, P-2X and P-2X-nH. The latter two ions if they appear at integral mass numbers cannot be differentiated from $\frac{P-2X}{2}$ and $\frac{P-2X}{2}-nH$ singly charged ions.

An interesting ion appears at $\frac{1}{2}P+1$, indicating a rearrangement of hydrogen from one triptycyl unit to the other. This ion is most apparent in the spectrum of 2,2'-dicarbomethoxy-9,9'-bitriptycyl. The 9,9'-bitriptycyls also show a $\frac{P}{2}-1$ ion.

Triply charged ions are also present. These ions are found at $\frac{P-2X-nH}{3}$.

Inspection of the abundant masses higher than $\frac{1}{2}$(P-2X) reveals that the major ions formed from the 9,9'-bitriptycyls correspond to loss of X, substituted benzyne, CH, and a combination of these fragments. The resulting ions are also accompanied by ions resulting from loss of an additional two or four hydrogen atoms. Thus, the ion at m/e 350, present in all the spectra, corresponds to the loss of two benzynes from 9,9'-bitriptycyl or two substituted benzynes from the substituted 9,9'-bitriptycyls; each process being accompanied by a loss of four hydrogens. This ion could have a stable structure such as LI.



LI

# Autobiography

The author, Constantine Koukotas, was born in Klisoura, Macedonia, Greece on July 20, 1940. He immigrated to the United States in 1954 and acquired citizenship in 1967. He attended The City College of New York where he has received his Bachelor of Science degree in June 1962 and a Master of Arts degree in June 1965.