PHOTOCHEMICAL REACTIONS OF BIPHENYLENE AND SOME DERIVATIVES

BY

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

1976

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

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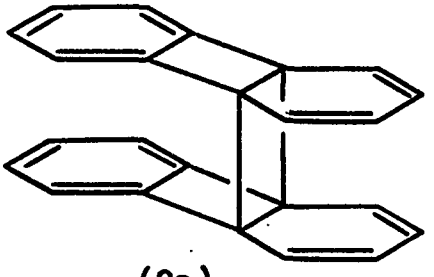
ABSTRACT

The photoreactivity of biphenylene and several 2-substituted biphenylenes was investigated. The most detailed study was made on the photodimerization of biphenylene itself, including the structure of the photodimer and the variation of the quantum yield for the disappearance of biphenylene with changes in wave length, concentration and solvent. A conclusion from the latter work is that the dimerization is a reaction of singlet biphenylene.

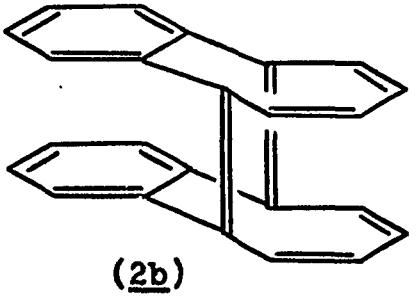
Initially, the photodimer was thought on the basis of the spectral data available and by hydrogenation studies to be syn-13,14,15,16-dibenzopentacyclo-$[6.4.2.2^{2,7}.0.0^{2,7}]$hexadeca-3,5,9,11,13,15-hexaene (2a), the product of syn-[2+2] addition of two biphenylenes across their 4a,8b-carbons.



(2a)

This structure could not be proved by the many degradative reactions carried out and was shown to be untenable when the ^{13}C spectrum showed all the carbons to be olefinic or aromatic. The apparent possibility that a dimer formed as previously thought, but isomerized by conversion of the central

cyclobutane ring to a diene, was demonstrated by an X-ray crystallographic study of the octahydrodimer. The initially assigned syn-stereochemistry was corroborated and the structure of the octahydrodimer was shown to be syn-5,12:6,11-dibutanodibenzo[a,e] cyclooctene (2c), and the photodimer is, therefore, syn-5,12:6,11-di [1,3] butadienodibenzo [a,e]-cyclooctene (2b).



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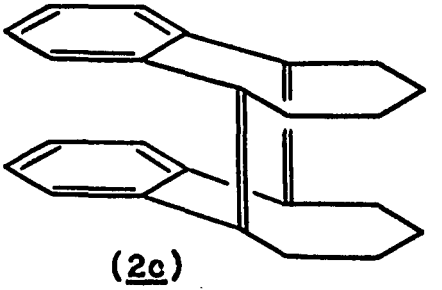


(2c)

Attempts to trap the photo-intermediate from biphenylene using maleic anhydride and other olefins did not produce any adducts.

Several 2-substituted biphenylenes were prepared and their photoreactivities studied. In the case of 2-methoxybiphenylene, this substance was found to be photo-inactive, contrasting with the known photodimerization of 2-methoxynaphthalene; also inactive was 2-benzoylbiphenylene. Irradiation of 2-benzoyloxybiphenylene produced a photo-Fries rearrangement to give 2-benzoyl-3-hydroxybiphenylene. The rate of this reaction was solvent dependent, and formed the same product observed from the thermal Fries rearrangement.

ACKNOWLEDGEMENTS

Appreciation is hereby extended to Dr. Norman L. Goldman, my research mentor, for his assistance in planning and carrying out this thesis study.

Special thanks are also extended to Dr. Robert Engel and Mr. Dennis Liotta of Quenns College, CUNY for the running of several mass spectra, and to Dr. George A. Gray of Varian Associates for the running of ^{13}C spectra.

A word of gratitude is also extended to my wife, Mary, whose love and moral support, while raising two infants, was beyond measure and will always be deeply treasured.

TABLE OF CONTENTS

TABLE OF CONTENTS

TABLE OF CONTENTS

TABLE OF CONTENTS

TABLE OF CONTENTS

TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF CHARTS, FIGURES AND SCHEMES

FACTORS EFFECTING THE PHOTODIMERIZATION OF THE POLYNUCLEAR AROMATIC HYDROCARBON BIPHENYLENE

I. INTRODUCTION

Biphenylene and some of its derivatives have been found to undergo photochemical reactions. Prior to this work there had been conflicting reports about the photoreactivity of biphenylene; claims of no reaction;[1,2] claim of reactivity, without specification of products;[3] and claim of a characterized product, tetraphenylene.[4]

The primary reaction described herein, the photodimerization of biphenylene, was investigated in detail with respect to structure and formation. The dimerization will be shown to involve a very interesting syn- [2+2] coupling of the 4a, 8b-carbons of two biphenylenes, followed by an isomerization of the cyclobutane ring so formed to a diene. Quantum yield studies involving variation of wave length, solvent, including heavy-atom solvents, etc. provided evidence about the nature of the reaction, judged thereby to involve singlet biphenylene.

The photoreactivity of substituted biphenylenes is also described. First, however, a review of the reported photochemistry of related aromatic systems is presented.

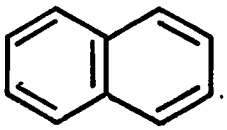
II. HISTORICAL

PHOTOCHEMISTRY OF POLYNUCLEAR AROMATIC HYDROCARBONS

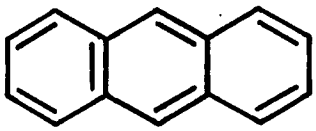
A. General Discussion

The photochemistry of polynuclear aromatic compounds has been of interest to chemists for over 100 years. The photodimerization of anthracene was first reported by Fritzsche in 1866.[5]

In order to better understand the photochemistry of biphenylene, it would be helpful to review the observed reactions of several polynuclear aromatic systems. The systems of most interest are the naphthalene system (A), with two fused rings and five formal double bonds; anthracene (B), with three fused rings and seven formal double bonds; acenaphthylene (C), with three fused rings and six formal double bonds, like the biphenylene system (D); and phenanthrene (E), with three fused rings and seven formal double bonds.



(A)



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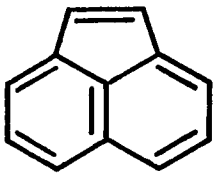

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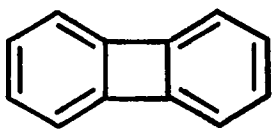

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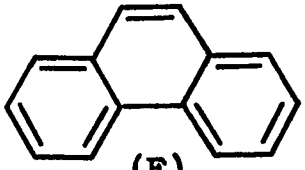


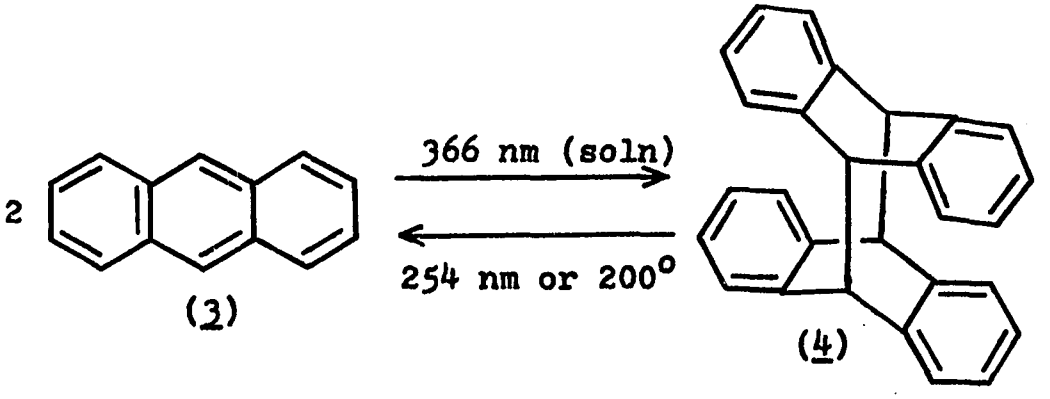
(E)

In general, the photodimerization of aromatic compounds depends on the formation of 1:1 complexes between excited and ground-state molecules of the monomer (hereafter referred to as excimers), and it has been generally accepted that the structure of the photodimer should reflect the preferred spacial orientation of the components in the excimer.[6]

There are two classes of photoreactions of aromatic compounds that this review will be concerned with: (1) photodimerizations, and (2) mixed photocycloaddition reactions. Since much work on the anthracene system appears in the literature,[7-12] what follows is only a summary of those points salient to the study of the biphenylene system.

B. Anthracene Photodimerization

It has been shown by Chandross that the photodimerization of anthracene in solution is a reversible reaction.[13]



(3) (4)

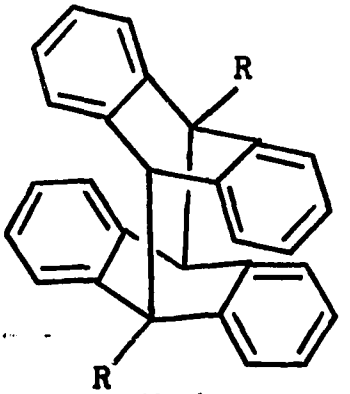
Using the technique of photolytic dissociation of photodimers of substituted anthracenes in glasses at 77°K., Chandross was able to produce pairs of parent anthracene molecules in close proximity. It was found that these photo-excited species exhibited fluorescence as well as having an absorption spectrum differing from that of the undissociated dimer. This was unusual because excimer fluorescence (under near-ultraviolet irradiation) had never been observed in solutions of anthracene and was also uncommon in substituted anthracenes.[10,11]

Two important facts should be noted at this point. First, photodimerization occurs at the 9,10-positions (meso) of the anthracene monomer; and secondly, the resulting dimer exists with the pairs of opposing aromatic rings not being parallel to one another.[14,15] The ability of the excited monomer to distort from planarity is apparently essential in those reactions where photodimerization is relatively facile.

It has been shown that substitution at the meso positions slows down the rate of dimerization, and that for many cases 9,10-disubstituted monomers fail to undergo reaction. For example, the reaction of 9-methylanthracene is slower than that of anthracene;[11] 9,10-dimethylanthracene does not react at all. The same results are observed for the corresponding cyano derivatives.[9] An explanation of these observations has been arrived at by a quantum-mechanical analysis. Results from extended Huckel M.O. calculations on distorted

molecules indicate that the free valence at the meso positions increases considerably in the first excited state.[16,17] Thus, factors which tend to decrease the ease of bending such as steric interaction of methyl groups with adjacent benzenoid hydrogens, and formation of partial double bond character, as a consequence of conjugation with an electron-withdrawing group (CN), will tend to inhibit the formation of the excimers that are required for photodimerization. A thorough discussion of these calculations is found in a paper by Burnelle, Lahiri, and Detrano.[12]

Anthracene and some of its derivatives undergo both relatively efficient dimerization and fluorescence.[18] All anthracene dimers formed in solution have been shown to have the head-to-tail stereochemistry as shown in 4a.[19]



(4a)

1. Photodimerization of 9-Anthroic Acid

It has been described that changes in substituents can produce changes in the rates of photodimerization in substituted anthracenes. Cowan and Schmiegel studied the photodimerization of 9-anthroic acid in ethanol and benzonitrile and the reaction of sodium 9-anthroate in water, deuterium oxide, and benzonitrile to learn more about the effects of the reaction medium on the rates of radiative and nonradiative processes.[20]

The observed overall rate for the photodimerization of anthroic acid is in accord with the steps described in Scheme I.

Scheme I. 9-Anthroic Acid Photodimerization

Process	Rate	Description	(Eq.)
$A + h\nu \longrightarrow A^s$	I_a	light absorption	(1)
$A^s \longrightarrow A + h\nu$	$k_f [A^s]$	fluorescence	(2)
$A^s \longrightarrow A$	$k_{IC} [A^s]$	internal conversion	(3)
$A^s \longrightarrow A^t$	$k_{ISC} [A^s]$	intersystem crossing	(4)
$A^s + A \longrightarrow D$	$k_{Dim} [A^s] [A]$	dimerization	(5)
$A^s + A \longrightarrow 2A$	$k_{CQ} [A^s] [A]$	conc'n quenching	(6)

$$1/\Phi_{Dim} = (k_{Dim} + k_{CQ})/k_{Dim} + \frac{[(k_f + k_{ISC} + k_{IC})/k_{Dim}]}{[A]} \quad (7)$$

They showed that in this case a plot of $1/\Phi_{Dim}$ vs. $1/[A]$ does not have an intercept of unity, concluding that concentration quenching reactions are very important in the overall photochemistry of this and, presumably, other anthracene compounds. The three major concentration-dependent deactivation mechanisms which would contribute to the overall lowering of Φ_{Dim}, as suggested by the authors, and which are applicable in general to photodimerizations are: (a) deactivation to the ground state via the triplet state through collisions with ground-state solute molecules; (b) formation of excimers followed by decay; and (c) formation of unstable covalently bonded dimeric species.

Concentration-assisted intersystem crossing can be measured (flash-photolytic triplet-counting methods), but this effect has not been conclusively demonstrated in the anthracene case, although it has been suggested.[21] If no new fluorescence band can be found in emission spectra, it is very difficult to distinguish excimer decay from unstable dimeric ground-state species.

Bowen and Tanner[7] and Cherkasov and Vember[22] proposed concentration quenching of anthracene involving the triplet state: $A^s + A \rightarrow A^t + A$. Livingston[23] suggested direct deactivation to the ground state: $A^s + A \rightarrow 2A$. Bowen[24] suggested, in a general review of the photochemistry of aromatic hydrocarbons in solution, that dimerization and concentration quenching are competitive processes involving

an excimer intermediate A^SA:

$$A^S + A \rightarrow A^SA.$$

$$A^SA \rightarrow A_2.$$

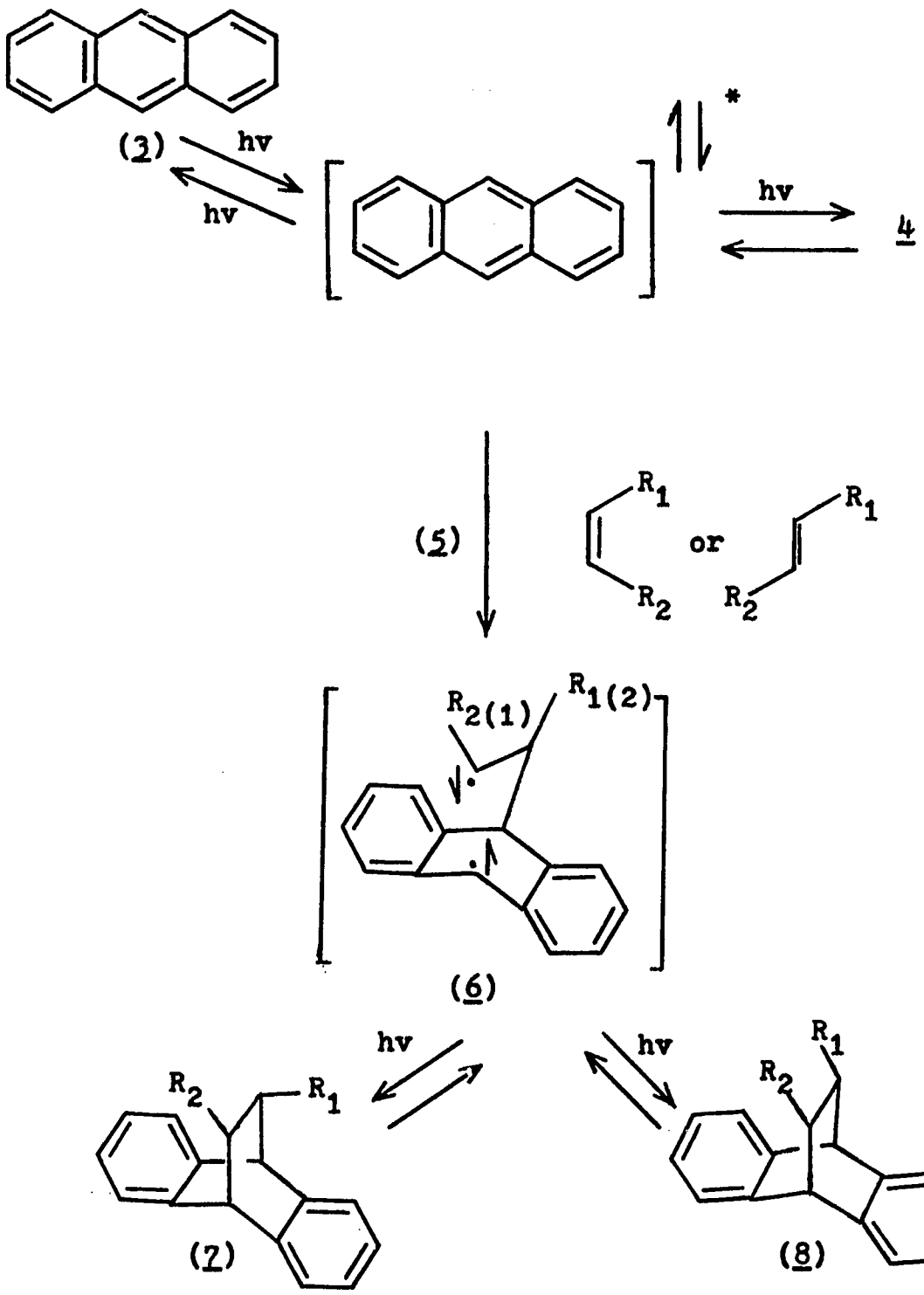
$$A^SA \rightarrow 2A.$$

Thus, the concentration quenching mechanisms have had different interpretations, all of which are subject to uncertainty due to the lack of direct measurements of second-order nonradiative decay. In the case discussed by Cowan and Schmiegel, the nonfluorescent excimer or unstable product alternatives were deemed most plausible.

C. Anthracene Photocycloadditions

Up to this point, only the ($4\pi + 4\pi$) dimerization reactions of anthracenes have been considered. It has been shown by Kaupp[25] that anthracene can also undergo photochemically induced cycloadditions to electron-deficient alkenes, via a ($4\pi + 2\pi$)-type of reaction. It was found that upon selective irradiation (above 330 nm) of anthracene in the presence of dimethylfurmarate and dimethylmaleate, the more stable trans-adduct (7) is formed as the principal product. In the case of more electron-rich olefins such as cyclopentene, cyclohexene, or stilbene, neither a quenching of anthracene fluorescence nor formation of adducts of type (7) or (8) as shown in Scheme II could be detected under standard conditions.

Scheme II



When $R_1 = R_2 = CO_2CH_3$; (7)/(8) = 98/2.

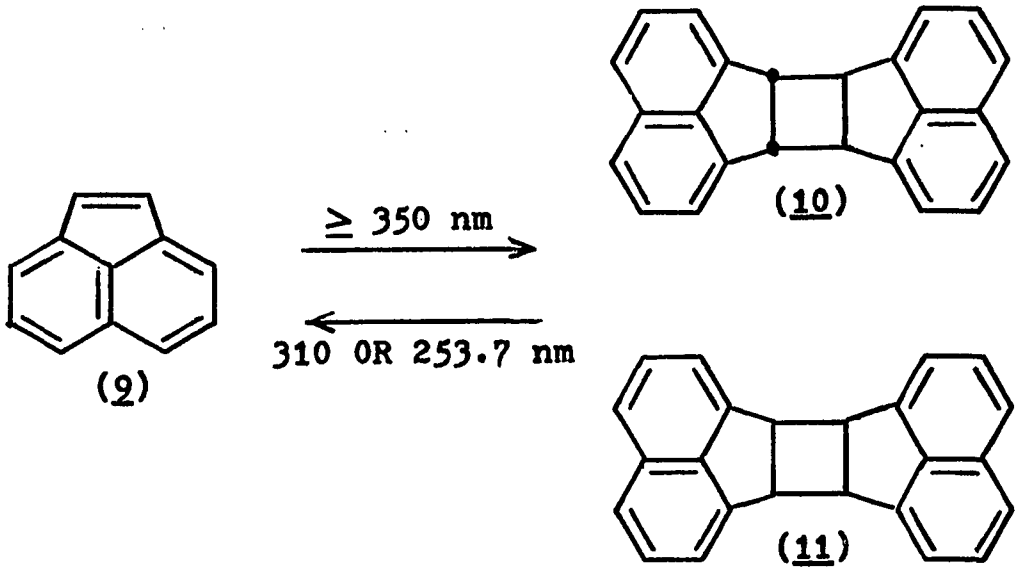
The singlet ($4\pi + 4\pi$)-dimerization of anthracene and its derivatives are interpreted by Kaupp as a symmetry allowed ($\pi 4_s + \pi 4_s$) reaction in which both new sigma bonds are formed simultaneously from an excimer with rehybridization at the four meso positions.

D. Acenaphthylene-Singlet and Triplet State Reactions

Thus far the importance of the photo-excited singlet-state in the reactions of aromatic hydrocarbons has been described. The case of the acenaphthylene system is, however, different. Although acenaphthylene undergoes both photodimerization and photo-addition reactions as does anthracene, acenaphthylene reacts by two photochemical pathways - the singlet state giving rise to one isomer; and the triplet state, which gives both isomers.

The photodimerization of acenaphthylene (9) was first reported in 1912 by Dziewonski and Rapalski[26] and was later studied quantitatively by Bowen and Marsh in 1947.[27] A more extensive study of the reaction was undertaken in the mid-1960's by Livingston and Wei.[28] It was found that in solution, the quantum yield for photodimerization increases with increasing concentration and is depressed by dissolved oxygen. Only the cis-dimer (11) is formed in oxygen-saturated solutions. In oxygen-free solutions, both dimers are formed; the trans-dimer (10) is the dominant species in dilute solutions and the cis-dimer dominates in concentrated solutions.

The dimers are efficiently photo-dissociated, reforming acenaphthylene. The quantum yield of the photo-dissociation was found to be independent of the concentrations of dimer or of oxygen.



(9) (10) (11)

1. Solvent and Heavy-Atom Effects

As was mentioned by Cowan and Drisko in 1966,[30] in their initial report on the solvent effect on the photodimerization of acenaphthylene, there had existed reports in the literature from as early as 1913, that the photodimerization in benzene solution produces the trans-cyclobutane isomer, while the same reaction performed in cyclohexane solution produces the cis-isomer.[26,27]

In 1970, Cowan and Drisko reported on their detailed study of solvent and heavy-atom effects on the photodimerization of acenaphthylene.[31] They found that the relative quantum yield of dimerization and the ratio of dimers (cis/

trans) depends linearly on the acenaphthylene concentration. The cis-dimer formation was found to be dominant in polar solvents and in the irradiation of concentrated solutions of acenaphthylene. Heavy-atom solvents, in small amounts, when admixed with solvents usually employed were found to increase the amount of trans-dimer and to reduce the amount of cis-dimer formed. Ferrocene and oxygen quench the triplet precursor of the trans-dimer but only slightly reduce the amount of cis-dimer formation. Cowan and Drisko suggest that their kinetic data is consistent with a mechanism involving two reactive species, a singlet excimer and an acenaphthylene triplet. The singlet excimer forms only cis-dimer and the triplet intermediate reacts to form both isomers (ratios depending upon solvent polarity).

2. Importance of Excimer

It is important to note that according to the above conclusions dimer formation via the excimer results only in the formation of the cis-dimer. Cowan and Drisko suggest that this is because of the geometrical requirements of maximum charge transfer and "exciton" interaction for excimer formation. The authors point out that Birks has shown that there is no solvent effect when only exciton-interactions are important, while others have observed a solvent effect on systems where charge-transfer interactions are important.[32]

The ability of heavy atoms to relax the forbidden transitions between singlet and triplet states has been known for some time in spectroscopy.[33] However, the effect of heavy atoms on the course of a photochemical reaction has only recently been studied in any detail, and has been observed only in a few cases: (1) the dimerization of acenaphthylene;[31,34] (2) the photocycloaddition of acrylonitrile to acenaphthylene;[35] (3) the Rhodamine B sensitized oxygenization of 2,5-dimethylfuran;[36] and recently (4) the photocycloaddition of maleic anhydride to acenaphthylene.[37]

E. Phenanthrene. Triplet Excimer Formation

Until recently, those reports appearing in the literature in which excited-state complexes (hereafter referred to as exciplexes) have been proposed to account for the observed kinetic results and observed changes in emission spectra, have advocated the intermediacy of a singlet-state species.[38-42] Forster[38a] found a change in the fluorescence spectrum that varied with the concentration of pyrene. The emission spectrum showed the presence of an isoemissive point which is indicative of two species in equilibrium; Chandra and Lim,[40] using Huckel-type M.O. calculations, were able to correlate the energy gap differences between selected states of the monomer and dimer (for a series of alternate hydrocarbons) with experimentally determined energy values from

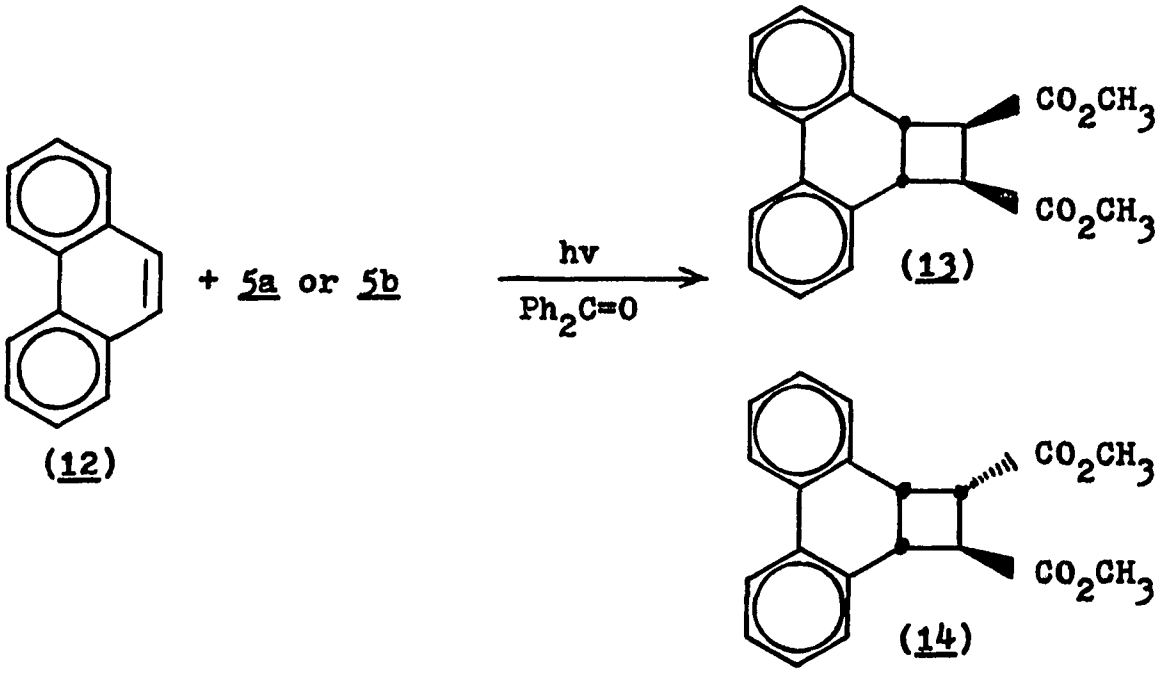
fluorescence measurements; Hammond,[41] studied the quenching of naphthalenes by conjugated dienes. These dienes, which in themselves can not function as classical electronic energy transfer species because they lack sufficiently low-lying excited states, were found to quench the fluorescence of the naphthalene compounds. This suggested to Hammond that there was the formation of a complex of the excited molecule and the quencher. This exciplex, in turn, undergoes rapid radiationless decay.

Other reports appearing in the literature inferred that their observations could only be due to a triplet exciplex,[43-47] although no measureable complex-phosphorescence could be detected in emission spectra. The presence of a triplet exciplex was suggested mainly by the correlation of kinetic results with proposed rate expressions in which a triplet intermediate is proposed.

More recently, Corey's work on the photoaddition of alkenes to cyclohexenone[48] suggests the intermediacy of a triplet exciplex. Such a species was proposed to account for (1) the observed orientational specificity of reactants, (2) the stereochemistry of photoaddition, and (3) the relative reactivity of different olefins with excited 2-cyclohexenone. Similarly, Kochevar's work on the quenching of butyrophenone triplets with alkenes[49] also suggests a triplet exciplex.

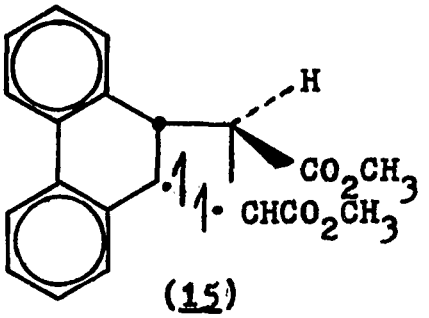
During the past few years Caldwell[50] used secondary deuterium isotope effects to distinguish excitation transfer and biradical formation in benzophenone-sensitized alkene isomerizations, and studied the benzophenone-sensitized photocycloaddition of phenanthrene (12) to electron-poor olefins.[51] The observed patterns of reactivity and stereoselectivity have been suggested by Caldwell as proof of a triplet exciplex intermediate.

Thus, the benzophenone-sensitized cycloaddition of 12 to dimethyl fumarate (5a) and maleate (5b) was shown to give rise to the photocycloadducts 13 and 14.[52]



(12) (13) (14)

Since the ratio of 14/13 (trans/cis) of 1.8 ± 0.05 was found to be independent of reaction time and of whether 5a or 5b was the reactant; and since the isomerization of 5a to 5b or of 5b to 5a was as low as 1.0% under the reaction conditions, Caldwell proposed the intermediacy of a triplet 1,4-biradical.[a,b]



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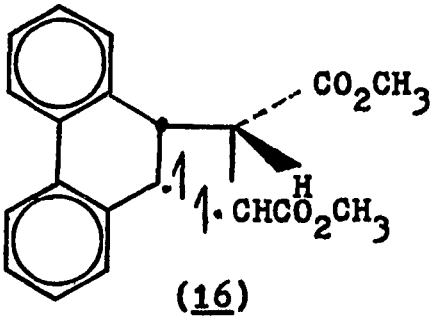

(16)

Two stereoisomeric biradicals, 15 of SR configuration and 16 of SS configuration (Cahn-Ingold-Prelog nomenclature) are possible. It can be seen that 15 can give rise to both 13 and 14, while 16 would give rise to only 14 and the isomeric cis-endo-diester; the latter was shown to be absent within experimental error (± 3%).

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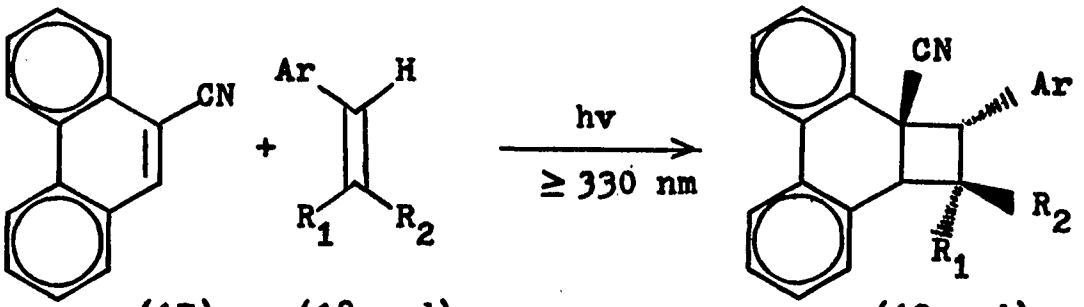
a. Quantum yield studies showed that triplet Phenanthrene and not triplet 5a was the reactive species.

b. An analogous intermediate had been proposed in other triplet-state photocycloadditions.[31,48-50,54]

1. Exciplex Emission

Early in 1974, Caldwell reported (private communication) that he had observed exciplex emission and efficient, stereospecific ($2\pi + 2\pi$) photocycloaddition simultaneously. Up to this time, exciplex emission had been observed only twice in a (2+2) photocycloaddition system. Farid[55] and Kaupp[56] both had studied the photocycloaddition of phenanthrene to dimethyl maleate and fumarate. Farid found that the fumarate quenched the fluorescence of phenanthrene and produced a new emission band (λ_{max} 450 nm in C_6H_6). Kaupp correlated luminescence measurements and kinetic rate expressions to derive a two-step singlet mechanism. Similarly, Taylor[57] measured luminescence from the 1-cyanonaphthalene:1,2-dimethylcyclopentene exciplex, but did not report any products. Quenching experiments revealed the presence of a singlet intermediate as evidenced by an isoemissive point in the emission spectrum.

Thus, irradiation of 9-cyanophenanthrene (17), in the presence of trans-β-methylstyrene (18a), trans- or cis-anethole (18b,c), or 1-anisyl-2-methylpropene (18d) was found to give rise to the cycloadducts 19a-d :



(17) (18 a-d) (19 a-d)

It was found that upon addition of the styrenes to a solution of 17, the fluorescence of 17 was quenched and a new long-wavelength emission was observed. In the case of the methoxystyrenes (18b-d), an isoemissive point occurred. Since the new emissions were absent in the fluorescence spectra of the methoxystyrenes and the Stern-Volmer plots from quenching experiments were linear, Caldwell assigned the new emissions to 1:1 exciplexes of 17 with the three methoxystyrenes. Also, through quenching experiments, it was proven that exciplex formation precedes cycloaddition. Either exciplex formation or cycloaddition could account for quenching of singlet 17 by 18b. The exciplex emission was found to be sharply attenuated by dimethyl acetylene-dicarboxylate (DMA). The quenching was found to be due to the interaction of DMA with the exciplex.

2. Factors Influencing Rate of Cycloaddition

Caldwell's work thus suggests that there are two important factors to be considered which influence the rate of photocycloadditions. There must be considered those factors which effect the initial rate of chromophore interaction, and those aspects which influence the rates of reactions of exciplexes (emission, collapse to cycloadducts, and collapse to the component cycloaddends).

When steric hindrance is absent; when the exciplex

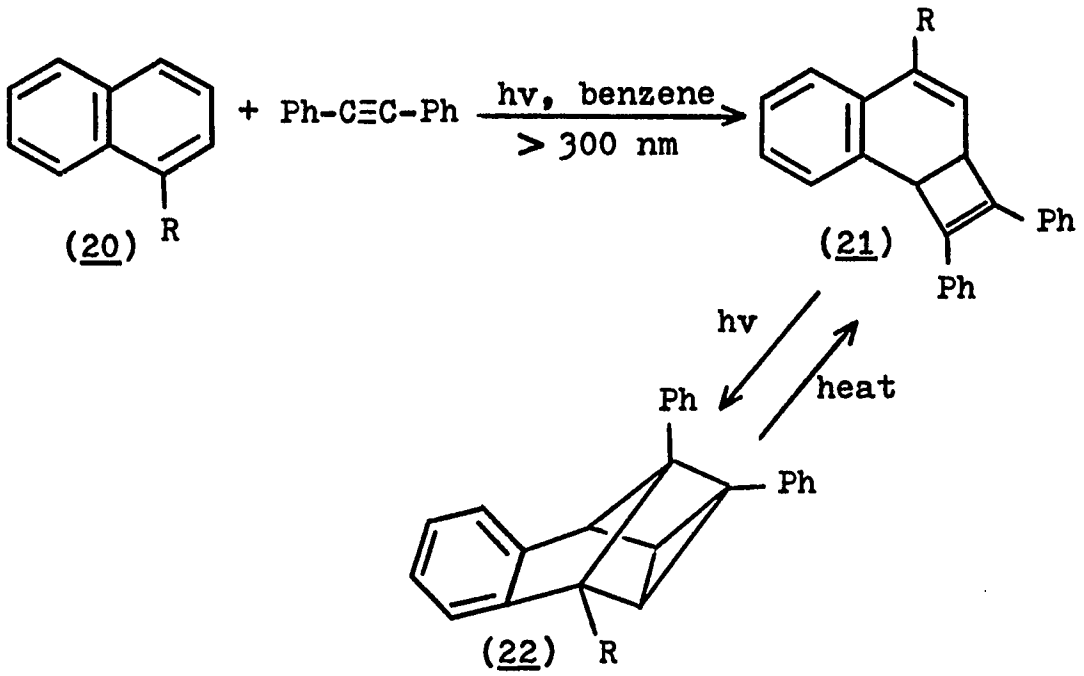
geometry is favorable; and when the exciplex binding is relatively strong, the collapse to cycloadduct should be expected to be fairly efficient.

The actual lifetimes of such exciplexes have not been measured as of now. However, Caldwell has estimated such lifetimes by measuring the effect of air saturation on fluorescence intensity. Thus, if one assumes diffusion-controlled oxygen quenching, an estimate of 11 nanoseconds for the 17:18b exciplex and 36 nanoseconds for 17:18d can be obtained.

F. Naphthalene

Unlike the previously cited cases, the photochemistry of naphthalene and its derivatives has led to more questions than to concrete answers.

The recent work of Sasse[58] on the photocycloaddition of diphenylacetylene (DPA) with alkoxynaphthalenes is a good example of the problems encountered. It was found that irradiation of 1-methoxy-, 1-ethoxy-, and 1-isopropoxy-naphthylene (20 a-c), in the presence of DPA gave rise to adducts 21a,b and 22 a-c; less than 1% yields of the adducts derived from addition to the unsubstituted ring were found. In addition, no dimers were formed in the absence of DPA.



(a) R = OMe (b) R = OEt (c) R = OPr^{iso}

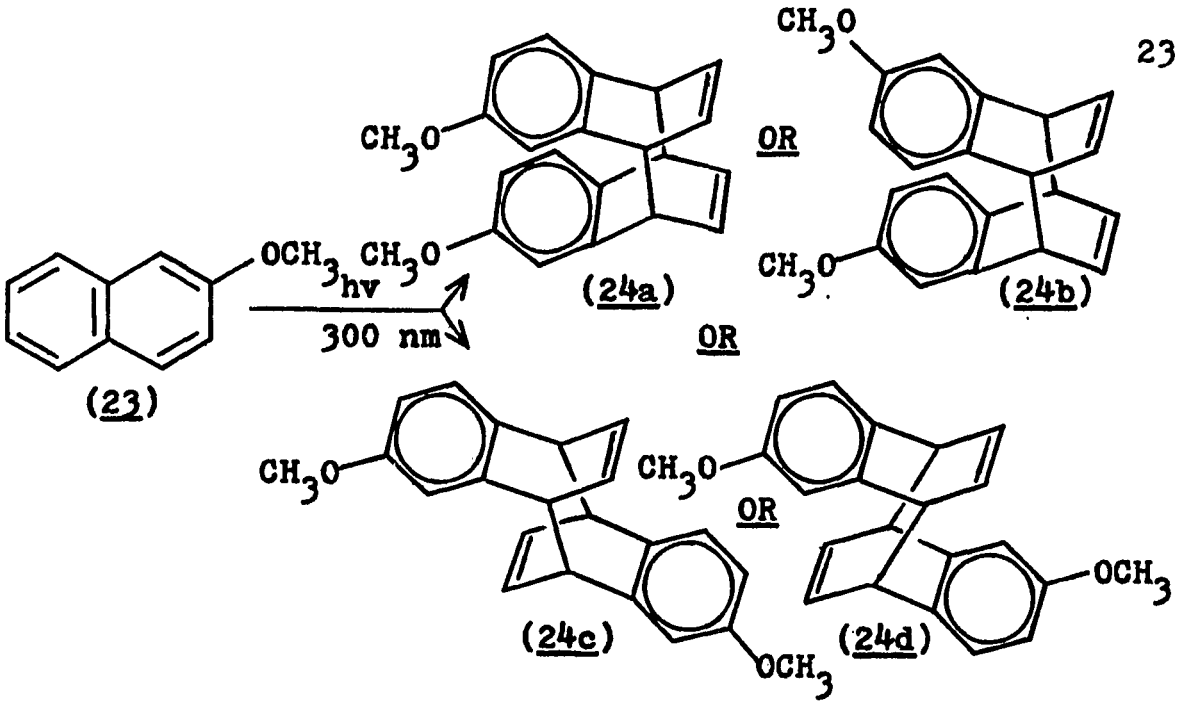
In striking contrast to the above results, the corresponding 2-alkoxynaphthalenes did not react detectably with DPA upon similar irradiation conditions. These results tend to suggest that the failure of the 2-alkoxy derivatives to form DPA photoadducts might be due to their ability to form photodimers. However, even in the presence of a five-fold molar excess of the naphthalenes, no more than ca. 50% yield of photodimer could be isolated. This excess of the naphthalenes, then, should have been sufficient to form detectable amounts of the DPA photoadducts. In contrast to the results with 2-alkoxy derivatives, 2-t-butylnaphthalene does form an adduct, but with DPA adding to the unsubstituted ring.

Thus, it was concluded by Sasse that the lack of reactivity of the 2-alkoxynaphthalenes in the DPA photoaddition is not caused by competing photodimerization or by the steric requirements of the substituent. Sasse, therefore, suggests that dimerization *via* formation of an excimer of 2-alkoxynaphthalene in its first excited singlet-state is favored to the exclusion of exciplex formation with DPA. This is consistent with the result that DPA does not quench the fluorescence of 2-isopropoxynaphthalene.

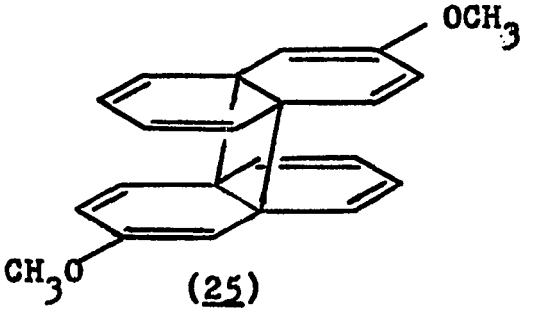
Investigation of the photodimerization of alkoxynaphthalenes has, in addition, led to conflicting evidence as to the structure of the photodimers.

1. Substituent Effects on Photodimerization

It was found that irradiation of 2-methoxynaphthalene (23) in a variety of solvents gave rise to a photodimer.[59] However, irradiation under identical conditions of 1-methoxy-, as well as 1- or 2-methyl-, hydroxyl-, bromo-, and aminonaphthalene derivatives failed to produce photodimers. Benzophenone was found to efficiently quench the formation of the 2-methoxy dimer. Spectral data indicated that the dimer was formed by a 1,4-1'4' dimerization of the unsubstituted ring.



In the first report on X-ray measurements of a single crystal of dimeric 2-methoxynaphthalene,[61] Selinger showed that the above structures 24 a-d can be ruled out and the centro-symmetric structure 25 was suggested instead.

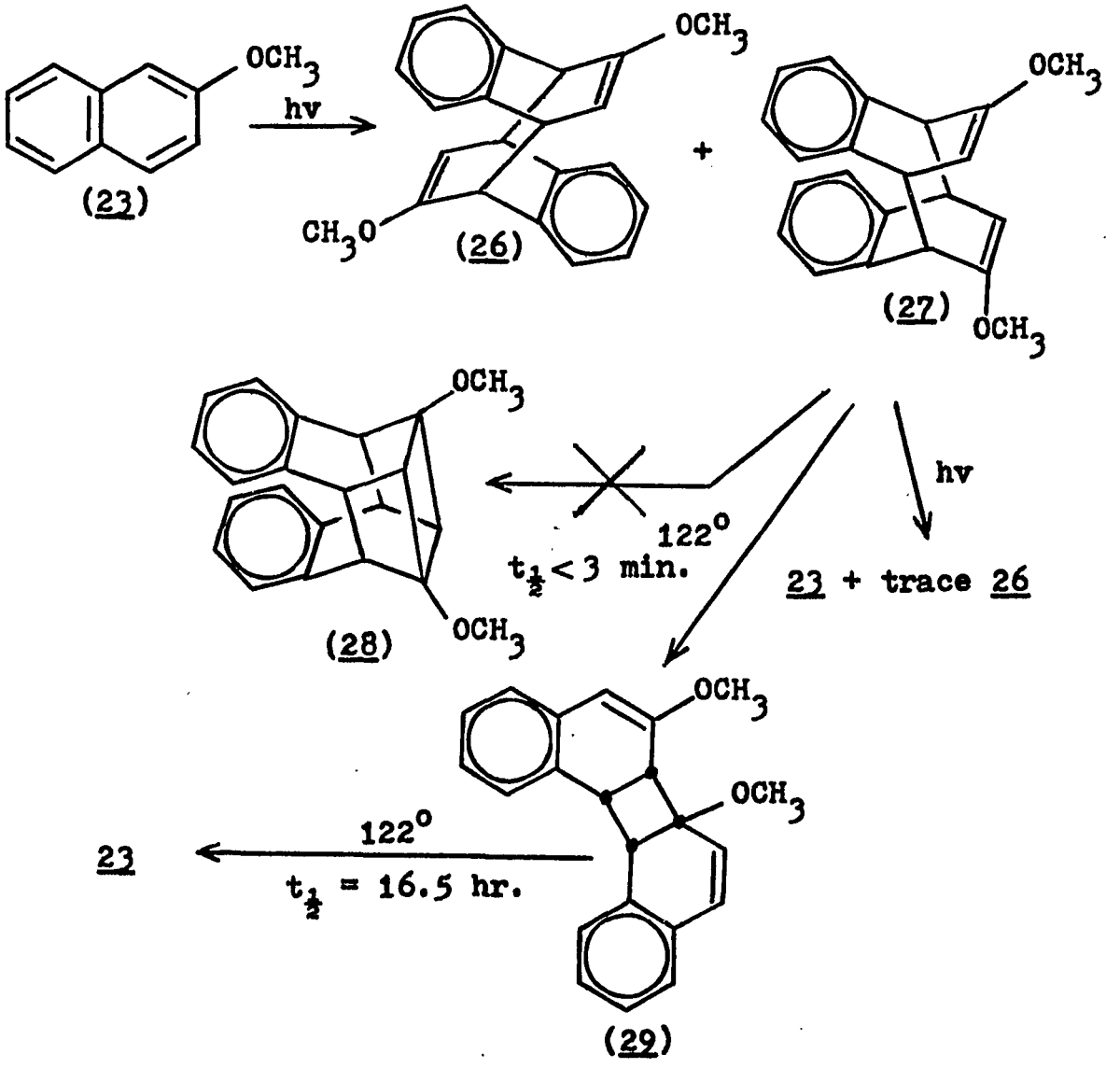


But, in a more recent report[60] the same investigators, using a more detailed X-ray structure analysis of 2-methoxy-naphthalene photodimer showed that the two halves of the dimer are linked in the 1,4-1',4' positions of the substituted rings in an anti-trans-configuration (26); this isomer also has a center of symmetry. The difficulties encountered in

the assignment of structure to this compound were due to its dissociation ability.

To further add to the complexity of the problem, Sasse has more recently reported[62] that the syn-trans-dimer (27) is also formed on irradiation of 2-methoxynaphthalene, but in much lower yields. The currently proposed pathway for the photodimerization of 2-methoxynaphthalene is shown in Scheme III.

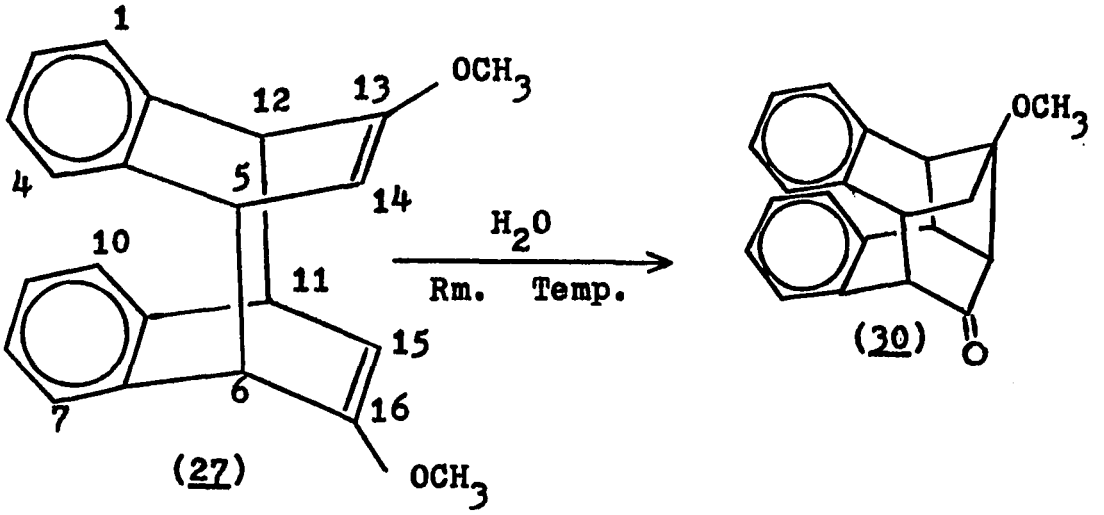
Scheme III. Photodimerization of 2-Methoxynaphthalene



2. Correlation of Kinetics with Rates of Observed Product Formation

Selinger[63] had tried to correlate the kinetics of the formation of the anti-trans-dimer (26) with the excimer fluorescence of 2-methoxynaphthalene, but was not successful. Sasse suggests that the existence of a second photodimer of 2-methoxynaphthalene may account for this unsuccessful correlation attempt.

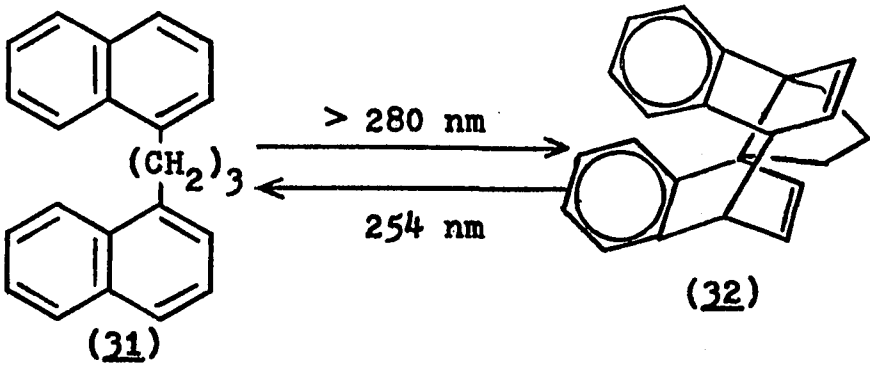
The structure of the syn-trans-dimer (27) was assigned as a result of the isolation of the ketone 30 which is formed on hydrolysis of 27. The structure of 30 rests in the interpretation of nmr data from contact-shift-reagent experiments as well as chemical degradation to identifiable products.



3. Proof of Structure - NMR[a]

The structure of 27 was suggested by its nmr spectrum which shows a slightly broadened singlet at 6.68 (8H); a singlet at 3.58 corresponding to two methoxy groups; and three doublets-of-doublets, each representing two protons: 3.60 (H-6 and H-12); 3.74 (H-5 and H-11); and 5.27 (H-14 and H-15).

These nmr assignments are similar to those made for the corresponding protons in the photodimer of 1,3-bis-(1-naphthyl)-propane (31), prepared by Chandross.[64]



(31) (32)

NMR correlation of structure 32: multiplet at 3.7 (1H, methinyl); unsymmetrical doublet at 6.1, 6.36 (vinyl); and a multiplet at 6.5-6.9 (8H, aromatic).

Thus, Sasse suggests that the assignment of structure 27 to the minor photodimer of 2-methoxynaphthalene seems to be justified.

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a. Throughout this thesis, nmr values will be reported in (δ) units of ppm downfield from tetramethylsilane.

To review, there have been several reports of the photodimerization of 2-substituted naphthalenes. Proof of the structure of the products was initially assigned based on interpretation of ir, uv, and nmr spectra, but such data by itself led to differing assignments of structure. The only fool-proof method of determination of structure is a complete and accurate X-ray study.

In Chart I, is found a summary of the evidence reported to justify various assigned structures of the photodimer of 2-methoxynaphthalene. From the evidence available in the literature, and presented in Chart I, it is very difficult to correlate the structures proposed for the syn- and anti-photodimers of 2-methoxynaphthalene with nmr parameters. All reports appearing in the literature since 1970 rely on the communication of Selinger[60] which provides only X-ray data for a proof of structure. There is no report of ir, uv, or nmr data to correlate with their determination that the two halves of the dimer molecule are linked in the 1,4-1',4'-positions of the substituted rings in an anti-configuration. For instance, if one had available the spectral data of pure syn- and pure anti-photodimers, one could possible correlate the difference in structure to the position of the vinyl protons relative to the ring-current effects of the aromatic ring. This would be the case since there should be a pronounced effect due to the shielding effect by π-electrons of

Chart I. Proposed Structure of 2-methoxynapthalene Photodimer

Spectral Characteristics of Photodimer

Mode of Dimerization	IR (cm^{-1})	UV λ_{max} nm. (ϵ)	NMR ($CDCl_3$) δ ppm	X-Ray	Ref.
1,4-1',4' syn or anti unsubstituted ring	(3010,3040,1650)[a] 1420-1470,1330-1340,1270,1170-1200,1140-1150, 775-780,750-755	(methanol) 223 (8400) 275 (1600) 282.5 (1800) b	c	d	59
1,4-1',4' syn or anti unsubstituted ring	d	263 (4500) 273 (4800) 283 (3500)	5.7 (vinyl protons)[e]	suggests trans configuration	63
9,10-9',10' anti	1650,1280,1210, 1150,1010,770 and 785.	232 273 (2900) 283 (3500) f	3.75(methoxy) 5.70(2H,s)[g] 6.0-7.1(olefin)	space group $P2_1/c$ (No. 14) centosymmetric	61
1,4-1',4' syn[h] and anti substituted ring	d	(isooctane) 235 (6400) 260 (1110) 268 (1000) 282 (1070) 289 (1260) i,j	6.68(8H,aromatic) 3.58(methoxy) 3.60,3.74(-CH) 5.27(vinyl)	d	62

Chart I. continued - footnotes

a. Such bands have been attributed, respectively, to the C-H and C=C stretching modes of cis-olefins.[66]

b. There is a similarity between the spectra of the dimer and o-xylene, with a distinct bathochromic shift attributed to the methoxy groups. Such similarity in the ultraviolet spectra of dianthracene and o-xylene has also been reported by Coulson and has been used to conclude that dianthracene has the structure formed by bonding the meso atoms of two anthracene molecules.[67]

c. Owing to a complete insolubility in almost all solvents, attempts to establish the structure of the photodimer more rigorously were not successful.

d. Not determined or reported.

e. Suggests that the vinyl proton is not adjacent to the methoxy group and that the methoxy group is in the aromatic ring.

f. This spectrum is not unlike that observed for 9,10-ethano-9,10-dihydronaphthalene.[68]

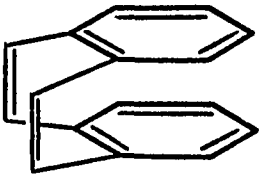
g. Claimed that deuteration studies showed that this absorption was due to the 1- and 1'-protons.

h. Ratio of isolated anti/syn = 6.

i. Refers only to the syn-dimer.

j. The uv spectrum reveals considerable interaction between the two vinyl ether moieties.[69]

the overlapping aromatic ring in the case of the syn-dimer. As an example of this effect, the nmr spectrum of dibenzocyclooctatetraene (33), presumed by Cava to have the syn-configuration, shows the aromatic protons shifted upfield to 7.08,[70] compared to the unshielded aromatic protons of anti-dibenzotricyclooctadiene (34), at 7.28.[71]



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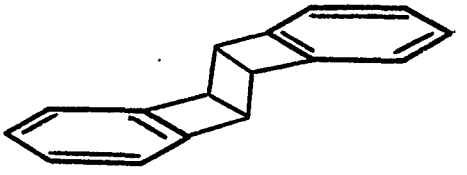
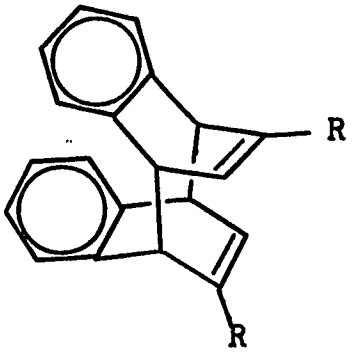


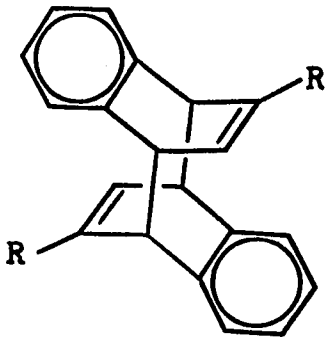
(34)

If the assignment of structures 26 and 27 to the anti- and syn-photodimers (respectively) of 2-methoxynaphthalene are accurate, then there should be a similar correspondence in the nmr spectrum relative to the above example. Unfortunately their spectra were not determined or made available, nor was an X-ray study performed at the time of this writing.

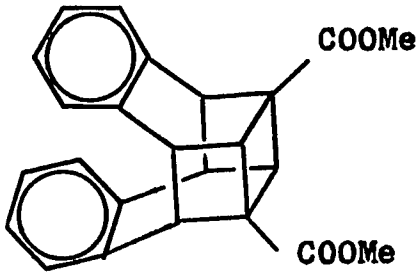
To summarize, although earlier reports on the structure of substituted naphthalene photodimers were conflicting, the latest view is that 2-alkoxynaphthalenes form photodimers Type I and Type II. In addition, it has been recently confirmed by X-ray,[72] nmr, and chemical studies that the related methyl naphthalene-2-carboxylate (35) forms the caged photodimer 36.[73]



Type II



Type I



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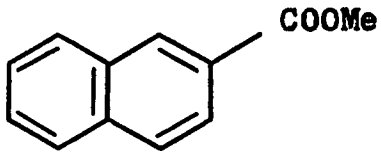


(35)

G. Biphenylene

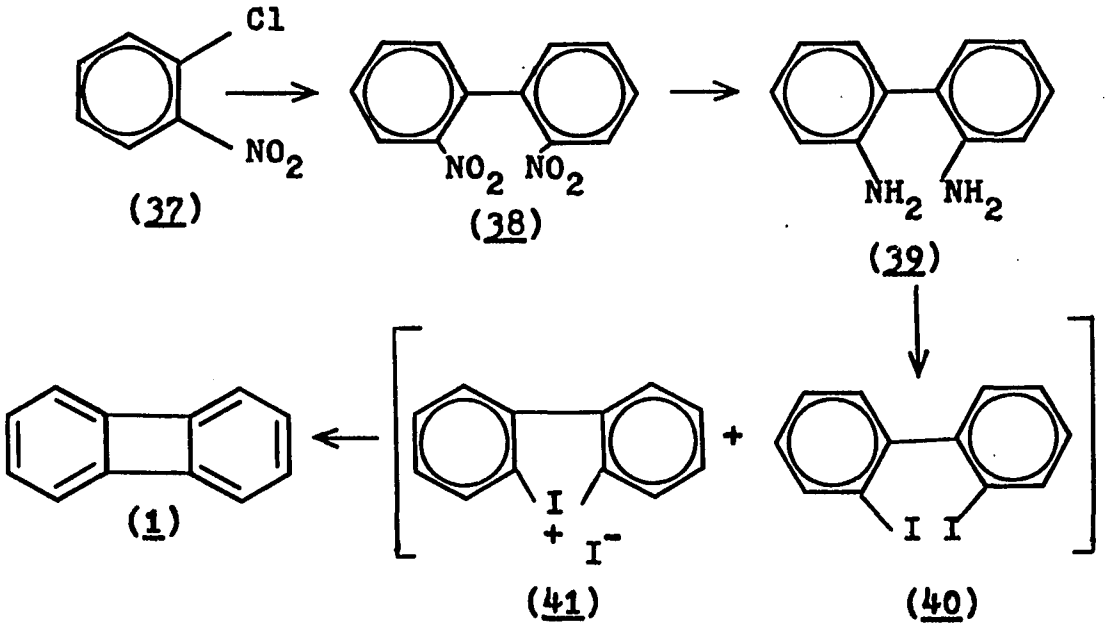
As can be seen, much work has been done on the photochemistry of the previously mentioned polynuclear aromatic hydrocarbons. Another interesting fused aromatic system is that of biphenylene. Much work appears in the literature on the syntheses of substituted biphenylenes, but little is known about the photochemistry of biphenylene or its derivatives.

It was due to this lack of information that an investigation into the photochemistry of biphenylenes was undertaken. The results of this work are presented as an introduction to the problem of understanding the primary photochemical reactions of a theoretically interesting molecule.

1. Syntheses from Biphenyls

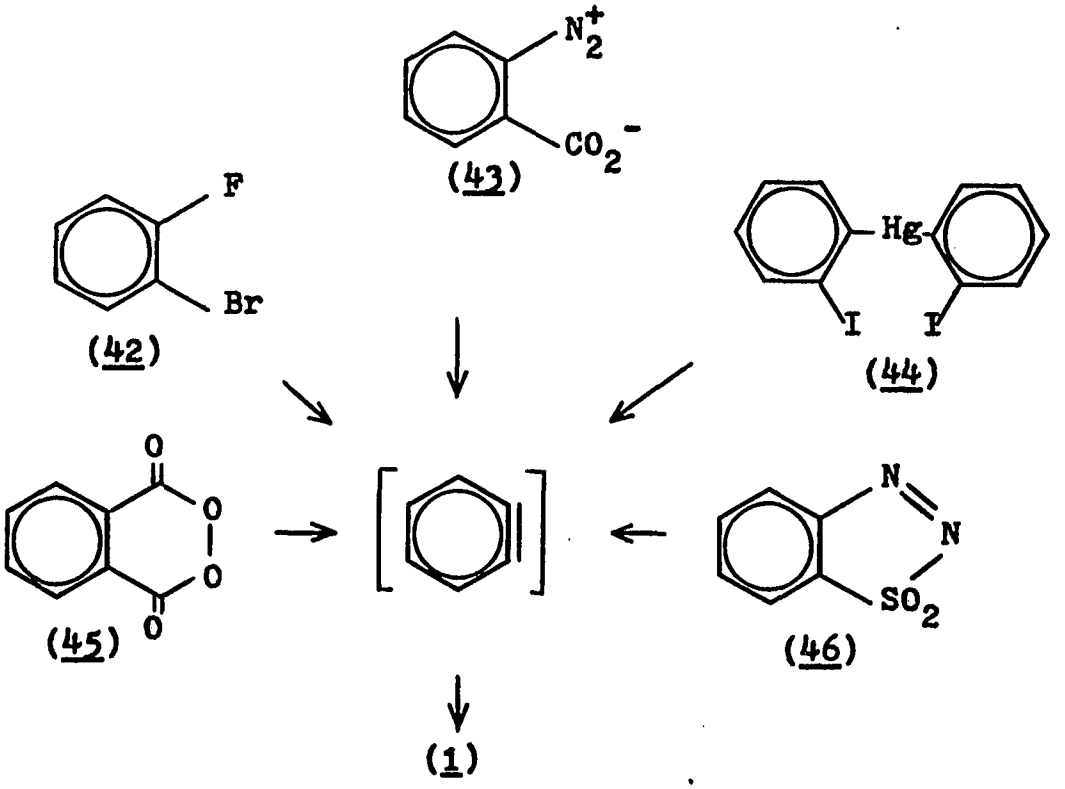
Biphenylene (1) was first successfully synthesized by Lothrop[74] in 1941 by heating 2,2'-dihalobiphenyls with cuprous oxide at 350°. Diiodobiphenyl has been converted into biphenylene in about 20% yield, using the Lothrop method.[75] It has been shown that the yields of this type of reaction depend on the state of the cuprous oxide used.[76]

An example of the Lothrop method is shown with the conversion of o-nitrochlorobenzene (37) into 2,2'-dinitrobiphenyl (38) by means of the Ullmann reaction, followed by reduction of the nitro compound to 2,2'-diaminobiphenyl (39). Tetraazotization of the diamine, followed by reaction with potassium iodide, gives a mixture of 2,2'-diiodobiphenyl (40) and biphenyleneiodonium iodide (41), which when reacted with cuprous oxide yield biphenylene.



2. Benzyne Pathways

Biphenylene has also been obtained by the dimerization of benzyne. The dehalogenation of o-fluorobromobenzene (42) with lithium amalgam in ether gave rise to biphenylene in 24% yield.[77] Different combinations of halogen and diffreent metals have produced biphenylene in yields lower than 10%.[78] Flash photolysis of solid o-benzenediazonium carboxylate (43) generates benzyne which rapidly dimerizes to biphenylene.[79] Biphenylene has also been generated by the high temperature pyrolysis of bis-(o-iodophenyl)mercury (44) and phthaloyl peroxide (45) in yields of 54% and 27%, respectively.[80] Pyrolysis of 1,2,3-benzothiadiazole-1,1-dioxide (46) in the presence of nitrous oxide has been shown to give rise to biphenylene in 52% yield, along with small amounts of 2-nitro-biphenylene.[81]



Biphenylene is also obtained in good yield (25-30%) by the rapid decomposition of benzenediazonium-2-carboxylate in ethylene chloride, followed by co-distillation of biphenylene with ethylene glycol (Friedman Method).[82]

Oxidation of 1-aminobenzotriazole with lead tetra-acetate in benzene solution produces benzyne, which in the absence of a trapping agent gives biphenylene in 83% yield.[83]

Substituted biphylenes have also been prepared by treatment of substituted o-dihalobenzenes with dehalogenation reagents.[84] A modification of the Ullmann reaction has been employed by Corbett and Holt in the synthesis of substituted biphenylenes.[85]

In addition, electrophilic substitution and transformation of functional groups has led to the isolation of many interesting biphenylene derivatives.[86-92]

3. Physical Properties

Biphenylene, $C_{12}H_8$, MW=152.18, forms pale yellow prisms, m.p. 110-111°. It sublimes, can be steam-distilled, and forms crystalline complexes with picric acid (m.p. 122°),[74,84b,95] trinitrofluorenone (m.p. 154°, dec.),[75a] and with trinitrobenzene (m.p. 127-128°).[80] Biphenylene is air-stable and is not readily decomposed by heat.

a. Ultraviolet Spectrum

The uv spectrum of biphenylene consists of two sets of bands.[96] The more intense absorption occurs at 235-260 nm., while the weaker is at 330-370 nm.

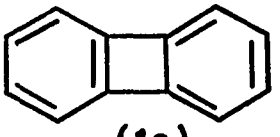
4. Chemistry of Biphenylene

Before attempting to understand the photochemistry of biphenylene, it would be instructive to review what is known about the chemistry of this molecule and the correlation of chemical behavior with predictions from theoretical chemistry.

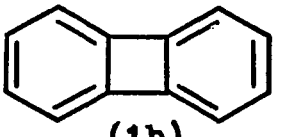
Theoretical calculations have led to results which predict that all reactions involving substitution into the ring, nucleophilic, electrophilic, and free radical, should occur exclusively at the 2-position.[93]

In the valence-bond approach, the five canonical structures in Chart II are considered. If the two cyclobutadienoid forms (1 d and e) are neglected, the results are close to that from a Huckel M.O. calculation, and the predicted bond lengths are similar to those observed and are shown in Table I.

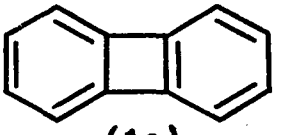
Chart II. Biphenylene Resonance Canonical Forms.



(1a)



(1b)



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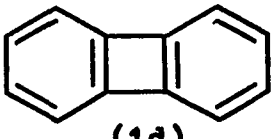
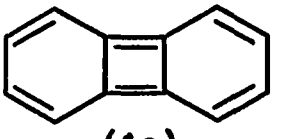


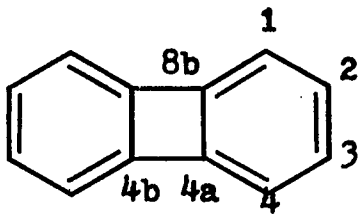
(1d)



(1e)

Table I. Biphenylene Bond Lengths

Bond	Cal'd Bond Length (A) Resonance Theory (without 1d,e)	M.O. Theory	Measured[128] (X-ray diffraction)
1,2	1.43	1.40	1.43
2,3	1.37	1.38	1.37
4,4a	1.37	1.38	1.37
4a,4b	1.54	1.47	1.52
4a,8b	1.43	1.41	1.43



a. Electrophilic Substitution

Biphenylene has been shown to undergo electrophilic substitution in fair yields and always at the 2-position, in accord with theory. Further electrophilic reaction of 2-substituted biphenylenes gives rise to substitution in the 3-position as the result of the directive action of electron-donating groups, and in the 6-position by direction from electron-withdrawing groups.

b. Nucleophilic Substitution

There have been no reported nucleophilic substitutions of biphenylene to compare with theoretical predictions.

c. Free-radical Substitution

Biphenylene is very resistant to free-radical attack: (i) bromination by N-bromosuccinimide fails to occur, and (ii) reaction with lead tetraacetate gives the 2-acetoxy compound in very poor yield (1.5%).[75a]

III. DISCUSSION OF RESULTS

A. Sources of Biphenylene

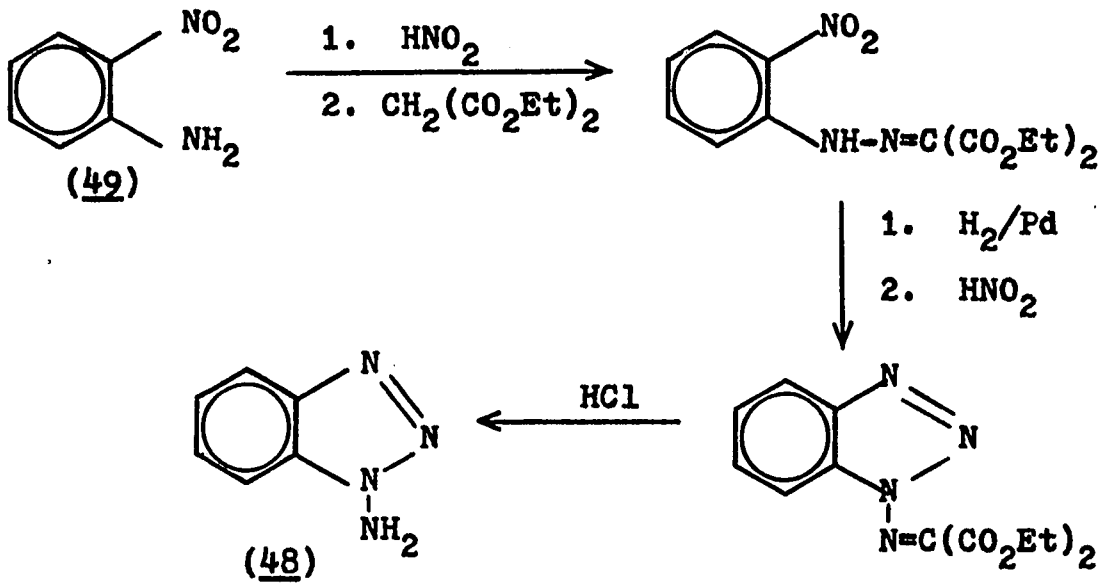
There are many methods available for the preparation of biphenylene. For the preparation of large quantaties, the method of Friedman[82] was used. The second method employed during the course of this research was that of Rees.[83]

Although Friedman's method involved the dangerous, controlled decomposition of benzenediazonium-2-carboxylate, this procedure was deemed more workable because of the commercial availability of the precursor, anthranilic acid.

According to Rees,[98] oxidation of 1-aminobenzotriazole (48) gives biphenylene in 83% yield and this would appear to be a safer and better method, but attempts at repeating the Rees' preparation of 48 by direct 1-amination of 1-H-benzotriazole (47), a commercially available material, were not successful.

It was later established in private communication with other investigators (L. Friedman and M. Jones, Jr.) that they too were having difficulties in duplicating this direct amination procedure of Rees', using hydroxylamine-O-sulfonic acid. Because direct amination seemed the most feasible and least time-consuming method for the preparation of 48, an investigation was undertaken into other methods of N-amination of 1-H-benzotriazole. The alternative to direct amination would be the known[97] synthesis of 48 from o-nitroaniline (49) as shown in Scheme IV.

Scheme IV. Synthesis of 1-Aminobenzotriazole



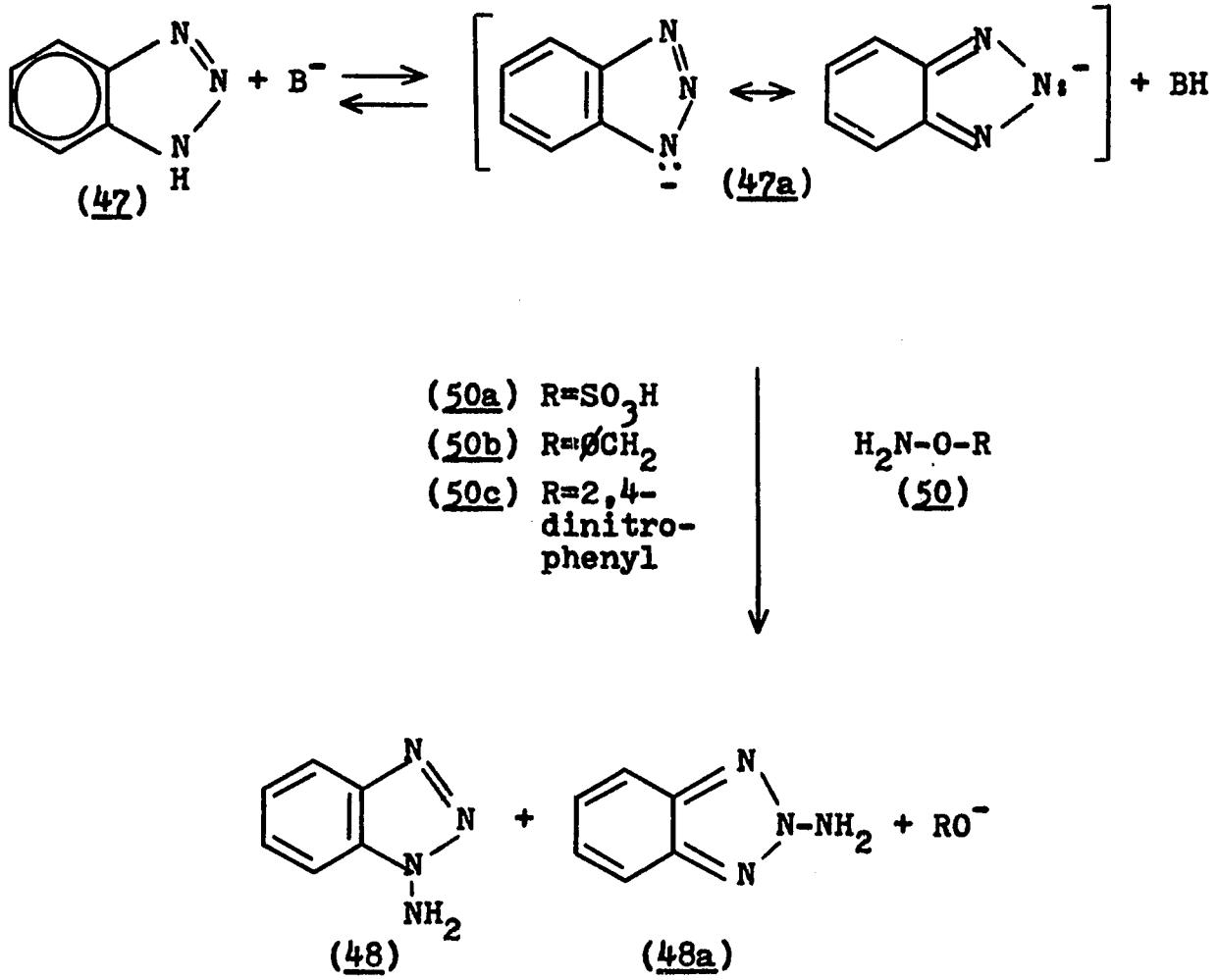
This preparation was repeated, and the product found to give biphenylene as described by Rees, but the procedure is too long to be convenient.

1. Attempted New Routes to 1-Aminobenzotriazole

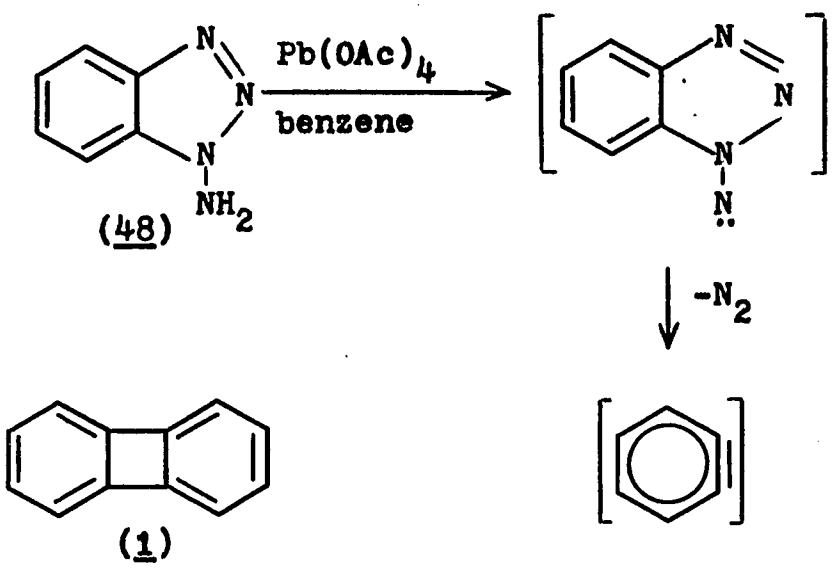
a. Direct N-Amination of Benzotriazole

Two methods were chosen for the synthesis of 48 from benzotriazole, a commercially available compound. The first involved direct amination by generation of anion 47a, followed by a nucleophilic attack on an aminating reagent, 50, possessing a good leaving group. This type of reaction is summarized in Scheme V.

Scheme V. N-Amination of Benzotriazole



From the structure of the anion it would appear that amination could take place at either the 1- or 2-position (statistically, 1-amination is favored). This could be tolerated, nevertheless, as the compounds are separable by chromatography.[98] The assumed intermediates in the formation of biphenylene from 1-aminobenzotriazole are shown:



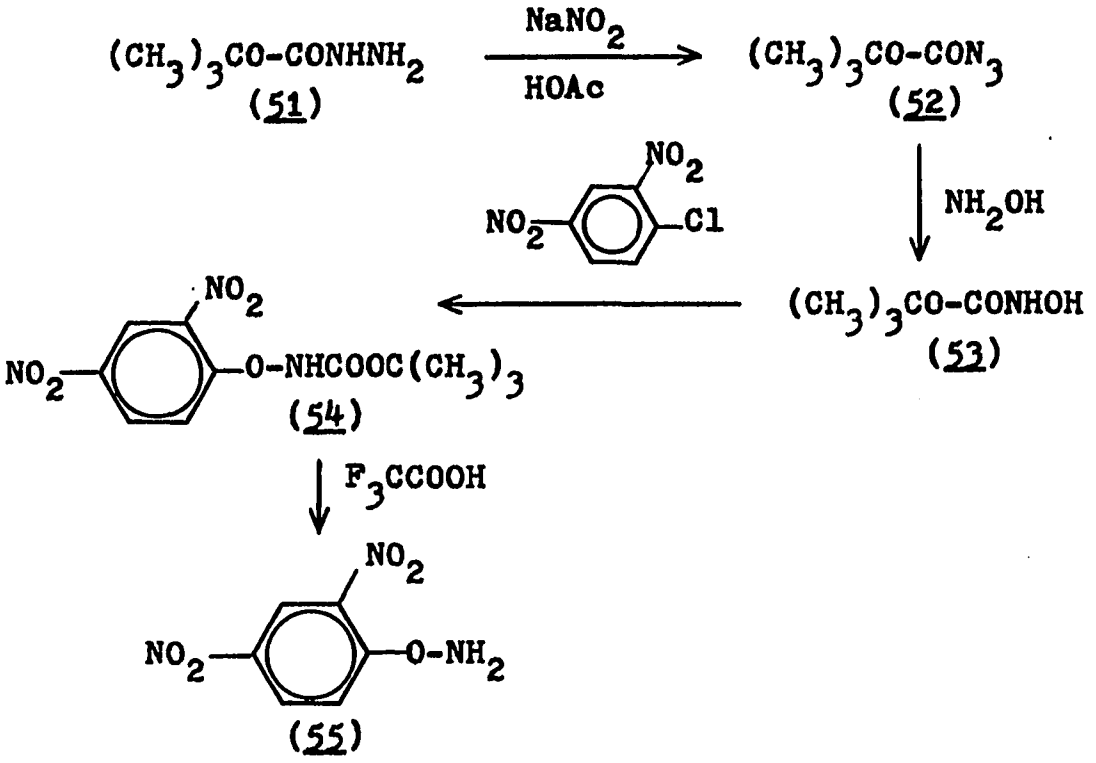
(48)

(1)

Initial experiments were conducted with the idea of isolating the solid sodium salt of the anion of 1-H-benzotriazole. It was discovered that isolation of the pure salt in air was not feasible due to its hygroscopic nature (forming a mixture of 1- and 2-H-benzotriazole upon protonation, as shown by nmr spectroscopy).

Therefore, the anion was generated *in situ* in the presence of a large excess of the aminating reagent. Thus, a solution of benzotriazole in benzene was added to a mixture of O-benzylhydroxylamine (50b) hydrochloride (commercially available) and two equivalents of sodium hydride in benzene and dioxane under an inert atmosphere. However, after separation of the resulting mixture into its various components (acidic, alkaline and neutral), no 1-aminobenzotriazole could be found (spectral and chromatographic comparison with authentic material).

The last attempt at direct amination employed a reagent with a more stabilized leaving group than the two previously used. The amination was performed using O-(2,4-dinitrophenyl)-hydroxylamine (55), described by Sheradsky,[99] and prepared as shown:



In this procedure, the sodium salt of benzotriazole was made by reaction with a freshly prepared solution of sodium methoxide, the methanol removed and replaced by DMF. An equivalent amount of the solid aminating reagent 55 was then added to the DMF solution at room temperature as described by Sheradsky for imides, sulfonamides, and pyrroles. When the reaction was worked up in the usual manner, no 1-amino-benzotriazole could be shown to be present (spectral and

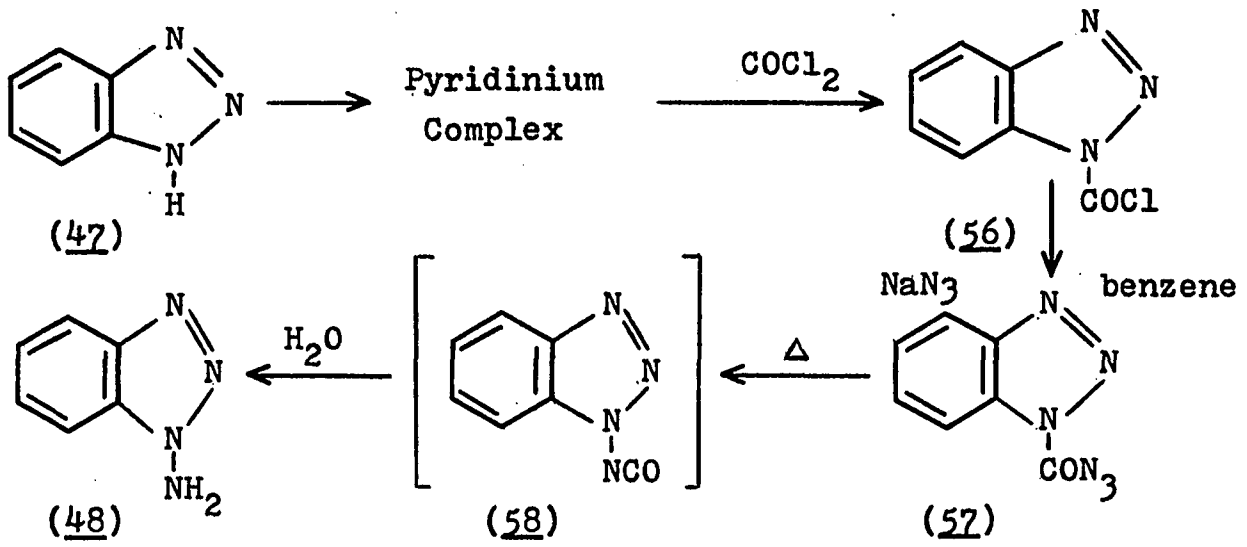
chromatographic comparison to authentic material). Thus, after failure with three aminating agents, this direct procedure was abandoned as a source of 1-aminobenzotriazole. It is suggested here that the benzotriazole anion is simply deprotonating the various aminating reagents more rapidly than acting as a nucleophile. This parallels the reaction of 1-chlorobenzotriazole[100] with sodium amide to give benzotriazole rather than the aminated benzotriazole.

b. Via Curtius Rearrangement of Acyl Azide

The second approach to 1-aminobenzotriazole was the attempt to use the Curtius rearrangement[101] of the azide, prepared from the acid chloride 56, corresponding to 1-H-benzotriazole-carboxylic acid. This acid chloride was synthesized by a modification of the phosgenation procedures of Roomi[102] and Staab[103] as applied to pyrroles and imidazoles, respectively. Thus, in a typical experiment, as outlined in Scheme VI, the complex resulting from the reaction of a benzene solution of benzotriazole (47) with pyridine was isolated as an uncharacterized yellow oil which was immediately dissolved in anhydrous ether. To this ethereal solution was added a saturated, phosgene-ether solution under a nitrogen atmosphere at -5°C. Removal of the ether by aspiration led to a dry solid which was dissolved in a mixture of dry benzene and acetone. This solution was immediately added to a mixture of sodium azide in dry benzene which led to the formation of a light brown solid,

m.p. 162-163° (dec), after purification. The ir spectrum showed the presence of -N=N=N at 4.6 μ and -C=O at 5.85 μ, typical for acyl azides.

Scheme VI. Proposed Curtius Rearrangement of Acyl Azide



Various methods were tried to cause the rearrangement of azide 57 to the corresponding isocyanate 58, which would be expected to give rise to the N-amino derivative 48 upon aqueous hydrolysis. All attempts at this procedure led only to the recovery of unreacted azide 57, or to the formation of benzotriazole itself. No 1-aminobenzotriazole was found, even in the crude reaction mixtures, when aliquots were tested against authentic material (tlc and ir analyses).

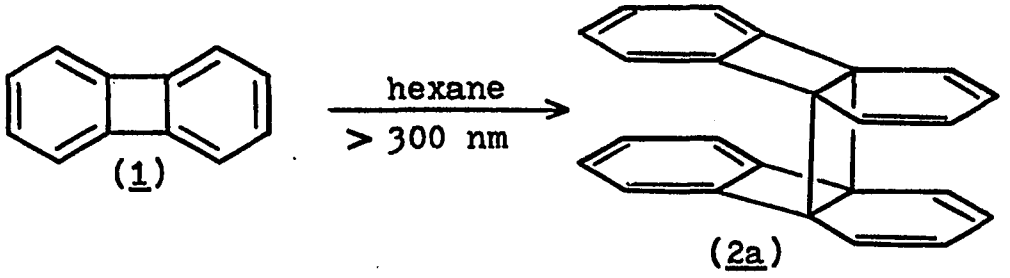
These results thus suggest that the Curtius rearrangement doesn't take place (if it did, the isocyanate formed would hydrolyze to the 1-aminobenzotriazole).

The formation of 1-aminobenzotriazole from benzotriazole was abandoned after the negative results of the approaches described.

B. Photochemistry of Biphenylene

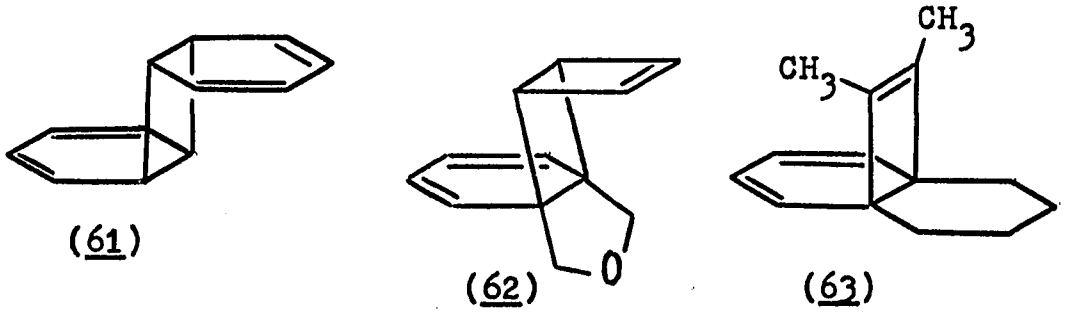
The photochemistry of biphenylene (1), until most recently,[4] has not been investigated in detail. Early in the 1960's, Fonken[3] alluded to the possible photoreactivity of biphenylene generated by irradiation of 2,2-diphenylene-mercury, although specific products were not reported. Lindow and Friedman[104] later reported that a small amount of tetraphenylene (59) is formed when a hexane solution of biphenylene is irradiated with either 2537 or 3500 angstrom light. In contrast, Goldman and Ruden,[4] found that when a 0.02 M hexane solution of biphenylene was irradiated through pyrex, at reflux, with a 275 W sunlamp, a single product was deposited. The product formed was a crystalline photodimer, molecular ion at m/e 304.1232 (calc'd for $C_{24}H_{16}$, m/e 304.1252). The assignment of structure 2a, syn-13,14,15,16-dibenzopentacyclo $\left[6.4.2.2^{2,7}.0.0^{2,7}\right]$ hexadeca-3,5,9,11,13,15-hexaene, that was made initially to the photodimer followed mainly from its proton nmr spectrum: singlet at 7.04 (8H; aromatic); and an AA'BB' system spanning 6.48-5.52 (8H; diene protons). The anti-isomer would be expected to show a downfield shift in the position of the aromatic protons to about 7.3, according to Cava[70] (a detailed discussion of nmr assignments follows shortly), and the vinyl protons would be expected

to move upfield, relative to the syn-isomer, due to the effect of the shielding aromatic ring.



(1) (2a)

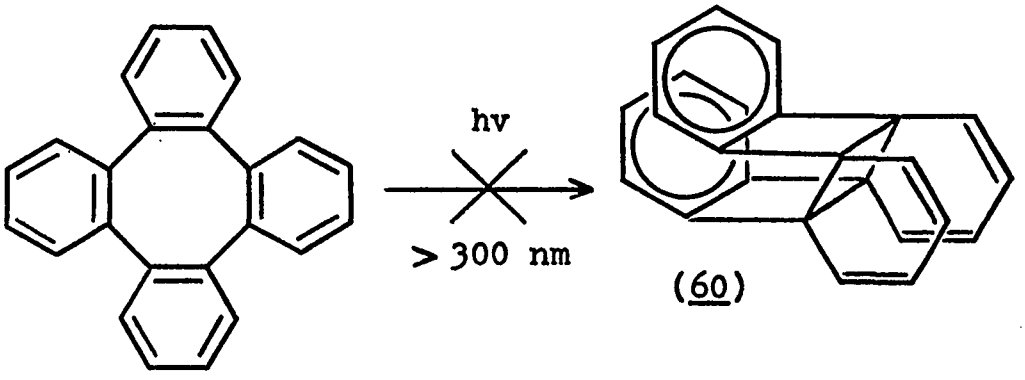
There are several systems in the literature having a cyclohexadiene ring fused to a four-membered ring, and in none of these cases is the center of the diene proton resonance found at a lower field than for the photodimer of biphenylene. Schroder[107] found the vinyl protons of cis-anti-cis-tricyclo $[6.4.0.0^{2,7}]$ dodeca-3,5,9,11-tetraene (61) at 5.62; Martin[108] assigned the value of 5.73 to the center of the system corresponding to the four vinyl protons of 12-oxa-tetracyclo $[4.4.3.0^{1,6},0^{2,5}]$ trideca-3,7,9-triene (62); and Paquette[109] found four vinyl protons of 11,12-dimethyl $[4.4.2]$ propell-2,4,11-triene (63) at 5.10-5.80.



(61) (62) (63)

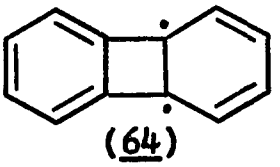
1. Alternative Structures for the Photodimer

Friedman[104] suggested that tetraphenylene (59) is formed when a hexane solution of biphenylene is irradiated at 2537A of 3500A, and it is possible that the photoproduct observed arises from a secondary photochemical reaction of tetraphenylene to form a product such as 60, which would have spectral characteristics similar to those of 2a. In order to test this possibility, tetraphenylene, synthesized independently by the thermal reaction of biphenylene,[104] was irradiated under identical conditions as for dimerization of biphenylene, and recovered completely unreacted.

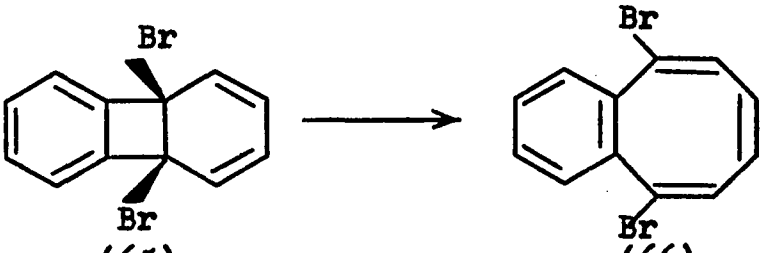


(59) (60)

It is suggested that the photodimer of biphenylene is derived by a $2\pi + 2\pi$ cycloaddition proceding through an intermediate which for purpose of illustration can be represented as the diradical 64. This kind of intermediate has been proposed by Barton[106] in his suggestion of structure 65 for the intermediate that gives rise to 3,8-dibromocyclooctatetraene (66) in the photobromination of biphenylene.

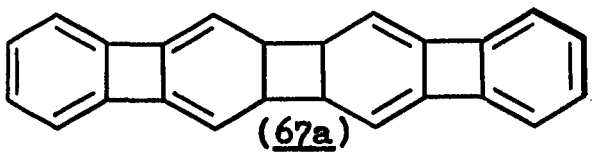


(64)

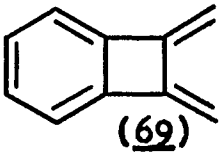


(65) (66)

It is also possible to visualize a $[2\pi + 2\pi]$ cycloaddition arising from reaction of the outermost 2,3-bond of biphenylene to give a symmetrical dimer of type 67a. This bond is the reactive one in the thermal reaction of biphenylene with ethyl diazoacetate, giving rise by a series of rearrangements to ethyl fluorene-2-carboxylate (68)[110] as shown in Scheme VII. However, structure 67a was rejected on the basis of uv and nmr spectral considerations. The uv spectrum of 67a would be expected to show similar absorption to that of biphenylene as does di-exo-methylene benzocyclobutene (69); the characteristic series of bands in the 350 nm region is absent in the photodimer.

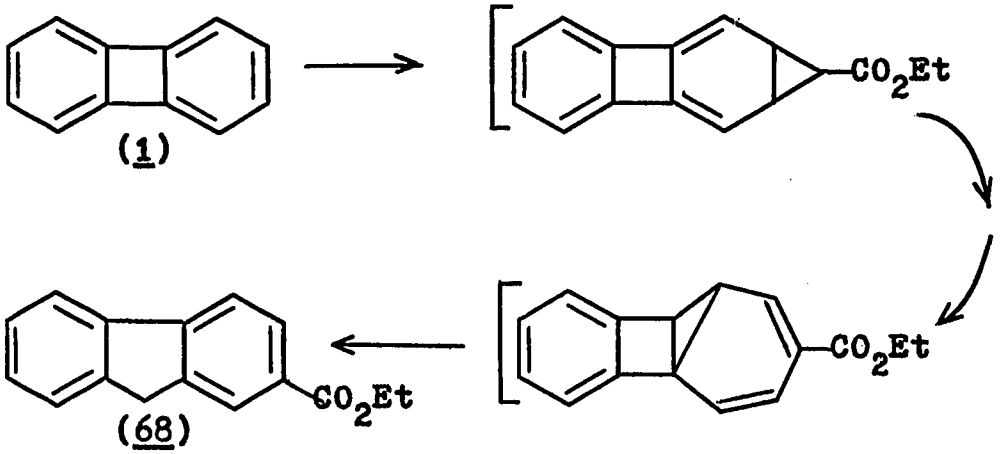


(67a)



(69)

Scheme VII.

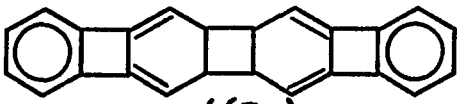


(1)

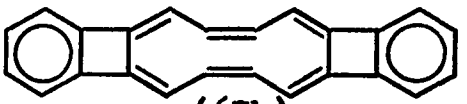
(68)

Also, the nmr spectrum of 67a would show three different types of protons: aromatic, vinylic, and bridge-head-allylic in the ratio of 2:1:1 (respectively). The observed nmr spectrum of the photodimer reveals only two different types of protons: aromatic and vinylic in the ratio of 1:1.

Furthermore, it is possible to conceive of the formation of a dimer corresponding to the ring opened form of structure 67a, namely, 67b. Such a structure would be in accord with a proton AA'BB' nmr system, but would also be expected to have an ultraviolet spectrum similar to (1) or (69).



(67a)

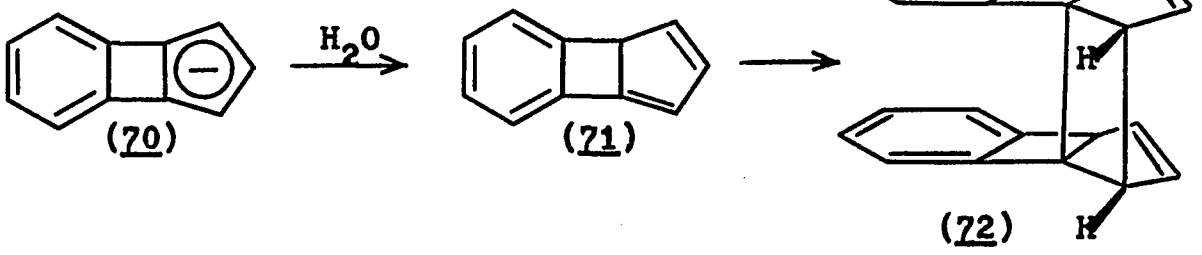


(67b)

Many other possible structures can be considered for the photodimer. A simple approach would be to consider 1,2-; 1,3-; and 1,4-addition of one biphenylene molecule with another.

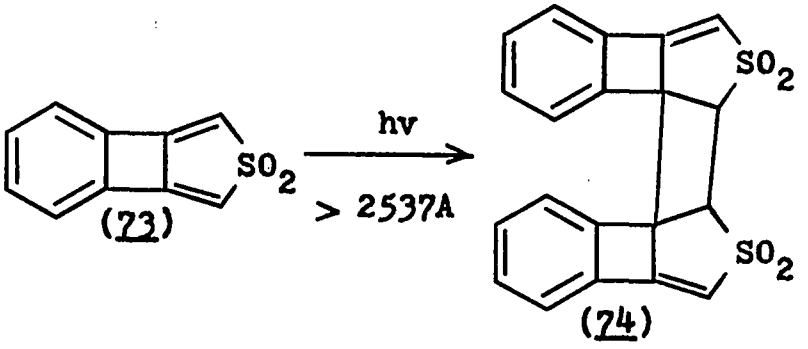
a. 1,2-Additions

Cava[111] has reported the formation of a dimeric hydrocarbon arising upon the protonation of the norbiphenylene anion (70). Protonation of the anion by water was suggested to give the highly strained, unstable monomer 71 which undergoes a thermal 1,2-cycloaddition across the strained bridgehead double bond of the five-membered ring. Two of the four possible dimers have been found. A detailed X-ray analysis on one of them has led Cava to assign structure 72 to this dimer.



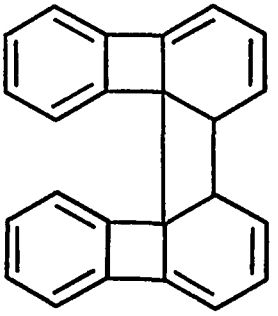
(70) (71) (72)

In another study of biphenylene analogs, Garratt[112] prepared 2-thianorbiphenylene-2,2-dioxide (73), and showed that this sulfone on irradiation through quartz gave rise to a dimer, to which he assigned structure 74. The stereochemistry was not defined, but the similarity in structure of the thermally formed dimer from 71 and the photodimer from 73 is noteworthy.



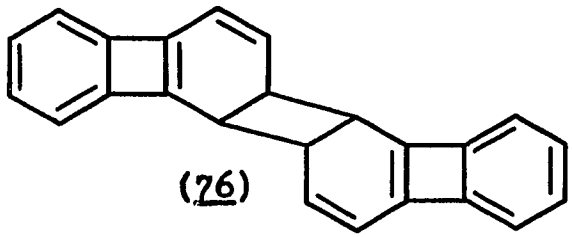
(73) (74)

If biphenylene were to undergo such a comparable dimerization, it would give rise to structure 75.



(75)

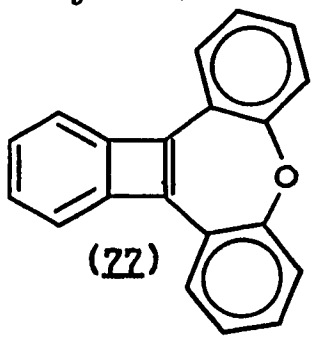
Alternatively, $[2\pi + 2\pi]$ dimerization could lead to the benzocyclobutadienoid, and, consequently, unstable structure 76.



(76)

Both structures 75 and 76 can be eliminated because neither would be expected to possess the AA'BB' nmr pattern observed with the actual photodimer of biphenylene. Furthermore, ring opening of the cyclobutane rings of both 75 and 76 can be excluded as each product would be expected to have the uv spectrum of a dimethylene benzocyclobutene, which is not observed.

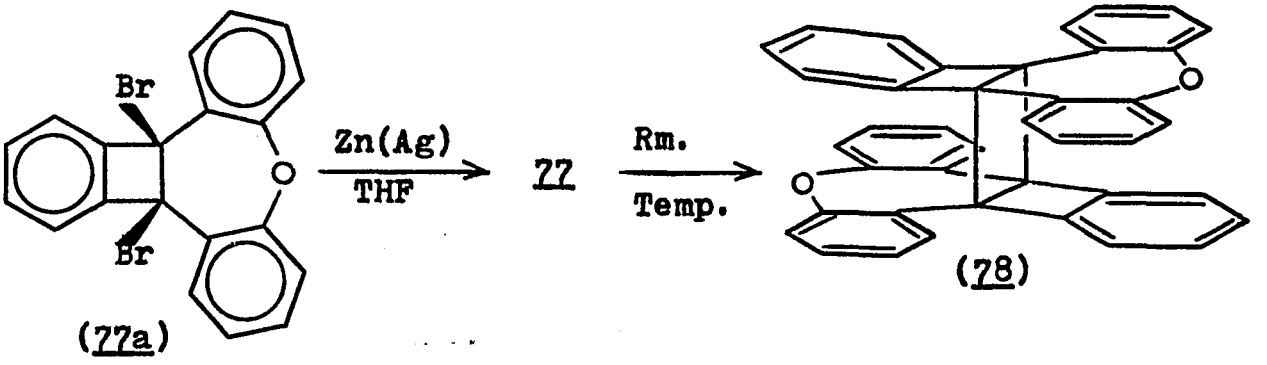
There is, however, precedence for the dimerization of a biphenylene-like system involving the central cyclobutadienoid portion of the molecule. Cava[113] has reported the synthesis of 3-oxahomobiphenylene (77), a biphenylene analog in which one of the benzenoid rings has been replaced by the nonaromatic (4n) oxepin system.



(77)

When 77 was generated from dibromide 77a with zinc-silver couple in warm THF, an orange-red solution (λ_{max} 496 nm)

was formed. It was found that solutions of 77 could be preserved unchanged for several hours at -78°, and that at -195° no esr signal could be detected, confirming a singlet ground state for the butadienoid structure 77; at room temperature, however, the red color vanished rapidly, and a colorless dimer of assigned structure 78 was reportedly formed.



(77a) (78)

In the cases of 67, 75, and 76, speculation was made about possible structures resulting from ring opening of the cyclobutene ring to the corresponding diene. Such consideration is foreclosed for 78, as the dibenzocyclooctatetraene (79) that would be produced on ring opening would have two trans-double bonds, which is structurally prohibitive. The syn-isomer of 78 would, however, be able to open to the stable, tub-shaped dibenzocyclooctatetraene, shown as 79b.

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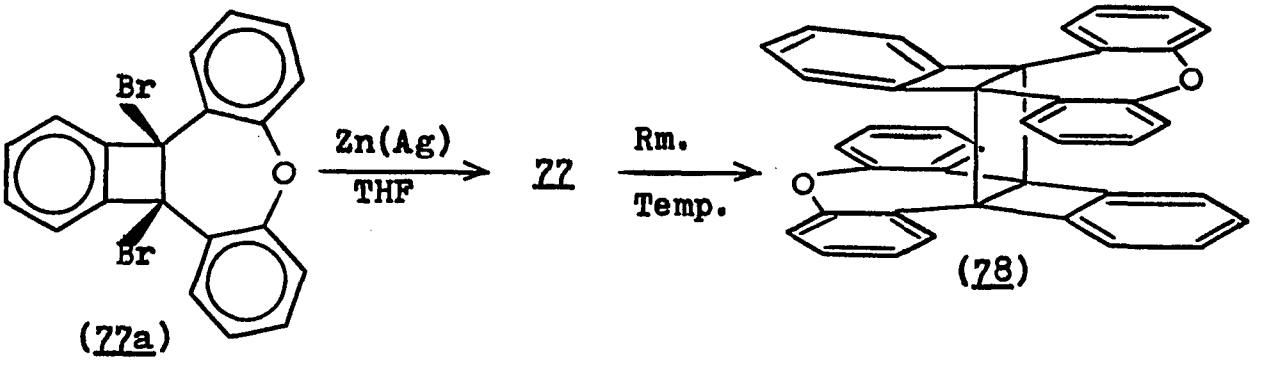

(77a) (78)

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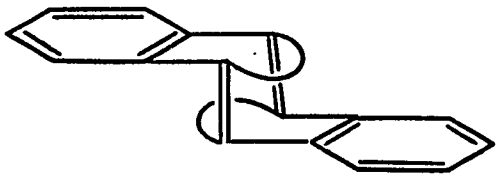
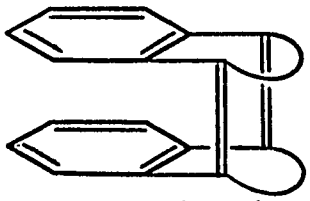
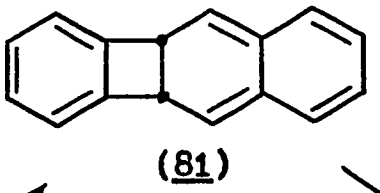


(79a)

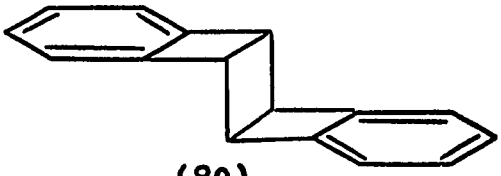


(79b)

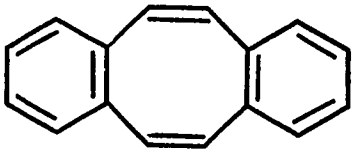
The reluctance of 3,4:7,8-dibenzotricyclo $\left[4.2.0^{2,5}\right]$-octa-3,7-dienes to undergo direct conversion to the corresponding dibenzocyclooctatetraenes is a well documented effect, and was first detailed by Cava[70] for 80, the anti-isomer of the parent member of this group. This compound gave 82 on heating at 150°, but via 81 which can undergo the thermally allowed electrocyclic reaction to 82. Proof of the intermediacy of 81 was provided by trapping experiments with dienophiles.



(81)



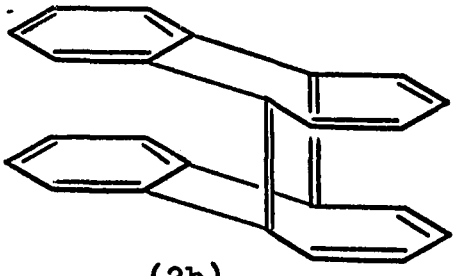
(80)



(82)

Unfortunately, the syn-isomer of 80 is not known, nor has any simple derivative of this system been reported in the literature. It would be interesting to determine if syn-80 would give 82 directly on irradiation; this would be an allowed reaction, and 82 would be produced in the stable, tub-configuration.

Analogous considerations can be made for photodimer 2a. The syn-structure originally proposed does incorporate the dibenzotricyclooctadiene system of interest and could have opened to the dibenzocyclooctatetraene (2b): (5,12:6,11-di [1,3] butadienodibenzo [a,e] cyclooctene), the proton nmr spectrum for which would have the symmetry associated with structure 2a. This would be the first example of the direct



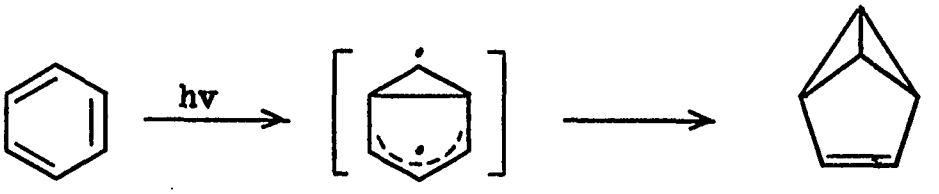
(2b)

ring opening transformation to a dibenzocyclooctatetraene; an intermediate similar to 81 is not possible because of the two unfavorable bridgehead double bonds. The anti-isomer of 2a would presumably be unable to undergo similar reaction because of the instability of the trans-double bonds in the enclosed dibenzocyclooctatetraene of the product system.

Further consideration of 2b as an alternative to 2a for the photodimer is postponed at this point to part C., after other modes of photoaddition known in other aromatic systems, as described in earlier sections, are considered.

b. 1,3-Additions

It has been known for some time that benzene undergoes photochemical 1,3-cycloadditions with a number of olefins.[114-117] The products derived from these reactions are believed to arise through the singlet diradical shown as 83, called prefulvene,[118] and can thus be visualized as derivatives of benzvalene (84).

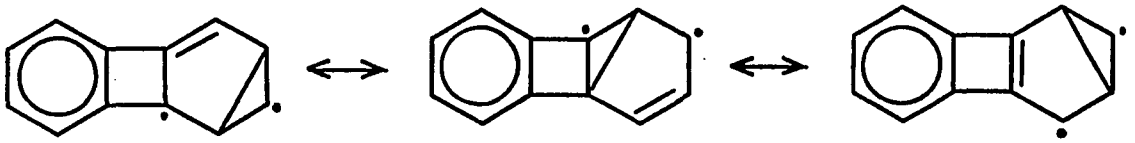


(83) (84)

Although numerous 1,3-additions are known for reaction of benzenes with olefins, 1,3-1',3'-dimerizations have not been reported. Known dimerizations result from 1,2-1',2'-, 1,2-1',4'-, and 1,4-1',4'-coupling.

Bryce-Smith points out that extention of these relationships to naphthalene and higher condensed aromatic hydrocarbons does not necessarily apply. But, if we consider the possible 1,3-1'.3'-combinations that can be derived from structures 85 a-c, all dimers thus derived can be ruled out

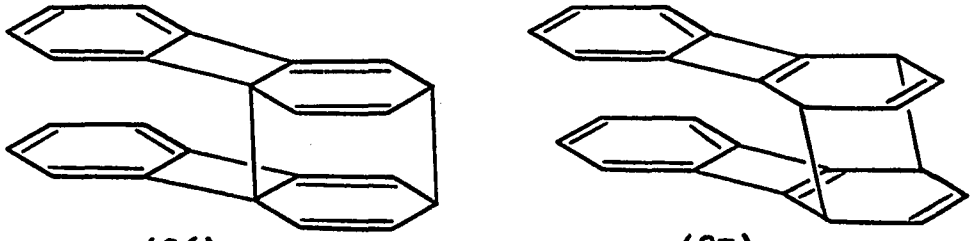
for not having the AA'BB' proton nmr system, and/or, for having cyclobutadienoid systems.



(85a) (85b) (85c)

c. 1,4-Additions

It was previously mentioned that in the case of 2-alkoxynaphthalenes, the suggested mode of dimerization was via 1,4-1',4'-addition.[60,62] If this analogy were carried over to the case of the biphenylene system, dimers 86 or 87 (or their anti-forms) could be considered.

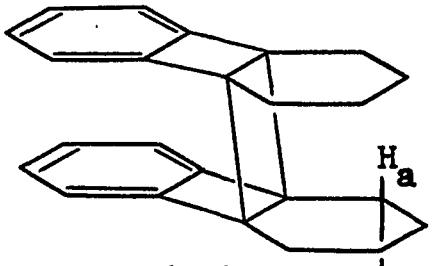


(86) (87)

Dimer 86 can be rejected because the expected proton nmr spectrum would not be in accord with the observed AA'BB' system. Likewise, dimer 87 can be rejected on the basis of the observed chemical shift for the protons of the photodimer, all of which are aromatic or vinylic, and because of the presence of a cyclobutadienoid system in 87.

C. Structure Proof of Photodimer

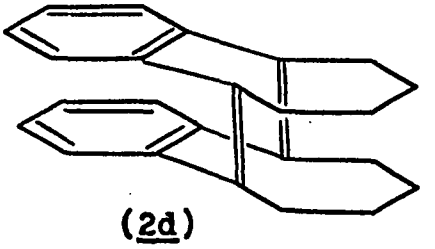
Catalytic hydrogenation of the biphenylene photodimer with Pd/C in ethyl acetate proceeded with the uptake of four equivalents of hydrogen to give an octahydrodimer which, on the basis of assignment of structure 2a for the photodimer, led to the assignment of structure 2c, syn-13,14,15,16-dibenzopentacyclo $\left[6.4.2.2^{2,7}.0.0^{2,7}\right]$ hexadeca-13,15-diene, molecular ion at m/e 312. The proton nmr spectrum showed a singlet at 6.93 (8H; aromatic), two multiplets centered at 2.80 (4H) and 2.12 (4H) assignable to H_a and H_b protons, respectively, and a broad band centered at 1.57 (8H) for the remaining protons.



(2c)

In part B., section a., the ring-opened form 2b of the structure initially assigned to the photodimer 2a was considered as a possible alternative, and rationalized on the basis of a photochemically allowed reaction of a syn-dibenzotricyclooctadiene to give a dibenzocyclooctatetraene in a stable configuration. This consideration, however, has

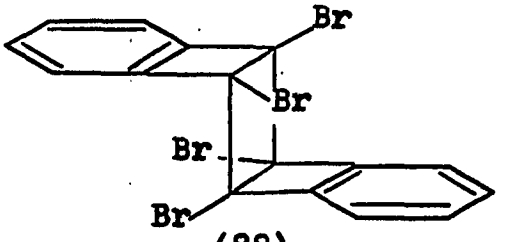
no precedent in the literature, as only anti-isomers of the dibenzotricyclo-system have been reported. Assuming 2b for the photodimer, the octahydro derivative would have structure 2d, syn-5,12:6,11-dibutanodibenzo [a,e] cyclooctene, with



(2d)

the remaining double bonds unreduced, probably because of steric hindrance to the surface of the catalyst.

The initially reported structure for 2a had the aromatic rings syn to each other, and this assignment was based on the chemical shift of 7.04 for the aromatic protons. This was compared to the aromatic protons at 7.28 in 80, which had been proved to be anti by chemical degradation, and the aromatic protons at 7.08 in 82, known to be in the tub form, with aromatic rings facing each other. The same argument has been extended by Cava[70] to the assignment of the anti-configuration to 88 with its aromatic protons at 7.25.



(88)

Thus, the syn-configuration for the photodimer appears secure on the basis of chemical shifts, whether in the cyclobutane 2a or cycloocatetraene 2b form, and also on a structural basis if 2b is formed by a ring-opening of initially generated syn-2a.

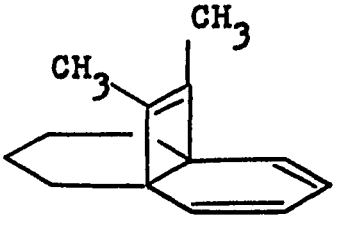
To differentiate between 2a and 2b, and in turn, 2c and 2d, more evidence was required, and this led to a conclusive proof of structure using ^{13}C magnetic resonance and an X-ray crystallographic study of the octahydrodimer. Preceding the availability of the latter two techniques, an extensive study of the attempted chemical degradation of both the photodimer and the octahydrodimer was carried out, but without conclusive results.

1. ^{13}C nmr Spectral Results

As was pointed out by Levy and Nelson,[120] the first advancement in the art of the ^{13}C nmr experiment came in 1965 with the perfection of wide-band proton decoupling techniques. It is only during the past several years, however, that this method of analysis has become more generally available with the development of commercial Fourier transform systems.

If the photodimer of biphenylene has structure 2a, the ^{13}C nmr spectrum should show the presence of a cyclobutane carbon. Cycloalkanes have been shown[121] to possess cmr

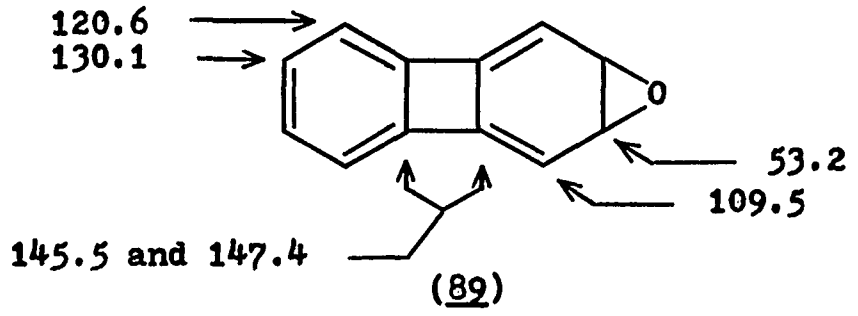
chemical shifts in the range of 25-29 ppm (all shifts are reported relative to TMS) for C-5 to C-10 compounds. Cyclobutane, itself, appears at 22.4 ppm. However, when the cmr spectrum of the photodimer was determined, no chemical shifts below 124 ppm could be found. The $\underline{sp}^2$ carbons of alkenes and aromatics appear downfield relative to alkanes.[122] Their chemical shifts appear 100 $\pm$ 20 ppm downfield, relative to the corresponding alkane resonance. On this basis, the structure of the photodimer accords more with the open form 2b, although cmr models for propellane cyclobutanes have not been available, until recently, to use for comparison. Also, this variety of cyclobutane is considered to have its bridgehead bond formed by $\underline{sp}^2$ orbitals, and its carbon magnetic resonances would be expected to be at a lower field than for other cyclobutanes. One of these cmr models for the comparison of carbon chemical shifts would be 63 prepared by Paquette[109] in 1974.



(63)

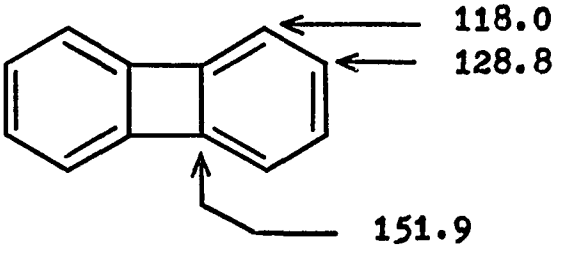
No actual assignment of the determined chemical shifts was made by Paquette, but the following values can be assigned: 8.44 (CH_3); 18.24, 28.65 (CH_2); 47.43 (bridgehead); 120.88, 133.08 (1,2-disub. olefin); 141.52 (tetra-sub. olefin). The

assignment of 141.52 for the tetrasubstituted double bond carbon is in very good agreement with the values of 145.5 and 147.4 assigned by Gunther[123] and the corresponding carbons of 2,3-epoxybiphenylene (89), and is also consistent



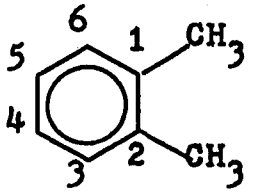
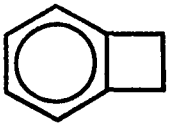
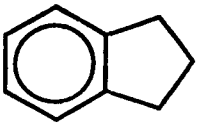
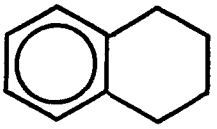
(89)

with the values assigned by Grant[124] to the parent hydrocarbon, biphenylene.



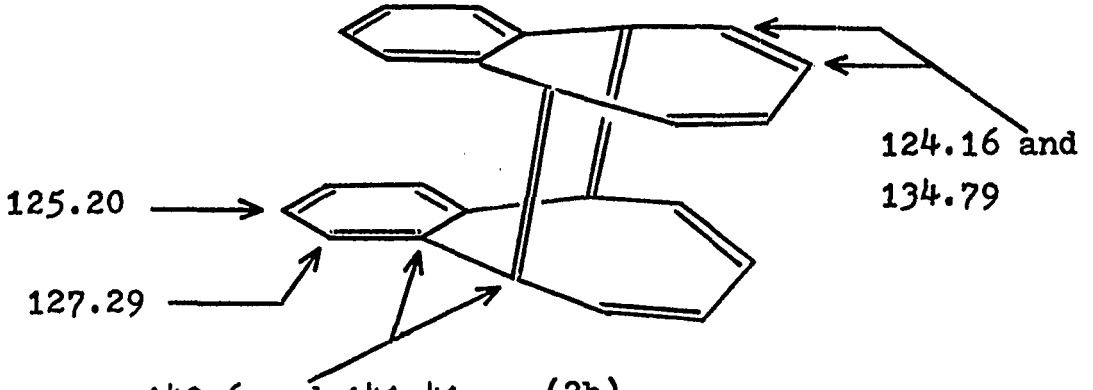
It should be noted, that in ortho-disubstituted benzene systems, the carbons bearing the substituents show the largest chemical shifts in the cmr spectrum. Kitching[125] has made a comparison of the carbon shift of the ortho-disubstituted positions of the various benzocycloalkanes shown in Table II, and the trends in evidence should provide a means of assigning chemical shifts to related systems.

Table II. ^{13}C Assignments of Ortho-Disubstituted Aromatics

Entry	Compound	$C_{1,2}$	$C_{3,6}$	$C_{4,5}$
1		136.3	129.8	126.0
2		145.6	122.1	126.6
3		144.0	124.4	126.6
4		137.0	129.2	125.2

Refering to the above ^{13}C chemical shifts, it becomes apparent that as the steric constraint of the ring attached at $C_{1,2}$ decreases, the chemical shift at $C_{1,2}$ approaches that of entry 1. $C_{4,5}$ values show the least change with ring size, as is to be expected, while $C_{3,6}$ values increase as bond-angle constraint decreases.

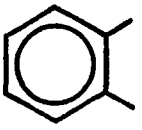
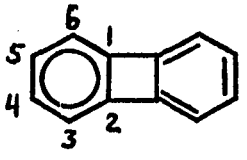
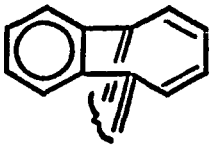
Thus, this trend should also be followed when comparing the carbon chemical shifts of biphenylene and the photodimer. The assigned ^{13}C chemical shifts for dimer 2b are shown:



(2b)

Looking at biphenylene, its photodimer, and its octahydrodimer as ortho-disubstituted benzenes, the carbon chemical shifts can be compared to o-xylene (Table III).

Table III. ^{13}C Assignments of Benzenoid Systems

Entry	Compound	$C_{1,2}$	$C_{3,6}$	$C_{4,5}$
1		136.3	129.8	126.0
2		151.9	118.0	128.8
3		141.41 140.6	127.29	125.20

Thus, it can be seen that as the steric constraint due to substitution at $C_{1,2}$ decreases from 2. to 4., the chemical shift at $C_{1,2}$ approaches that of o-xylene. As in the previous case of benzocycloalkanes, $C_{4,5}$ values show very little change due to substituents at $C_{1,2}$.

2. Infrared and Raman Spectroscopy.

Determination of Centrosymmetry

One of the problems associated with photodimerizations in which a cyclobutane ring or a directly rearranged product is generated is determining the stereochemistry about the ring system. Since the photodimerization of biphenylene could have led to formation of an anti-dimer as well as a syn-dimer, a simple procedure for distinguishing the anti-dimer from the syn would be useful in a structural determination. Thus, since only the anti-dimer can possess an inversion center, Raman spectroscopy, which is capable of identifying centrosymmetry in molecules, was used to examine the photodimer of biphenylene.

The difference in vibrational selection rules for infrared and Raman transitions of such molecules provides a theoretical basis for determining the presence or absence of a center of symmetry through the Rule of Mutual Exclusion,[126] which states that for centrosymmetric molecules a vibrationally active infrared transition cannot be active in the Raman; and, conversely, a vibrationally active Raman transition cannot be active in the infrared. If a molecule should

be lacking such an inversion center, vibrations of the same frequency (coincidences) appear in both spectra. In the case of small molecules, Raman and infrared spectral comparisons are frequently employed to detect this symmetry element.[127]

In the case of large molecules, such as is presented in the biphenylene photodimer problem, there are a relatively large number of atoms (forty) and, consequently, a very complex vibrational spectrum is expected.

The infrared spectrum of the photodimer was recorded with the sample in the form of a KBr disk and compared to the Raman spectrum of the pure solid as a powder. Raman displacements and infrared frequencies are accurate to $\pm$ 2 cm^{-1}. However, transitions within 5 cm^{-1} for the infrared and Raman comparisons were considered coincidences (This is general practice).[127] This range of 5 cm^{-1} for coincidences should allow for crystal perturbations associated with the Raman spectrum of a pure solid. Table IV summarizes the infrared and Raman data for the photodimer of biphenylene.

Table IV

Comparison of the Raman Displacements and Infrared Frequencies for the Biphenylene Photodimer

Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}
270	268		755	1206	
304		762		1234	
332			835		1240
354		906	905	1268	1270
362	360		948	1308	1310
	445		960		1390
	480	970		1418	1420
494		1002	1000		1450
	570		1030		1470
642	640	1038		1550	
678	675		1100		1570
	725	1158	1160		1610
746			1190	1622	

Ten coincidences are observed in harmony with the initial assignment of a syn-configuration to the photodimer. This evidence is, however, not conclusive, as the presence of forty atoms in the photodimer necessitates a total of one hundred fourteen vibrational fundamentals (3n-6); and since overtone and combination bands commonly appear in the infrared spectrum, there is the strong possiblity that there are accidental coincidences between the infrared and Raman spectra.

It would, of course, be more desirable to have both isomers to establish a trend rather than to require a strict mutual exclusion for the C_i molecule or a complete set of coincidences for the C_2 molecule. Also, for nonplanar cyclobutane derivatives or twisted cyclooctatetraenes that do not contain a center of symmetry, the application of the Rule of Mutual Exclusion may be invalid. A final proof of structure by physical means for the photodimer can be made with certainty by X-ray crystallography.

3. X-ray Analysis of the Octahydrophotodimer

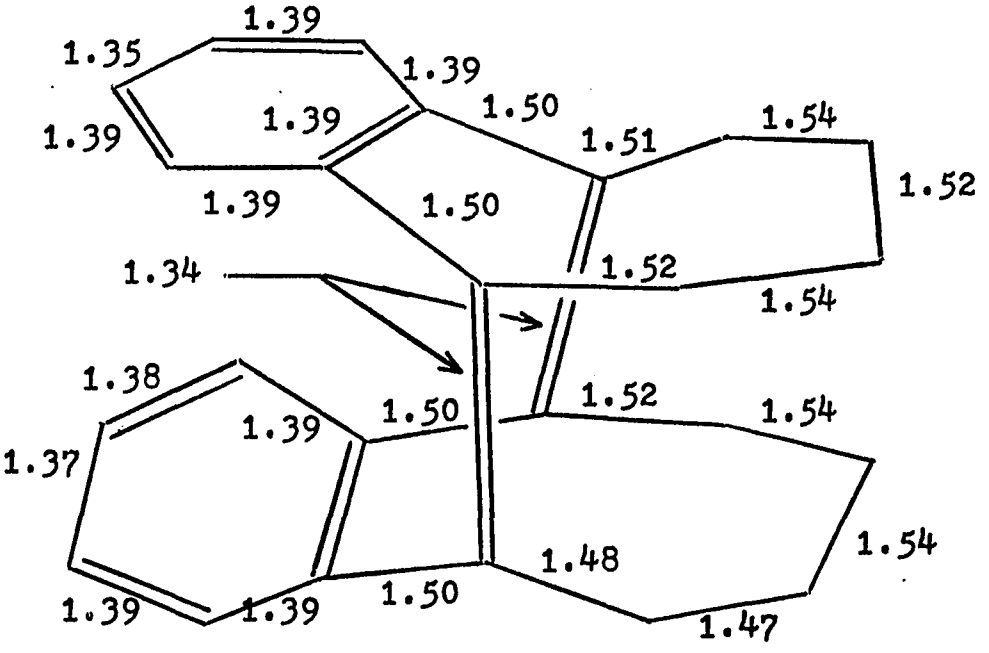
When the ^{13}C nmr results for the photodimer were first obtained, it became apparent that assignment of structure 2a and 2c to the photodimer and octahydrophotodimer, respectively, were in doubt, and that structures 2b and 2d were more probable.

The open, cyclooctatetraene form of the photodimer became firmly established with the completion of an X-ray study on the octahydrodimer by Prof. J. White of Fordham University and his student, Eugene Passer; the octahydrodimer was used in their study because it forms better crystals than the photodimer. The results of this study support structure 2d based on measured interatomic distances between carbon atoms.

White finds that the octahydrodimer crystallizes as monoclinic prisms with cell parameters:
a=13.167908 A, b=8.608985 A, c=21.325012 A, $\beta = 134.350^{o}$.

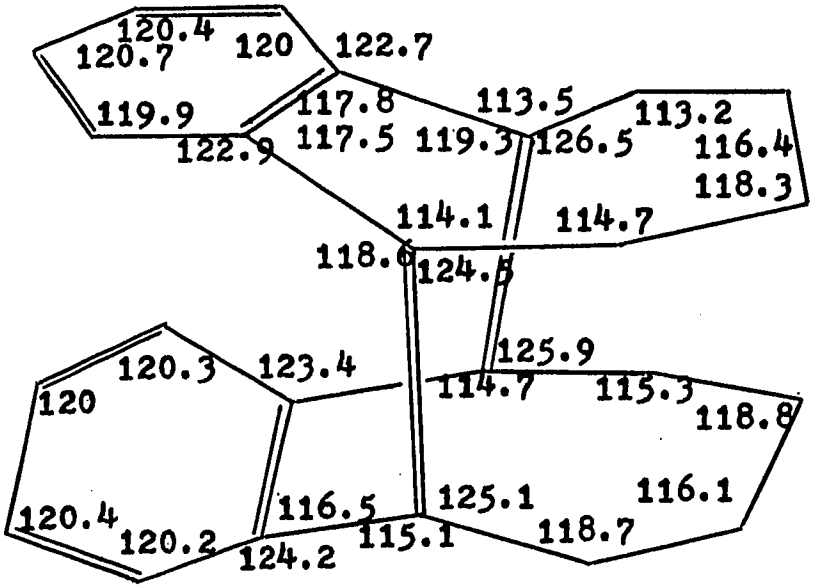
Using the Cu-K_{α} line, 1.54178 A with an Enraf Nonius Diffractometer, Model CAD-4, White is able to Classify the octahydrodimer as belonging to the Space Group $P2_1/c$ and of possessing four molecules per unit cell. The calculated bond distances and bond angles are shown in Figures 1 and 2, respectively, and result from application of the Sayre equation to the diffraction data, to an R value of 0.06.

Figure 1. Bond Distances in the Octahydrophotodimer (A)



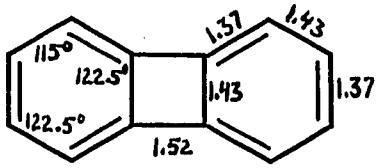
Further details on the structure will be given in the Experimental Section (section U.).

Figure 2. Bond-Angles Around Carbon Atoms of Octahydrodimer



X-ray crystallographic studies on the parent hydrocarbon[128], biphenylene, show that in the solid state the molecules are planor (D_{2h}), and the bond lengths reveal the bond alternation predicted by LCAO calculations.[129] This has recently been reconfirmed by Bauer[130] using electron diffraction techniques as applied to biphenylene in the gas phase. The calculated bond distances and bond angles for the parent hydrocarbon are shown in Figure 3.

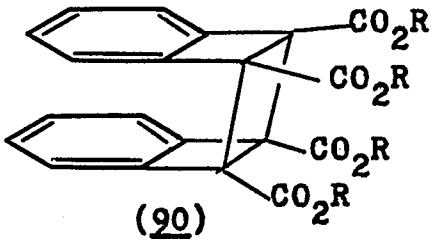
Figure 3. Bond Lengths and Bond Angles in Biphenylene.[130]



4. Attempted Characterization by Chemical Means

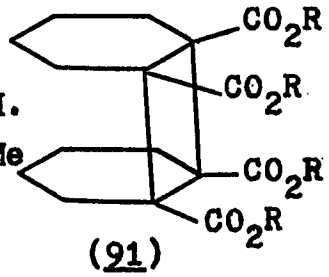
Prior to having the cmr results, the cyclobutane 2a was the apparent structure for the photodimer; and several methods were employed to verify the structure and the syn-configuration.

It was hoped that oxidative degradation of the cyclohexadiene portions of the dimer would result in the formation of the tetracarboxylic acid 90a, which could be characterized as the corresponding methyl ester 90b.



(90)

(a) R=H.
(b) R=Me



(91)

Likewise, if the octahydrodimer were of type 2c, it should be possible to isolate the tetracarboxylic acid 91a, which could also be characterized as its corresponding methyl ester 91b.

Thus, in a series of oxidative degradations utilizing procedures described by Lemieux and von Rudloff[131] (periodate-permanganate oxidation); Lemieux and Johnson[132] (periodate-osmium tetroxide oxidation); Caputo and Fuchs[133] (periodate-ruthenium tetroxide oxidation); Moriconi and Salce[135] (ozonolysis, alkaline-peroxide work up); and Meinwald[136] (ozonolysis, acetic acid), attempts were made to

degrade the photodimer and the octahydrodimer to the cyclobutane carboxylic derivatives mentioned above.

In the degradations performed on the photodimer itself, various types of products were obtained depending on the degree of degradation. However, in none of these cases could any compound corresponding to 90a or 90b be isolated. Those products which were isolated proved to be mixtures of hydroxy-acids, carbonyl-containing acids, and aldol-type condensation products (based upon interpretation of ir and nmr spectra). There were in some of the experiments results which supported the assignment of structure 2b for the photodimer; in several cases, o-phthalic acid was isolated in low yields (5-20%). The formation of o-phthalic acid could also be explained in terms of the further degradation of the cyclobutane ring in photodimer 2a.

A summary of the methods used follows, with details given in the experimental section.

a. Periodate-Permanganate Oxidation[131]

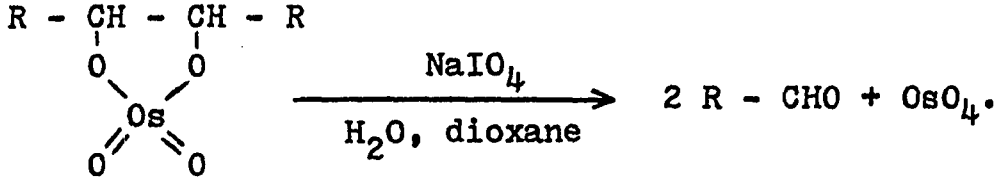
When an aqueous solution of potassium permanganate reacts with an olefin, it is believed that there is formed a cyclic manganese ester by cis-addition to the double bond. If the solution is kept alkaline, a 1,2-diol will form. If the reaction mixture is kept neutral, the permanganate oxidation results in cleavage, or in the formation of α-hydroxyketones.[137-140]

However, in the periodate-permanganate procedure in which the aqueous solution is maintained at pH 8, and in which only a catalytic amount of the permanganate is required, the α-hydroxyketones and the 1,2-diols resulting from reaction with the olefin are cleaved by the periodate to form carbonyl compounds. Any aldehydes produced during the periodate cleavage are further oxidized to carboxylic acids.

Since the isolation of carboxylic acid products is predicated on the initial formation of a cyclic permanganate ester, it is not so surprising that structures such as 2b or 2d not be cleaved at all of their double bonds because of steric factors.

b. Periodate-Osmium Tetroxide Oxidation[132]

In this modified osmylation procedure, the initially formed cyclic osmylate ester is continuously oxidized with sodium periodate to reform osmium tetroxide. In this procedure, there is no further oxidation of the cleavage product.



This procedure, too, failed to give rise to compounds that could be readily identified. A direct osmylation procedure described by Criegee,[141] in which pyridine is used

to catalyze the reaction of osmium tetroxide with an olefin, also failed to produce the anticipated result, a clean polyhydroxy derivative of the photodimer, as evidenced by ir and nmr spectroscopy.

c. Periodate-Ruthenium Tetroxide Oxidation[133]

Ruthenium Tetroxide prepared by the method of Nakata,[134] by the oxidation of water-insoluble ruthenium dioxide with aqueous sodium metaperiodate, and used in catalytic amounts with excess sodium periodate according to the procedure of Caputo and Fuchs,[133] also produced complex mixtures which could not readily be separated into identifiable products.

d. Ozonolysis. Alkaline Peroxide Work Up[135]

Using the procedures of Moriconi and Salce,[135] naphthalene was subjected to ozonolysis in order to determine the conditions required to oxidize this hydrocarbon to o-phthalic acid. Ozonolysis of a methylene chloride solution of naphthalene at dry-ice temperature for sixty minutes was required to oxidize 0.01 mole of the hydrocarbon to a 78% yield of isolated phthalic acid.

The above procedure was used on an equivalent amount of the photodimer. From the reaction mixture was isolated a neutral fraction (16%), which showed the presence of unreacted starting material (ir); a water-insoluble acidic fraction (39%), which showed the presence of a mixture of aromatic acids and anhydrides (nmr and ir); and a water-soluble acidic fraction (44%) isolated by Soxhlet extraction

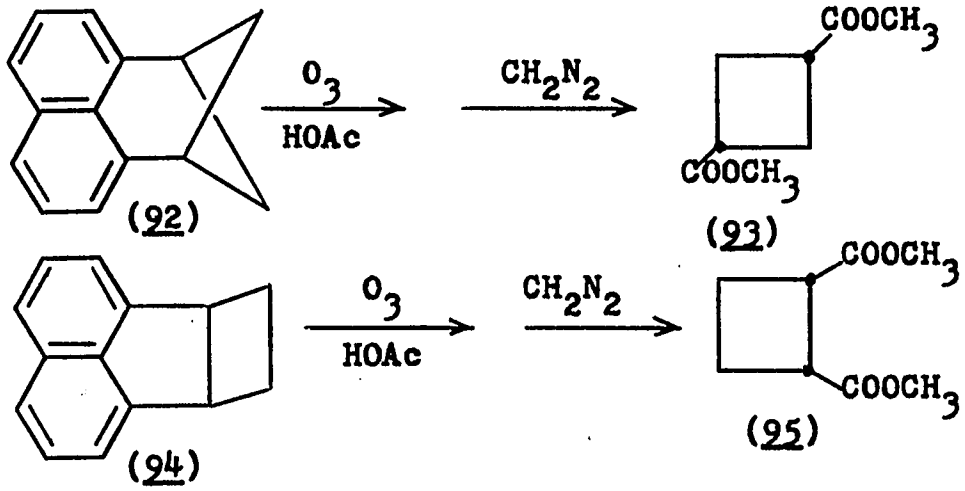
of the evaporated aqueous acidified portion, which showed the presence of a mixture of aliphatic acidic compounds (nmr and ir) that could not be resolved.

e. Ozonolysis in Acetic Acid[136]

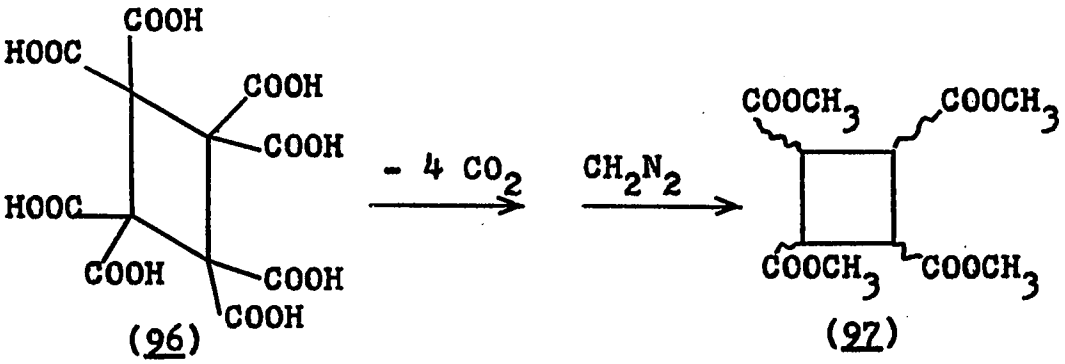
Following the procedures outlined by Meinwald,[136] the octahydrodimer 2c was ozonized in 80% aqueous acetic acid and worked up with 30% hydrogen peroxide in an attempt to generate tetracarboxylic acid 91a. The crude acidic material was taken up into methanol and esterified with excess diazomethane in ether (prepared from N-methyl-N'-nitro-N-nitrosoguanidine according to the procedure described by McKay[142]) in an attempt to generate tetracarboxylic ester 91b, which it was thought could be synthesized from commercial starting materials (see part f). The resulting mixture was separated by vacuum distillation into three main fractions. The high boiling fraction showed the presence of a mixture of methyl esters (ir and nmr). However, there was still present an aromatic ring in the molecule which would preclude a tetraester of the cyclobutane system anticipated.

Meinwald had demonstrated that a molecule containing a cyclobutane system in the presence of an aromatic system was oxidized down to the corresponding cyclobutane system, using the ozonolysis procedures mentioned in the above. When peri-naphthobicyclo [3.11] heptene (92) and peri-naphthobicyclo-[3.2.0] heptene (94) were subjected to ozonolysis followed by diazomethane esterification, there was isolated diesters

93 and 95, respectively.



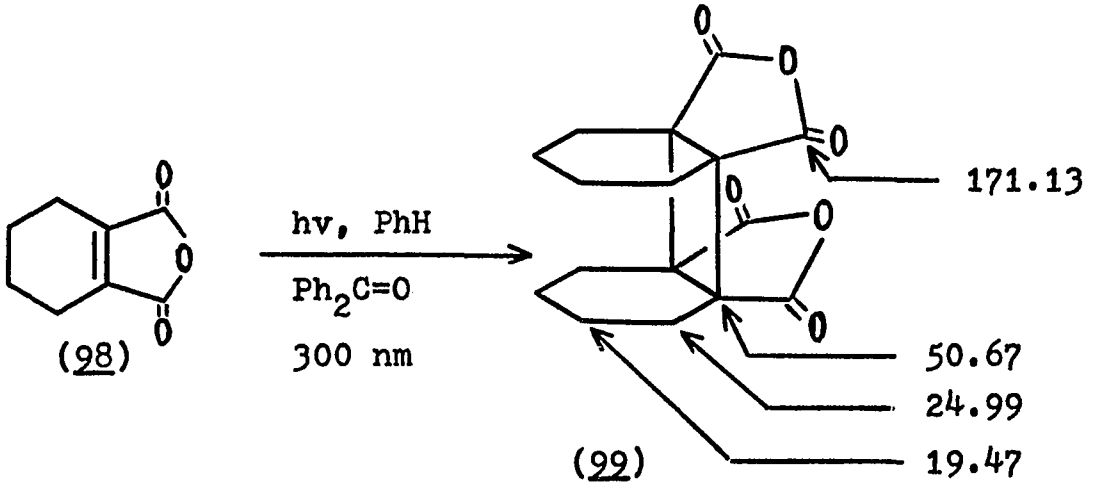
Thus, it was anticipated that application of these procedures to the photodimer (2a) should give rise to the cyclobutane derivative 96, which after decarboxylation and esterification should give rise to a mixture of the well-characterized tetracarbomethoxycyclobutanes (97).[143b]



f. Model Degradation Product for Octahydrodimer

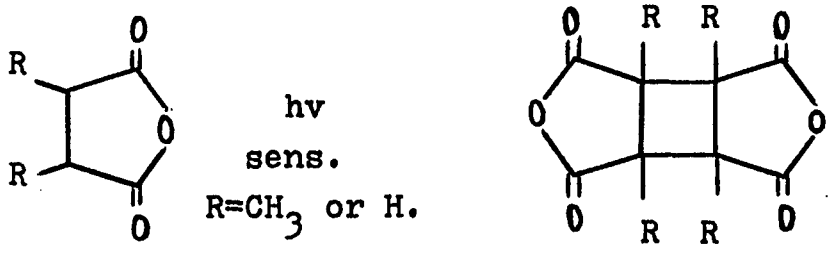
In an attempt to prepare a hoped-for degradation product of the octahydrodimer (2c), 3,4,5,6-tetrahydrophthalic anhydride (98) was submitted to benzophenone-sensitized photodi-

merization. From the crude reaction mixture was obtained an ether-insoluble solid, m.p. 276-280°, which showed characteristic cyclic anhydride ir bands at 5.5 and 5.65 microns and also showed the expected upfield shift to 2.03 and 1.5 of the resonances at 2.45 and 1.82 for the protons in the starting material. The mass spectrum showed the presence of a dimer, m/e 304. The ^{13}cmr results indicate one isomer only, structure 99, rather than a mixture.



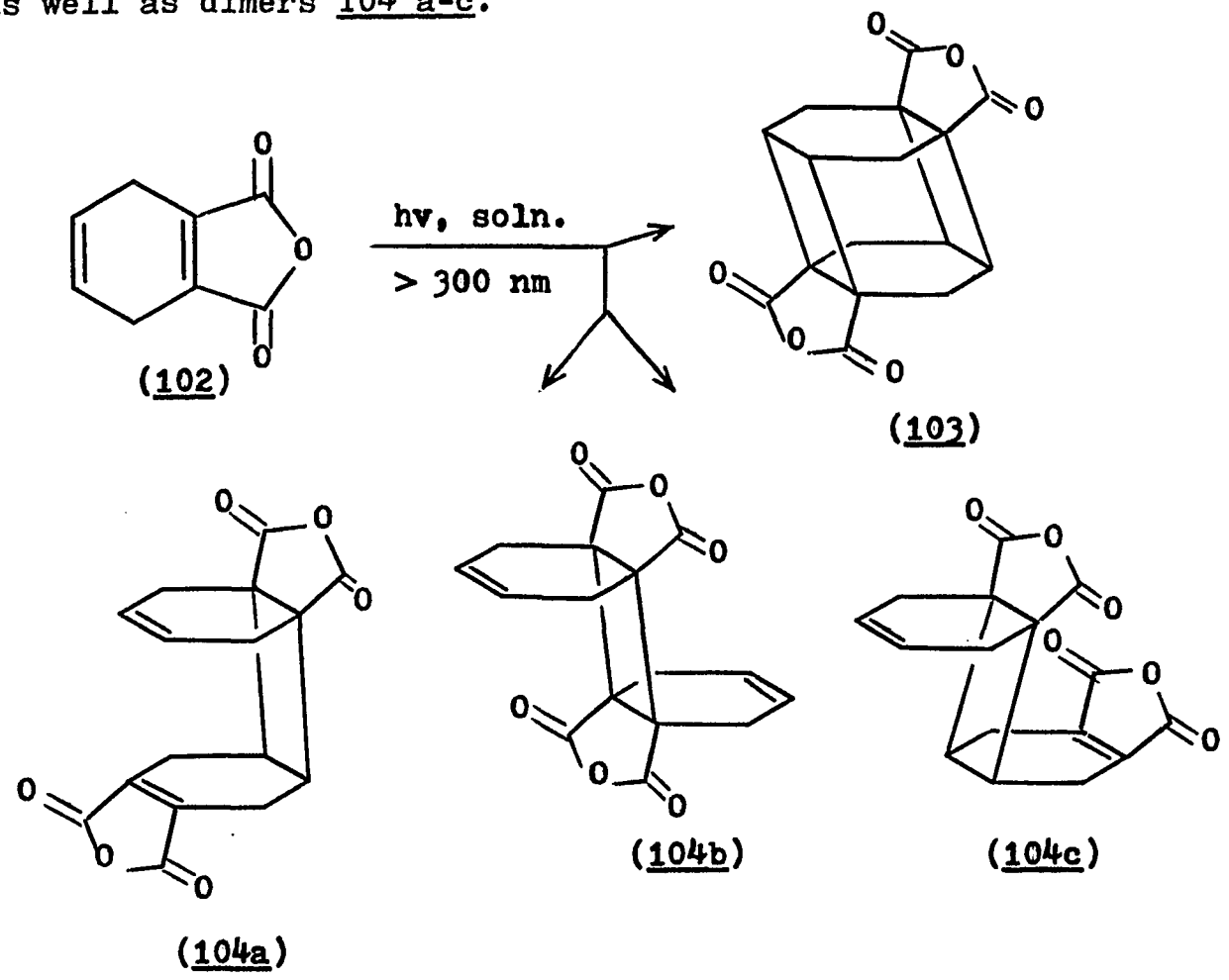
(98) (99)

Such a dimer as 99 would be expected in light of the cycloaddition products 101 obtained by Griffin[143] and Schenck[144] when compounds of type 100 were irradiated in the presence of benzophenone.



(100) (101)

More recently,[145] it has been reported that irradiation of a solution of 1,4-cyclohexadiene-1,2-dicarboxylic anhydride (102) in various solvents gave rise to cage dimer 103 as well as dimers 104 a-c.



(102) (103) (104a) (104b) (104c)

The inability to obtain cyclobutane products of chemical degradation is understandable in view of the rearranged structure of the photodimer as the cyclooctatetraene 2b.

D. Nature of Biphenylene Photodimerization

In order to consider a mechanism for the photodimerization of biphenylene, it is necessary to discuss, first of all, the absorption and emission properties of biphenylene.

1. Absorption Spectrum

The ultraviolet spectrum of biphenylene contains two sets of separated bands[146] which distinguishes its uv spectrum from that of biphenyl, which has only one absorption maximum. The more intense band coming at 235-260 nm has been ascribed to the second electronic transition in biphenylene, while the less intense band at 330-370 nm has been assigned to the first electronic transition.[147]

The long-wavelength absorption characteristics of representative aromatic systems, some previously discussed in the introduction, are shown below in Table V.

Table V. Ultraviolet Absorption Characteristics of Representative Aromatic Systems[a]

Compound	Number of Rings	Number of Double Bonds	λmax (nm)	log
Naphthalene	2	5	311	2.38
Biphenyl	2	6	245	4.25
Biphenylene	3	6	358	4.00
Acenaphthalene	3	6	322	4.04
Anthracene	3	7	355	3.89
Phenanthrene	3	7	329	2.51

[a] Absorption maxima are reported for the band of maximum intensity in the long-wavelength region.

2. Emission Spectra

In the early 1960's there appeared two articles purporting that biphenylene, prepared by the method of McOmie, possessed dual emission properties.[148] These emissions, however, were later shown, by comparison with results from a sample purified by zone-refining commercially available material, to be most likely caused by the presence of an impurity that absorbs light near 280 nm and shows fluorescence at 300 nm and phosphorescence at 410 nm.

Thus, Hochstrasser concluded that a purified sample of biphenylene did not exhibit the common radiative processes associated with an excited state molecule: fluorescence from an excited singlet-state, or phosphorescence from an excited triplet-state. This suggested to Hochstrasser that there must be a very efficient radiationless process by which excited states of biphenylene could be effectively depopulated.

Furthermore, work by Hochstrasser at 4.2°K using a mixed crystal of biphenyl[149b] led to the conclusion that biphenylene must undergo a considerable geometry change upon excitation. This change in geometry is suggested to be necessary to increase the overlap of vibrational levels of the excited state with those of the ground state. This distortion ability has the net effect of increasing the probability, and thus the efficiency, of a radiationless transition back into the ground state.

In addition, Rentzepis[155] has shown that although biphenylene exhibits neither fluorescence nor phosphorescence under conventional means of irradiation, biphenylene does show emission when subjected to strong excitation such as supplied by Q-switched laser sources. Rentzepis has estimated that in the case of biphenylene, repopulation of the ground state from a geometrically distorted excited state takes approximately 10^{-11} seconds, whereas, in the case of a non-distorted planar aromatic molecule in the excited state, repopulation of the ground state usually takes place twice as slow.

3. Radiationless Processes

The transfer of excitation energy from a donor capable of undergoing fluorescence, $^1D^*$, to a fluorescent acceptor A in the process $^1D^* + A \longrightarrow D + {}^1A^*$ leads to the simultaneous quenching of donor fluorescence and sensitization of acceptor fluorescence.

In the absence of an acceptor, it is possible for the donor to interact with a ground state molecule D. In the case of aromatic systems, it has been suggested by Forster[151] that such a process (self-quenching) involves primary photoassociation to an excimer $^1D_2^*$: $^1D^* + D \longrightarrow {}^1D_2^*$. This excimer can either undergo radiative relaxation, $^1D_2^* \longrightarrow 2D + h\nu$,[152] or can undergo several non-radiative processes:
(1) internal conversion to the ground state, $^1D_2^* \longrightarrow 2D$;
(2) intersystem crossing to a triplet state, $^1D_2^* \longrightarrow {}^3D_2^*$;

(3) dissociation, $^1D_2^* \rightarrow {}^1D^* + D$; or (4), dimerization by a localization of intermolecular forces, $^1D_2^* \rightarrow D_2$.

If excimer dissociation (3) is an extremely rapid process, as it is in the case of naphthalene and phenanthrene,[152] the self-quenching constants would be expected to be very low.

Assuming that both donor $^1D^*$ and excimer $^1D_2^*$ fluoresce, then it would be possible to express the overall reaction kinetics of the above dimerization process in terms of six rate parameters: the radiative transition probabilities of $^1D^*$ and $^1D_2^*$; their non-radiative probabilities; and the rates of the forward and reverse reaction $^1D^* + D \rightleftharpoons {}^1D_2^*$. These parameters have been evaluated experimentally for several aromatic solution systems[153] from observations of the concentration dependence of the monomer and excimer fluorescence quantum yields, and from measurements of their fluorescence intensities as a function of time, using nanosecond (10^{-9} sec.) flash photolytic procedures.

However, in the case of biphenylene photodimerization in which the monomer does not emit, it is not possible to apply this general technique to determine the rate of dimerization occurring through a self-quenching, excimer process.

Because of the lack of these emission properties, the photodimerization of biphenylene could not be investigated in as much detail as originally hoped for using conventional irradiation techniques. It is apparent from Rentzepis'

initial work, that the fluorescence quantum yields for biphenylene excited by Q-switched mode-locked lasers is attainable. However, Rentzepis has not yet reported the results of further investigation into high-energy excitation of biphenylene. Also, it has not been shown by Rentzepis that, under this high-energy irradiation of biphenylene, photodimer is produced.

Therefore, it was possible only to monitor the net disappearance of biphenylene and/or the net appearance of photodimer as a function of the following: temperature, solvent and heavy-atom effects, potential quenchers, and initial concentration of biphenylene; and to search for intermediates by examining ultraviolet spectra. A kinetic reaction scheme is presented later on that is consistent with a photochemical process in which dimerization is the only apparent product-forming process.

4. General Observations

Irradiation of solutions of biphenylene (0.05M to 0.08M) in solvents of varying viscosities and boiling points led to an almost quantitative conversion of biphenylene to photodimer when yields were corrected for recovered unreacted biphenylene. Thus, dimerization is the only product-forming process occurring when biphenylene solutions are irradiated at wavelengths greater than ca. 3200 A; dimer was shown to be not formed at appreciable rates at lower wavelengths.

E. Kinetic Methods and Materials

Materials. Biphenylene was prepared from either anthranilic acid[82] or from 1-aminobenzotriazole[83] and recrystallized several times from ethanol and then further purified by chromatography on a silica gel column using purified hexane as the elutant. This material has a melting point of 111.5-112.0°. Biphenylene from either of these two sources was found to give identical results.

The solvents used were of analytical reagent or spectrograde, or, as in the case of n-hexane, purified to remove alkenes (see experimental section, part A).

Determination of Quantum Yields. The number of photons absorbed was determined by the use of a trans-stilbene actinometer, following the procedure outlined by DeBoer.[156] Since it was shown that the isolated photodimer does not undergo further photochemical reaction either to new products or photodissociation under the conditions of irradiation, no correction for back-reaction was necessary.

Solutions of biphenylene were irradiated alongside actinometer solutions in a Rayonet reactor equipped with a cooling fan and a merry-go-round accessory. For the determination of the optimal wavelength for photodimerization, the solutions were contained in either quartz or Pyrex reaction vessels, (Southern New England RQV-7 and RQV-8 cells, respectively) 10.0 mm in diameter and filled to a volume of 10.0 ml. A bank of sixteen lamps was used as the

light source. After determining that the optimal wavelength were greater ca. 3200, all kinetic determinations were performed using only 3500 A lamps and Pyrex cells.

The concentration of the biphenylene monomer was measured spectrophotometrically before and after illumination, using light of 358 nm which is not absorbed by the dimer. Alternatively, complete ultraviolet spectra were determined during the course of the reaction by diluting 0.10 ml. aliquots to appropriate concentrations. These results were checked by evaporating the irradiated solutions to dryness, extracting unreacted biphenylene with pentane, and then evaporating the pentane to determine the weight of recovered biphenylene.

Since the concentration of the photodimer could not be determined spectrophotometrically due to its insolubility in the solvent used for irradiation, the weight of the dimer was determined as the weight of the residue remaining after extraction of biphenylene with pentane.

Absorbance of aliquots from irradiated samples was determined on a Gilford Model 2400 spectrophotometer or on a Cary Model 14 spectrophotometer which was also used to record complete ultraviolet spectra.

Experimental Limitations. It was found that concentrations of biphenylene in the range of 0.05 M to 0.08 M led to the optimum chemical yields of photodimer in preparative runs using the sunlamp apparatus described in part F of the

experimental section. In order to prevent precipitation of biphenylene during pipetting in the kinetic runs, and thus permitting reproducible analyses, the range of 0.02 M to 0.05 M was used when comparing the effects of solvent change, addition of heavy-atom solvents, and effects of potential quenchers.

If biphenylene showed fluorescence, it would have been possible to determine the optimal concentration to maximize the quantum yield; this would be done by measuring the quantum yield of fluorescence as a function of concentration and temperature. This is expressed in the following simplified form of the Stern-Volmer equation,[157] where c_h is the mean self-quenching concentration constant, φ is the measured quantum yield at concentration c, and φ_m is the maximum quantum yield:

$$\varphi = \frac{\varphi_m}{1 + (c/c_h)}$$

F. Rate of Biphenylene Disappearance

H. A. Hammond[150] has demonstrated that the quantum yield for the sensitized photoisomerization of trans-stilbene was constant at 0.55 ± 0.02 for stilbene concentrations of 0.01 M or greater, and for seven sensitizers with phosphorescence energies greater than 57 kcal. It was shown by DeBoer[156] that if conditions of irradiation are adjusted so that less

than 5% isomerization occurs, no corrections have to be made for back reaction and that benzene solutions of trans-stilbene with benzophenone as sensitizer may be used as an actinometer in other photochemical studies.

Thus, it was found that a benzene solution of trans-stilbene (0.03 M) containing benzophenone (0.10 M) when irradiated with a bank of sixteen 3500 A lamps in a Rayonet reactor for a period of 100 seconds produced 3.26% isomerization.

Therefore, using the value of 0.56 for the quantum yield of trans/cis isomerization, a value of 1.0×10^{17} photons per second per unit volume was obtained for the photon flux of the Rayonet reactor using the following equation:

$$\text{Photon Flux} = \frac{W\lambda}{hc} = n \times (6.024 \times 10^{23}) / \Phi_I t,$$

where W is the power-output of the source in Watts, λ is the wavelength of the light source, h is Planck's constant, c is the speed of light, n is the number of moles of material that has reacted in any process (light-induced) in a period of time (t) for a given unit volume of solution (V).

$$\Phi_I = \frac{\text{molecules reacted per unit time per unit volume}}{\text{photons of light absorbed per unit time per V}} .$$

When 5.00×10^{-2} M hexane solutions of biphenylene were irradiated alongside the stilbene actinometer solutions, it was found that there was a loss of 2.5% of biphenylene in

the initial 4,000 seconds of irradiation. Using the photon flux calculated from the actinometer, a value of 0.019±0.002 was calculated for the quantum yield for the initial rate of disappearance of biphenylene. The 10% experimental error reported is based on the average per cent deviation of the values obtained from gc analyses.

G. Quantum Yield for Loss of Biphenylene in Comparison to Rate of Formation of Photodimer

The photon flux of a Rayonet reactor fitted with a bank of sixteen 3500A lamps and a merry-go-round accessory was measured periodically with the stilbene actinometer previously mentioned and found to be constant at 1.0×10^{17} photons per second per unit volume within an error of ± 10%.

The reaction vessels were Southern New England RPV-8 Pyrex cells, 10.0 mm in diameter and containing a 95% ethanol solution (5.00×10^{-2} M) of biphenylene (10.0 ± 0.1 ml.). The samples were used without degassing and the temperature around the reaction vessels was maintained at ambient by means of a cooling fan located in the bottom of the reactor.

At intervals of 24 hours, pairs of samples were removed, combined,* and diluted to exactly 100.0 ml. with 95% ethanol.

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*It was found that by combining pairs of irradiated samples, sufficient amounts of dimer could be obtained for analysis, and that the results of uv analyses were more reproducible following this procedure.

Aliquots of 0.100 ml. were removed and diluted to exactly 25.0 ml. Complete spectra were determined in the range of 2900-3900 A and compared to unirradiated samples (4.00×10^{-5} M in biphenylene). Further dilution of a 5.0 ml. aliquot of the above solution to 25.0 ml. enabled determination of spectra over the range of 1900-2900 A and comparison to unirradiated samples (8.00×10^{-6} M in biphenylene). By comparing the spectra of irradiated and nonirradiated samples of biphenylene at the principal maxima (3580, 3390, 2500, and 2410 A), it was possible to determine the concentration of remaining biphenylene, and thus, the amount consumed.

The remaining solution from the pairs of irradiated samples was evaporated to dryness. Unreacted biphenylene was removed by extraction with pentane. The weight of the pentane-soluble fraction (recovered biphenylene) was compared to the weight of the insoluble fraction (photodimer). The results are summarized in Tables VI and VII.

Table VI. Loss of Biphenylene

Sample	Wt. Pentane-Soluble Fraction (mg.)	Wt. Biphenylene from uv spectra (mg.)	Wt. Diff.* (mg.)	Length of Irrad'n (hrs.)
Ref.	146	152	06	0
1	142	134	08	24
2	139	118	21	48
3	127	107	20	72
4	114	96	18	96
5	95	83	12	120
6	76	73	03	144

* Average per cent deviation of Weight of Pentane-Soluble Fraction from calculated Wt. of Biphenylene (uv) = 11%. This gravimetric error is used to estimate the gravimetric error for the determination of photodimer, also determined gravimetrically.

Table VII. Loss of Biphenylene vs. Dimer Formation

Length of Irradiation (hrs.)	Wt. Dimer (mg.)	Calc'd. moles* of Dimer ($\times 10^5$)	Calc'd. moles** of Biph. Consumed ($\times 10^5$)
24	1.0	0.30	8.00
48	7.0	2.30	18.0
72	22.0	7.20	26.0
96	43.0	14.1	33.0
120	73.0	24.0	41.0
144	93.0	30.6	48.0

* Determined from Wt. of Pentane-Insoluble extract.

** Determined from uv spectra of irradiated samples.

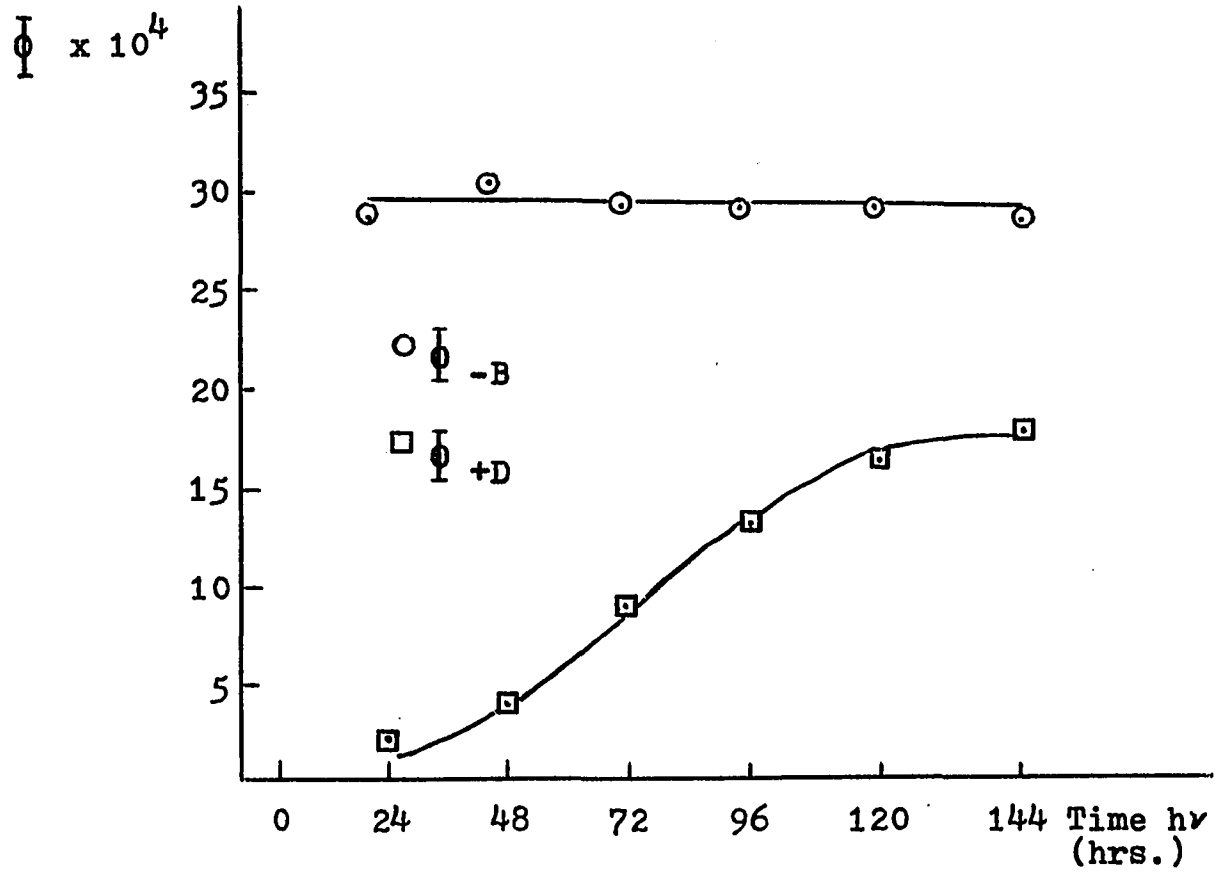
Using the values for the number of moles of biphenylene consumed relative to the number of moles of dimer produced in the same time period, the quantum yields for the loss of biphenylene relative to the quantum yields for dimerization corrected to a unit volume of 10.0 ml. were calculated and are shown in Table VIII. In addition, the quantum yields have been plotted as a function of time and represented in Figure 4.

Table VIII. Quantum Yields Corrected to Unit Vol. of 10.0 ml.

Length of Irradiation (hrs.)	$\Phi_{-B} \times 10^4$	$\Phi_{+D} \times 10^4$	Φ_{-B} / Φ_{+D}
24	27.9	1.10	26.6
48	31.4	4.00	7.8
72	30.2	8.40	3.6
96	28.8	12.4	2.3
120	28.6	16.8	1.7
144	27.9	17.7	1.6

Average $\Phi_{-B} = 29.1 \times 10^{-4}$; average dev. $= 1.1 \times 10^{-4}$;
Average Per Cent Dev. in $\Phi_{-B} = 3.8\%$.

Figure 4. Quantum Yields as a Function of Time.



Since the uv spectra of the irradiated samples showed no new bands, the presence of an intermediate that absorbs light in the region of biphenylene excitation (> 2600 A) can be ruled out. This would be especially apparent in the 2600-2900 A region where biphenylene and dimer shown essentially transparent.

The initially low values for the quantum yield of dimer formation calculated from the weight of isolated product is most likely due to the presence of a supersaturated solution of photodimer. The apparent leveling off of the quantum yield for dimerization relative to the quantum yield for the

loss of biphenylene is in accord with the observed chemical yield. Also, due to the small conversion rate of biphenylene to dimer, the isolation of these small amounts of dimer is subject to large errors relative to the errors associated with the uv analysis of biphenylene consumption. Since previous attempts at analysis of photodimer by gas phase chromatography did not lead to reproducible results (insolubility of dimer in most solvents), the above procedure was the more acceptable method.

By comparing the ratio of Φ_{-B} / Φ_{+D} in the region of the graph where the rate of change of the quantum yields appear to be linear, it is possible to show that the rate of biphenylene consumption is twice the rate of dimerization, consistent with observed chemical yields and indicative of a photochemical process in which dimer is the only product being formed. The above ratio approaches 2.0 with an estimated error of 16%, likely reflecting high apparent weights for the dimer because of solvent incorporation.

The result of a ratio of Φ_{-B} / Φ_{+D} of two is in accord with the usual scheme for photodimerization, as follows, where $(BB)^*$ is either an excimer or the excited cyclobutane 2a that gives the cyclooctatetraene product, D is the isolated dimer, B and B^* are the biphenylene monomer and its excited-state, respectively.

		Rate Expression
1.	$B + h\nu \longrightarrow B^*$	I_a
2.	$B^* + B \longrightarrow (BB)^*$	$R_2 \quad [B^*] \quad [B]$
3.	$(BB)^* \longrightarrow D$	$k_3 \quad [BB^*]$
4.	$(BB)^* \longrightarrow 2B$	$k_4 \quad [BB^*]$
5.	$B^* \longrightarrow B$	$k_5 \quad [B^*]$

The presence of an association dimer in solution prior to irradiation was essentially ruled out by the Beer's Law study, previously discussed, in which there was found neither change in molar extinction coefficients with changes in biphenylene concentration nor appearance of new bands in the ultraviolet spectrum with concentration changes.

H. Quantum Yield for Loss of Biphenylene as a Function of Biphenylene Concentration

The loss of biphenylene at varying initial concentrations (1.00×10^{-4} M to 5.00×10^{-2} M) was determined relative to a reference actinometer sample for a series of hexane solutions irradiated at 3500 A for 10,000 seconds in a Rayonet reactor. The results are summarized in Table IX. A plot of the reciprocal of biphenylene concentration versus the reciprocal of the quantum yield for the loss of biphenylene was made and is shown in Figure 5.

Table IX. Quantum Yield for the Loss of Biphenylene at Various Initial Concentrations.*

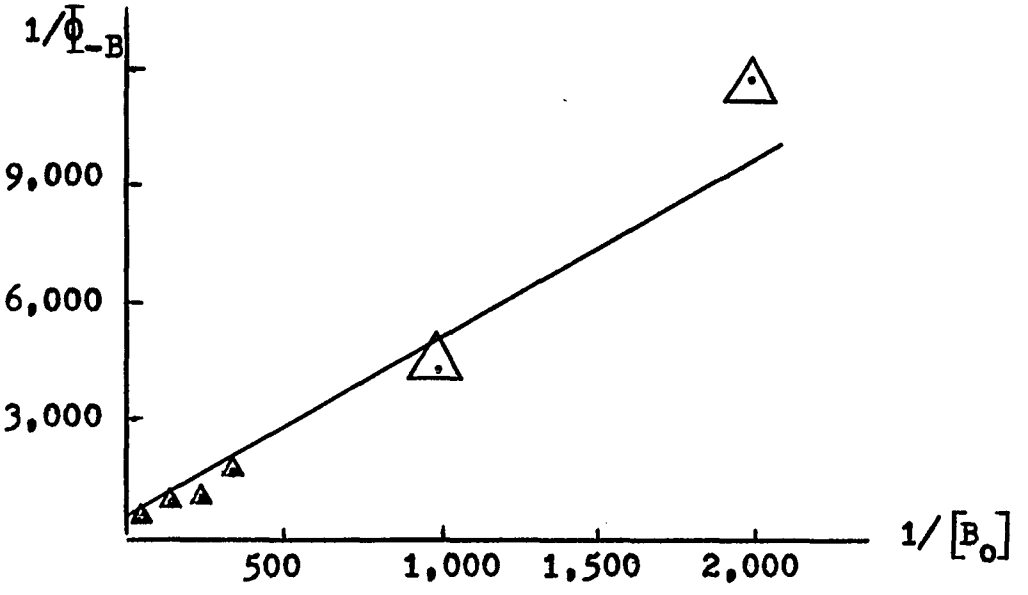
$[B_o]$**	Φ_{-B}***
5.00×10^{-4}	8.30×10^{-5}
1.00×10^{-3}	2.60×10^{-4}
5.00×10^{-3}	9.80×10^{-4}
1.00×10^{-2}	4.50×10^{-3}
2.50×10^{-2}	7.50×10^{-3}
5.00×10^{-2}	1.70×10^{-2}

* Hexane solutions irradiated at 3500 A for 10,000 seconds.

** Initial concentration of biphenylene solutions.

*** Based on a photon flux of 1.00×10^{17} photons/sec/unit vol.

Figure 5. Reciprocal quantum yield for loss of biphenylene as a function of reciprocal concentration of biphenylene



The slope was graphically determined to be 5.2, and the intercept, by the point-slope equation, to be 85.

If the usual scheme for photodimerization were applicable (see page 93), a linear equation of the form $y = mx + b$ would obtain in which the slope is equal to $(k_3 + k_4)\, k_5 / 2k_2k_3$ and the intercept is equal to $(k_3 + k_4) / 2k_3$. For all intercept values greater than unity, k_4 (rate of decay of excimer to ground-state biphenylene) will be greater than k_3 (rate of dimerization) which coincides with the observed experimental results.

I. Test for Heavy Atom Effects on the Photodimerization of Biphenylene

In order to test for a heavy atom effect by ethyl bromide in the photodimerization of biphenylene, aliquots of 0.05 M biphenylene (10.0 ml.) in hexane containing varying amounts of ethyl bromide (12.5-37.5% by volume) were irradiated at 3500 A in a Rayonet reactor alongside reference samples of biphenylene (containing no ethyl bromide) for a period of 24 hours.

The quantum yield for the loss of biphenylene in the absence of ethyl bromide was compared to the quantum yield in the presence of ethyl bromide. If the ratio of Φ_o/Φ (quantum yield in absence/quantum yield in presence of EtBr) could be shown to increase linearly with increase in the concentration of ethyl bromide, then the quenching rate constant could be found from a plot of this ratio versus ethyl bromide concentration.

It was found that the quantum yield in the absence of ethyl bromide was 0.019 $\pm$ 0.002 while the quantum yield for the loss of biphenylene over the range of ethyl bromide concentrations was found to be constant at 0.011 $\pm$ 0.001. Over the range of concentrations used, therefore, no heavy atom effect is observed, and the decreased rate of loss of biphenylene by 40% may be a simple polar effect.

Also, since no new dimeric product could be found, a process involving enhanced transition from a singlet to a

triplet species caused by the presence of a heavy atom was not found.

Cowan and Drisko[13] had found that the ratio of cis/trans-dimers of acenaphthalene could be changed by the addition of small amounts of a heavy-atom solvent. This was attributed to the enhanced intersystem-crossing of a singlet excimer (which forms only cis-dimer) to a triplet intermediate which reacts to form both isomers (ratios depending upon solvent polarity).

J. Attempted Quenching by Piperylene

It was apparent from earlier preparative photodimerization, and later shown in quantum yield studies, that the presence of air in irradiated biphenylene solutions does not change the rate of dimer formation within the experimental error of ± 11%. This is suggestive of a singlet excited-state intermediate.

In order to provide further evidence for this conclusion, solutions of biphenylene (0.02 M) in both n-hexane or cyclohexane containing piperylene (0.1 M and 0.5 M) were irradiated at 3500 A for 10,000 seconds in the presence of reference samples of biphenylene containing no piperylene.

Within experimental error, the quantum yield for the disappearance of biphenylene was not effected by the presence of piperylene, indicating that a triplet-state intermediate is not involved.

Prolonged irradiation of biphenylene solutions (0.05 M) in a mixture of hexane and piperylene using the sunlamp procedure gave rise to quantitative yields of dimer after correction for recovered biphenylene, showing that no new processes occurred.

K. Quenching Studies with Napthalene

Ethanol solutions of biphenylene (0.02 M) containing naphthalene in varying concentrations (1.00×10^{-5} M to 1.50×10^{-2} M) were irradiated at 3500 A for a period of 48 hours alongside reference solutions of biphenylene (no naphthalene present).

Aliquots of irradiated and non-irradiated samples were taken and diluted appropriately so that the entire ultraviolet spectrum of each aliquot could be determined. The concentration of the remaining biphenylene was calculated by comparing the absorbance at several maxima of irradiated samples relative to non-irradiated reference samples.

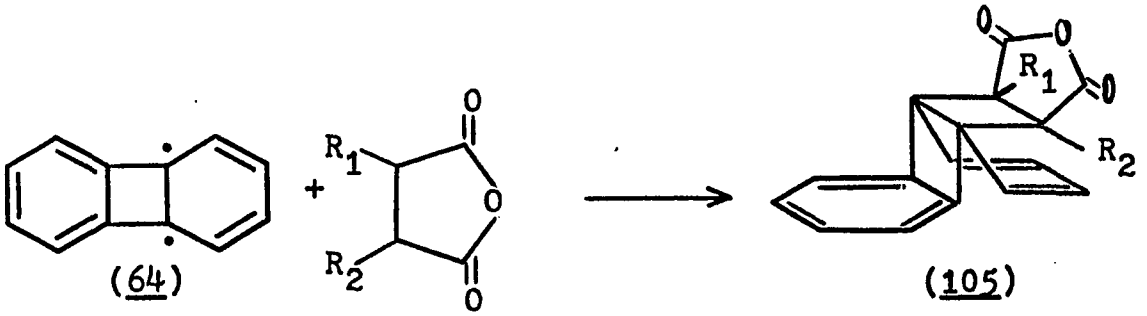
It was found that the average rate of disappearance of biphenylene was 21.06% $\pm$ 0.42% in the presence or absence of naphthalene. Thus it would appear that the biphenylene was absorbing all the incident light to produce the excited-state intermediate that leads to photodimer without any appreciable transfer of energy to the naphthalene system.

Work-up of the irradiated samples resulted in the recovery of unreacted biphenylene, unreacted naphthalene, and

biphenylene photodimer, but no cross-product of biphenylene and naphthalene.

L. Attempted Trapping of Biphenylene Photo-Intermediate

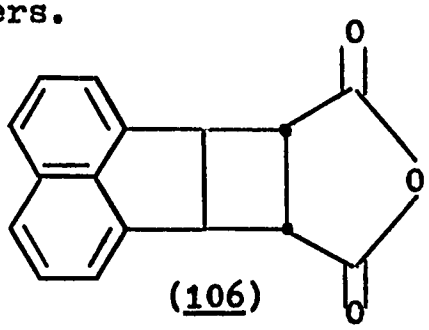
It is suggested that the photodimer of biphenylene is derived by a $[2\pi + 2\pi]$ cycloaddition initiated by excited biphenylene which, for purposes of illustration and with the structure of the photodimer in mind, can be represented as a diradical 64. In order to prove the presence of such an intermediate, trapping experiments were tried with various active olefins. In the case of maleic anhydride (100, R_1 = R_2 = H) and its derivatives (R_1 = R_2 = Cl and R_1 = H, R_2 = Br), reaction of these dienophiles with the excited state of biphenylene would give rise to products of the following structure, if bonding were to take place at the same carbon atoms as in the photodimer.



(64) (100) (105)

In an analogous case, Hartmann and Heine[37a] had shown that irradiation with a mercury high-pressure lamp through Pyrex, of maleic anhydride and acenaphthylene in dioxane,

acetone, or acetonitrile led to the formation of a copolymer and/or the dimers of acenaphylene. However, if halogenated methanes were used as solvent, the reaction was found to proceed differently, with the formation of a cycloaddition adduct 106, with a corresponding decrease in acenaphylene dimers and copolymers.



(106)

This result can be explained as a heavy-atom effect, with cycloadduct 106 a product of triplet acenaphylene.

Similarly, Meinwald[37b] found that irradiation of a solution of acenaphthylene and maleic anhydride in n-propyl bromide with a Hanovia 450 W lamp, using a uranium glass filter sleeve ($\lambda > 320$ nm), resulted in the conversion of acenaphthylene to the same cycloadduct in about 50% yield relative to a yield of 10% for acenaphthylene dimers (mixture of both isomers). Based on recovered starting material, the overall conversion to dimers and cycloadducts was about 50%.

Before quantitative results were obtained on the heavy atom effect for biphenylene, there were preliminary experiments indicating that the effect did, in fact, take place (small amounts of ethyl bromide added to hexane solutions of

biphenylene appeared to increase the rate of dimer formation). Consequently, heavy atom solvents or maleic anhydride derivatives containing heavy atoms could increase the rate of intersystem crossing to the triplet and, thereby, reduce singlet-derived dimerization.

In this event, irradiation at reflux (sunlamp) or at ambient temperature (Rayonet reactor, 3500 A) failed to produce any cycloaddition products when biphenylene was irradiated in the presence of maleic anhydride or its derivatives (bromo-, or dichloro-) in hexane solutions containing ethyl bromide. In all instances, biphenylene was recovered unreacted in yields of 80-95%. The remaining 5-20% consisted of intractable oils and polymers and, in the case of maleic anhydride, about a 10% yield of maleic anhydride dimers (ir and nmr spectra).

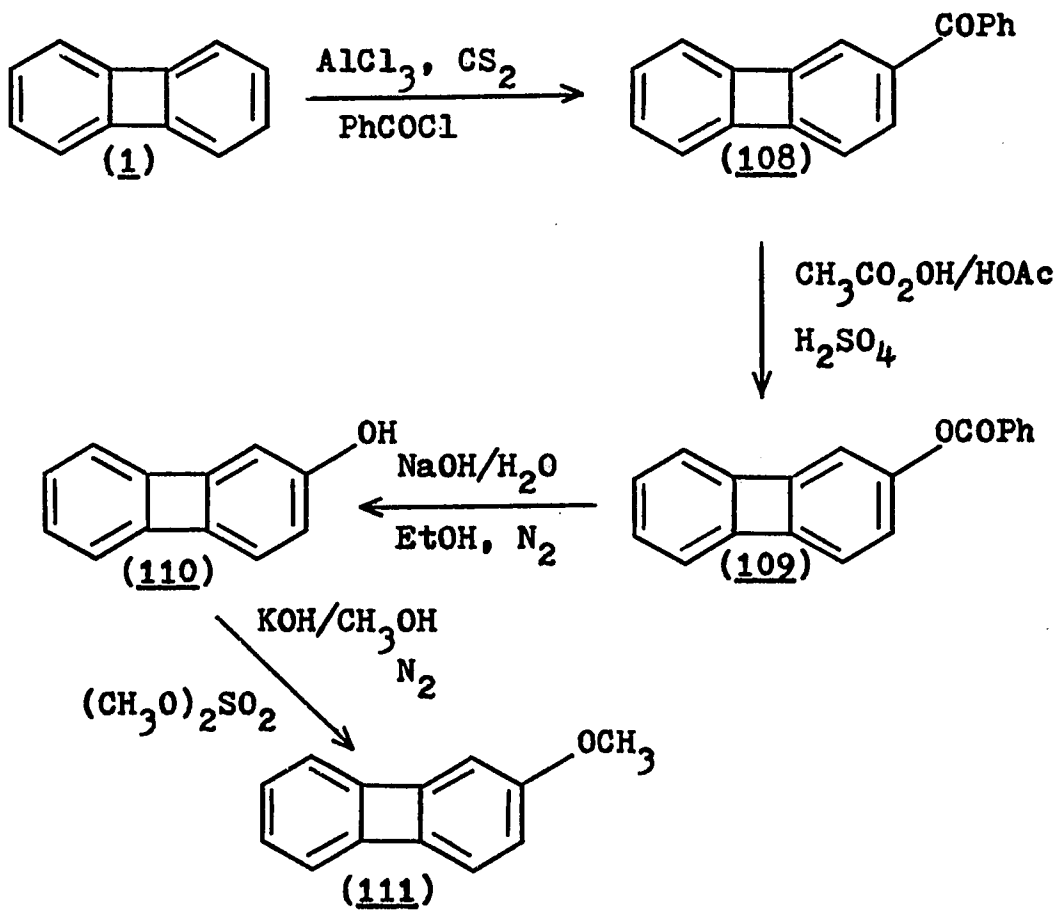
In none of the above cases could any biphenylene photodimer be found, suggesting that excited-state biphenylene was being quenched by energy transfer to the anhydride systems more efficiently than reaction with ground-state biphenylene to form photodimer.

M. Substituent Effects on Biphenylene Photodimerization

It is known that the addition of a substituent to an aromatic hydrocarbon can alter the normal course of the photoreaction of the parent hydrocarbon. This has been demonstrated in the case of naphthalene in which the nature of

the substituent (steric bulk), as well as its location in the aromatic ring, effected the overall photochemical reaction.[58-62] Photodimerization was found to be the primary reaction of several 2-alkoxynaphthalenes. In the case of the 2-methoxy derivative 23, two dimers have been reported (see page 24).

Therefore, it was anticipated that 2-methoxybiphenylene (111), synthesized as outlined below, might lead to the formation of another photodimer of the biphenylene system.



Biphenylene reacted with benzoyl chloride in the presence of powdered aluminum chloride to give 2-benzoylbiphenylene (108) in 57% yield. When 108 was treated with peracetic acid in acetic acid containing sulphuric acid (modification of McOmie's[89] procedure), the ketone underwent the Baeyer-Villiger reaction to give rise to 2-benzoyloxybiphenylene (109) in 66% yield. Alkaline hydrolysis of 109 under a nitrogen atmosphere gave an 89% conversion to 2-hydroxybiphenylene (110). Reaction of 110 with 10% methanolic potassium hydroxide in the presence of dimethylsulfate gave a 74% yield of 2-methoxybiphenylene (111). Thus, biphenylene was converted in four steps to 111 in ca. 25% overall yield.

1. Irradiation of 2-Methoxybiphenylene (111)

Irradiation of 111 under identical conditions used for preparative photodimerization of biphenylene (275 W sunlamp, refluxing hexane solution, one week) led to a 96% recovery of the starting material. No other compounds could be detected in the photolyzed solution (tlc and uv spectrum).

2. Irradiation of 2-Benzoylbiphenylene (108)

Similarly, irradiation of hexane and ethanol solutions (0.02 M) of 108 using a 275 W sunlamp as in the above, failed to produce any reaction. Starting material was completely recovered.

3. Irradiation of 2-Benzoyloxybiphenylene (109)

When a hexane solution (0.018 M) of 109 was irradiated, as in the previously cited cases, a rapid visible reaction

was observed. Within several hours of irradiation (275 W sunlamp), the originally pale-yellow solution of 109 began to turn orange in color. After irradiating for 24 hours, an aliquot was removed, diluted to an appropriate volume, and its uv spectrum determined and compared to the spectrum of an unirradiated sample. Analysis of the spectrum revealed that 57% of the starting ester had disappeared. At the end of three days, only a trace of starting material could be detected (tlc and uv spectrum).

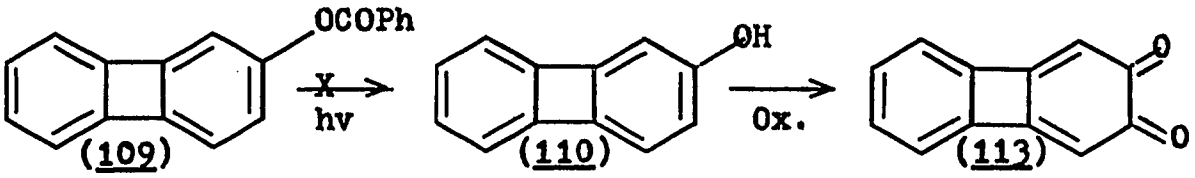
From the irradiated solution was isolated an 88% yield of a mixture of orange solids, m.p. 123-145°, along with unreacted starting material (12%), m.p. 140-148°. The photoproduct gave a brick-red color when treated with ethanolic ferric chloride, indicating the presence of a phenol. The starting ester 109 failed to react with the same test reagent. This reaction was then investigated in more detail, as described in the following section.

N. Photo-Fries Rearrangement of 2-Benzoyloxybiphenylene

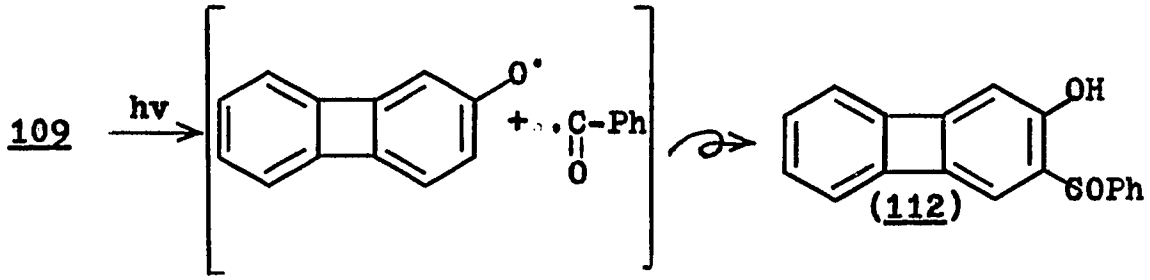
It was apparent from the fact that the photoproduct isolated from the irradiation of 109 gave a positive test for a phenol that a cleavage must have occurred at the ArO-COPh bond, presumably homolytic.[173] Two modes of reaction are available to the radicals thus produced: (1) hydrogen abstraction by ArO· to form 2-hydroxybiphenlene (110), or (2) molecular rearrangement within a solvent cage to

produce 2-benzoyl-3-hydroxybiphenylene (112) or 1-benzoyl-2-hydroxybiphenylene.

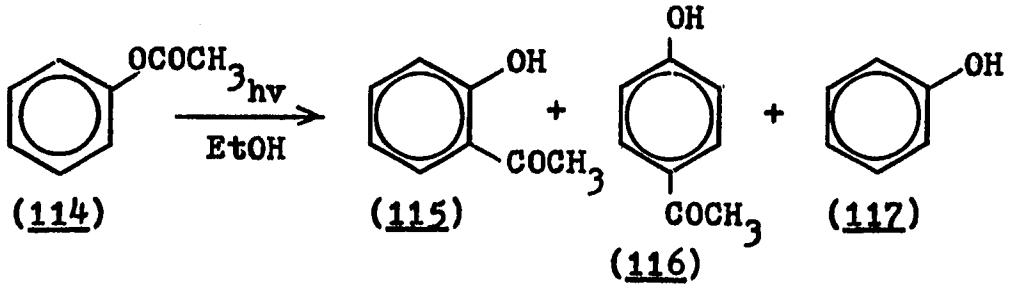
2-Hydroxybiphenylene and its known oxidation product, biphenylene-2,3-quinone[89] can be ruled out based on the mass spectrum of the product.



Instead, the second process occurs with migration of the benzoyl group to the 3-position (as shown later by comparison to the product of the thermal Fries rearrangement).



The photo-Fries rearrangement was first observed by Anderson and Reese in 1960.[158] The rearrangement of phenyl acetate in ethanol to give o- and p-hydroxyacetophenones and phenol is an example of this reaction.



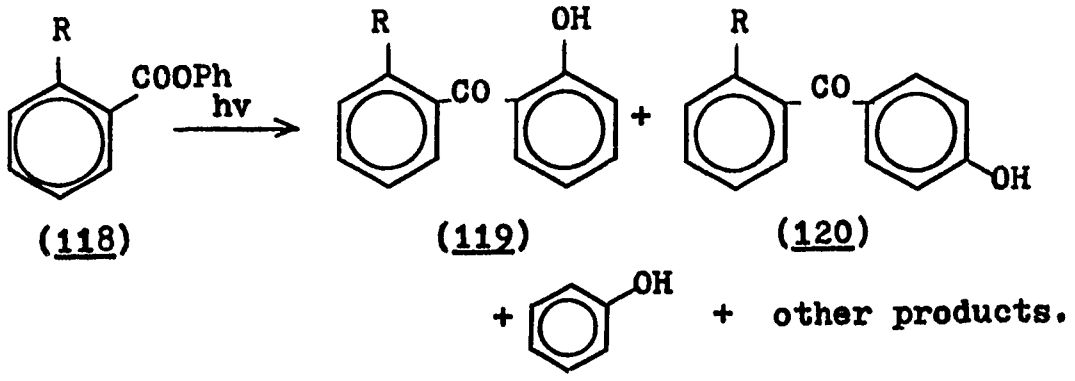
The rearrangement has been shown to occur for many derivatives of phenol: phenyl esters,[159-162] aryl alkyl carbonates,[163-164] phenoxyacetic acids,[165] and hydroxyphenyl cinnamates.[166] A review of the photo-Fries rearrangement has been published by Bellus.[167]

Although there is agreement that the photo-Fries rearrangement is intramolecular, the nature of the excited state of the reactive intermediate has been disputed. The presence of a triplet intermediate has apparently been ruled out since attempts to quench the rearrangement with triplet quenchers such as naphthalene, ferric acetylacetonate,[168] and 1,3-cyclohexadiene[169] have been unsuccessful. Attempts at triplet sensitization with acetophenone were also unsuccessful.[170-171]

It has been reported by some investigators that the rearrangement is unaffected by the nature of the solvent.[171] However, it has also been reported that the rearrangement is indeed influenced by the solvent.[172,173]

Plank[173] studied the photo-rearrangement of phenyl benzoate (R = H) and phenyl o-toluate (R = CH_3) in several solvents. The irradiations were run in sealed Vycor tubes using a Rayonet reactor fitted with 3000 A lamps.

It was apparent from the relative yields of 119 and 120 compared to the yield of phenol that the rearrangement is dependent on the nature of the solvent. The yield of rearrangement products increased from 36% in ether to 79% in



methanol. The yield of phenol was found to decrease as methanol was added to ether solutions. In the presence of t-butyl alcohol, there was a 98% conversion of phenyl benzoate to a combined yield of 119 and 120 (R = H) of 84% with a relative yield of 57% for the ortho isomer 119.

Polar solvents were found to favor rearrangement, and the non-polar solvents found to favor phenol formation. Since both benzene and ether (non-polar solvents) were found to give the same yield of Fries product (33%), the solvent effect is not solely due to a partitioning between an intramolecular rearrangement process and an intermolecular hydrogen abstraction process (phenol-forming). Sandner and Trecker[171] have found that the quantum yield for the rearrangement of p-tolyl acetate was unaffected by a 100-fold change in viscosity of the reaction medium.

Plank, therefore, suggests that these results are consistent with a mechanism involving two reactive excited states: one leading to the rearrangement products, and the other to the formation of phenol.

In the case of 2-benzoyloxybiphenylene (109), a rearrangement is the exclusive pathway no matter if a polar (t-butyl alcohol) or non-polar (hexane, cyclohexane) solvent is used.

Irradiation of cyclohexane solutions of 109 (0.01 M) in a Rayonet reactor equipped with 3500 A lamps resulted in a 93% conversion of the ester to rearrangement product (55%) and unidentified polymeric material (30%), which also gave a positive test for the presence of a phenol when treated with ethanolic ferric chloride.

The rearrangement product was further resolved by several separations on silica gel (ptlc) giving an orange compound, m.p. 129-131°. The uv, ir, nmr and mass spectral fragmentation were in accord with structure 112 and the same as that for the thermal; aluminum chloride induced Fries rearrangement.

In the previous instance, reaction was complete in about 48 hours. When the same procedure was repeated using t-butyl alcohol as solvent, irradiation for only 150 minutes resulted in a 40% conversion to rearrangement product. The reaction was stopped at this time to see if the rearrangement product was the same as with cyclohexane as solvent. This insured that primary, rather than products of further irradiation, were observed.

It was found that the rearrangement was not accompanied by formation of polymer under these conditions. Further

purification of the initially isolated material (ptlc) gave rise to orange crystals, m.p. 130-134°, with the same spectral properties as the rearrangement product in cyclohexane.

These results are consistent with a mechanism proposing a solvent-caged diradical intermediate that undergoes intramolecular rearrangement within the solvent-cage. The apparent lack of formation of 2-hydroxybiphenylene (110), or its oxidation 2,3-quinone product 113, suggests that the rate of intramolecular rearrangement is more rapid, or that this process is more efficient than hydrogen abstraction from the solvent.

O. Thermal $AlCl_3$-Induced Fries Rearrangement of 2-Benzoyloxybiphenylene

When a pulverized mixture of 2-benzoyloxybiphenylene and three equivalents of powdered aluminum chloride were heated between 150-160° for a period of 20-25 minutes, there resulted a ca. 66% conversion to rearrangement product. The orange material was resolved by several separations on silica gel until pure yellow-orange needles, m.p. 129-130°, were isolated. The uv, ir, nmr, and mass spectral fragmentation patterns were identical to those found for the photo-Fries product.

IV. EXPERIMENTAL

A. Materials

Hexane was purified by vigorously stirring a mixture of technical grade n-hexane (1500 ml.) with concentrated sulfuric acid (400 ml.) for several days. The alkene-free layer was separated, washed with: water (2 x 200 ml.), saturated aqueous sodium carbonate (2 x 200 ml.), water (2 x 200 ml.), and saturated aqueous sodium chloride (2 x 100 ml.); dried (anhydrous calcium sulfate) for three hours; filtered; refluxed over calcium hydride; and distilled at 67.5 - 68.0°.

Benzene was purified by distillation from calcium hydride, and stored over sodium metal.

Ethyl acetate was purified by washing with: 10% aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride; dried (anhydrous magnesium sulfate); filtered; and distilled at 77.0 - 78.0°.

Acetone was purified by distillation from solid potassium permanganate.

Other solvents and liquid reactants used in photochemical experiments were purified by distillation. All other solvents used in extraction procedures were commercial materials used without further purification. Solids not purchased explicitly for photochemical use were purified by recrystallization to constant melting point.

B. Analytical Procedures

All melting points (m.p.) and boiling points (b.p.) are uncorrected. Infrared (ir) spectra were recorded on a Perkin-Elmer Model 237B grating spectrophotometer. Ultraviolet (uv) spectra were recorded on a Cary Model 14 spectrophotometer. Absorbance of aliquots from photochemical runs were determined on a Gilford Model 2400 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian Model A-60A spectrometer or on a Varian EM-360 instrument. Mass spectra were determined by Dr. Robert Engel and Mr. Dennis Liotta using a Varian-MAT Model CH-7 instrument. ^{13}C magnetic resonance (cmr) spectra were recorded by Dr. George A. Grey of Varian Associates on an XL-100 or a CFT-20 instrument.

Thin layer chromatographs (tlc) were run on microscope slides coated with Silica Gel G. Column chromatography was done using the specified grade and quantity of Baker Analysed neutral alumina in a 25 mm. diameter column, unless otherwise specified. Gas chromatography (gc) was performed using a Varian-Aerograph Model 1200 instrument with flame detection. Elemental analyses were performed by the Micro-Tech Laboratory of Skokie, Illinois.

C. Preparation of Biphenylene

1. Method of Friedman.[82]

Anthranilic acid was diazotized according to the

procedure of Friedman with freshly prepared isoamyl nitrite. Solid benzenediazonium-2-carboxylate prepared from 34.5 g. of anthranilic acid was rapidly decomposed in 1.5 liters of boiling 1,2-dichloroethane. The combined material from five of these runs was reduced to a volume of 200 ml. at 35-40° using a continuous-feed rotatory evaporator.

Purification by ethylene glycol co-distillation led to the isolation of straw-colored crystals of biphenylene (22.4 g., 24%), m.p. 110-111° (Lit. m.p. 111-112°). Recrystallization from n-hexane gave rise to almost-white crystals, m.p. 111.5-112.0°.

2. Method of Campbell and Rees.[83]

Decomposition of 1-aminobenzotriazole, prepared by the method of Trave and Bianchetti,[97] using lead tetraacetate under a nitrogen atmosphere, led to the formation of biphenylene (74%), m.p. 111-112°. Mixed melting point determination with a sample prepared by the method of Friedman showed the two samples to be identical.

D. 1-Aminobenzotriazole (48)

1. Method of Trave and Bianchetti.[97]

Using the sequence of reactions reported in the literature,[97] o-nitroaniline (82.8 g., 0.6 mole) was diazotized and converted with diethyl malonate to the corresponding diethylmalonic nitrohydrazone (70.0 g., 40%), m.p. 68-69° (Lit.[97] m.p. 72-74°). Catalytic reduction of the

nitrohydrazone (61.8 g., 0.2 mole), followed by diazotization and recrystallization of the crude product, led to the isolation of light yellow crystals of the diethyl malonate derivative of 48 (27.7 g., 48%), m.p. 95-97° (Lit.[97] m.p. 99-100°). Hydrolysis of the above derivative (50.9 g., 0.176 mole), followed by recrystallization, led to the isolation of colorless crystals of 1-aminobenzotriazole (17.7 g., 75%), m.p. 80-81° (Lit.[97] m.p. 82-83°).

2. Attempts at Direct Amination of Benzotriazole

a. Hydroxylamine-O-sulphonic Acid (50a)

To a stirred suspension of benzotriazole (6.45 g., 0.05 mole), in dry benzene (120 ml.) kept at 0° was added sodium hydride dispersion in mineral oil (2.4 g., 0.05 mole). The resulting mixture was refluxed for one hour, after which time 50a (5.65 g., 0.05 mole) in water (10 ml.) was added dropwise over a period of 20 minutes.

The solid material gradually dissolved and a two-phase (benzene/water) solution resulted. The aqueous phase developed a turbid appearance and the benzene layer became yellow. These two phases were allowed to stir at room temperature (R.T.) overnight.

The resulting mixture was filtered and the filtrate extracted with ether (4 x 50 ml.); dried ($MgSO_4$); filtered and evaporated to give rise to 2.21 g. of a light orange and brown powder, m.p. 72-76°.

The aqueous phase remaining from the above ether extraction was made alkaline with 10% aqueous sodium hydroxide; extracted with ether (100 ml.) and benzene (100 ml.); dried ($MgSO_4$); filtered and evaporated to an orange and red powder (2.03 g.), m.p. 72-76°. The solids from the ether extractions were combined and recrystallized from benzene/pet. ether to give rise to off-white crystals (3.1 g.), m.p. 89-90°, which proved to be unreacted starting material when it was compared to benzotriazole. The ir spectrum did not show the presence of any 1-aminobenzotriazole.

b. Modification using 50a

To a stirred mixture of 50a (5.65 g., 0.05 mole) in water (10 ml.) and benzene (50 ml.) at 60° was added dropwise a solution of benzotriazole (6.45 g., 0.05 mole) and sodium hydroxide (6 g., 0.15 mole) in water (25 ml.). An additional amount of benzene (50 ml.) was added, and the mixture refluxed for 1.5 hours.

The mixture was cooled, filtered and the filtrate thoroughly extracted with ether (3 x 100 ml.); dried and concentrated. No 1-aminobenzotriazole could be detected (ir spectrum and tlc against authentic sample).

c. O-Benzylhydroxylamine (50b)

A mixture of 50b-hydrochloride (1.6 g., 0.01 mole) and sodium hydride dispersion (50% by wt., 1.04 g., 0.02 mole) in benzene (50 ml.) and dioxane (20 ml.) was stirred at 50-60° under a nitrogen atmosphere for 30 minutes. To this

was then added dropwise a solution of benzotriazole (1.19 g., 0.01 mole) in benzene (100 ml.)

After refluxing for one day, the mixture was cooled and diluted with ether (200 ml.) and extracted with water (3 x 200 ml.). The alkaline organic phase was extracted with 50% aqueous hydrochloric acid (2 x 250 ml.), then washed with water, saturated aqueous sodium carbonate, and saturated aqueous sodium chloride. Continued work-up of the organic layer in the usual manner gave rise to a yellow liquid containing several components (tlc).

Neutralization of the HCl-extracts with saturated aqueous sodium carbonate (500 ml.) and solid Na_2CO_3, followed by extraction with ether (4 x 400 ml.), and evaporation of the dried solution, gave rise to a yellow oil. Trituration with low boiling pet. ether (100 ml.) failed to induce crystallization. Removal of the pet. ether gave rise to a yellow oil which was as complex as that obtained from the benzene layer. No evidence for the presence of 1-aminobenzotriazole could be found (ir and tlc).

d. O-(2,4-Dinitrophenyl)hydroxylamine (50c)

This aminating reagent was prepared by a series of reactions described by Sheradsky[99] and Carpino.[100] Thus, tert-butyl carbazate (51) was converted to tert-butyl azidoformate (52) in 86% yield and used without further purification for conversion into tert-butyl N-hydroxycarbamide (53) in 74% yield, purified by recrystallization from

pet. ether to give rise to 53, m.p. 53-55° (Lit.[100] m.p. 55-57.5°). Reaction with 2,4-dinitrochlorobenzene gave rise to tert-butyl N-(2,4-dinitrophenoxy)carbamate (54) in 52% yield as yellow crystals after being recrystallized from ethyl acetate/hexane, m.p. 75-77° (Lit.[99a], m.p. 74-75°). The carbamate was hydrolyzed with trifluoroacetic acid to give rise to golden crystals (87%) when recrystallized from ethanol, m.p. 100-101°, dec. (Lit.[99a], m.p. 112°). Thus, the overall yield of 50c based on 51 was 29% (Lit.[100], 33%).

To 50 ml. of dry methanol under a nitrogen atmosphere was added sodium metal (0.23 g., 0.01 mole). After all the sodium had dissolved, benzotriazole (1.29 g., 0.01 mole) was added and stirred until dissolved.

The solvent was then evaporated under reduced pressure (140 mm. Hg) at 100° while under a nitrogen atmosphere. The resulting residue was immediately dissolved in dry DMF (50 ml.).

One equivalent of the aminating reagent 50c (1.99 g., 0.01 mole) was added to the above DMF solution at R.T., stirred for 20 minutes and then poured into 250 ml. of cold water. (The expected precipitate failed to appear).

The resulting dark solution was extracted with ether (3 x 200 ml.), benzene (2 x 200 ml.), and ethyl acetate (2 x 100 ml.). The individual extracts were dried ($MgSO_4$); filtered; and evaporated to give rise to mixtures of oils and/or liquids, none of which showed the presence of 1-aminobenzotriazole.

3. Application of the Curtius Reaction[101]

a. Benzotriazole-1-Carboxylic Acid Chloride (56)

To a stirred saturated solution of phosgene gas in dry ether (250 ml.) kept between -5° and 0° under a nitrogen atmosphere was added, dropwise, a solution of benzotriazole (4.76 g., 0.04 mole) in anhydrous ether (200 ml.).

After the addition had been completed, the system was allowed to warm up to R.T. and then evaporated (red. pressure) to a paste. The paste was dried by warming on a hot water-bath while passing a stream of dry nitrogen over the material.

b. Benzotriazole-1-Carboxylic Acid Azide (57)

To a well-stirred mixture of sodium azide (3.25 g., 0.05 mole) in dry benzene (250 ml.) at 50° and under a nitrogen atmosphere was added a suspension of the acyl chloride from above (a) in a mixture of benzene/acetone (100/200 ml.). The resulting mixture was allowed to stir for one day at 45-50°.

The mixture was then cooled to R.T., diluted with water (100 ml.) and stirred vigorously at 0° for about one hour, saturated with solid sodium chloride (25 g.), and separated. The aqueous phase was extracted with ether (2 x 100 ml.) and the ethereal extracts combined with the previously separated benzene layer, dried ($MgSO_4$), filtered, and concentrated to give crude product (4.83 g., 65%).

The above crude material was washed with ether

(3 x 75 ml.) until the washings were colorless. There resulted a light brown residue (708 mg.), fraction 1, m.p. 154-156° (dec.). The filtrates from the washing procedure were chilled and filtered to give rise to an off-white residue (90 mg.), fraction 2, m.p. 161-162° (dec.). Evaporation of this filtrate gave rise to a viscous yellow oil which solidified as nitrogen was passed over it (3.58 g.), fraction 3.

Fraction 3 was washed with small portions of ice-cold ether to leave a residue (665 mg.), fraction 4, m.p. 160-162° (dec.), and a yellow filtrate, which upon evaporation gave rise to a golden yellow oil which crystallized slowly upon standing (2.70 g.), fraction 5. Repetition of this ether wash procedure gave a residue (220 mg.), fraction 6, m.p. 160-162° (dec.). Evaporation of the filtrate, followed by recrystallization from hot ethanol (50 ml.) with the aid of Norite, then recrystallization from ethanol/water produced a slightly yellow compound. The ethanolic solution from above was decanted from the solid, diluted with an equal volume of water and extracted with ether (3 x 70 ml.), dried ($MgSO_4$), and concentrated to a brown crystalline compound (2.124 g.), fraction 7, m.p. 79-82°.

Total amount of recovered benzotriazole: 2.70 g.

Amount consumed: 2.06 g., 0.0173 mole.

Fractions 1,2,4 and 6 combined: 1.68 g. (52%).

Ir (KBr): 4.65, 5.75, 6.23 μ.

c. Attempted Rearrangement to Isocyanate (58)

To well-stirred decalin (100 ml.) kept at 125° was added portionwise solid acyl azide (1.56 g., 0.083 mole). As the solid was added, the decalin took on an orange color which gradually darkened to a deep purple hue.

After allowing the solution to cool slowly to 60°, water (80 ml.) was added to hydrolyze any isocyanate that might have formed. The mixture was then cooled to 5°, acidified with 6M hydrochloric acid (25 ml.), and separated.

The decalin was further extracted with 6M HCl (2 x 25 ml.), washed with saturated aqueous sodium carbonate (25 ml.), dried ($MgSO_4$), and concentrated. The resulting orange-colored liquid was distilled to remove decalin (32-35°/0.85-0.95 torr). The residue was crystallized from ether to give rise to unreacted acyl azide (147 mg.), m.p. 162-163°.

The acid extracts were neutralized with solid sodium carbonate, extracted with ether, dried ($MgSO_4$), filtered, and evaporated to give a mixture of an oil and solid. Crystallization of this mixture from benzene triturated with pet. ether led to the isolation of a solid (200 mg.), m.p. 94-95°. A second crop of benzotriazole was also obtained (121 mg.), m.p. 92-93°, after concentration of the mother-liquor and further trituration with pet. ether. It was concluded that the Curtius rearrangement did not take place, and that benzotriazole was formed during the hydrolytic

work-up procedure.

E. Beer's Law Study of Biphenylene in Hexane

(i): A stock solution of biphenylene in purified dry n-hexane was prepared at 1.0×10^{-4} molar concentration. Various aliquots were taken and diluted to 25.0 ml. and the absorbance of these solutions was measured at 339, 344, and 358 nm using 1.000 cm. matched quartz cells.

A plot of absorbance vs. molar concentration yielded a straight-line curve for all concentrations studied at the principal uv maxima of biphenylene (2.0×10^{-6} M to 8.0×10^{-5} M).

(ii): The same procedure was followed using a stock solution of 1.0×10^{-3} M biphenylene. Plotting the absorbance vs. concentration at the principal uv maxima also gave a straight-line (2.0×10^{-4} M to 1.0×10^{-3} M).

F. Preparative Photolysis of Biphenylene

A solution of biphenylene (1.00 g., 6.58 mmole) in purified hexane (100 ml.) in a 250 ml. pyrex conical flask fitted with a reflux condenser and under a nitrogen atmosphere was irradiated with a G. E. 275 W sunlamp. The flask was mounted 15 cm. above the center of the lamp and the whole system completely surrounded with aluminum foil.

After a period of one week, irradiation was stopped and the contents of the flask cooled and filtered to give photodimer (292 mg.), m.p. 258-266° (dec.). The filtrate was

concentrated to 60 ml. and irradiated for another four days. Work-up in the same manner afforded a second crop of photodimer (242 mg.), m.p. 260-266° (dec.), for a combined yield of dimer (53.4%). The residue from the evaporation of solvent contained mainly unreacted biphenylene and photodimer (ir and tlc) which was purified by column chromatography and then co-distillation of crude biphenylene with ethylene glycol at 150-197°.

The slightly brown photodimer was purified by vacuum sublimation at 110-148° and 0.1-0.25 mm Hg. to produce white crystals, m.p. 260-263° (dec.): molecular ion at m/e 304.1232 (calc'd. for $C_{24}H_{16}$: m/e 304.1252); ir (KBr) 13.25, 13.80, 14.81 μ; nmr ($CDCl_3$) 7.04 (8H, s), 6.48-5.52 (8H, AA'BB').

G. Reduction of Biphenylene Photodimer

1. Octahydrodimer

A mixture of photodimer (600 mg., 1.98 mmole), purified ethyl acetate (175 ml.), and 10% Pd/C (310 mg.) was stirred under hydrogen maintained at atmospheric pressure throughout reduction.

After the theoretical uptake of hydrogen had been consumed (65 min.), the reduction mixture was filtered through a Celite filter pad and washed with hot benzene. Evaporation of the benzene/ethyl acetate solution gave rise to white crystals, m.p. 174-178°, in a quantitative yield.

Vacuum sublimation at 120-130° and 0.55 mm Hg. afforded a pure white crystalline powder, m.p. 177.5-179.0°; molecular ion at m/e 312; ir (KBr) 13.25, 13.70 μ; nmr ($CDCl_3$) 6.93 (8H, s), 2.80 (4H, m), 2.12 (4H, m), 1.57 (8H, m).

Analysis. Calc'd. for $C_{24}H_{24}$: C, 92.29; H, 7.71. Found: C, 92.10; H, 7.88.

2. Octadeuterodimer

A mixture of photodimer (177 mg., 0.582 mmole), purified ethyl acetate (70 ml.), and 10% Pd/C (25 mg.) was stirred under a deuterium atmosphere maintained at atmospheric pressure.

After the theoretical uptake of deuterium had been consumed (113 min.), the mixture was worked up as in the above (1.) to give rise to a white solid (177 mg., 95%), m.p. 173-179°.

Vacuum sublimation at 120-130° and 0.5 mm Hg. afforded a white solid, m.p. 180.0-181.5°; ir (KBr) 12.55, 13.20, 13.83 μ; nmr ($CDCl_3$) 6.93 (8H, s), 2.72 (4H, m), 1.62 (4H, m). Mass spectrum, m/e (relative intensity) 321 (50.5), 320 (100), 319 (87.5), 318 (48.8) showing that the deuterated dimer contains d_6, d_7, d_8, and d_9 species.

H. Attempted Elucidation of Photodimer Structure by Chemical Means

1. Periodate-Permanganate Oxidation[131]

Biphenylene photodimer (100 mg., 0.33 mmole) in dry acetone (15 ml.) was oxidized according to the method of Lemieux and von Rudloff[131] using a mixture of potassium permanganate (60 mg., 0.4 mmole) and sodium meta-periodate (1.9 g., 8.9 mmole) in dry acetone (20 ml.).

After stirring for three days at room temperature, the reaction mixture was worked up in the usual manner. Extraction with benzene (2 x 200 ml.) and ether (2 x 100 ml.) followed by drying ($MgSO_4$) and evaporation led to the isolation of a mixture of solids and oils (225 mg.): ir ($CHCl_3$) 2.9 (OH), 8.3, 9.3 (C-O), 5.9 (C=O) μ.

A partial separation was effected by crystallization from benzene/pet. ether to give a solid (40 mg.), m.p. 62-85° (dec.). The nmr spectrum revealed the loss of the original vinyl AA'BB' system (5.5-6.5).

Evaporation of the filtrate from the above crystallization gave rise to a mixture of several products (68 mg.) which was not resolvable.

2. Periodate-Permanganate Oxidation - Modified

After several modifications in the above procedures had been made (ratio of periodate to permanganate, solvent system, work-up conditions), a solution of the photodimer

(200 mg., 0.66 mmole) in acetone (30 ml.) was oxidized by the dropwise addition to a mixture of sodium meta-periodate (3.8 g., 17.8 mmole) and potassium permanganate (200 mg., 1.3 mmole) in aqueous acetone (100 ml. of 20% acetone/water). During the course of the addition (35 min.), solid sodium carbonate was added to maintain the pH between 7 and 8.

After work-up in the usual manner to remove MnO_2 and periodate, the filtrate was made alkaline with 40% aqueous sodium hydroxide, filtered through Celite, and extracted with benzene (2 x 250 ml.) to give rise to base-insoluble materials (258 mg.) which when crystallized from chloroform/pet. ether afforded a white amorphous solid (18 mg.), m.p. 190-215°. The ir and nmr spectra gave no indication that the desired product had been formed.

The alkaline solution from above was acidified (Congo Red) with 6M hydrochloric acid, extracted with benzene (3 x 250 ml.) and ether (2 x 250 ml.), and dried ($MgSO_4$) to give rise to a mixture of acid-insoluble materials (413 mg.). Recrystallization from chloroform/pet. ether gave a high-melting residue (25 mg.), m.p. > 280°, and a mixture (seven spots on tlc) upon evaporation of the filtrate (228 mg.) that still showed an aromatic system in the nmr spectrum.

3. Osmylation[141]

To a stirred solution of photodimer (0.515 g., 1.7 mmole) in dry benzene (30 ml.) containing 1 ml. of dry pyridine was added a freshly prepared solution of osmium tetroxide

(0.500 g., 1.97 mmole) in dry benzene (10 ml.), while under a nitrogen atmosphere. After four days, work-up in the manner described by Criegee[141] gave rise to a dark purple solid (256 mg.). Chromatography from neutral alumina, grade 2, (20 g.) and elution with chloroform gave 196 mg. of a solid (yellow), m.p. 232-250° (dec.) and two fractions as films (total of 53 mg.). The ir and nmr spectra indicated mainly unreacted starting material and small amounts of a hydroxy compound.

4. Oxidative Osmylation[132]

To a stirred solution of the photodimer (100 mg., 0.33 mmole) in dioxane (10 ml.) was added 5.1 ml. of a stock solution (0.01 M on osmium tetroxide and 0.1 M in sulfuric acid). The resulting black suspension was added to a stirred solution of potassium chlorate (0.322 g., 2.62 mmole) in a mixture of dioxane (4 ml.) and water (10 ml.).

After stirring an additional day at room temperature, the resulting yellow solution was concentrated to one-half volume, saturated with solid sodium chloride, extracted with ethyl acetate (3 x 100 ml.), dried ($MgSO_4$), filtered and concentrated to a volume of 25 ml.

After removal of osmium according to the method of Lemieux and Johnson,[127] followed by evaporation of the ethereal filtrate, there was isolated an oil which crystallized from chloroform/ether to give a yellow crystalline compound (220 mg.), foams at 98°, melting at 105°. Tlc, ir,

and nmr revealed the presence of an apparently complex mixture of hydroxy- and carbonyl-containing compounds.

5. Peracetic Acid Oxidation

To a solution of photodimer (100 mg., 0.33 mmole) in chloroform (10 ml.) was injected 40% commercial peracetic acid (0.5 ml., 3.8 mmole). After stirring at room temperature overnight, unreacted peracetic acid was hydrolyzed with saturated aqueous sodium bicarbonate (2 ml.). The solution was reacidified with 10% aqueous hydrochloric acid, extracted with chloroform (3 x 50 ml.), washed with water (25 ml.), dried ($MgSO_4$) to give rise to a white solid (139 mg.), m.p. 136-260° (dec.). Tlc, ir, and nmr revealed mainly unreacted starting material, plus several other components. An epoxide was ruled out due to the absence of expected ir bands at 8.0, 10.53-12.35, and 11.90-13.33 μ.

6. Ozonolysis. Aromatic Model

In order to work out the conditions to partially oxidize a polynuclear aromatic hydrocarbon, naphthalene was subjected to ozonolysis according to the method of Moriconi and Salce.[135]

Thus, when a solution of naphthalene (1.28 g., 0.01 mole) in methylene chloride (125 ml.) at dry-ice temperature no longer absorbed ozone (potassium iodide indicator trap), the reaction mixture was purged with nitrogen, then oxidized at 0° with a 1:1 mixture (50 ml.) of 10% aqueous sodium

hydroxide and 30% hydrogen peroxide.

After one hour, the mixture was transferred and refluxed with an additional 50 ml. of the oxidizing mixture for 3.5 hours, and then allowed to stir overnight at room temperature. Unreacted naphthalene (518 mg.) was removed by extraction with methylene chloride.

After concentrating the alkaline solution to a volume of 150 ml., the solution was chilled and then acidified (Congo Red) with 12 M hydrochloric acid, cooled and filtered to give rise to a white solid (1.29 g., 78%) of phthalic acid, m.p. 204-205° (sealed tube). Mixed melting point with authentic acid showed no depression. The ir spectrum was superimposible with that of phthalic acid.

7. Ozonolysis of Photodimer

Ozone was passed through a solution of the photodimer (273 mg., 0.9 mmole) in methylene chloride (100 ml.) for a period of 17 minutes. Work-up in the manner previously described led to the recovery of unreacted photodimer (31 mg.). The acidified solution failed to form a precipitate; however, extraction of the sodium chloride saturated solution with methylene chloride gave rise to a yellow and brown solid (75 mg.), m.p. 212-215° with the evolution of a gas (previous softening at 180°). Ir (KBr) 5.55 and 5.9 μ.

An additional acid fraction (167 mg.) was obtained by evaporating the aqueous acid layer to dryness and extracting with acetone in a Soxhlet extractor for two days. Crystal-

lization of the oil, thus obtained, gave rise to a solid (84 mg.), m.p. 168-172° (open tube). The infrared spectrum showed this substance to be impure phthalic acid.

8. Ozonolysis, Meinwald Method[136]

According to the method of Meinwald,[136] ozone was bubbled through a suspension of the photodimer, previously purified by vacuum sublimation (193 mg., 0.63 mmole) in 80% aqueous acetic acid (50 ml.) at room temperature for one day.

To the above was added 30% hydrogen peroxide (5 ml.) and the resulting mixture stirred at room temperature for 70 hours. Evaporation at 30-35° and 1.0-1.16 mm Hg. led to a residue which was taken up into methanol (10 ml.) and esterified with excess diazomethane in ether at 0°. Evaporation of the ethereal solution led to the formation of a viscous liquid. Tlc and ir revealed the presence of a highly complex mixture. No further attempt was made to separate the mixture.

I. Attempted Elucidation of Octahydrodimer Structure by Chemical Means

1. Permanganate Oxidation

To a suspension of the octahydrodimer (130 mg., 0.4 mmole) in a mixture of refluxing dioxane (20 ml.) and water (10 ml.) was added dropwise an aqueous solution of potassium permanganate (0.79 g., 5.0 mmole) in water (20 ml.).

After refluxing overnight, 20% aqueous sodium hydroxide (40 ml.) was added to the brown mixture and the whole was allowed to stir at 50-60° for one hour. The mixture was then filtered (hot), and the residue washed with 20% aqueous sodium hydroxide and water and concentrated to one-half volume, poured into a 10% excess over the equivalent amount of concentrated sulfuric acid, cooled, and extracted for one day with chloroform (100 ml.).

Ir and nmr spectra of the residue obtained from the above extraction revealed the possible presence of a carboxylic acid, but among many other components; the mixture appeared to be too complex to separate on this scale.

2. Periodate-Ruthenium Tetroxide Oxidation[133]

To a mixture of sodium meta-periodate (2.57 g., 12 mmole) in water (100 ml.) and a carbon tetrachloride solution of ruthenium tetroxide (20 ml.) prepared from ruthenium dioxide by the method of Nakata,[134] was added a solution of the octahydrodimer (312 mg., 1.0 mmole) in carbon tetrachloride (50 ml.).

The resulting mixture was stirred at 60° for five days (an additional 6.0 g. of solid periodate was added over the five-day period until a yellow solution persisted). After removal of excess tetroxide according to the procedure of Caputo and Fuchs,[133] the aqueous layer was extracted with chloroform (2 x 50 ml.), dried (Na_2SO_4) and evaporated to

give rise to a yellow and white solid (134 mg.). The nmr (DMSO-d_6) spectrum still showed the presence of an aromatic system.

Various modifications of this procedure did not lead to the isolation of readily identified compounds. Conditions which did lead to the complete oxidation of the aromatic system, as evidenced by nmr spectra, gave rise to a mixture of acidic compounds (ir) which could not be separated and identified.

3. Ozonolysis, Alkaline-Peroxide Method[135]

Ozone was passed through a suspension of octahydrodimer (327 mg., 1.05 mmole) in methylene chloride (80 ml.) at -78° for 25 minutes.

After oxidation with alkaline-peroxide in the usual manner, the mixture was separated into base-insoluble and base-soluble fractions. The base-insoluble fraction gave rise to an oily mixture (246 mg.) which when crystallized from ether/pet. ether gave an insoluble residue (65 mg.), m.p. 100° (dec.). Evaporation of the filtrate gave a film (200 mg.) which was mainly unreacted starting material, along with a mixture of hydroxy and carbonyl compounds (ir and nmr spectra) which could not readily be separated for identification.

4. Ozonolysis, Modified

The octahydrodimer (1.05 g., 3.36 mmole) was ozonized

for a period of 60 minutes and worked up with alkaline-peroxide. After separation of the base-insoluble material (400 mg.), the alkaline phase was acidified, etc., to give rise to acid-insoluble materials (279 mg.) which were taken up into methanol (20 ml.) and refluxed for 17 hours in the presence of 15 drops of concentrated sulfuric acid.

After removing unreacted methanol under reduced pressure, the resulting residue was taken up into benzene (75 ml.) and washed free of acids. Evaporation of the benzene led to a film (186 mg.) which was crystallized from chloroform/pet. ether to give a yellow solid (54 mg.), having no definite m.p., and a residue (after evaporation of filtrate) in the form of a film (92 mg.).

The nmr spectrum was very complicated, showing the presence of a mixture of compounds. In addition to bands attributable to the $-OCH_3$ group (3.6-4.0), there still remained bands associated with the starting material as well as other aromatic compounds (7.0-8.0). This complex mixture could not be resolved into readily identifiable components.

5. Exhaustive Ozonolysis

The octahydrodimer (1.248 g., 4.0 mmole) was ozonized at -78° for seven hours and worked up with alkaline-peroxide.

After separation in the usual manner, there was

obtained base-insoluble material (226 mg.): ir ($CHCl_3$) 5.7, 5.85, 6.25, 7.75 and 7.9 μ. The base-soluble material (580 mg.) appeared to contain an anhydride (5.65 and 5.85 μ).

Various crystallization procedures failed to give any solids from the above fractions. The nmr spectra revealed the presence of complex mixtures for both of the above, and the fractions could not be resolved into identifiable components.

6. Ozonolysis. Meinwald Method[136]

Ozone was bubbled through a well-stirred suspension of the octahydrodimer (500 mg., 1.6 mmole) in 80% aqueous acetic acid (100 ml.) at room temperature for 24 hours.

The resulting solution was oxidized with 30% hydrogen peroxide (20 ml.) for a period of 74 hours and worked up in the usual manner; dissolved in methanol (30 ml.); esterified with excess diazomethane in ether solution at 0°.

The mixture was distilled and gave fractions boiling between 31-150° at 0.7 torr. These fractions were each shown to contain several components which did not lend themselves to ready separation.

J. Possible Model Compound for Structure Proof of Octahydrodimer. THPA Photodimer (99)

A solution of 3,4,5,6-tetrahydrophthalic anhydride (THPA) (4.56 g., 0.03 mole) and benzophenone (1.82 g., 0.01 mole) in spectrograde benzene (650 ml.) was purged of oxygen

by bubbling nitrogen through the solution for 30 minutes and then irradiated with a Hanovia medium-pressure mercury-vapor lamp (200 W) for a period of 130 hours.

Evaporation of the solution led to a mixture of solids (6.3 g.) which was repeatedly recrystallized from ether/pet. ether to give rise to a white solid (1.5 g., 33%), m.p. 276-280°: ir (KBr) 5.5 and 5.65 u; nmr ($CDCl_3$) 2.03 (m) and 1.50 (m) with protons in the ratio of 1:1; ^{13}cmr ($CDCl_3$) 19.47, 24.99, 50.67 and 171.13.

Analysis. Calc'd. for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.07; H, 5.26.

K. Factors Influencing Photodimerization

1. Light Source

a. Wide Bandwidth

Equal volumes of hexane solutions of biphenylene (40.0 ml. of 0.08 M) were irradiated for five days (same apparatus as for preparative runs) using a G. E. 275 W sunlamp, and a Hanovia 140 W portable medium-pressure lamp. The photodimer was isolated in the usual manner and the residues were chromatographed on silica gel (25 mm. x 25 cm. column). The residues were found to contain between 85-90% unreacted biphenylene and between 10-15% other material, mainly polymers and some residual photodimer. Correction of the yield of photodimer to reacted biphenylene gave

almost quantitative yields for the 275 W lamps and an average yield of 86% for the 140 W lamp.

In all the above cases, the wavelength of the irradiating light was greater than 3000 A (Pyrex cut-off at about 3000 A with a corresponding 80% transmission of incident light) and was continuous over the range 3000-3600 A.

b. Narrow Bandwidth - Under Reflux

A solution of biphenylene in hexane (400 ml. of 0.08 M) was irradiated while under reflux in a Rayonet reaction apparatus fitted with a bank of sixteen 3500 A lamps; or alternatively, a bank of sixteen 3100 A lamps; or a bank of sixteen 2537 A lamps. After seven days of irradiation, the solutions were chilled and filtered, and the filtrates evaporated to dryness and chromatographed to recover any unreacted biphenylene and secondary products.

Only the 3500 A lamps gave rise to photodimer (890 mg.), 89%, based on the reaction of 1.0 g. (6.58 mmole) of biphenylene. In the other two cases, biphenylene (97-98%) was recovered unreacted.

c. Narrow Bandwidth - Ambient Temperature

A hexane solution of biphenylene (250 ml. of 0.08 M) was irradiated for six days in a Hanovia reaction vessel fitted with a Pyrex water-jacketed immersion-well containing a medium pressure 200 W lamp, and, alternatively, a hexane solution of biphenylene (600 ml. of 0.08 M) was irradiated in the same apparatus with the addition of a uranium-glass

filter-sleeve around the lamp.

In the presence of the filter, there was a loss of 4% of biphenylene with the production of a quantitative yield, corrected for recovered biphenylene, of photodimer (300 mg., 0.99 mmole). In the absence of the filter, there was an 18% loss of biphenylene with the formation of an 89% yield of photodimer (495 mg., 1.63 mmole).

Similarly, irradiation of a hexane solution (400 ml. of 0.08 M) of biphenylene using a Rayonet reactor fitted with a bank of sixteen 3500 A lamps caused a loss of only 2% of biphenylene with the quantitative formation of photodimer (105 mg., 0.345 mmole), corrected for recovered biphenylene.

The ambient temperature during the above irradiations was approximately 40°.

2. Temperature Effects

Solutions of biphenylene (0.08 M) in hexane (b.p. 69°), cyclohexane (81°), ethanol (78°), octane (125°), and nonane (151°) were irradiated under reflux with 275 W sunlamps for seven days using the same apparatus as for preparative runs.

After isolation of photodimer by filtration, conversion rates were determined based upon reacted biphenylene. The rates were comparable when the solvent was hexane, cyclohexane, or ethanol (85-100%); as the temperature of the refluxing solvent increased, so did the solubility of the dimer in that solvent. In octane, only a 25% conversion to dimer relative to the above solvents was found by filtration, and with

nonane, 6%. In both these cases, column chromatography of the residues obtained after evaporation of filtrates revealed the apparent presence of several secondary photoproducts, each less than 10 mg., which did not lend themselves to characterization, in addition to unreacted biphenylene and residual photodimer.

L. Rate of Biphenylene Disappearance

1. Quantum Yield for Loss of Biphenylene

A stock solution of biphenylene was prepared by the dilution of solid (0.7600 g., 5.00×10^{-3} mole) to exactly 100.0 ml. with purified hexane to give a 5.00×10^{-2} M solution.

For one series of determinations, 10.0 ml. aliquots were degassed by several freeze-pump-thaw cycles using an oil diffusion-pump (10^{-5} torr); for another series, the aliquots were not degassed.

An actinometer was prepared by diluting a mixture of Aldrich analytical grade trans-stilbene (1.2840 g., 7.13 mmole) and benzophenone (4.7054 g., 0.026 mole) to exactly 250.0 ml. with purified benzene.

Aliquots (10.0 ml.) of the actinometer solution were degassed as above and irradiated at 3500 A alongside of biphenylene aliquots in a Rayonet reactor equipped with a merry-go-round accessory.

The actinometer samples were irradiated for 100 seconds

intervals, producing 3.26% isomerization as measured by gas chromatography, at the start, middle, and end of the biphenylene irradiations, 2.5% loss after 4000 seconds.

Analyses: Aliquots of irradiated and non-irradiated samples were injected onto a 6 ft. column of 30% SE 30 supported on acid washed Chromasorb P (60/80 mesh), column temperature 200°; He flow-rate, 60 ml./min.

Quantum Yield: The value of 0.56 was used for the quantum yield of trans/cis isomerization of stilbene,[150] and was used to determine the photon flux of the Rayonet reactor at 1.0×10^{17} photons/sec./unit volume. Thus, the calculated quantum yield for the loss of biphenylene, Φ_{-B}, was found to be 0.019± 0.002, ave. % dev. of ± 10%.

2. Quantum Yield (Φ_{-B}) in Comparison to Formation of Photodimer (Φ_{+D}).

a. Samples were prepared by diluting biphenylene (76 mg.) to exactly 10.0 ml. with 95% ethanol.

b. The samples (5.00×10^{-2} M) contained in Pyrex vessels were irradiated at 3500 A in a Rayonet reactor equipped with a merry-go-round accessory.

c. At intervals of 24 hours, pairs of samples were removed, combined, and diluted to exactly 100.0 ml. with 95% ethanol.

d. Aliquots of 0.100 ml. were removed from c. and further diluted to 25.0 ml. Complete ultraviolet spectra were determined in the range of 2900-3900 A and compared to

unirradiated samples (4.00×10^{-5} M in biphenylene).*

e. Additional dilution of 5.0 ml. aliquots of d. to 25.0 ml. were made to determine spectra over the range of 1900-2900 A and compared to unirradiated samples (8.00×10^{-6} M in biphenylene).

f. The concentration of the remaining biphenylene was obtained by comparison of the spectra of irradiated and non-irradiated samples at $\lambda_{max.}$ 3580, 3390, 2500, 2410 A.

g. Sample pairs of c. were evaporated to dryness and unreacted biphenylene removed by extraction with pentane. The weight of the pentane-soluble fraction (recovered biphenylene) was compared to the weight of the insoluble fraction (photodimer) and the results are summarized in Tables VI, VII, and VIII.

h. Plots of the change in Φ_{-B} and Φ_{+D} as a function of time were made and the ratio of the limiting value of Φ_{-B} / Φ_{+D} was found to be approximately 2.0.

3. Quantum Yield (Φ_{-B}) as a Function of Initial Biphenylene Concentration

Hexane solutions of biphenylene (1.00×10^{-4} M to 5.00×10^{-2} M) were prepared. Aliquots of 10.0 ml. were

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*It was found that the procedure of combination (c) and dilution (d) gave the most accurate results for quantum yield studies and isolation of the photodimer.

irradiated alongside a reference sample (2.50×10^{-2} M) at 3500 A for 10,000 seconds in a Rayonet reactor.

The loss of biphenylene at the various concentrations was determined relative to the reference actinometer sample and the quantum yields for the loss of biphenylene determined and summarized in Table IX. A plot of the reciprocal of the quantum yield for the loss of biphenylene versus the reciprocal of initial biphenylene concentration was made and found to be linear, indicating a reaction that is second order in biphenylene concentration. The slope was determined from the graph (5.2) and an intercept of 85 was determined by application of the point-slope equation for a straight line.

4. Heavy Atom Effects

Kinetic Method: A series of solutions was prepared by diluting biphenylene (0.7600 g.) and varying volumes of ethyl bromide (5.0 - 25.0 ml.) to exactly 100.0 ml. with purified hexane. The resulting biphenylene concentration is 5.0×10^{-2} M.

Aliquots (10.0 ml.) of the above mixtures were irradiated simultaneously with a reference sample of biphenylene in pure hexane (without added ethyl bromide) and an actinometer sample (stilbene/benzophenone) at 3500 A for a period of 24 hours using a Rayonet reactor equipped with a merry-go-round accessory.

At various time intervals the samples were removed and analyzed by uv and gc methods to determine the quantum yield for the loss of biphenylene as a function of the added ethyl bromide. For a discussion of the results, see pp. 97-98.

Preparative Method: A series of hexane solutions were prepared by diluting 500 mg. of biphenylene and varying volumes of ethyl bromide or ethyl iodide to exactly 40.0 ml. (0.08 M in biphenylene). After irradiation with 275 W sunlamps for 4 days, photodimer was isolated by filtration, and reacted biphenylene determined by evaporation of the filtrate to dryness and weighing the residue. The results were questionable because of solvent incorporation.

The use of ethyl iodide gave rise to iodine-containing products, and the heavy atom effect due to iodine could not therefore be determined.

M. Quenching Studies with Naphthalene

(i): Solutions of biphenylene and naphthalene were prepared by weighing out solid samples of biphenylene (304 mg.) and varying amounts of solid naphthalene (1.25×10^{-3} M to 1.50×10^{-2} M) and diluting to exactly 100.0 ml. with 95% ethanol. Aliquots (10.0 ml.) of the naphthalene-containing biphenylene solutions were irradiated alongside of a reference sample containing only biphenylene (2.0×10^{-2} M).

(ii): Solutions were made by diluting weighed biphenylene (304 mg.) and varying aliquots of naphthalene (1.0×10^{-2} M) to exactly 100.0 ml., so that the range of naphthalene concentration varied from 1.0×10^{-5} M to 1.0×10^{-3} M.

As in (i), aliquots of 10.0 ml. were irradiated at 3500 A for a period of 48 hours in a Rayonet reactor equipped with a merry-go-round accessory and analyzed for the loss of biphenylene.

(iii): The quantum yield for the disappearance of biphenylene in the presence of naphthalene relative to the quantum yield in its absence was found to be unchanged within an error of ± 5%.

N. Attempted Quenching by Piperylene

Solutions of biphenylene (2.0×10^{-2} M) in either n-hexane or cyclohexane containing piperylene (0.1 or 0.5 M)

were irradiated at 3500 A for 10,000 seconds in the presence of a reference sample of biphenylene containing no quencher.

Within experimental error (± 5%), the quantum yield for the disappearance of biphenylene was not affected by the presence of piperylene.

O. Attempted Trapping of Biphenylene Photo-Intermediate

Mixtures of biphenylene (500 mg., 3.3 mmole) and equivalent amounts of maleic anhydride or its derivatives (bromo-, or dichloro-) in hexane solutions (60 ml.) containing ethyl bromide (5 ml.) were irradiated for a period of five days with a G. E. 275 W sunlamp.

After evaporation of the irradiated samples to dryness, the residues were subjected to column chromatography (Silica) and the isolated fractions submitted to spectral analysis (ir and nmr). In all instances, biphenylene was recovered unreacted in yields of 80-95%. The remaining 5-20% consisted of intractable oils and polymeric materials. No biphenylene photodimer or cross-product dimers could be detected.

P. Derivatives of Biphenylene - Synthesis

1. 2-Acetoxymercuribiphenylene (105)

Biphenylene (600 mg., 3.95 mmole) was converted to 105 according to the procedure of McOmie.[86] The crude product thus obtained (815 mg.) was extracted with warm benzene in

a Soxhlet apparatus for 24 hours, giving rise to a mixture (650 mg.) containing primarily 105. Unreacted biphenylene (258 mg.) was removed by extraction with pet. ether, leaving 105 (400 mg., 43% corrected for unreacted biphenylene) which crystallized from benzene/pet. ether as a yellow powder, m.p. 166-172° (Lit.[86] m.p. 176-177°).

2. 2-Bromobiphenylene (106) - from (105)

2-Acetoxymercuribiphenylene (2.53 g., 6.2 mmole), suspended in chloroform (100 ml.), was treated by the dropwise addition of a brominating solution (20 ml. of a mixture of 1 ml. of bromine in 50 ml. of chloroform). The resulting mixture was filtered, giving unreacted 105 (985 mg.). The chloroform filtrate was washed with aqueous sodium bisulfite, dried ($MgSO_4$), filtered and evaporated to a yellow oil (1.05 g.) which crystallized slowly upon standing.

The crude 2-bromobiphenylene was purified according to the procedure of McOmie.[86] Thus, conversion to the 2,4,7-trinitrofluorenone complex (2.85 g., scarlet powder, m.p. 125-141°), recrystallization from ethanol (m.p. 134-137°), regeneration by passing its benzene solution through neutral alumina (5 cm. x 40 cm. column) and eluting with benzene, afforded 2-bromobiphenylene (727 mg., 83% corrected for unreacted 105, m.p. 63-65° (Lit.[86] m.p. 64-65°).

3. 2-Bromobiphenylene (Direct Bromination)

A solution of bromine in carbon tetrachloride (84 ml.; from a solution of 2 ml. of bromine in 100 ml. of carbon tetrachloride) was added to a mixture of biphenylene (3.0 g., 0.02 mole) and pyridine (9 ml.) over a period of 30 minutes. After the addition of the first 50 ml. of brominating solution, the mixture was warmed on a steam-bath for 5 minutes. Addition of the remaining brominating solution was followed by warming on a steam-bath for an additional 15 minutes.

The cooled reaction mixture was filtered to remove a brown tar (150 mg.), and the filtrate was washed: 3 M hydrochloric acid (150 ml.), cold water (125 ml.), aqueous sodium bicarbonate (125 ml.), cold water (50 ml.), and saturated sodium chloride (100 ml.). After drying ($MgSO_4$), the carbon tetrachloride solution was evaporated to a viscous yellow oil (3.06 g.) which solidified upon standing. Tlc revealed the presence of unreacted biphenylene, 2-bromobiphenylene, and other components of similar R_f value.

The crude mixture was converted into the 2,4,7-trinitrofluorenone complex and recrystallized from acetic acid/water to give rise to scarlet crystals (6.23 g., 86%), m.p. 134-137°.

The complex (3.9 g.) was taken up into hot benzene and passed through a column of neutral alumina to give rise to 2-bromobiphenylene (1.01 g., 61%, corrected for unreacted biphenylene, m.p. 66-67°).

4. 2-Iodobiphenylene (107) - (Direct Iodination)

A mixture of biphenylene (1.0 g., 6.6 mmole), iodine (2.0 g., 7.9 mmole), sodium persulfate (8.0 g., 3.4 mmole), and acetic acid (50 ml.) was refluxed overnight, cooled, diluted with water (500 ml.), and extracted with ether (4 x 100 ml.). After washing the ethereal extracts with water (100 ml.), saturated sodium carbonate (100 ml.), saturated sodium thiosulfate (100 ml.), water (100 ml.), and saturated sodium chloride (50 ml.), the extracts were dried ($MgSO_4$), filtered and evaporated to a yellow-brown mixture (1.11 g.) which was heated with pet. ether (30-60°), chilled and filtered to give rise to a dark residue (262 mg.), which decomposed without melting; starting at 115°.

Evaporation of the pet. ether filtrate was followed by recrystallization from ethanol (Norite) and trituration with water to afford yellow crystals of 2-iodobiphenylene (435 mg., 24%), m.p. 60-63° (Lit.[86] m.p. 63-64°).

5. 2-Benzoylbiphenylene (108)

To a stirred suspension of powdered aluminum chloride (2.8 g., 0.028 mole) in carbon disulfide (50 ml.) was added dropwise a solution of biphenylene (3.04 g., 0.02 mole) and benzoyl chloride (2.6 ml., 3.15 g., 0.0224 mole) in carbon disulfide (50 ml.). After work-up in the manner prescribed by McOmie,[89] the crude material (5.51 g.) was recrystallized from ethanol (Norite) to give rise to yellow crystals

(2.92 g., 57%), m.p. 114-116° (Lit.[89] 59%, m.p. 115-117°). Recrystallization from ethanol afforded bright yellow platelets (2.38 g.), m.p. 117.0-117.5°.

6. 2-Benzoyloxybiphenylene (109) - Baeyer-Villiger Oxidation

The following preparation is a modification of the procedure described by McOmie for this compound.[89]

2-Benzoylbiphenylene (1.0 g., 3.9 mmole) in acetic acid (50 ml.) was treated with freshly prepared 20% peracetic acid (100 ml., made by diluting 50 ml. of 40% commercial peracetic acid with 50 ml. of glacial acetic acid).

After stirring at room temperature for 21 hours, the solution was chilled in an ice-water bath for 15 minutes, and concentrated sulfuric acid (25 ml.) was added dropwise. In about two hours a precipitate formed, and it was filtered and then washed with glacial acetic acid. The filtrate was returned to the reaction vessel and stirring continued until a second crop of precipitate had formed (6 hours). The filtering procedure was again repeated and the filtrate allowed to stir overnight at room temperature.

The residues from the above filtering procedure (700 mg., 66%), m.p. 144-147° (dec.) were combined and recrystallized from ethanol (Norite) to give rise to 2-benzoloxybiphenylene as yellow straw-like needles (480 mg.), m.p. 151.5-152.0° (Lit.[89] m.p. 150-151°). A second crop of crystals (67 mg.) was obtained by trituration of the ethanolic

filtrate with water.

The remaining reaction mixture was cooled and poured onto chipped ice producing a yellow sludge. Chloroform (250 ml.) was added, and the resulting mixture was stirred for 30 minutes.

After separation of the chloroform layer, the aqueous layer was extracted with chloroform (100 ml.). The two chloroform layers were combined and washed as follows: water (2 x 250 ml.), saturated sodium carbonate (2 x 150 ml.), aqueous sodium chloride (250 ml.), and saturated sodium chloride (50 ml.). The extracts were dried ($MgSO_4$), filtered, and evaporated to give rise to unreacted starting material (150 mg.), m.p. 110-115°.

The alkaline solution from the above washing procedure was chilled and then made acid by the gradual addition of concentrated hydrochloric acid (Congo Red). The acidic solution (no visible precipitate present) was extracted with chloroform (2 x 125 ml.). Evaporation of the dried extracts led to the formation of an off-white powder (48 mg.), m.p. 110-114° (impure starting material).

It was pointed out by McOmie[89] that the yields in this Baeyer-Villiger oxidation of 2-benzoylbiphenylene varied from 47% to 90%. Several other modifications in McOmie's procedure (change in concentration of peracid; temperature; frequency of filtering crude material as formed) led to no improvement in the yield of isolated ester).

7. 2-Hydroxybiphenylene (110)

A mixture of 2-benzoyloxybiphenylene (500 mg., 1.84 mmole), ethanol (15 ml.), and aqueous sodium hydroxide (1 g. of solid dissolved in 20 ml. of water) was heated on a steam-bath for three hours while under a nitrogen atmosphere.

After evaporation of ethanol under reduced pressure, the resulting alkaline residue was extracted with ether, dried, and evaporated to give rise to crude material (103 mg.), m.p. 141-142°. The remaining aqueous phase was acidified with 50% hydrochloric acid (Congo Red) and extracted with ether. Evaporation of the dried extracts led to the recovery of a solid (425 mg.), m.p. 89-96°.

The low-melting solid (425 mg.) was taken up into 150 ml. of ether and extracted with saturated sodium bicarbonate (3 x 25 ml.), washed with water and saturated sodium chloride, dried, filtered, and evaporated to give rise to a yellow solid (171 mg.), m.p. 139-141°.

The sodium bicarbonate extracts were acidified with hydrochloric acid, extracted with ether, washed with water, dried, and evaporated to afford benzoic acid (197 mg., 88%), m.p. 120-121° (no freezing point depression when admixed with authentic benzoic acid, 50:50).

The combined crude hydroxy-compounds (274 mg., 89%) were recrystallized from ethanol (Norite) to afford 2-hydroxybiphenylene as yellow needles (185 mg., 60%), m.p. 142.5-143.0° (Lit.[89] 50%, m.p. 139-140°). A brick-red

color was obtained on addition of ethanolic ferric chloride, confirming the phenolic structure.

8. 2-Methoxybiphenylene (111)

To a stirred solution of 2-hydroxybiphenylene (795 mg., 0.47 mole) in anhydrous methanol (30 ml.) under a nitrogen atmosphere was added 3 ml. of a 10% methanolic potassium hydroxide solution. After cooling the solution to 0°, dimethylsulfate (1.0 ml., 1.35 g., 0.011 mole) was added and the resulting mixture stirred for one hour at room temperature (the reaction was followed by testing a drop of the mixture with ethanolic ferric chloride - a brick-red color indicating the presence of the starting phenol). After the addition of 2.0 ml. of 10% methanolic potassium hydroxide and 1.0 ml. of dimethylsulfate and refluxing for 90 minutes, the spot test showed the complete absence of starting material.

The mixture was diluted with an equal volume of water, concentrated to 50 ml., extracted with ether (2 x 50 ml.), washed with water (50 ml.), aqueous sodium carbonate (100 ml.), water (50 ml.), and saturated sodium chloride (50 ml.). The ethereal extracts were dried (Na_2SO_4), filtered, and evaporated to give rise to an orange solid (820 mg.).

The solid was triturated with pet. ether (2 x 50 ml.) and filtered to give rise to a brown powder (95 mg.), m.p. 134-139° (unreacted starting material), and after evaporation of the pet. ether filtrate, a yellow solid (700 mg.), m.p. 56-60°.

Column chromatography (2 cm. x 22 cm.) on silica gel with benzene afforded 2-methoxybiphenylene as yellow crystals (576 mg., 74% corrected for recovered starting material), m.p. 66-67° (Lit.[154] m.p. 69-70°).

Q. Derivatives of Biphenylene - Photochemistry

1. Irradiation of 2-Methoxybiphenylene (111)

A hexane solution (0.06M) of 111 was irradiated at reflux temperature under a nitrogen atmosphere with a G. E. 275W sunlamp (identical conditions used for preparative photodimerization of biphenylene). The course of the reaction was followed by removing small aliquots of the reaction mixture from time to time and analyzing for the disappearance of 111, and appearance of new components by the comparison with an unirradiated aliquot of the hexane solution.

After a period of one week, irradiation was stopped and the contents of the flask cooled and filtered to give unreacted starting material (96% recovery), m.p. 65-68°.

2. Irradiation of 2-Benzoylbiphenylene (108)

Similar irradiations of hexane or ethanol solutions (0.02M) of 108 failed to produce any detectable reaction (tlc and uv analyses of aliquots). Starting material was quantitatively recovered, m.p. 113-115°.

3. Irradiation of 2-Benzoyloxybiphenylene (109)

Irradiation of a hexane solution (0.018M) of 109, under conditions identical with those cited in the above, produced

a rapid visible reaction. The initially pale-yellow hexane solution changed to a bright orange colored solution within a matter of several hours of irradiation.

Further irradiation of the solution produced a 57% conversion of the starting ester 109 during a 24-hour period (determined by comparative uv analysis of irradiated and unirradiated aliquots). The reaction was continued until no more ester could be detected (within sampling and analytical limits).

Thus, after three days of irradiation, the reaction mixture was evaporated to dryness, and partially resolved by ptlc (silica gel) into a mixture of orange solids (88%), m.p. 123-145°, and unreacted starting material (12%), m.p. 140-148°. The orange photoproduct gave a positive test result when tested for the presence of a phenol with ethanolic ferric chloride solution. The recovered, unreacted starting material (ester 109), failed to give a positive reaction with the same test reagent.

R. Detailed Study of the Photochemistry of 2-Benzoyloxybiphenylene (109) - (Photo-Fries Rearrangement)

1. Irradiation in Cyclohexane (Non-polar Solvent)

Cyclohexane solutions (0.010M) of 109 contained in Pyrex vessels were irradiated at 3500A in a Rayonet reactor equipped with a merry-go-round accessory.

After an apparent 93% conversion of the ester (uv analysis), the photo-residue was separated by ptlc (silica gel) into three main fractions: rearrangement product (55%), unidentified polymeric material (30%), both of which gave positive reactions with ethanolic ferric chloride solution; and unreacted starting material (15%).

Further resolution of the orange material (ptlc on silica gel) gave rise to orange crystals, m.p. 129-131°. The uv, ir, nmr and mass spectral fragmentation pattern were in accord with assigned structure 112.

Analysis. Calc'd. for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.51; H, 4.48.

2. Irradiation in t-Butyl Alcohol (Polar Solvent)

Irradiation of t-butyl alcohol solutions (0.010M) of 109 under identical conditions, as in the previously cited case, gave rise to a rapid conversion to rearrangement product.

While in the previous instance (cyclohexane as solvent) a 93% conversion was accomplished in 48 hours, it took only 150 minutes to effect a 40% conversion to rearranged product without formation of polymeric material using the more polar alcohol solvent.

Resolution of the photo-residue (ptlc) gave rise to orange crystals, m.p. 130-134°, with the same spectral properties as for the rearrangement product obtained from the cyclohexane irradiations.

Analysis. Calc'd. for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.15; H. 4.53.

S. Thermal $AlCl_3$-Induced Fries Rearrangement of 2-Benzoyloxybiphenylene (109)

A pulverized mixture of 109 (0.1373g., 0.5 mmole) and anhydrous aluminum chloride (0.2000g., 1.5 mmole) was heated under a nitrogen atmosphere between 150-160° for a period of 20-25 minutes.

The resulting brick-red material was added with stirring to a mixture of ice (10g.) and concentrated hydrochloric acid (5ml.), extracted with methylene chloride (4 x 25 ml.), washed with water (50 ml.), and saturated sodium chloride (50 ml.). The dried ($MgSO_4$) methylene chloride extract was filtered and evaporated to give rise to a brown-orange solid (100 mg., 73% wt. recovery).

Recrystallization from 95% ethanol (Norite), followed by several separations on silica gel (ptlc) gave rise to light orange needles, m.p. 129-130°. The uv, ir, nmr and mass spectral fragmentation patterns were identical to those found for the photo-Fries product.

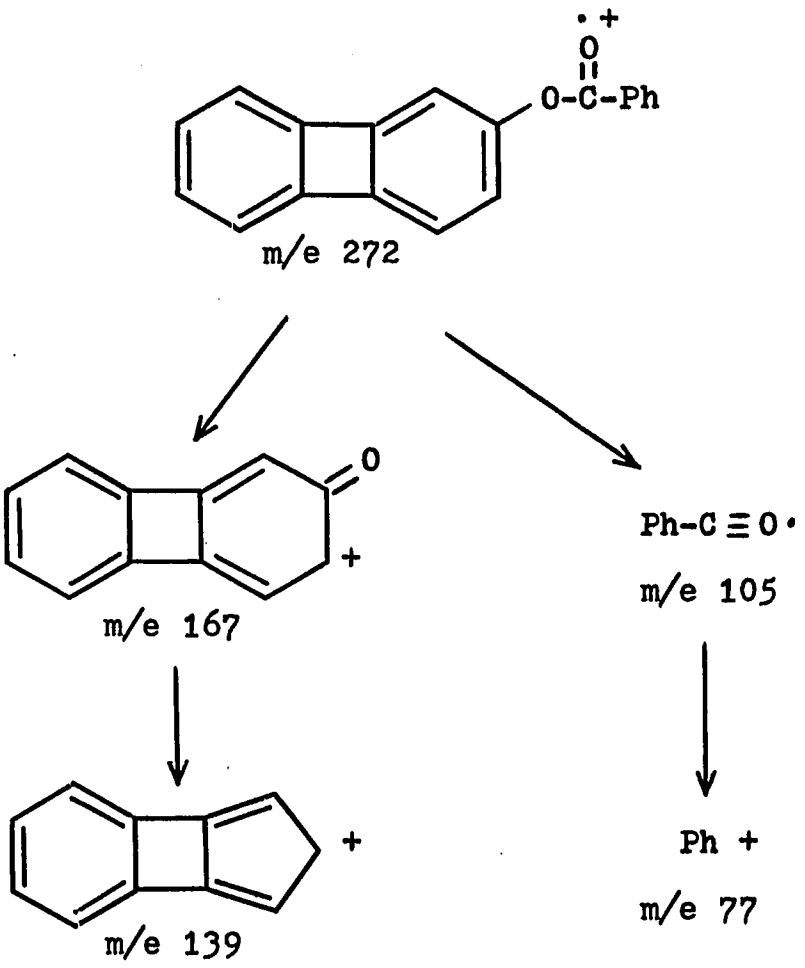
Analysis. Calc'd. for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.40; H, 4.69.

T. Mass Spectral Fragmentation Patterns

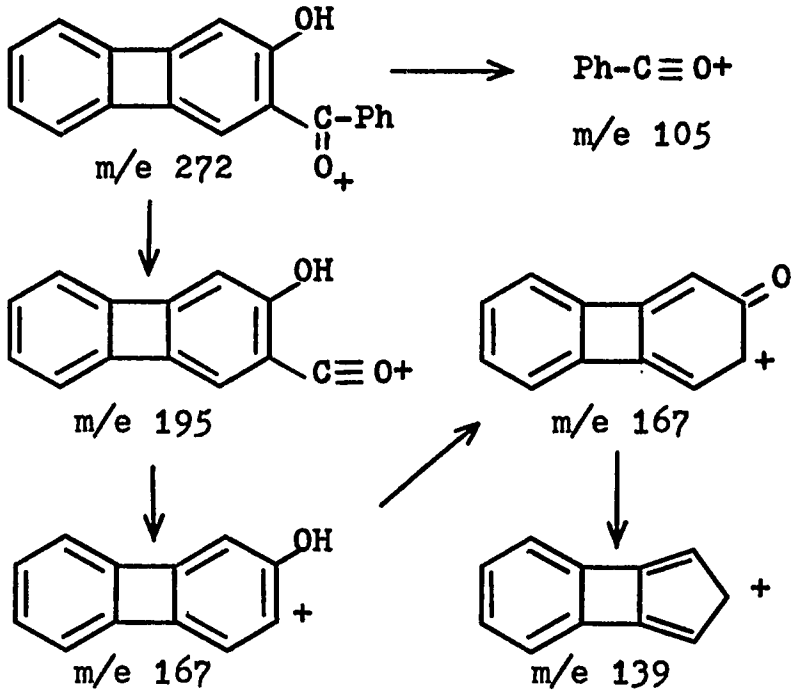
Differences in the structure of the starting material (ester 109) and the Fries rearrangement product were apparent from the mass spectrum of both compounds.

The Fries product, 2-benzoyl-3-hydroxybiphenylene (112), and 2-benzoyloxybiphenylene both exhibit parent ion peaks at m/e 272 and base peaks (100% relative intensity) at m/e 105. The source of the base peak, as well as other major fragments are proposed in the following correlation diagrams:

1. Fragmentation of 2-Benzoyloxybiphenylene



2. Fragmentation of 2-Benzoyl-3-hydroxybiphenylene (112)



The fragment corresponding to m/e 195 appears only in the mass spectrum of the Fries rearrangement product and is absent in the spectrum of the starting ester.

U. Detailed X-ray Analysis of Reduced Photodimer of Biphenylene (2d)

I am deeply indebted to Prof. J. White of Fordham University and his student, Eugene Passer, for their X-ray study performed on the octahydrodimer, op. cit., p. 68 of this thesis.

The crystallographic study has been completed, and the material to follow (through p.167) has been excerpted from the data of White and Passer (complete details can be found in the dissertation of Eugene Passer, Fordham University, 1976). It is presented here because of the collaborative nature of the work and the obvious interest for this dissertation:

1. Crystal Data

a. Morphology

Octahydrodimer (2d) was recrystallized from spectral grade ethyl acetate to give rise to flat transparent plates. Approximately cubic crystals of about 0.2 cm. on each edge were used to take equi-inclination Weissenberg photographs about all three crystallographic axes.

b. Number of Molecules per Unit Cell

The number of molecules in the unit cell was found to be 4.0 by the flotation method using a solution of carbon tetrachloride and hexane. This is in agreement with the results found by crystallographic methods.

c. Cell Constants

Based on the Weissenberg photographs, preliminary values for the unit cell constants were determined and found consistent only with the monoclinic space group $P2_1/n$. Precise cell constants were then determined from diffractometer data for the above space group.

The researchers found it convenient to convert the $P2_1/n$ space group to the $P2_1/c$ space group in order to correspond with the commonly used International Tables. The values for the cell constants in space group $P2_1/c$ were determined to be:

$$a = 13.168A$$

$$b = 8.609A$$

$$c = 21.324A$$

$$\beta = 134.35^{\circ}$$

A crystal measuring approximately 0.25 mm. x 0.2 mm. x 0.2 mm. was selected for data collection and found by photographic methods to be of good quality. Intensity data was collected on an Enraf Nonius CAD-4 Diffractometer using Cu - K radiation and Ni filters. Reflections were scanned at a constant rate of 0.574760° per minute.

A total of 3562 reflections were collected. The ratio of observed data to structural parameters (carbon atoms only) was 3562/216 = 16.5.

d. Direct Phasing

Inherent in all X-ray crystallographic studies is the problem of determining the signs of the structure factors (the structure factor is a vector quantity). From the X-ray data only the magnitude but not the direction (phase angle) of the vector can be measured. However, by use of Sayre's equation and the corresponding computer programs, these phase angles can be determined.

Although the actual form of the Sayre equation and the computer programs used will not be cited here, it should suffice to mention that the Sayre equation takes into account the following parameters: the number of, and type of reflections; the total number of atoms in the unit cell; the scattering angles of the atoms corrected for thermal vibration; and the degeneracy in the vectors caused by reflections that are located at symmetry equivalent positions in reciprocal space.

The results obtained by use of the Sayre equation were submitted to a full matrix least squares program in order to refine the previously determined phase factors. This new data was further refined with the aid of an error analysis program to produce data from which a difference electron density map could be prepared in order to locate the hydrogen atoms.

The difference electron density map was then compared to the results obtained from a computer program which theoretically located the 24 hydrogen atoms, assuming that a carbon atom in a tetrahedral chain has ideal tetrahedral symmetry and that the hydrogens are 1.08A from the carbon atom. It was found that the 24 peaks on the difference map coincided with positions predicted theoretically.

The theoretical hydrogen positions were then refined by an error analysis. The values thus obtained for the 24 hydrogens were placed into the carbon structure and the

resultant system submitted to refinement procedures.

Final values of the atomic parameters were then determined from the Sayre equation to an R value of 0.06, corresponding to a 99% confidence level.

2. Distances and Angles

The carbon to carbon bond distances in the octahydrodimer (2d) are listed in Table X. The value of 1.355A determined for C_2-C_3 is considered too short a bond distance and may be a reflection of the large thermal motion at C_2 and C_3 - i.e. the X-ray data do not give real bond distances when the thermal motion is very high. The values of 1.365A for C_5-C_6 and 1.336A for C_{11}-C_{12} are more consistent for a cyclooctatetraene than for a cyclobutane. The corresponding bond angles for 2d are found in Table XI.

Shown in Figures 6 and 7 are structural representations for the bond lengths and angles. Note that the numbers on the hydrogens do not necessarily correspond to the carbon numbers; this is a common practice amoung crystallographers. It is the case that the inside H's on the right hand ring have even numbers, whereas the inside H's for the left hand ring have odd numbers.

Table X

Carbon to Carbon Bond Distances in Octahydrodimer

Atoms	Distances (A)*	Atoms	Distances (A)
$C_1 - C_2$	1.397 (5)	$C_{10} - C_{23}$	1.390 (3)
$C_1 - C_{21}$	1.386 (2)	$C_{11} - C_{12}$	1.336 (3)
$C_2 - C_3$	1.355 (6)	$C_{11} - C_{17}$	1.516 (4)
$C_3 - C_4$	1.392 (4)	$C_{11} - C_{23}$	1.494 (2)
$C_4 - C_{22}$	1.389 (4)	$C_{12} - C_{13}$	1.504 (3)
$C_5 - C_6$	1.365 (3)	$C_{12} - C_{21}$	1.501 (3)
$C_5 - C_{16}$	1.516 (3)	$C_{13} - C_{14}$	1.544 (4)
$C_5 - C_{22}$	1.499 (2)	$C_{14} - C_{15}$	1.530 (3)
$C_6 - C_{20}$	1.471 (3)	$C_{15} - C_{16}$	1.535 (4)
$C_6 - C_{24}$	1.500 (2)	$C_{17} - C_{18}$	1.545 (4)
$C_7 - C_8$	1.385 (3)	$C_{18} - C_{19}$	1.543 (5)
$C_7 - C_{24}$	1.390 (3)	$C_{19} - C_{20}$	1.480 (6)
$C_8 - C_9$	1.373 (4)	$C_{21} - C_{22}$	1.393 (3)
$C_9 - C_{10}$	1.385 (3)	$C_{23} - C_{24}$	1.398 (3)

*The quantities enclosed in brackets are the estimated standard deviations.

Table XI

Octahydrodimer Bond Angles

Atoms	Angle*	Atoms	Angle
$C_{2, 1, 21}$	120.3 (2)	$C_{12, 13, 14}$	113.2 (2)
$C_{1, 2, 3}$	119.7 (3)	$C_{13, 14, 15}$	116.2 (2)
$C_{2, 3, 4}$	120.8 (3)	$C_{14, 15, 16}$	118.2 (2)
$C_{3, 4, 22}$	120.1 (3)	$C_{5, 16, 15}$	114.8 (2)
$C_{6, 5, 16}$	124.3 (2)	$C_{11, 17, 18}$	115.1 (2)
$C_{6, 5, 22}$	118.7 (2)	$C_{17, 18, 19}$	118.6 (3)
$C_{16, 5, 22}$	114.2 (2)	$C_{18, 19, 20}$	115.8 (3)
$C_{5, 6, 20}$	125.3 (2)	$C_{6, 20, 19}$	118.4 (2)
$C_{5, 6, 24}$	118.3 (2)	$C_{1, 21, 12}$	122.7 (2)
$C_{20, 6, 24}$	115.2 (2)	$C_{1, 21, 22}$	119.7 (2)
$C_{8, 7, 24}$	120.3 (2)	$C_{12, 21, 22}$	117.5 (2)
$C_{7, 8, 9}$	120.4 (2)	$C_{4, 22, 5}$	122.9 (2)
$C_{8, 9, 10}$	120.0 (2)	$C_{4, 22, 21}$	119.4 (2)
$C_{9, 10, 23}$	120.2 (2)	$C_{5, 22, 21}$	117.7 (2)
$C_{12, 11, 17}$	125.7 (2)	$C_{10, 23, 11}$	123.4 (2)
$C_{12, 11, 23}$	118.7 (2)	$C_{10, 23, 24}$	119.8 (2)
$C_{17, 11, 23}$	114.7 (2)	$C_{11, 23, 24}$	116.9 (2)
$C_{11, 12, 13}$	126.5 (2)	$C_{6, 24, 7}$	124.4 (2)
$C_{11, 12, 21}$	119.3 (2)	$C_{6, 24, 23}$	116.4 (2)
$C_{13, 12, 21}$	113.6 (2)	$C_{7, 24, 23}$	119.3 (2)

*The quantities enclosed in brackets are the estimated standard deviations.

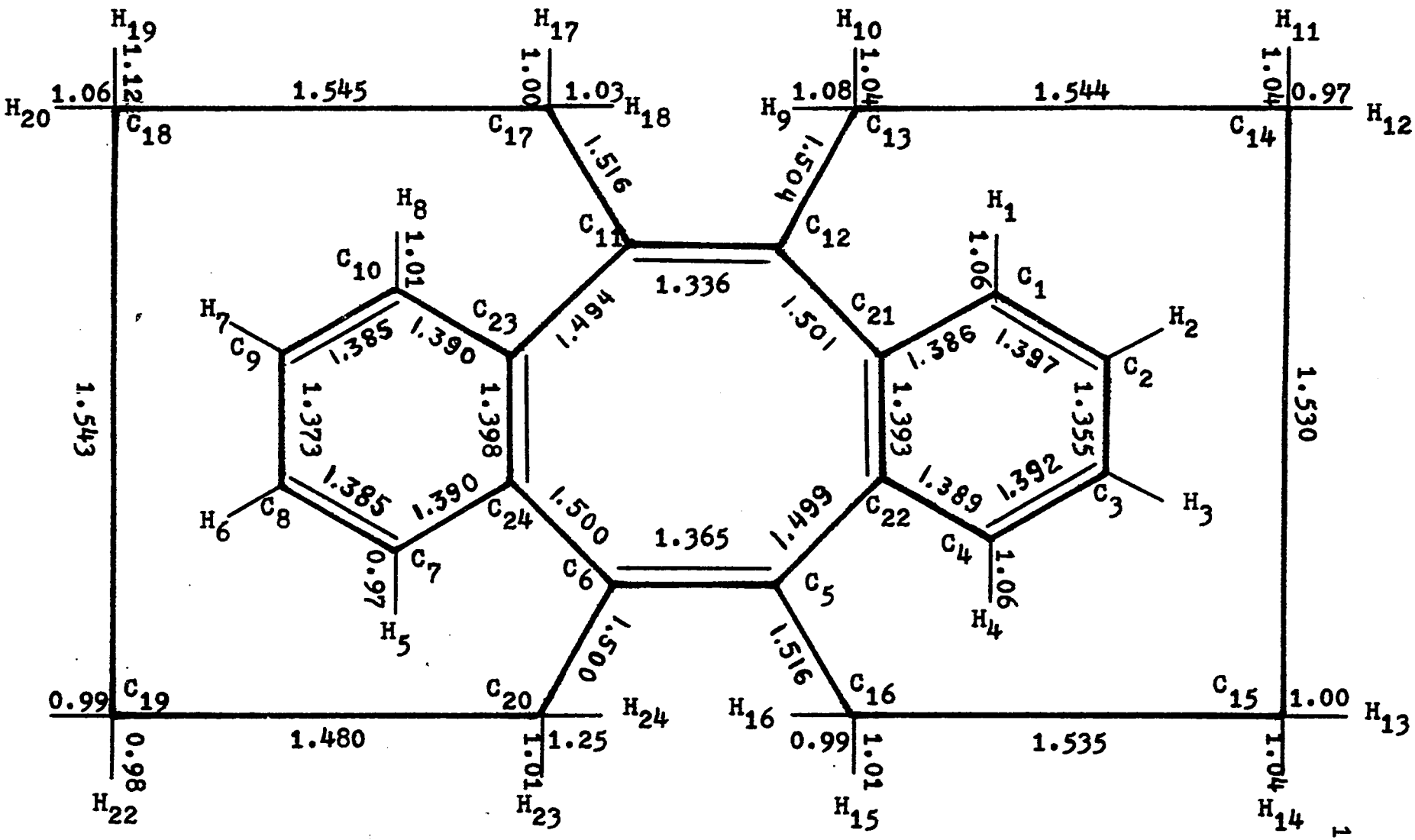


Figure 6. Octahydrodimer Bond Lengths

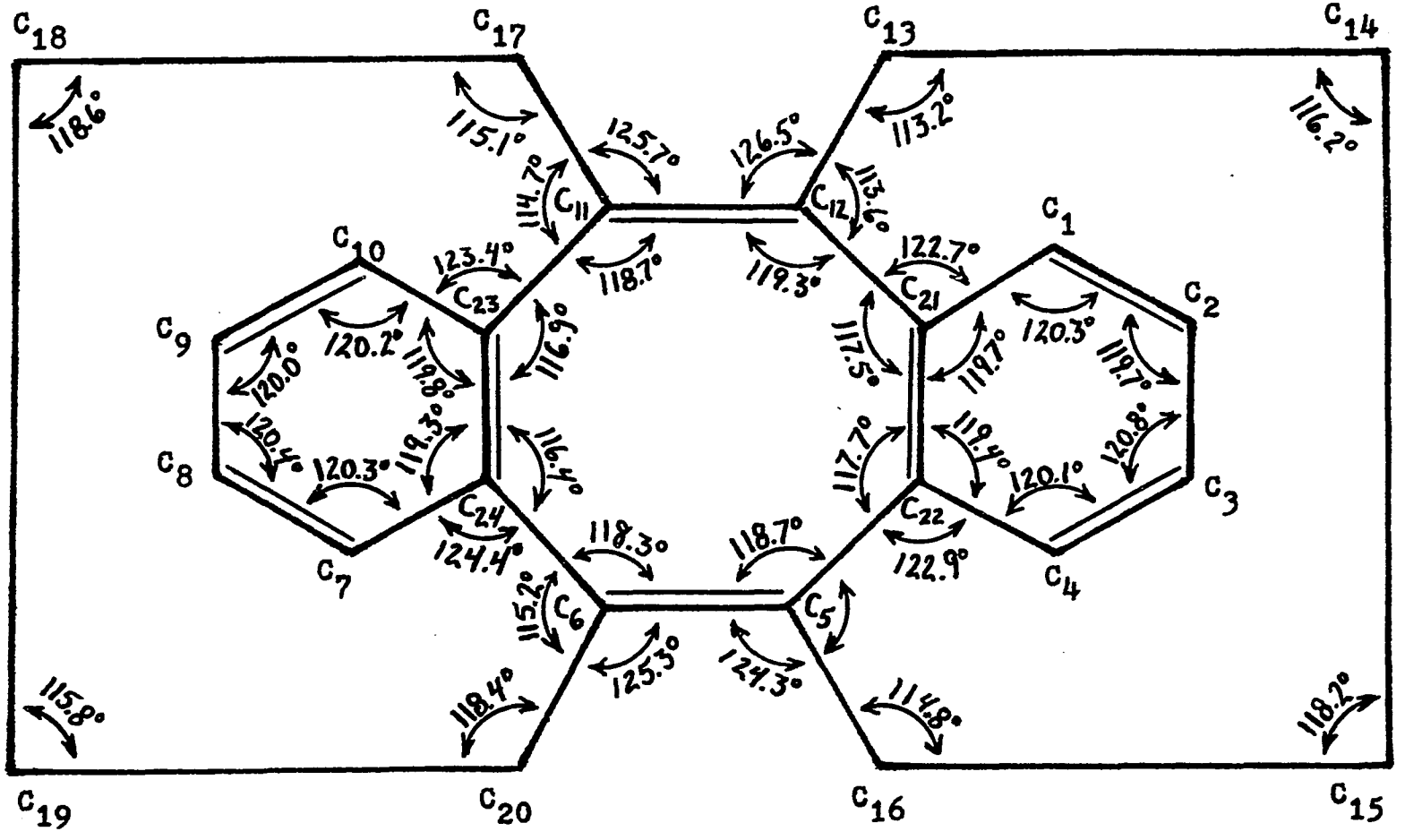


Figure 7. Octahydrodimer Bond Angles

3. Conformational Data

Each of the hydrogens in the tetramethylene ring C_{17}-C_{20} which participate in transannular interactions are displaced slightly in the direction of the C_{11}= C_{12} double bond, as can be seen in Figure 8. These small displacements increase the distance between the interacting hydrogens, thereby lowering the repulsive forces between them. To accommodate these displacements, two conformational changes have occurred. First, C_{20} is displaced 0.138A towards the C_{11}= C_{12} double bond. Second, the bond angle $C_{6,20,19}$ has opened up to 118.37°.

The two double bonds make an angle of 2.32° with each other. If the octahydrodimer possessed a perfect tub form, this angle would be 0°. The distance between the mid-points of the two double bonds (C_{11}= C_{12} and C_5= C_6) is 2.760A. This distance and the bond lengths show that there are two double bonds rather than a cyclobutane, thus confirming the assigned structure 2d.

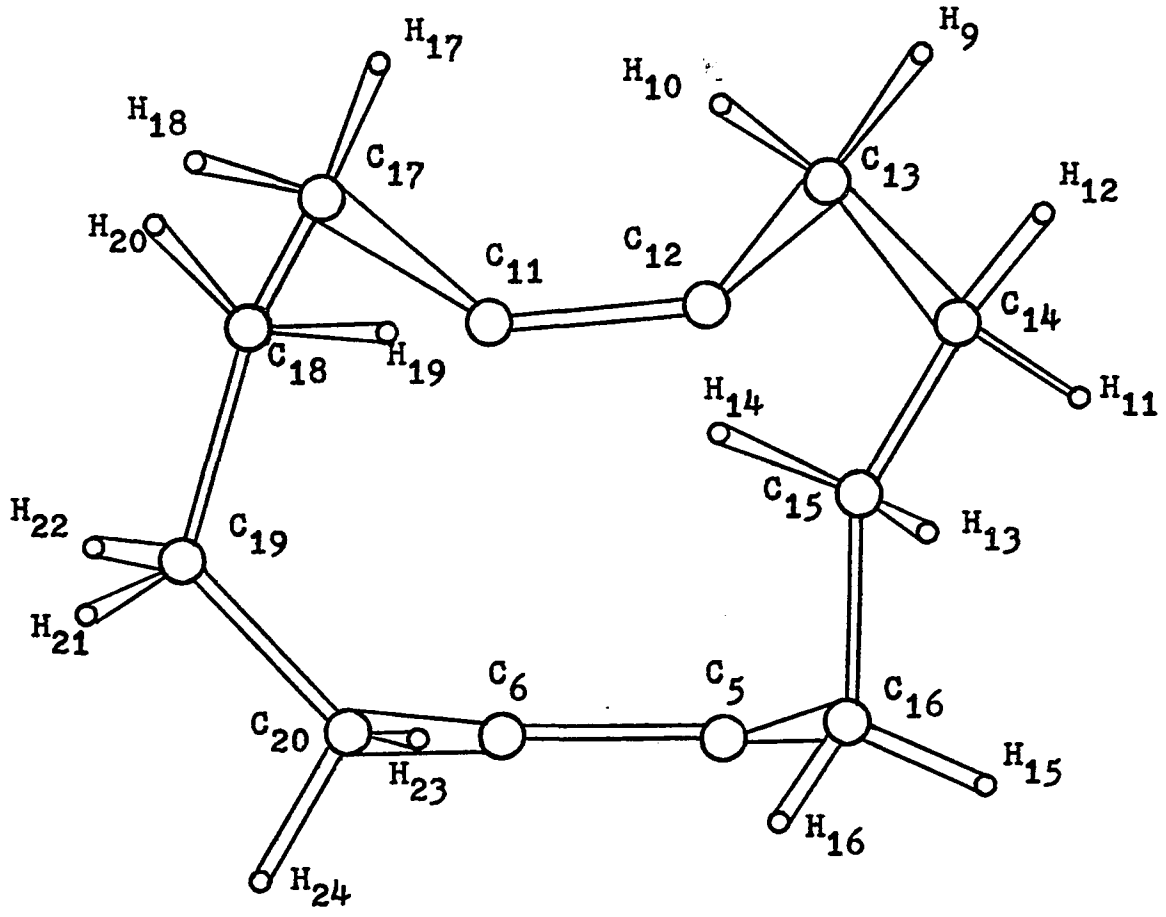


Figure 8. Conformation of the Cyclododecadiene Ring of Octahydrodimer Showing Transannular Interactions.

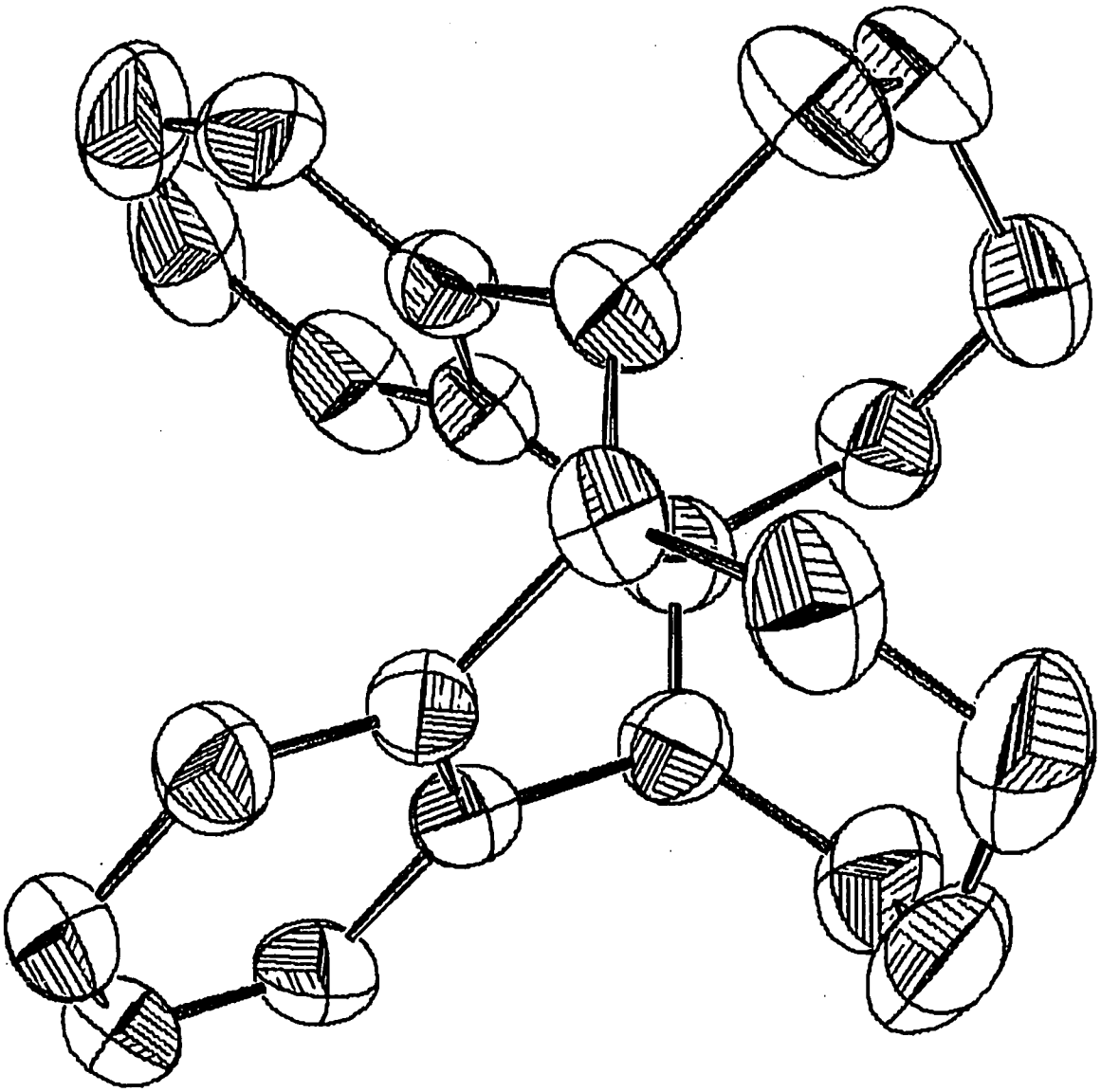


Figure 9. ORTEP (Oak Ridge Thermal Ellipsoid Program) Diagram

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