SYNTHESIS AND REACTIONS OF 2,3-DEHYDROBIPHENYLENE

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY
EUGENE N. LOSEY

1973

This is to certify that the

thesis entitled

SYNTHESIS AND REACTIONS OF 2,3-DEHYDROBIPHENYLENE

presented by

Eugene N. Losey

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Eugene Le Goff
Major professor

Date January 12, 1973

O-7639

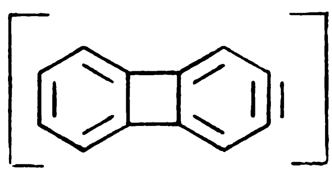
ABSTRACT

SYNTHESIS AND REACTIONS OF 2,3-DEHYDROBIPHENYLENE

By

Eugene N. Losey

Biphenylyne 24 (2,3-dehydrobiphenylene) was generated



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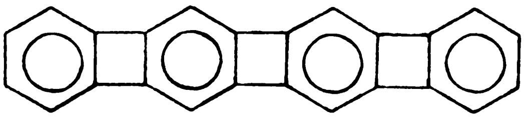
in situ by decomposition of 3-biphenylenediazonium-2-carboxylate 57. The inner salt was prepared by diazotization of 3-aminobiphenylene-2-carboxylic acid 25 with isoamyl nitrite in tetrahydrofuran.

The precursor 25 was synthesized from 2-acetamido-3-bromobiphenylene 39 by cyanide displacement of the bromine to yield 2-acetamido-3-cyanobiphenylene 40. Sequential hydrolysis of the cyano group and the amide afforded the amphoteric precursor 25.

The initial goal was to dimerize biphenylyne 24 to obtain hydrocarbon 4 or cross the former with benzyne 12 thus preparing hydrocarbon 5.



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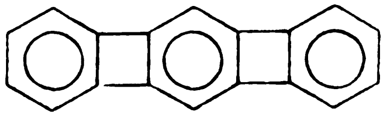

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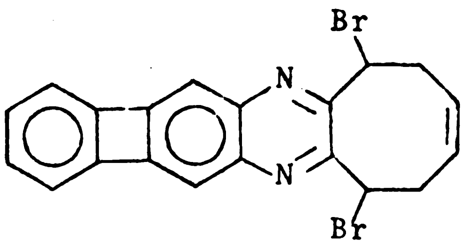
Attempts to do so were not successful, giving polymeric material and complex mixtures of isolable products. Generation of biphenylyne 24 in 1,2-dichloroethane gave small yields of 2-chlorobiphenylene 58 and a compound postulated to be the biphenylene analog of benzocoumarin. In benzene small amounts of the biphenylenobarrelene 69, arising from 1,4-addition of biphenylene 24 to benzene, were isolated.

Crossing attempts yielded mostly biphenylene 1, from independent reaction of the benzyne 12. The presence of the phenyl ester of biphenylene-2-carboxylic acid 74 was also indicated by the spectral data. Biphenylene 24 was trapped *via* its tetracyclone adduct which, through spontaneous loss of carbon monoxide, affords 1,2,3,4-tetraphenylbenzo[b]biphenylene 72.

Finally, two quinoxaline derivatives (79 and 80) of 2,3-diaminobiphenylene 75 were prepared as model compounds for extended biphenylene systems.



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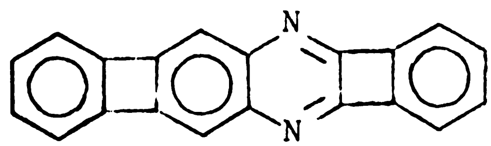

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SYNTHESIS AND REACTIONS OF 2,3-DEHYDROBIPHENYLENE

By

orman
Eugene N. Losey

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1973

G81347

To My Wife Mary

This is only a token of my appreciation
of her support —— tangible and intangible.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Eugene LeGoff for his guidance, encouragement and patience during the course of this work. The sharing of his expertise and enthusiasm as a chemical researcher has been an invaluable and vital part of this degree.

Special thanks must also go to Dr. Thomas Kowar not only for his suggestions and for the use of compounds prepared by him, but, above all, for serving as a model throughout the four years.

Financial support provided by the National Science Foundation and by Michigan State University, Department of Chemistry, is also gratefully acknowledged.

Finally, thanks should go to my fellow graduate students for making this experience an enriching and enjoyable one.

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SYNTHESIS AND REACTIONS OF 2,3-DEHYDROBIPHENYLENE

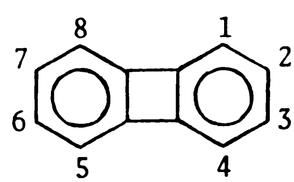
INTRODUCTION

An important contribution of synthetic organic chemistry is the validation of theoretical hypotheses. For example, laboratory preparation is the ultimate test of stability, especially for highly strained molecules such as cubane or unique species like stable carbonium ions. Examination of interesting, yet calculated properties such as resonance or strain energy must also be preceded by synthesis and purification of representative compounds. So too, postulated reaction paths, e.g. electrocyclic transformations, often require creation of molecules with special constraints as well as identifications of final products.

The concept of aromaticity has provided perhaps the largest and most diverse source of theoretically interesting molecules for synthesis. In 1931 Hückel[1] predicted special (aromatic) stability for fully conjugated, planar, monocyclic polyolefins having $4n + 2$ π-electrons (n = any integer), and no such stability for those containing $4n$ π-electrons. In fact $4n$ systems have been shown to be less stable than their acyclic counterparts, possessing negative delocalization stability.[2a,b]

All aspects of Huckel's rule have since been tested and some of its limitations expanded. For example, fused *poly*cyclic systems such as naphthalene and anthracene also show aromatic stability; having the requisite $4n + 2$ π-electrons and being planar.

However, fusion of two benzene rings at their respective *ortho* positions creates a unique system containing a four membered ring. Biphenylene **1**



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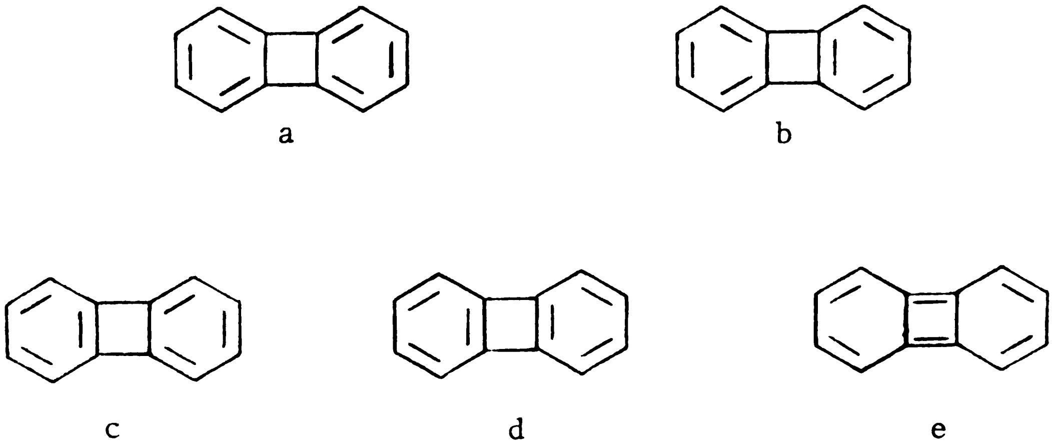
(referred to as diphenylene in the older literature) is basically a 12 π-electron system (4n), but it might also be viewed as two separate 6 π-electron (4n + 2) moieties, depending on the interaction (or lack of it) between the two benzene rings.

The properties of 4n + 2 as compared to 4n π-systems of course are very different, so biphenylene might be expected to unambiguously reveal its true identity. The following discussion will show that this does not happen and biphenylene exhibits traits characteristic to both above mentioned systems.

Examination of the five canonical resonance forms of biphenylene (**1**, a-e) reveal that not all



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should be expected to contribute equally. Two (d and e) include a formal cyclobutadiene moiety, while two (b and c) contain a cyclobutenequinoid structure.[3]

Molecular orbital calculations of bond order have proven incorrect when all forms are weighted equally, but are in accordance with observed values if **1a** is taken as the major contributor, with lesser contribution from b and c, little from d, and none from e.[4a-c] These arguments would lead one to expect that biphenylene would behave as two isolated benzene rings, with no interaction (*via* the cyclobutadienoid forms) between these rings.

Indeed, biphenylene does behave as a polycyclic aromatic hydrocarbon. It crystallizes in straw-yellow needles, is extremely stable to air and high temperature, undergoes the usual aromatic substitution reactions with very few addition reactions, and even has an odor reminiscent of naphthalenes or biphenyl. These factors seem to dominate the behavior of biphenylene, but an extension of the π-interaction between the benzene rings is alluded to in several properties of the molecule.

The ultraviolet spectrum of biphenylene exhibits two band systems. The short-wavelength system at 235-260 nm is of high intensity, while the long-wavelength system at 330-370 nm is a low intensity absorbance.[5a-c] The long-wavelength bands seem to indicate interaction between the benzene rings, despite the central C-C bond length of 1.52 Å.[6a,b] The uv spectrum of biphenyl, where interaction is certainly negligible, shows only one band at 250 nm.

In addition the long-wavelength absorption of biphenylene falls in between those of naphthalene and anthracene which have one less and one more formal double bond respectively than biphenylene (see Table 1),[7] and which of course contain total bond interaction.

Table 1. UV Absorptions of Polycyclic Aromatic Compounds

Compound	number of formal double bonds	λ_{max} (nm)*
(biphenyl)	(6)	(250)
naphthalene	5	314
biphenylene	6	358
anthracene	7	380
1,2,4,5-dibenzopentalene	8	415
tetracene (naphthacene)	9	480

*longest wavelength absorption

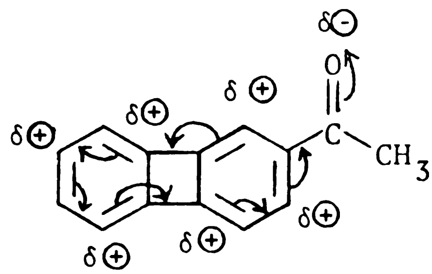
It must be kept in mind that uv spectroscopy is a measure of an excited state interaction and interaction here may differ from that in the ground state.

The nmr chemical shifts of both the C_1 (δ = 6.598 ppm) and C_2 (δ = 6.702 ppm) hydrogens of biphenylene occur at higher field than benzenoid fused aromatics or biphenyl. This is apparently not due to a change in hydridization caused by the system's strain, as benzocyclobutene shows an aromatic multiplet centered at δ 7.0.[8] This upfield shift in biphenylene has been attributed to the presence of a paramagnetic ring current in the central "cyclobutadiene" ring in addition to a decrease in the two possible diagmagnetic ring currents in the benzene rings.[9a-c]

Using calculated values of the diamagnetic ring currents in the benzene rings (+0.563) and a paramagnetic ring current in the four membered ring (-1.028) (benzene = 1.00) the contributions of each ring can be summed giving chemical shifts which are in good agreement with the experimental values. This paramagnetic ring current then also alludes to cyclobutadienoid type interaction between the benzene rings in biphenylene.

A final evidence for ring interaction might be the disubstitution reaction patterns of biphenylene. Electrophilic substitution occurs most readily at position 2. Initial substitution of an electron withdrawing group should lead to attack of the next substituent at position 6 or 7 with equal probability if the rings do not interact. However, dinitration and diacetylation lead *exclusively* to 2,6-disubstituted products.

This pattern can be explained *via* resonance forms which include both rings.



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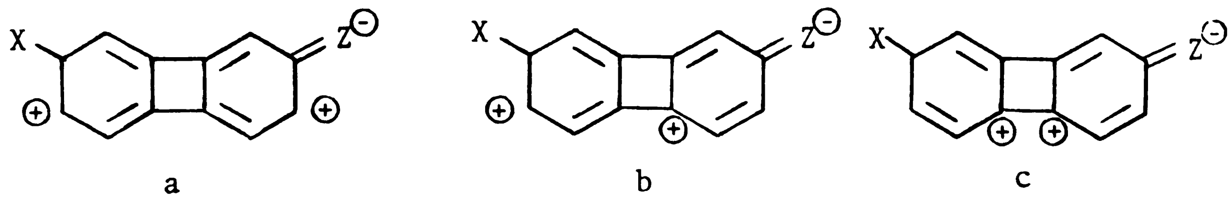
The resonance deactivated sites (δ⊕) are shown in 2.[10] Since position 8 is really an unfavorable 1-position, the second substitution should be predicted only at position 6.

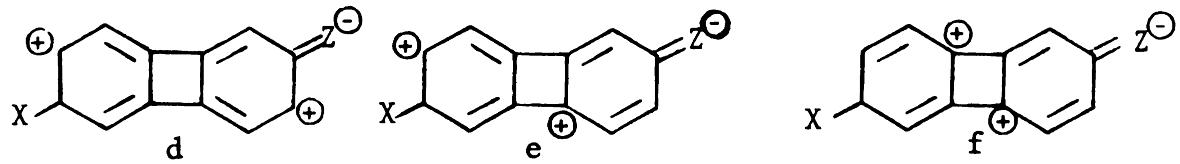
Cava and Mitchell[11] have explained these same experimental observations *via* Wheland structures of the postulated intermediate in disubstitution as shown in 3a-f.

None of these involve a cyclobutene or cyclobutadiene, and the results are explained in terms of unfavorable structures b and c, where the ⊕ centers are in conjugation and adjacent to one another respectively. Substitution at position 6 (d-f) however, gives only structures where the ⊕ centers are cross-conjugated.

Attack at 7-position



Attack at 6-position



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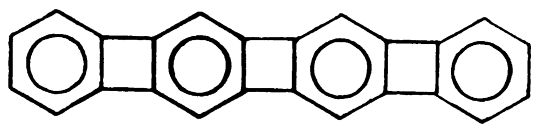
The purpose of the research described in this thesis was to prepare compounds in which the π-system would be bacically the same as in biphenylene, but with more electrons. The target was compound 4.

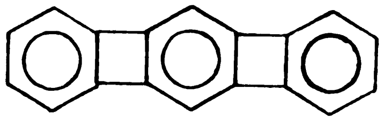


4

This hydrocarbon is a 24 π-electron biphenylene-type system. Preparation of 4 would enable one to see what effect extension to a larger 4n system would have on the unique properties of biphenylene type compounds.

Specifically, it was hoped that the ring interaction discussed above would be altered in 4.

In addition, the 18 π-electron system 5 was also a goal of this research, in that it would provide the 4n + 2 biphenylene analog.



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Its properties (e.g. nmr ring currents) could be investigated and compared to the 4n biphenylene systems 1 and 4.

It has been predicted that the aromatic stability of 4n + 2 systems and the aromatic destability of analogous 4n systems are less amplified in the larger π-systems of 26-30 electrons.[12]

Sondheimer has demonstrated this experimentally in the annulenes, the monodehydro[26]annulenes exhibiting a small amount of aromaticity[13] while the dehydro[30]annulenes are merely polyolefinic.[14] If there is substantial ring interaction in 4 and 5, this limit hypothesis could be tested in the more planar biphenylene systems.

Hydrocarbons 4 and 5 should also have some constraints on them which biphenylene does not, e.g. a completely quinoidal structure for the central four membered rings cannot be drawn. Their properties therefore might be unique and informative.

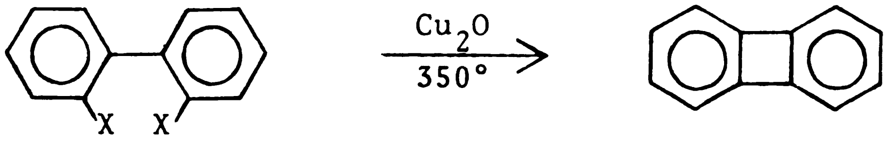
From a synthetic viewpoint, 4 would be a challenge to prepare in that generation and dimerization of a "biphenylyne" should be one possible route. This aryne would also be requisite for 5, crossing it with benzyne. The latter attempt would reveal something about the reactivity of the new aryne. It was expected, too, that trapping experiments would lead to a series of new biphenylene derivatives.

Finally, a number of new π-electron systems stemming from biphenylene were envisioned. These will be discussed as they arise in the discussion of functionalized biphenylenes.

The most straightforward approach to synthesizing hydrocarbon 4 was viewed as a dimerization of two biphenylenes in the same fashion as two benzenes combined to yield biphenylene itself. Consequently, the reactions used in this latter, well-known preparation were investigated. Below is a brief summary of the useful biphenylene syntheses.

Synthetic Approaches to Biphenylene

Lothrop first synthesized biphenylene by treatment of 2,2'-dihalobiphenyl 6a or 6b with cuprous oxide at high temperature.[15] The latter biphenyl

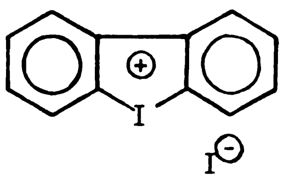


6a X = Br

6b X = I

1

or biphenyleneiodonium iodide 7 gives highest



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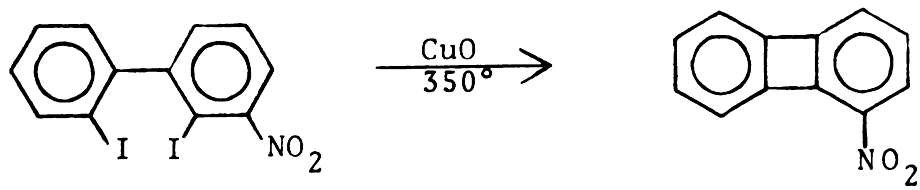
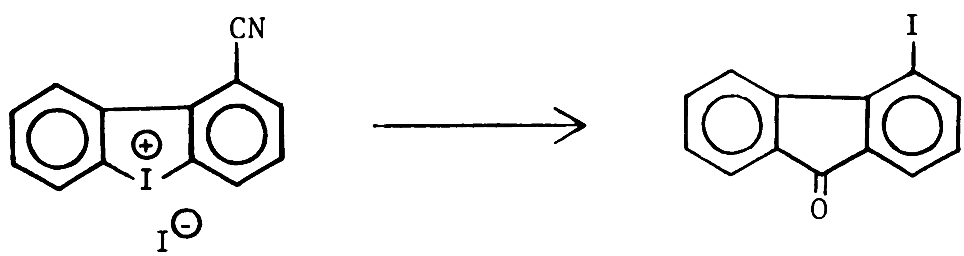
yields, and although this synthesis is dependent on several factors (some undetermined) it remained, until recently, the method of choice for preparation of biphenylene.

This route is especially useful in preparing derivatives not easily obtained by substitution of biphenylene itself. For example, 1-substituted biphenylenes such as 1-nitrobiphenylene 8[16] cannot be prepared from biphenylene because electrophilic substitution occurs most readily at the 2-positions. Treatment of 3-nitro-2,2'-diiodobiphenyl 9 with CuO at 350° yields the desired derivative in 14.5% yield.



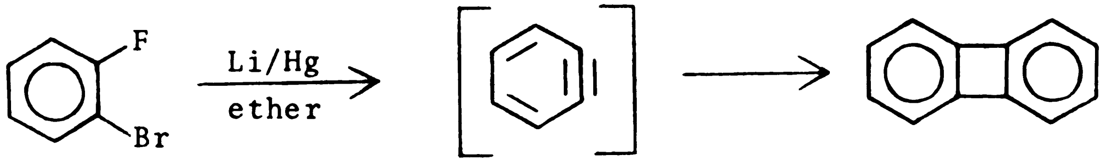
9 8

It is interesting that even though yields for this reaction are often low, it fails only if a competing side reaction predominates; such as in the case of 4-cyanobiphenylene iodonium iodide 10, which yields 4-iodofluorenone 11.[17]



10 11

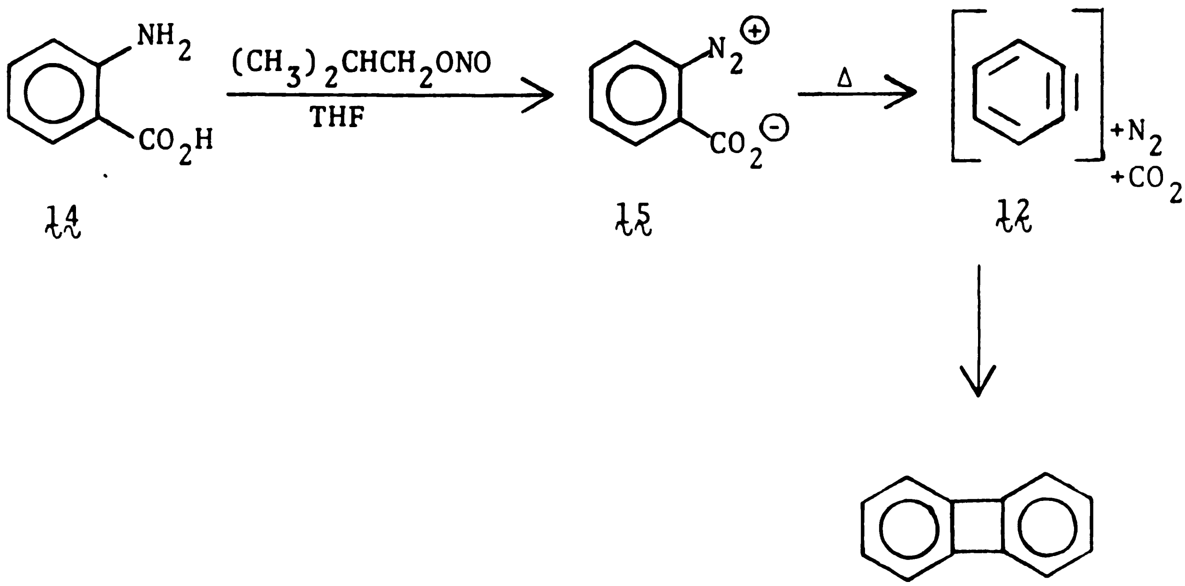
More recently the dimerization of dehydrobenzene (benzyne) has been used in the synthesis of biphenylene. Benzyne 12 can be generated several ways,[18] but only in nonpolar solvents with avoidance of strong nucleophiles does this reactive intermediate dimerize. This happens in 24% yield during the dehalogenation of o-fluorobromobenzene 13 by lithium amalgam in ether.[19a,b]



13 12 1

Other dehalogenations have been used, but less successfully.[20a-c] This procedure is also applicable to synthesis of biphenylene derivatives such as the methyl derivatives.[21]

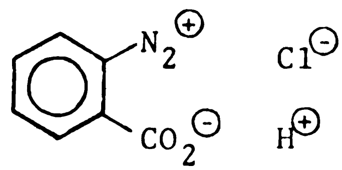
The easiest procedure involves diazotization of anthranilic acid 14 in aprotic media, followed by decomposition of the benzenediazonium-2-carboxylate 15 in an inert solvent.[22] The reaction is easily monitored by



14 15 12

1

the evolution of nitrogen and carbon dioxide and final clarification of the solution. Precautions must be taken, however, as the inner salt 15 is easily detonated when dry. The more stable hydrochloride salt 16



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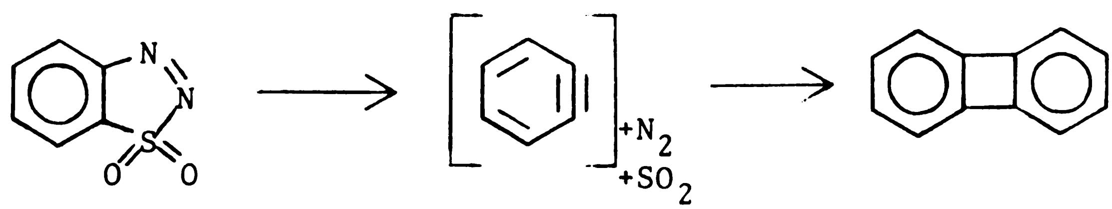
cannot be used to prepare biphenylene.[23]

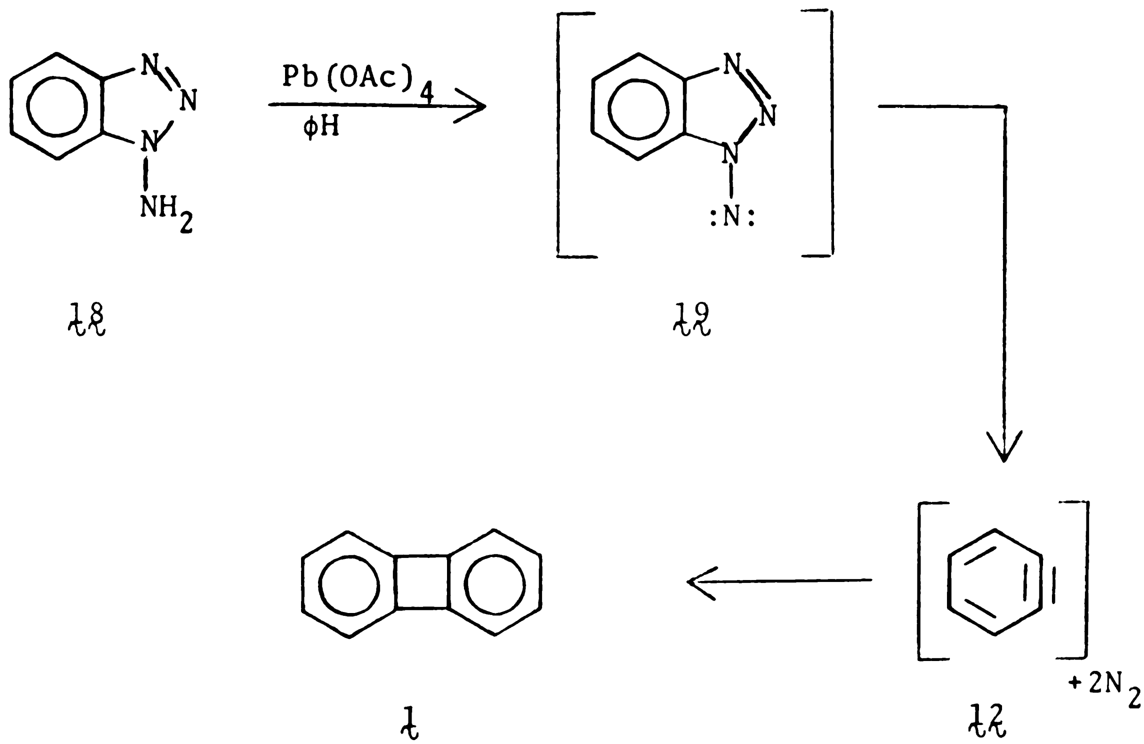
Substituted biphenylenes can also be prepared by this method, but nitro and haloanthranilic acids fail to react.

Decomposition of benzo heterocycles also leads to benzyne. Benzothiadiazole-1,1-dioxide 17 readily fragments to benzyne, nitrogen and sulfur dioxide in organic solvents at 20°C.[24] The yield (52%) is quite good but the precursor 17 is difficult to prepare.



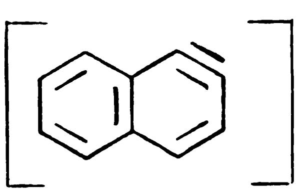
17 12 1

Oxidation of 1-aminobenzotriazole 18 with lead tetraacetate leads to a nitrene 19 which collapses to nitrogen and benzyne.[25a,b]



18 19 12 1

This reaction has been used to prepare other arynes including naphthynes 20 and 21[26] and 9,10-phenanthryne 22.[27] These can de dimerized or "crossed" with different arynes to give numerous benzobiphenylenes such as tribenzo[a,c,h]-biphenylene 23.



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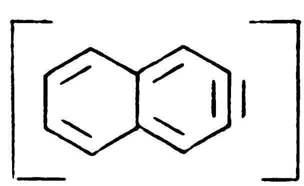

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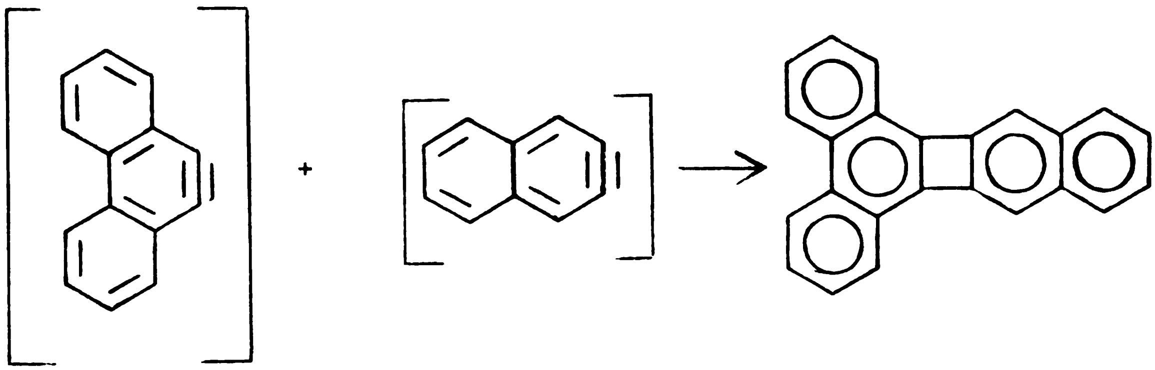


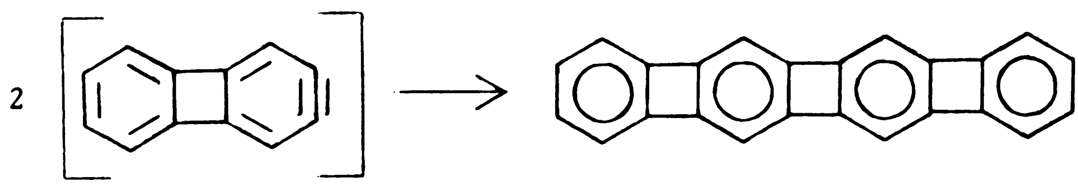
22 21 23

The sequence suffers only from the difficulty in preparing the requisite 1-aminotriazoles.

Several other methods have been used to synthesize biphenylenes and are described in two excellent reviews.[28a,b] These routes have not been synthetically useful due to low yields or experimental complexity, and will not be discussed here.

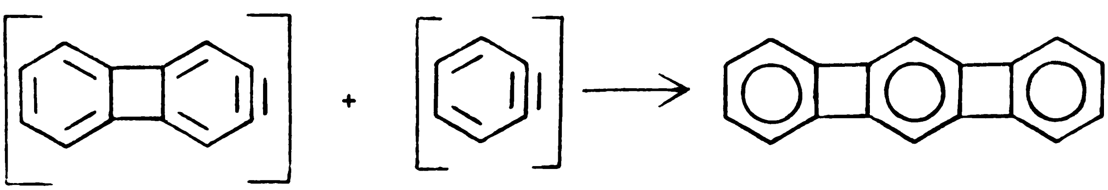
RESULTS AND DISCUSSION

As mentioned above the synthesis of hydrocarbon **4** might easily be carried out *via* a dimerization of 2,3-dehydrobiphenylene **24**.



24 **4**

The 18 π-electron analog **5** could be prepared in like manner by crossing benzyne **12** with biphenylyne **24**. Therefore a large amount of effort was expended in obtaining a precursor

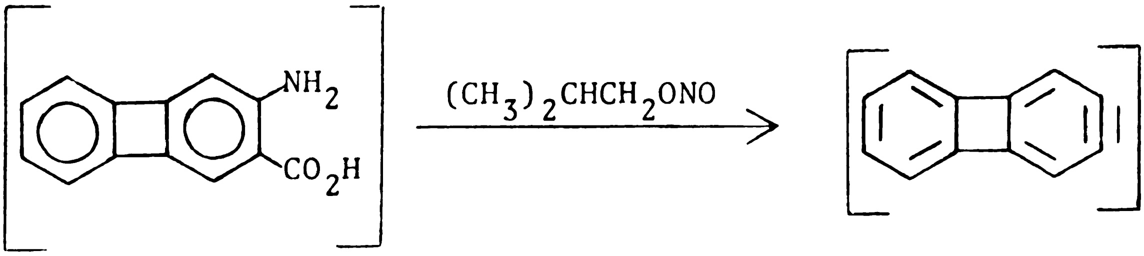


24 **12** **5**

to the requisite aryne **24**. The aryne reactions were then investigated and finally some novel biphenylene aromatic systems were synthesized.

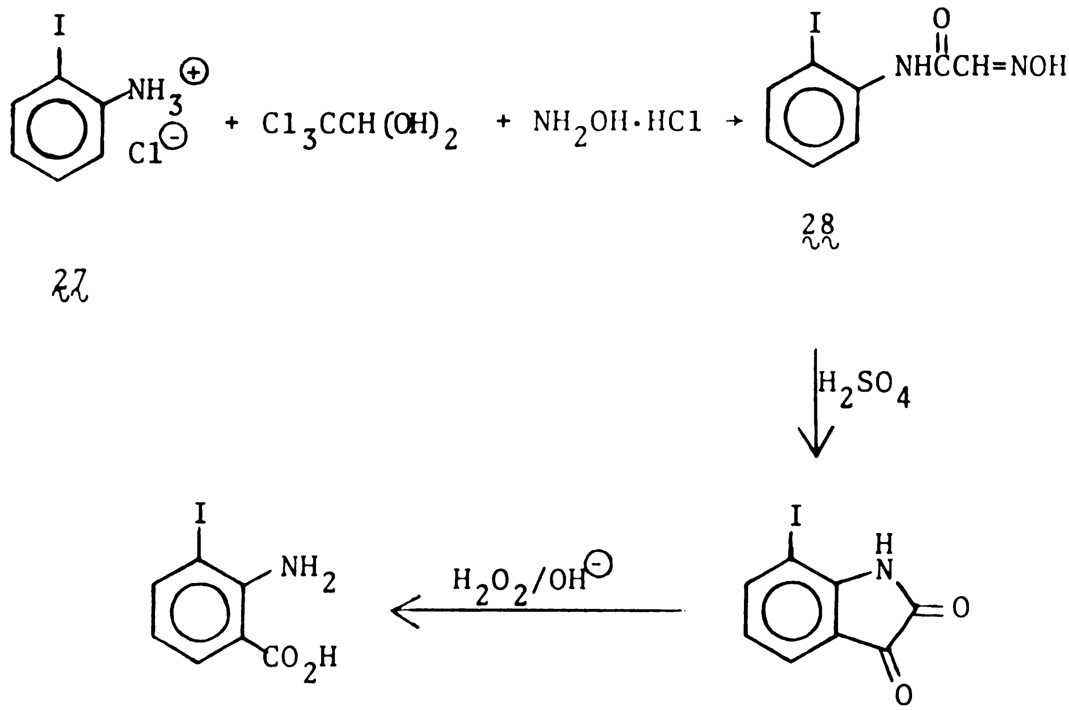
Preparation of 2,3-Dehydrobiphenylene Precursors.

By analogy with benzyne dimerizations, it seemed that 3-aminobiphenylene-2-carboxylic acid 25 would be the easiest precursor to prepare and, in addition, could be easily converted to biphenylyne 24 by treatment with isoamyl nitrite.



25 24

Substituted anthranilic acid derivatives, which are difficult to prepare by direct substitution have been synthesized by oxidation of the corresponding isatin.[29a,b] For example, synthesis of 3-iodoanthranilic acid 26 begins with conversion of 2-iodoaniline hydrochloride 27 to 2-iodo-α-isonitrosoacetanilide 28 by treatment with chloral hydrate and hydroxylamine hydrochloride in aqueous medium. The isonitrosoacetanilide 28 is then cyclized in sulfuric acid to 7-iodoisatin 29 and the isatin oxidized with basic hydrogen peroxide to yield the anthranilic acid 26. This three-step scheme seemed appropriate for synthesis of the precursor 25 (see Scheme I).

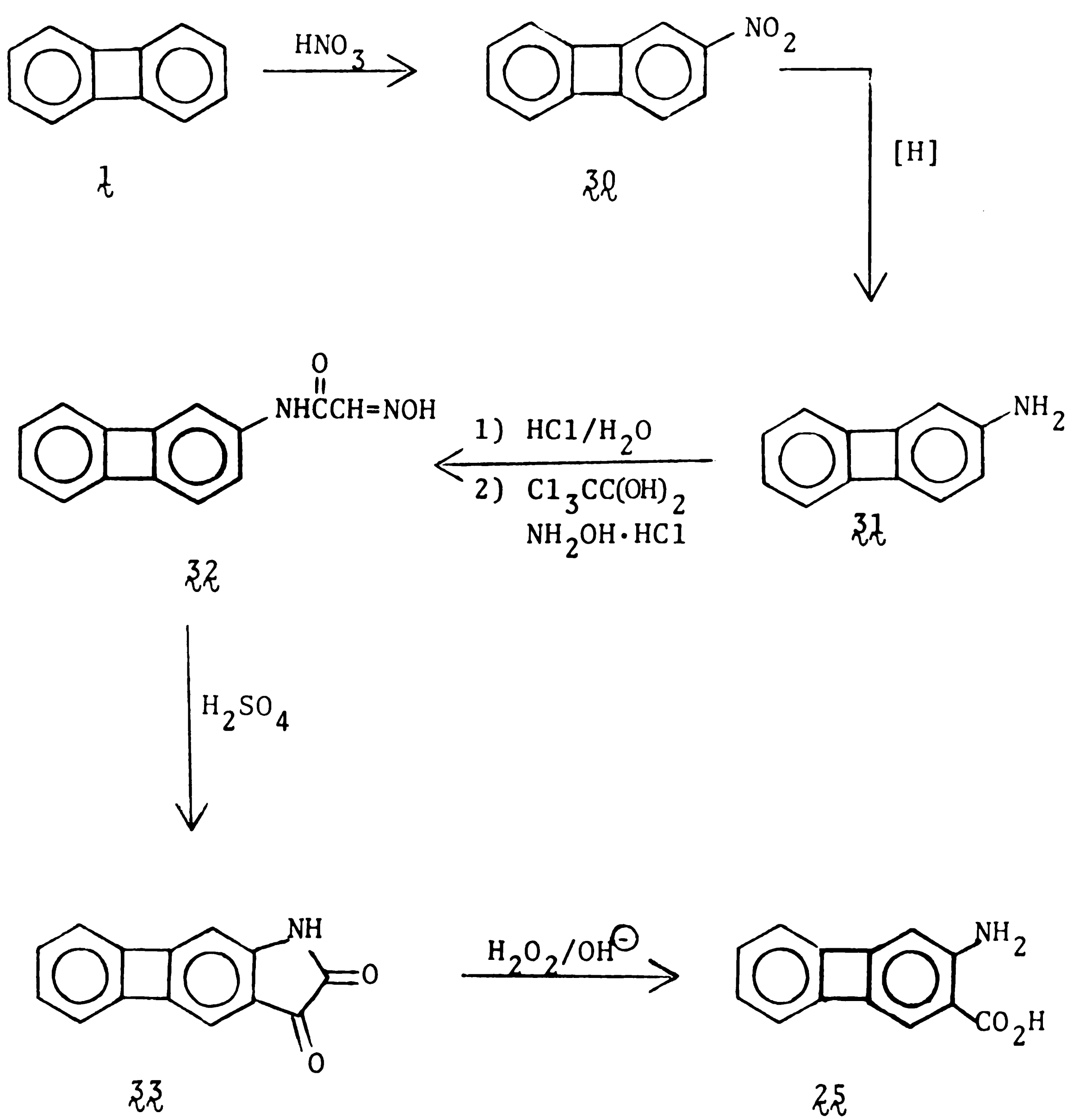


27 28 29 26

The 2-nitrobiphenylene 30 has been prepared by nitration with acetic acid/nitric acid in acetic anhydride (24% yield),[30] but the work-up involves a steam distillation in which one liter of distillate yields 90 milligrams of product. Consequently, an alternative nitration procedure was sought.

A simple heterogeneous nitration yielded 2-nitrobi-biphenylene 30 in 30% yield. Concentrated nitric acid was added dropwise to a cooled, dilute solution of biphenylene in methylene chloride until thin layer chromatography showed exhaustion of starting material. The mixture was washed well with water, dried, and the residue chromatographed on neutral alumina, eluting the product with methylene chloride or chloroform. This entire procedure

Scheme I


HNO3
NO2
[H]
NH2
1) HCl/H2O
2) Cl3CC(OH)2
NH2OH·HCl
NHCCH=NOH
O
H2SO4
NH
O
O
H2O2/OH⊖
NH2
CO2H
1
30
31
32
33
25

requires about 2 hours time.

Attempts at maximizing yield by changing temperature and dilution were unsuccessful. Although orientation in the dinitro product has been shown to be directed by the initial electron withdrawing substituent, the second ring is not sufficiently deactivited by the first substituent to supress dinitration. Thus, the reactivity of the second ring is quite independent and the limit for mononitration is 30% yield.

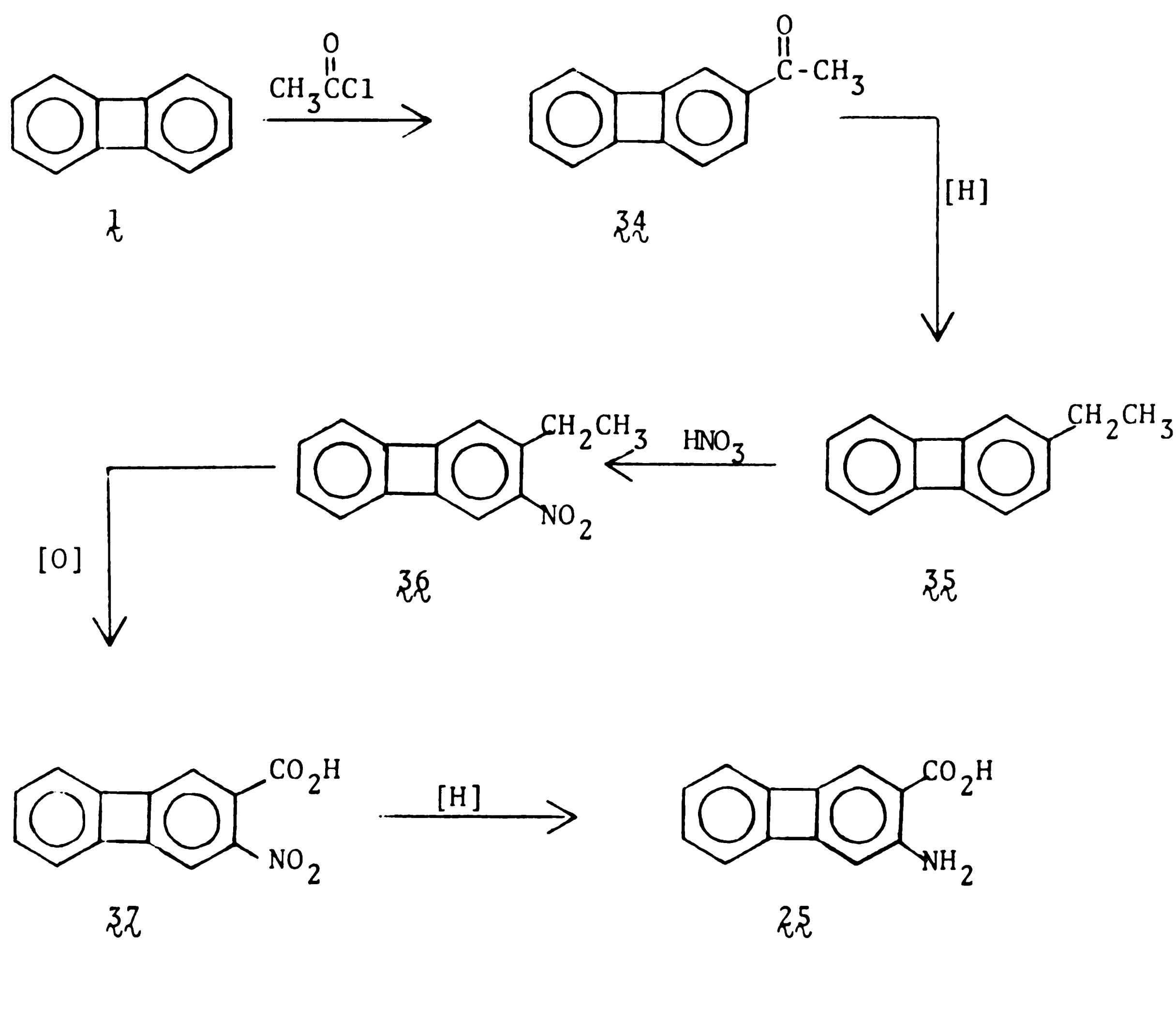
Reduction of 2-nitrobiphenylene **30** has been carried out in 73% yeild using stanuous chloride/hydrochloric acid,[30] but this procedure also requires steam distillation in the workup, complicated by heavy precipitates of inorganic salts.

However, amines can be rapidly prepared by reduction of nitro compounds with ethanolic hydrazine in the presence of 10% palladium-on-charcoal.[31a,b] The reaction is easily monitored by evolution of nitrogen and discharge of color (nitrobiphenylene is bright orange) and the workup consists of filtration of the catalyst followed by dilution with water and collection of product. The yield of 2-aminobiphenylene **31** was 67%.

The formation of the isonitrosoacetanilide **32** was not successful. A representative procedure[29b,32] calls for addition of the amino compound as its hydrochloride salt dissolved in aqueous hydrochloric acid. The 2-aminobiphenylene hydrochloride was not soluble in the solution, and if a suspension was added the reaction yielded only dark, insoluble material. The reaction was also attempted in acetic acid with the same result. This method was therefore abandoned.

A second approach to precursor 25 is outlined in Scheme II.

Scheme II



The preparation of 2-acetylbiphenylene 34 was carried out as described by McOmie and coworkers[33] except that the final product was purified by chromatography on neutral alumina.

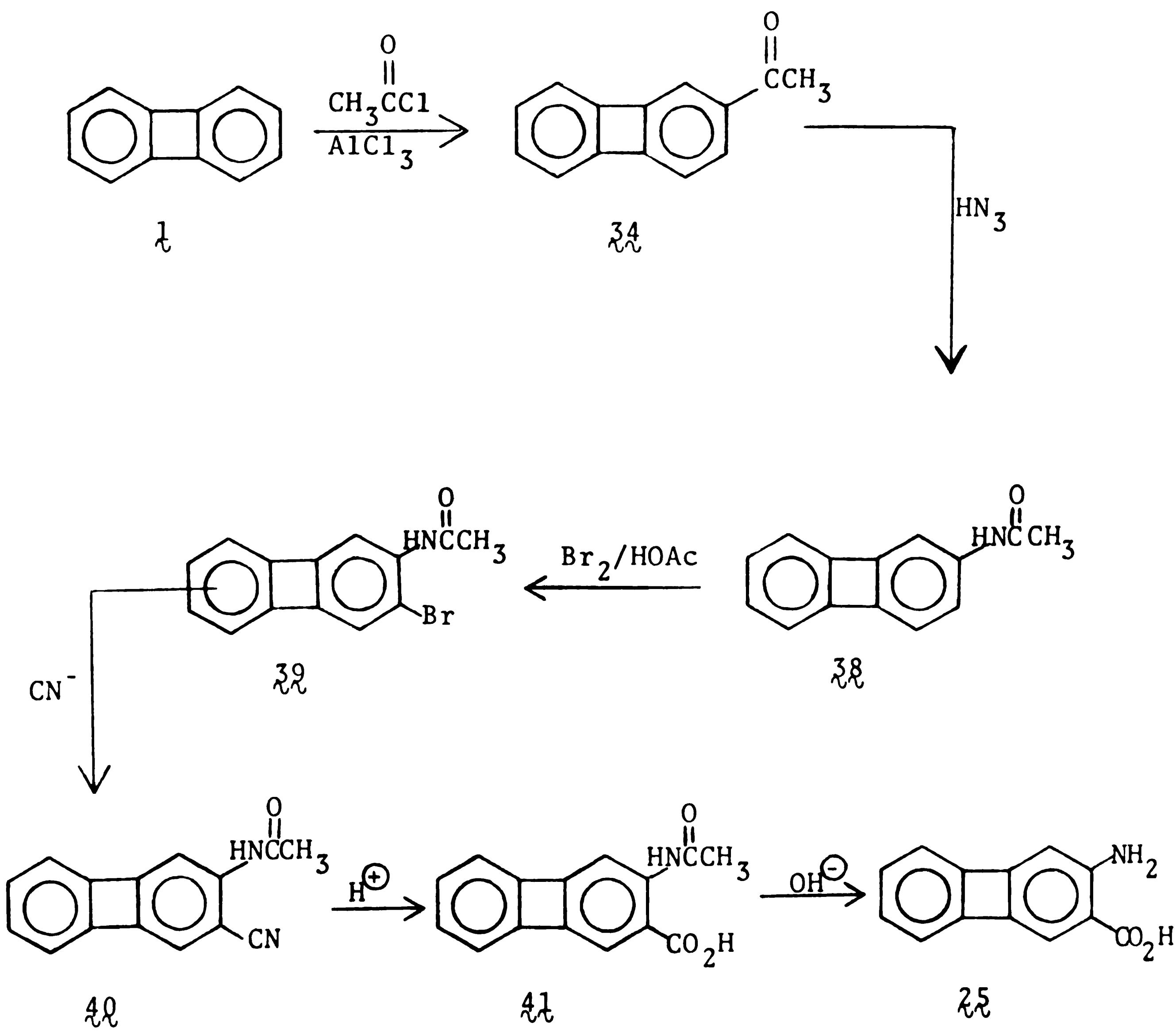
Conversion to 2-ethylbiphenylene 35 via the Huang-Minlon modification of the Wolff-Kishner reduction has also been reported by McOmie[34] and this procedure proved best. The Clemmensen reduction did not react to completion during six hours reflux, due to the insolubility of 2-acetylbiphenylene 34 in the water/concentrated hydrochloric acid medium.

Nitration of 2-ethylbiphenylene 35 was carried out using the heterogeneous procedure described above for the preparation of 2-nitrobiphenylene 30. The nitration was erratic, reacting surprisingly slow, even when stirring at room temperature in the presence of a large excess of nitric acid. Chromatography of the reaction mixture after the usual water workup yielded 23% of unreacted starting material and 19% of 2-ethyl-3-nitrobiphenylene 36 (lit[34] yield = 13%).

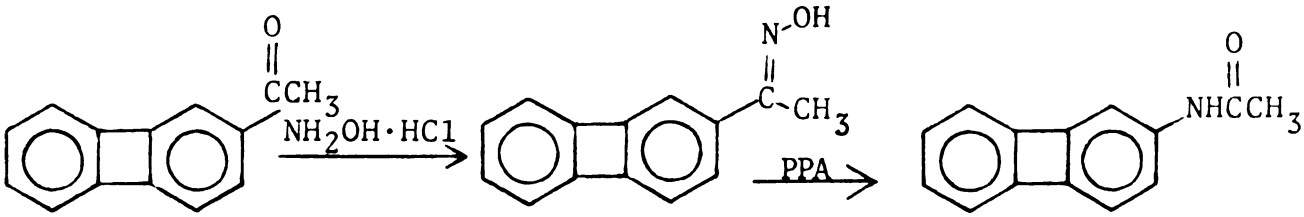
Oxidation of the ethyl side chain in 36 to the corresponding carboxylic acid 37 by refluxing in aqueous basic permanganate could not be accomplished because the 2-ethyl-3-nitrobiphenylene 36 was again too insoluble. Starting material was recovered from this reaction and neutralization of the aqueous layer yielded no carboxylic acid.

The third route to the amino carboxylic acid proved successful and is revealed in Scheme III.

Scheme III



Rearrangement of the 2-acetylbiphenylene 34 described above to 2-acetamidobiphenylene 38 can be carried out *via* the Beckmann rearrangement of the oxime 42[33,36] or directly



34 42 38

by the Schmidt reaction.[30]

The compound 38 was prepared using both methods. The oxime used in the Beckmann rearrangement was obtained in greater than 67% yield and the reaction itself was carried out as reported in polyphosphoric acid, yielding pure 2-acetamidobiphenylene 38 in 75% yield.

Generation of hydrazoic acid *in situ* was attempted two ways. The procedure of Smith and Dice[37a,b] involving addition of sodium azide to a solution of the 2-acetylbiphenylene 34 in molton trichloroacetic acid provided the best results (>80% yield). It was not necessary to add tetraphosphoric acid as reported by McOmie.[30]

The reaction was also carried out in a chloroform/sulfuric acid solution, but a solid precipitated from the reaction mixture before any sodium azide could be added and only a small yield of an oily solid was obtained. It was postulated that sulfonation of the biphenylene occurred upon addition of the sulfuric acid.

Bromination of **38** was carried out exactly as reported in the literature[36] yielding 2-acetamido-3-bromobiphenylene **39**.

The synthesis of aryl nitriles by cyanide displacement of halogen in aryl halides is an old reaction, but recently has been improved by the use of cuprous cyanide in dimethylsulfoxide.[38] Dewar and Grisdale have prepared a number of cyano napthoic esters by this displacement reaction,[39] varying the workup slightly. It was found that this latter method could be modified to give 2-acetamido-3-cyanobiphenylene **40** from the bromo compound **39** in good yield.

A solution of **39** in DMF was heated to 140° for several hours then the nitrile-cuprous bromide complex decomposed by addition of ammonium hydroxide and water. The solid obtained was recrystallized or chromatographed along with material extracted from the decomposition solution to yield fluffy, yellow needles, mp 244-245°.

The ir spectrum (Nujol) showed a weak N-H absorption at 3275 cm^{-1} and a sharp absorption at 2220 cm^{-1}, denoting a cyano function. A medium strong carbonyl absorption occurred at 1700 cm^{-1}.

The aromatic region of the nmr spectrum consisted of a singlet at δ 7.80 corresponding to one hydrogen. A slightly split singlet and a sharp singlet at δ 6.89 and δ 6.70 respectively integrated for five hydrogens total. The single low field aromatic hydrogen is that at C-4, i.e. *ortho* to the cyano group. The acetyl methyl occurred at

δ 2.22 and the integration was consistent with its three hydrogens. The amide hydrogen occurs as a broad signal, integrating for one hydrogen, at δ 7.55.

The uv spectrum (cyclohexane) of **40** was typical of that for a biphenylene showing maxima at 247 nm (sh, ε 37,000), 264 nm (ε 69,600), 327 nm (sh, ε 2600), 346 (ε 4770) and 365 nm (ε 7160).

A molecular formula of $C_{15}H_{10}N_2O$ for the cyano compound **40** was confirmed by elemental analysis and *via* the mass spectrum which exhibited a parent peak of m/e 234.

It was hoped that the hydrolysis of the cyano group and the amide in compound **40** could be accomplished simultaneously in concentrated hydrochloric acid. A suspension of **40** in acid was heated to 85° and a yellow solid obtained in 87% yield.

The mass spectrum of this material showed a parent peak at m/e 253 and a peak at m/e 250, denoting P-H_2O. The latter is typical of an aromatic carboxylic acid bearing an *ortho* substituent capable of donating a hydrogen. Elemental analysis also supported the formula of $C_{15}H_{11}NO_3$, suggesting that only the cyano group had been hydrolyzed, forming 3-acetamidobiphenylene-2-carboxylic acid **41**.

The ir spectrum (Nujol) revealed a very weak NH absorption at 3700 cm^{-1}, a double carbonyl absorption at 1675 cm^{-1} and 1660 cm^{-1}; and an amide II band, i.e. N-H bending absorption, at 1520 cm^{-1}. The expected broad O-H stretch was obscured by Nujol.

The nmr spectrum could not be obtained in deuteriochloroform, but spectra were obtained by using trifluoroacetic acid (TMS internal standard) and basic D_2O (DSS internal standard).

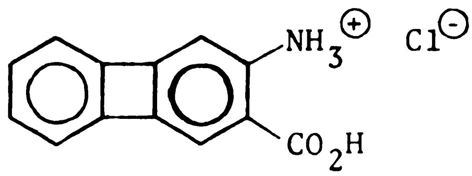
The former consisted of an aromatic multiplet at δ 7.4-6.7 which appeared to be superimposed on a broad resonance, arising from the N-H group. A sharp singlet appeared at δ 2.96 corresponding to the acetyl methyl group. A smaller singlet was also observed at δ 2.42.

The aromatic region of the latter spectrum contained a singlet at δ 7.42, a singlet at δ 7.02 and a multiplet of at least ten lines between δ 7.0 and δ 6.5. The acetyl methyl occurred as a sharp singlet at δ 2.07. The two portions of this spectrum integrated in a ratio of 7 to 3.

The uv spectrum was consistent with the above facts and the hydrolysis product was assigned structure **41**; 3-acetamidobiphenylene-2-carboxylic acid.

Further hydrolysis of **41** was carried out in a refluxing mixture of 20% aqueous sodium hydroxide and 95% ethanol. Water was then added to the mixture and it was neutralized with hydrochloric acid to a pH below 7, yielding a yellow solid in 94% yield.

It is interesting that the amphoteric precursor **25** could be isolated in slightly acidic solution. The hydrochloride salt **43** does not form rapidly because the neutral compound is very insoluble in aqueous medium. Even allowing the compound 25 to stand overnight in concentrated hydro-



43

chloric acid produces no visible change in the crystals suspended in the mixture.

The structure of 25 was established by spectral methods. The yellow solid showed an ir spectrum (Nujol) consisting of a two sharp absorptions above 3000 cm^{-1}. These N-H absorptions lie at 3475 cm^{-1} and 3340 cm^{-1}. The broad O-H is again obscured by Nujol. The carbonyl stretch appears as a triple absorption at 1675 cm^{-1}, 1660 cm^{-1} and 1640 cm^{-1}.

Again the nmr spectrum had to be taken in solvents other than deuteriochloroform. In basic D_2O (DSS internal standard) the aromatic region consisted of a singlet at δ 7.03, a split singlet at δ 6.80 and a third singlet at δ 6.35. Integration of these signals showed them to be in a ratio of 1 to 4 to 1.

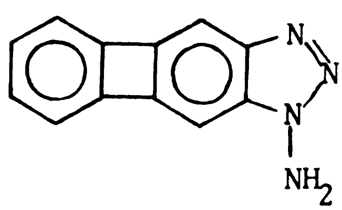
In acetone-d_6 (TMS internal standard) the aromatic region showed the same three singlet pattern (δ 7.19, δ 6.93, δ 6.49) in addition to a very broad NH_2 resonance at δ 3.45. Integration of the aromatic portion was correct, although the NH_2 integration was proportionately too large as expected for such a broad resonance. Finally, the nmr spectrum in trifluoroacetic acid (TMS internal standard) showed only aromatic hydrogens.

The uv spectrum (cyclohexane) contained bands at 259 nm (ε 38,400), 266 nm (ε 50,700), 328 nm (ε 4230), 345 nm (ε 8450) and 363 nm (13,700). This corresponds to a typical biphenylene type spectrum.

The mass spectrum not only confirmed the molecular formula (parent peak at m/e 211), but showed the typical "*ortho* effect" peak at m/e 193, denoting loss of water. A molecular formula for 25 of $C_{12}H_9NO_2$ was determined from the mass spectrum, as mentioned, and by elemental analysis.

Precursor 25 had a mp 193° and decomposed upon melting to a red liquid. Material isolated from the reaction mixture was quite pure, and could be used directly to prepare the biphenylyne 24. Recrystallization from 95% ethanol gave darkened material, so analytical samples were obtained by sublimation at 175° (0.2 mmHg).

Another probable precursor to biphenylyne 24 is 1-aminobiphenylenotriazole 47. The oxidation of aminated triazoles

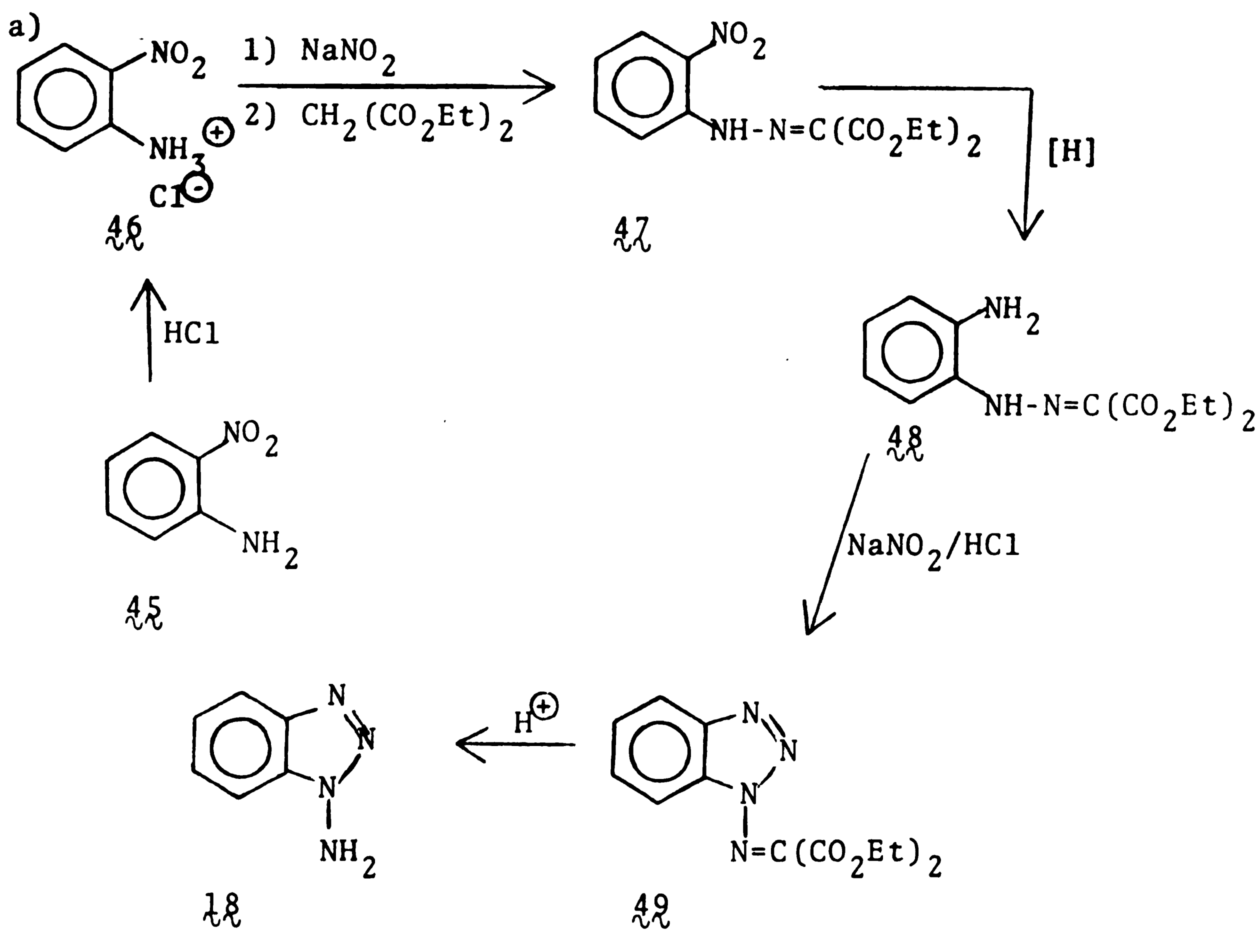


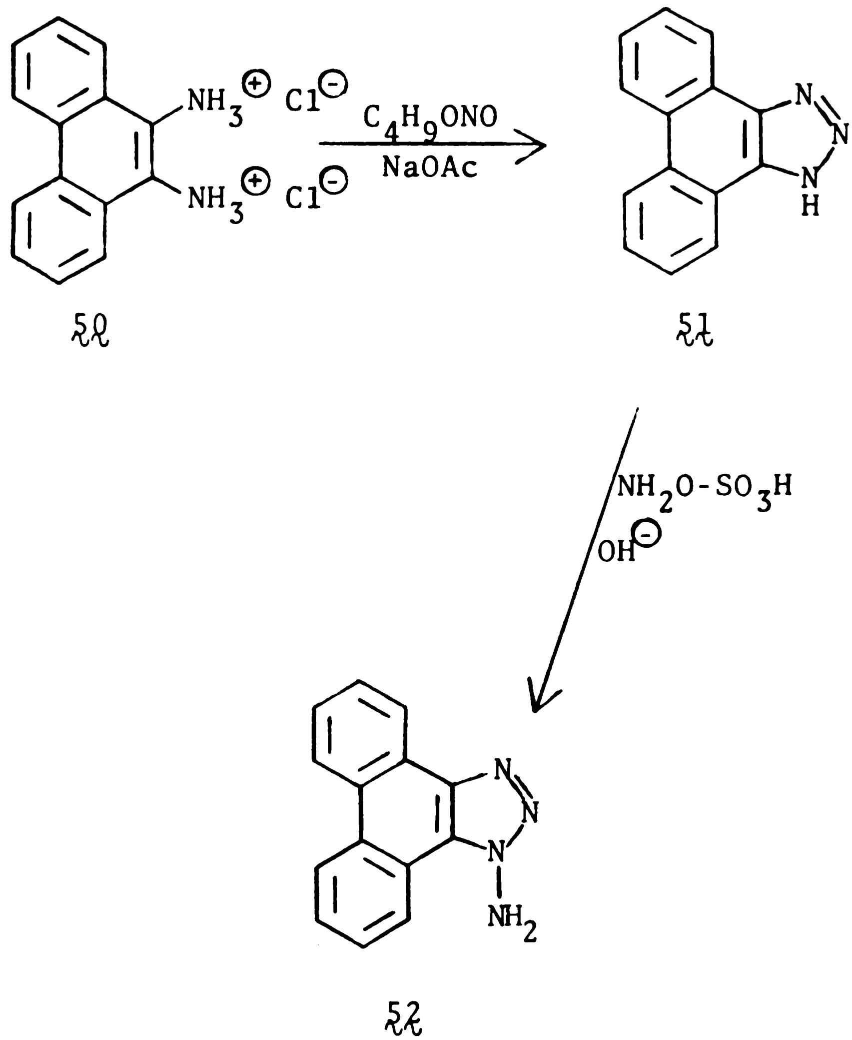
44

to prepare arynes was mentioned in the introduction of this thesis,[25-27] but preparation of the requisite 1-aminotriazoles themselves was not discussed.

The 1-aminotriazoles have been prepared in two ways: a) directly *via* diazotization of protected o-aminoarylhydrazines, followed by removal of the protecting group.[25a,b,26] or b) by amination of the appropriate triazole itself.[25a,b,26,27] Representative routes are shown below for the preparation of 1-aminobenzotriazole 18 and 1-aminophenanthro[9,10-d]triazole 52.

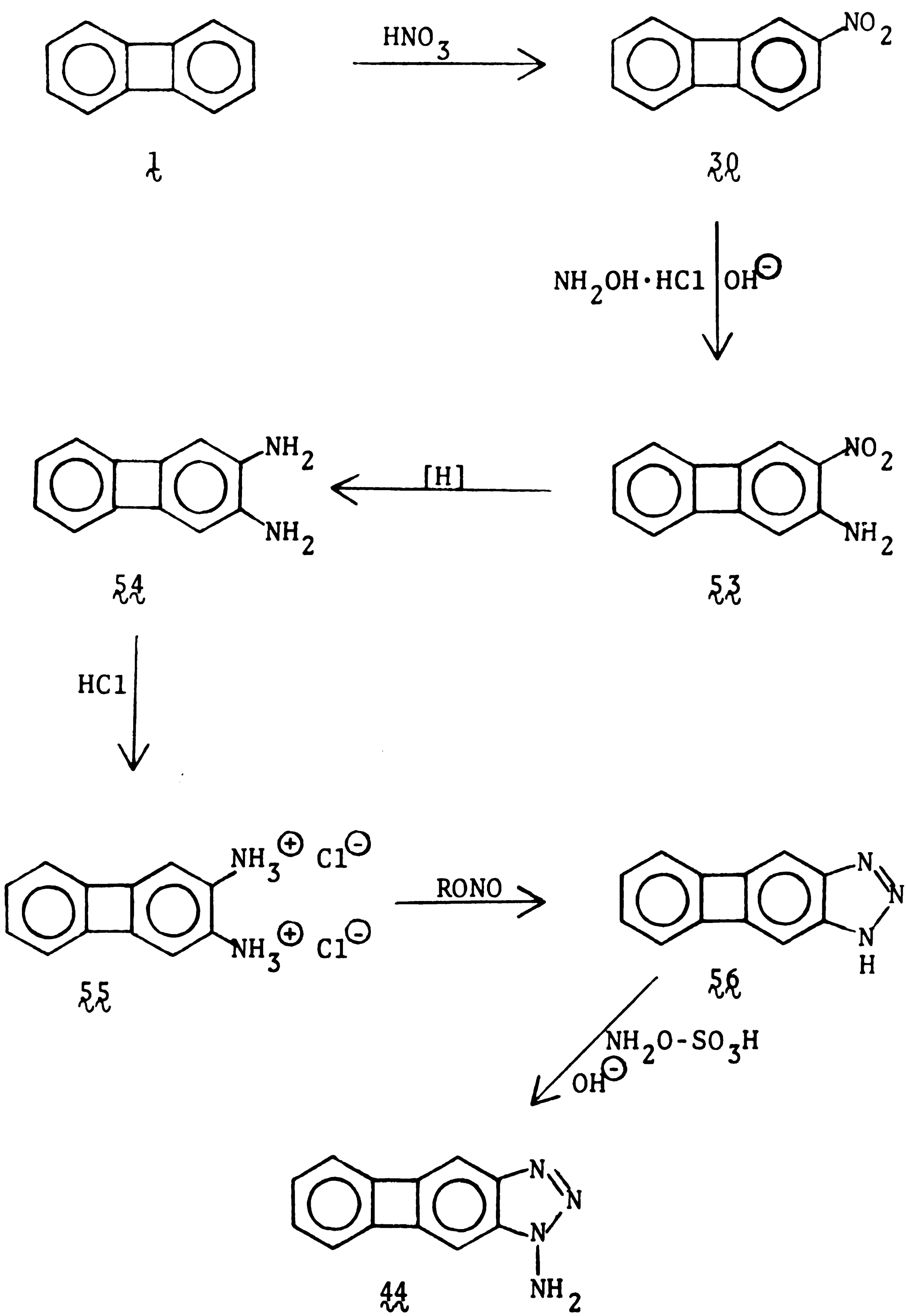
Route (a) to Aminated Aryl Triazoles



b) 

It appears that for more complex systems the latter method is best and this route was envisioned for preparation of precursor 44 (Scheme IV).

Scheme IV

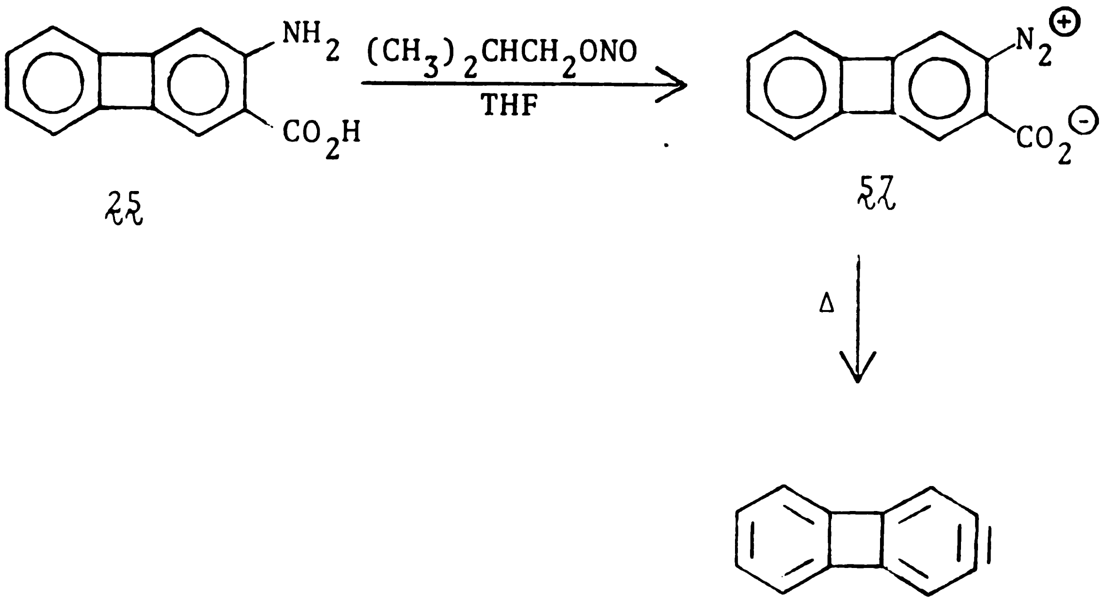

HNO3
NO2
1
30
NH2OH·HCl
OH⊖
NH2
NH2
[H]
NO2
NH2
54
53
HCl
NH3⊕ Cl⊖
NH3⊕ Cl⊖
RONO
N
N
N
H
55
56
NH2O-SO3H
OH⊖
N
N
N
NH2
44

Both compounds 53 and 54 were prepared by Barton's procedures,[40] but attempts to prepare the dihydrochloride salt 55 directly were unsuccessful, yielding only dark material. Addition of water to the $SnCl_2$/HCl reduction of 53, yielded golden plates assumed to be this salt. Reaction of this compound with isoamyl nitrite afforded only a small amount of brown solid.

Attempts to prepare the precursor 44 were therefore abandoned in light of the success in obtaining precursor 25 and the results of reactions of the subsequent biphenylyne 24 which are discussed below.

Preparation and Attempted Dimerization of Biphenylyne

Biphenylyne 24 was prepared by Friedman's method for

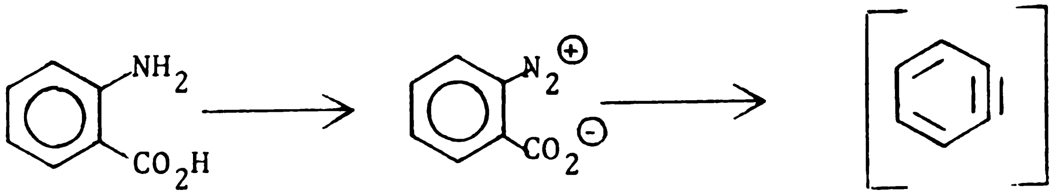


25

57

24

conversion of anthranilic acid 14 to benzyne 12.[22]



14 15 12

Isoamyl nitrite was added to a cooled (trichloroacetic acid catalyzed) solution of 25 in tetrahydrofuran and the mixture stirred for 3-4 hours. Upon addition of the isoamyl nitrite a green color formed, accompanied by immediate formation of a dark precipitate. This color gave way to a reddish solution containing the tan to brown colored precipitate of the diazonium carboxylate 57. In the anthranilic acid reaction this is also observed except that the initial precipitate and solution are a very deep red color.

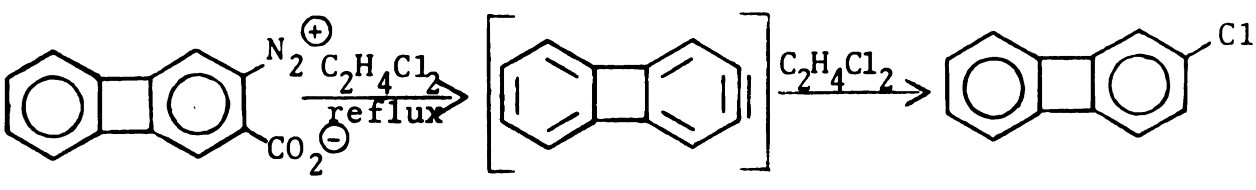
The precipitate was filtered and washed first with fresh tetrahydrofuran, then with the solvent to be used in the decomposition to biphenylyne 24. Special caution was used when handling this new unstable diazonium carboxylate 57 because dry benzenediazonium-2-carboxylate 15 has been known to detonate violently if scraped or heated.[22] (Note: during several preparations of these arynes no incident of explosion occurred!)

The first dimerization attempt was carried out in 1,2-dichloroethane. The moist 2-biphenylenediazonium-3-carboxylate 57 was suspended in 1,2-dichloroethane and added all at once (portionwise addition recommended for large amounts) to a refluxing solution of the same solvent. The mixture was refluxed several minutes, during which time the solution cleared and turned dark red.

Room temperature evaporation of the solvent yielded a dark, complex mixture of products which was chromatographed on a neutral alumina column. Elution with pentane yielded a solid which was further chromatographed on a thick layer plate (silica/pentane).

The major band of several from the plate yielded an off-white solid, mp 69-70°. The mass spectrum of this solid revealed a parent peak at m/e 186 and a P+2 peak (m/e 186) whose relative intensity was 33.8% of the parent. In addition, a P-35 peak occurred at m/e 151, all signaling the presence of one chlorine atom in the molecule.

Hence the compound was postulated to be



57 24 58

2-chlorobiphenylene 58. Its molecular weight is 186.64 grams/mole and its melting point is reported as 66-67°.[30]

The ir and nmr spectra of 58 were consistent with this structure and the uv revealed a typical biphenylene envelope, shifted slightly to higher wavelengths.

The yield of 2-chlorobiphenylene 58 was only 8.7%, the major reaction product being a dark material which remained at the origin of the initial column even after elution with acetone.

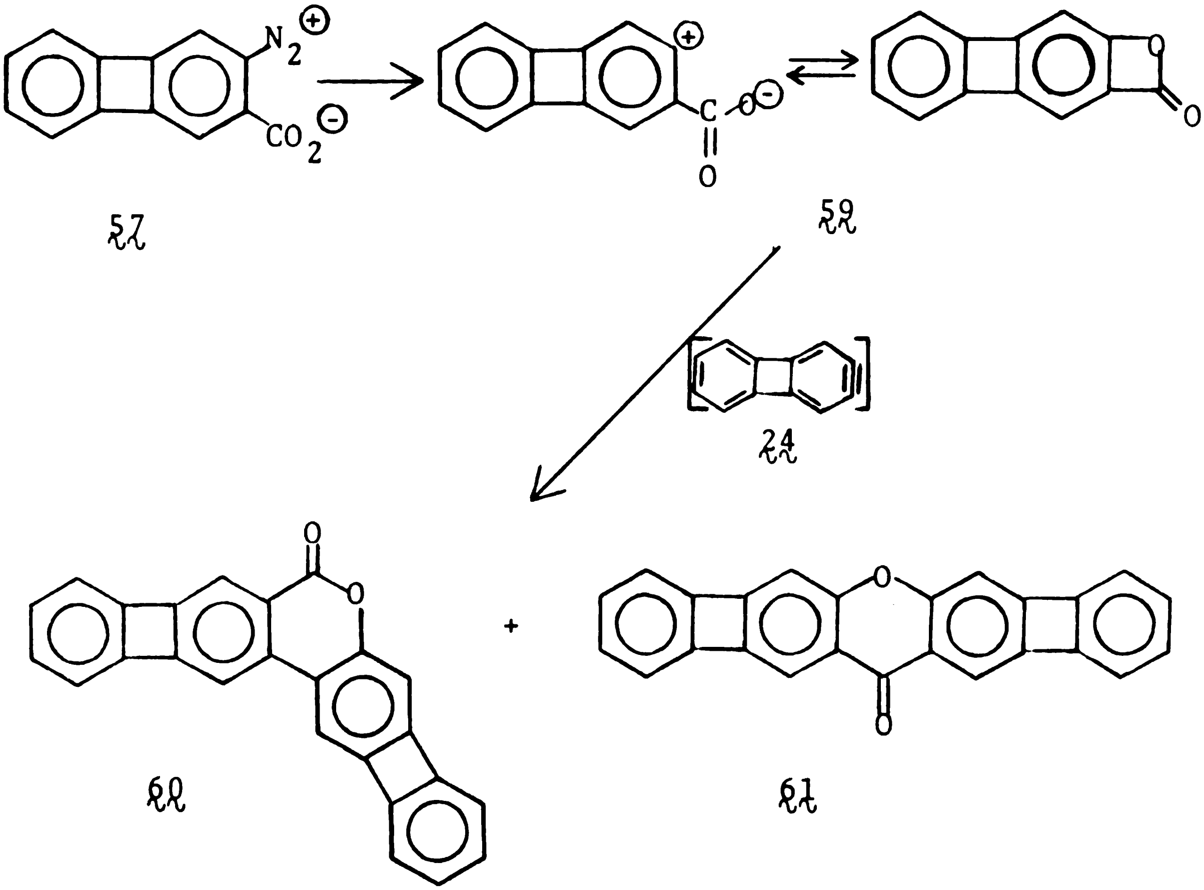
None of the hydrocarbon 4 could be isolated. Instead, polymerization is the major reaction course. It was felt the due to the high reactivity of biphenylyne 24, dimerization is only one of many possible reaction paths and, as for benzyne 12 dimerization, conditions for this reaction may be extremely difficult to obtain.

To obtain 2-chlorobiphenylene 58, biphenylyne 24 must act as a diradical, abstracting a chlorine from the 1,2-dichloroethane solvent. This is unusual as this solvent was chosen for its low reactivity with arynes. However, in the presence of the limitations against dimerization this reaction succeeds to a small degree.

Continued elution of the original column afforded another fraction which was further purified by thick layer chromatography. The major band here afforded a bright yellow solid of mp > 300°. Its uv spectrum showed an array of bands typical of a biphenylene, (but shifted considerably to longer wavelengths) and also included absorbances at λ_{max} = 430 nm and λ_{max} = 456 nm. The ir spectrum of this bright yellow compound exhibited a carbonyl at 1710 cm^{-1}.

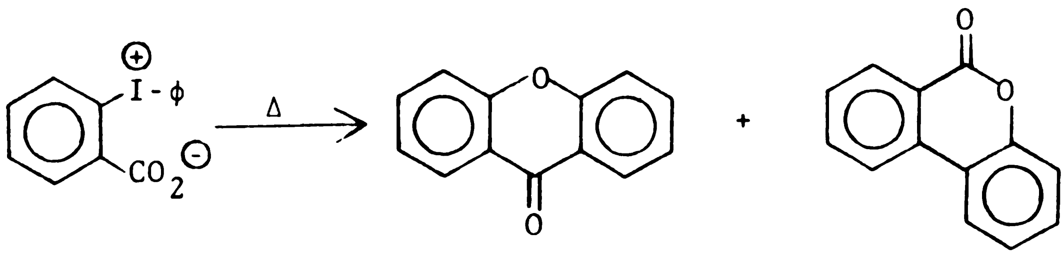
The mass spectrum showed a large peak at m/e 344 and a very small peak at m/e 368 (relative intensity less than one percent). This latter peak was thought to be an impurity peak, as the thin layer chromatogram showed a slight impurity in the sample. In addition, most biphenylene compounds observed to date have shown very strong parent peaks.

Based on the molecular weight, two isomeric structures 60 and 61 were proposed for this bright yellow compound. They were postulated to have arisen by the route outlined below.



57 59 24 60 61

It has been shown in the benzyne sequence that nitrogen is lost first from the diazonium carboxylate 15 and in the absence of aryne trapping agents, the transient existence of a highly reactive β-lactone analogous to 60 has been suggested.[41] Moreover, in the generation of benzyne by thermal decomposition of diphenyliodonium-2-carboxylate 62, xanthone 63 has been isolated in addition to benzo-coumarin 64.[42a,b]



62 63 64

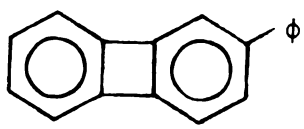
Although the small amount of material obtained permitted only spectral analyses, it appears that the coumarin structure 60 is the correct one for this compound. The carbonyl absorption at 1710 cm^{-1} is consistent with the coumarin, as coumarin itself absorbs at 1710 cm^{-1}. Xanthone 63, on the other hand, is typical of a diaryl ketone, absorbing at 1658 cm^{-1}.

Another solvent was then sought in which to carry out the decomposition. It has been shown that decomposition of benzenediazonium-2-carboxylate 15 in benzene takes place quite slowly,[43] but biphenylene 1 has not been isolated in this solvent. On the other hand, benzene is the solvent of choice when biphenylene 1 is prepared by oxidation of 1-aminobenzotriazole.[25a,b] It was also felt that radical attack on the solvent would be minimized in benzene. This mode of decomposition was therefore undertaken and its products studied.

The reaction was carried out as described in the 1,2-dichloroethane case and, indeed, decomposition was noticeably slower. A very deep violet residue was obtained and column chromatography afforded a crude fraction which was a complex mixture of colorless to yellow products. Again the major reaction product consisted of polymeric material which remained at the column origin.

The column-eluted material was rechromatographed on a thick layer plate and the primary band collected was a light yellow solid. The mass spectrum of this compound showed parent peak at m/e 228, thus, the yield of this compound was 1.3%. A second major peak in the mass spectrum occurs at m/e 202.

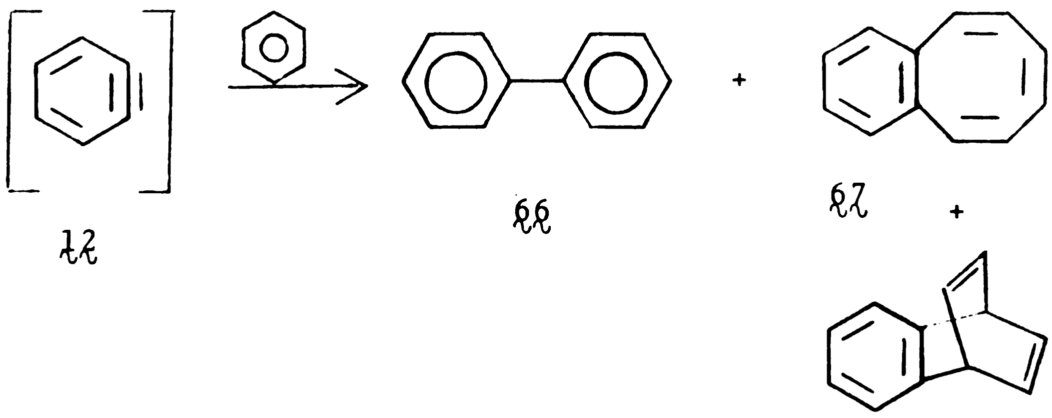
It was felt that this compound was 2-phenylbiphenylene 65 but its melting point (156-158°) and uv spectrum did



65

not correlate with that described by McOmie and coworkers.[44] The nmr spectrum further discredited the proposed structure of 65 in that it showed an expected multiplet at δ 7.2-6.3 but also included a multiplet as δ 5.0-4.7. These integrated in the ratio of 10 to 2.

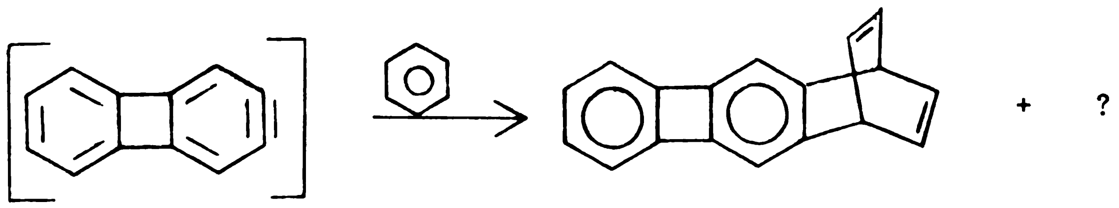
Miller and Stiles[45] have prepared benzyne 12 in benzene and from the major polymeric product, have separated three isomeric hydrocarbons: biphenyl 66, benzocyclo-öctatetraene 67 and benzobicyclo[2.2.2]octatriene 68 (benzobarrelene).



12 66 67 68

By analogy with the above work, the product isolated from the biphenylyne reaction appears to be the biphenylene analog of 68, i.e. biphenyleno[2.2.2]octatriene 69.

Comparison of the nmr spectra of these two barrelenes substantiated this. The nmr spectrum of benzobarrelene 68 shows a symmetrical, complex pattern for the aromatic



74 69

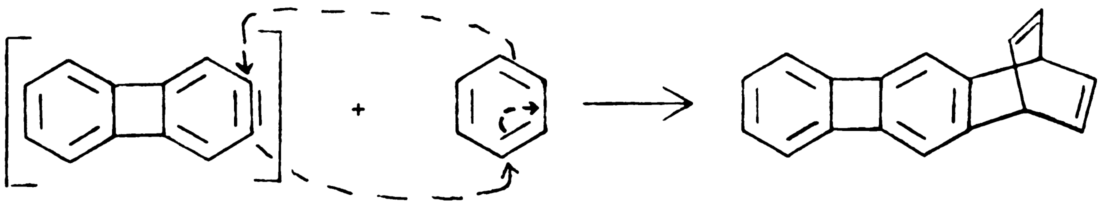
hydrogens at δ 6.9 and a quartet centered at δ 6.8 for the vinyl hydrogens. The spectrum of 69 is consistent with this, but any symmetry in the pattern is obscured by what appears to be a biphenylene singlet occurring in the midst of the array.

The chemical shifts of the bridgehead methine hydrogens correlate well in these two compounds. In both 68 and 69 they appear as a multiplet centered at δ 4.8.

The peak at m/e 202 (P-26) in the mass spectrum of 69 suggests the loss of a C_2H_2 fragment from the parent. Indeed, benzobarrelene 68 has been shown in the above work to thermally decompose, giving napththalene and presumably acetylene.

None of the other $C_{18}H_{12}$ isomers were isolated, but the mass spectrum of the band which remained at the origin on the thick layer plate revealed a mixture whose major peak was also at m/e 228. Use of larger amounts of starting material and tedious isolation techniques could undoubtedly lead to isolation of the remaining two isomers.

The barrelenes 68 and 69 arise from a thermal 1,4-addition of the aryne to benzene. The dienophilic nature



24

69

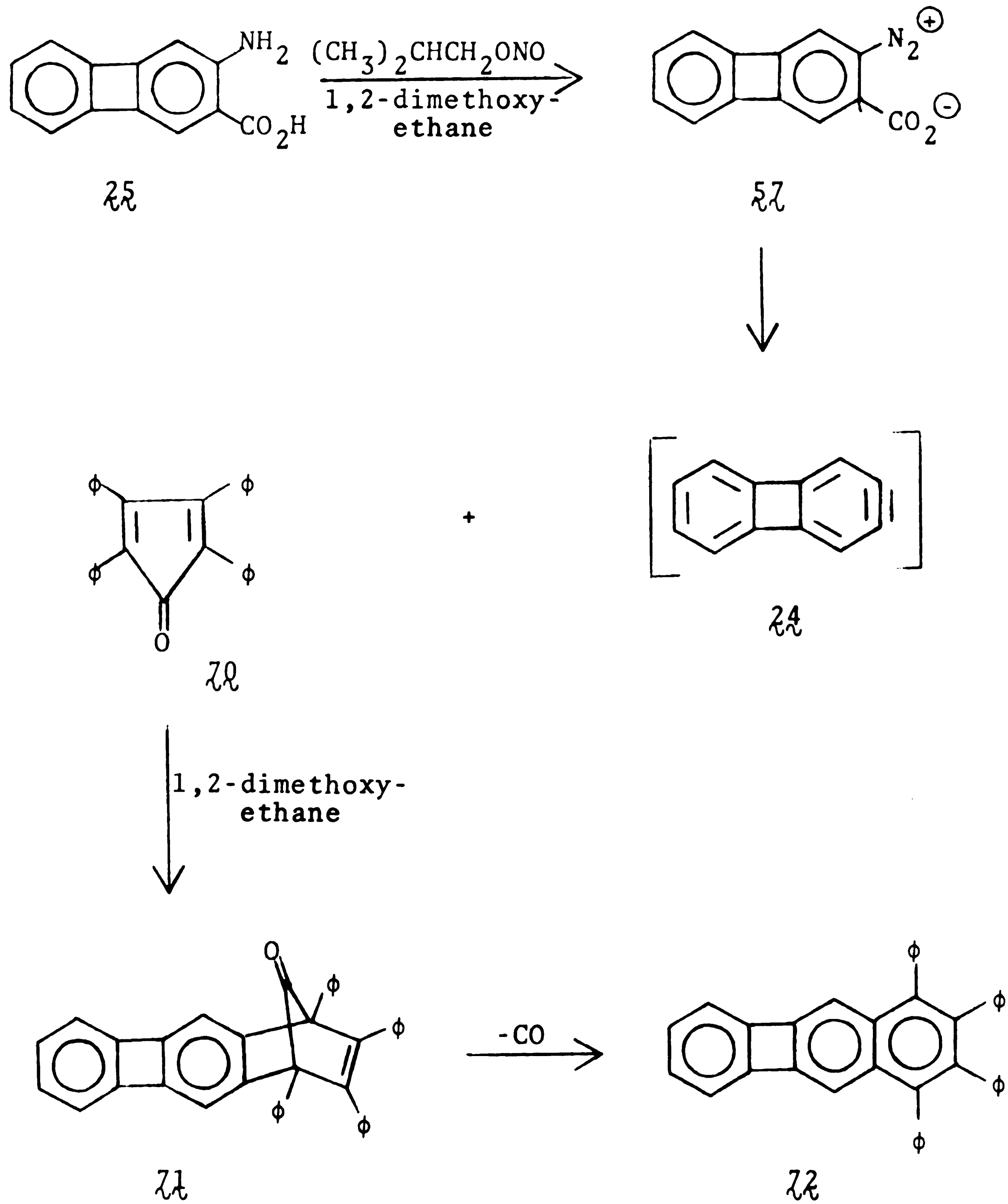
of arynes is, of course well known, but the participation of benzene as a diene is quite rare.[45]

In summary, it was shown that dimerization of biphenylyne 24 does not take place in solvents known for their efficacy in aryne dimerizations. Instead, a radical reaction takes place. In benzene, a poor solvent, 24 behaves as expected, adding in a 1,4-fashion to the solvent.

In light of these results it was decided to attempt the trapping of biphenylyne 24 in a normal fashion to see if this new aryne would behave "normally" under these favorable conditions.

Trapping of Biphenylene 24

Biphenylyne 24 was trapped as its tetracyclone adduct 72.

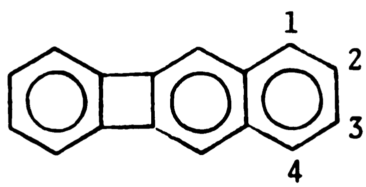


Solutions of the amino carboxylic acid 75 and isoamyl nitrite in 1,2-dimethoxyethane were added to refluxing a solution of tetraphenylcyclopentadienone 70 in the same solvent. A trace amount of trichloroacetic acid was added to the latter solution as catalyst.

The adduct 1,2,3,4-tetraphenylbenzo[b]biphenylene 72 was obtained in 10% yield as a white solid, mp 316-317.5°. The nmr spectrum of 72 consisted of three singlets at δ 7.15, δ 6.80 and δ 6.76. The low-field singlet integrates for ten hydrogens, while the closely spaced upfield signals correspond to sixteen hydrogens.

The phenyls on carbons 1 and 4 give rise to the δ 7.15 singlet, being closer to and more deshielded by the adjacent diamagnetic ring current in biphenylene's phenyl ring. The phenyls furthest from the diamagnetic ring current (C_2 and C_3) plus the biphenylene hydrogens themselves comprise the high-field singlets.

Hydrogens in the unsubstituted benzo[b]biphenylene 73 show this same relation of chemical shifts, i.e. those on carbons 1 and 4 appearing at lower field than those on



73

carbons 2 and 3.[9a,b]

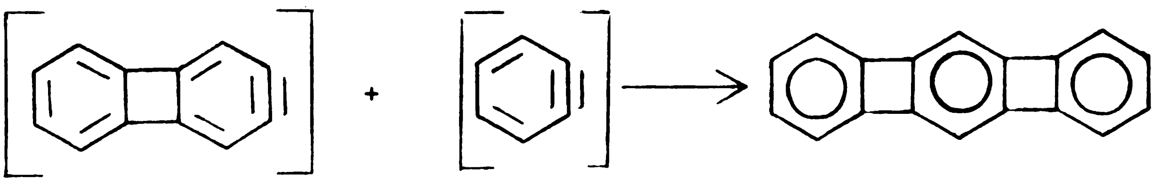
The uv spectrum of 72 is typical of a benzo[b]-biphenylene[46] showing a bathochromic shift of the short-wavelength biphenylene band system (enhanced by the phenyl groups in 72) and revealing an expanded long-wavelength system, which shows four distinct absorbances of increasing intensity.

In addition a new band system appears in both benzo[b]-biphenylene 73 and adduct 72. This is comprised of two absorbances near 300 nm.

The parent peak at m/e 506 and an elemental analysis confirmed the molecular formula of $C_{40}H_{26}$.

Attempted Crossing of Biphenylyne with Benzyne

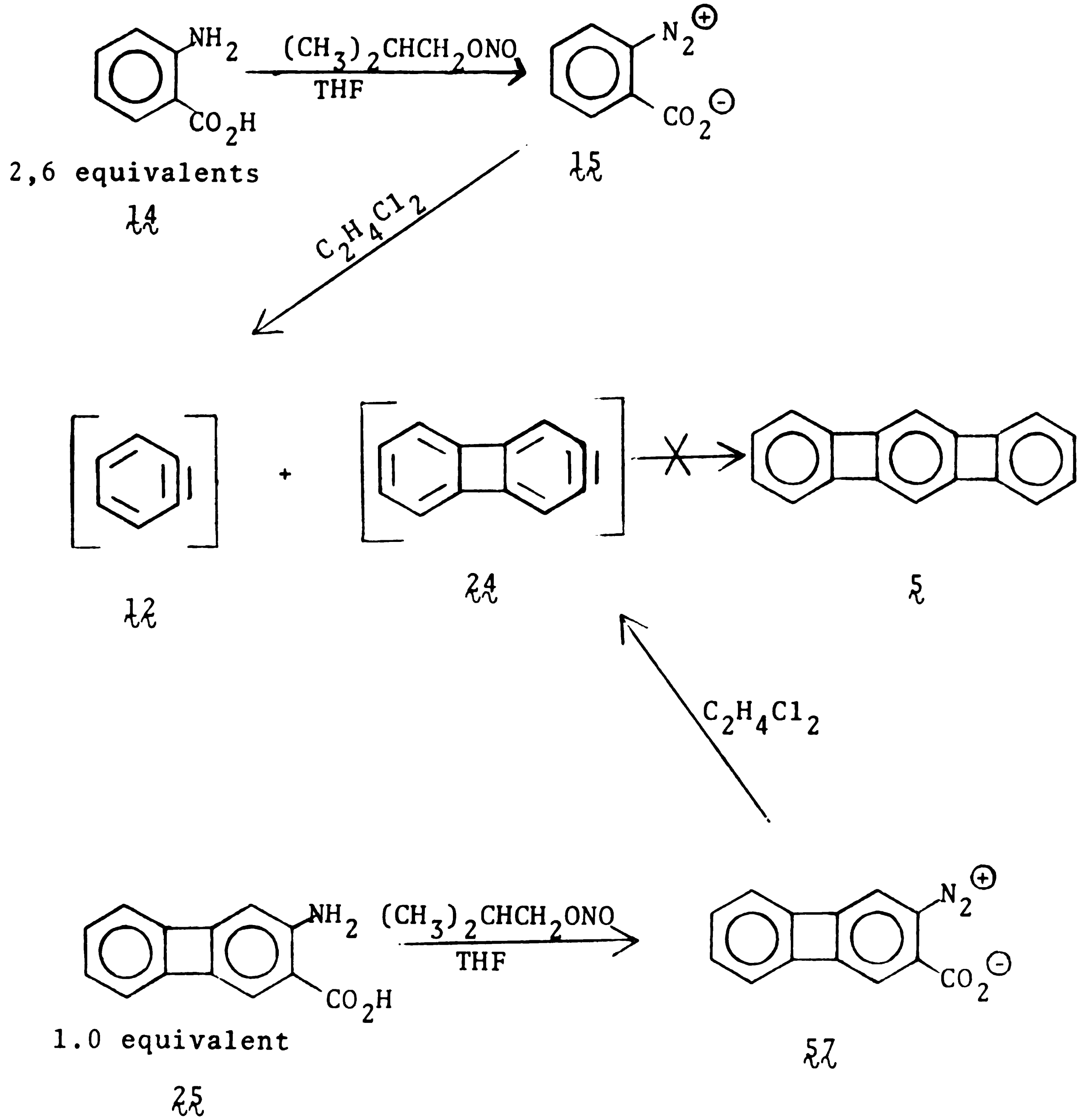
It was also decided to attempt the crossing biphenylyne 24 with benzyne 12, hoping to obtain the 18 π-electron system 5.



24 12 5

hydrocarbon 5 is a 4n + 2 π-electron system and its synthesis might be more favorable than the 4n system 4 attempted earlier.

A mixture of the requisite aryl diazonium carboxylates 15 and 57, prepared from 2.6 equivalents and 1.0 equivalent of the respective amino carboxylic acids 14 and 25, was decomposed in 1,2-dichloroethane.


NH2
CO2H
(CH3)2CHCH2ONO
THF
N2
CO2
2,6 equivalents
14
15
C2H4Cl2
12
24
5
C2H4Cl2
NH2
CO2H
(CH3)2CHCH2ONO
THF
N2
CO2
1.0 equivalent
25
57

The reaction was worked up as usual and, in addition to dark, polymeric material, yielded two major products. The band which traveled fastest on the thick layer plate yielded predominately biphenylene 1, determined from the nmr spectrum and the parent peak (m/e 152) of the mass spectrum. A small impurity of 2-chlorobiphenylene (could not be separated by thick layer technique) was revealed by the presence of a peak at m/e 186 (m/e 188 also present at 1/3 of the relative intensity of the parent m/e 186) in the mass spectrum.

It is interesting that biphenylene was produced in good yield (*ca.* 25% based on anthranilic acid 14) indicating that the conditions of the reaction are certainly favorable for the dimerization of benzyne 12. However, even in these conditions conducive to dimerization of the simple aryne, no aryne coupling products (e.g. hydrocarbons 5 or 4) deriving from biphenylyne 24 were isolated.

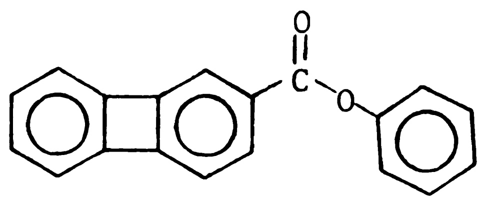
Instead, the only other substantial band obtained was a yellow brown solid which showed a large carbonyl in the infrared spectrum. The nmr spectrum of this compound consisted solely of aromatic absorptions.

The mass spectrum suggested the presence of more than one compound, therefore, this solid was rechromatographed on a thick layer plate.

Indeed, the subsequent plate showed at least three components, which again could not be entirely separated.

However, the nmr spectrum of the major component showed resonances typical of both phenyl and biphenylene type hydrogens, and even though the mass spectrum was indicative of a mixture, one series of strong peaks at m/e 272, 179 and 151 could be easily recognized.

It was speculated that this series arose from the ester 74, showing the usual aromatic ester cleavage pattern of P, P-OR and $P{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR$. Loss of the phenoxy moiety from the phenyl ester 74 or P-93 gives m/e 179, while cleavage of the entire ester function is the loss of 121 mass units and gives rise to m/e 151.

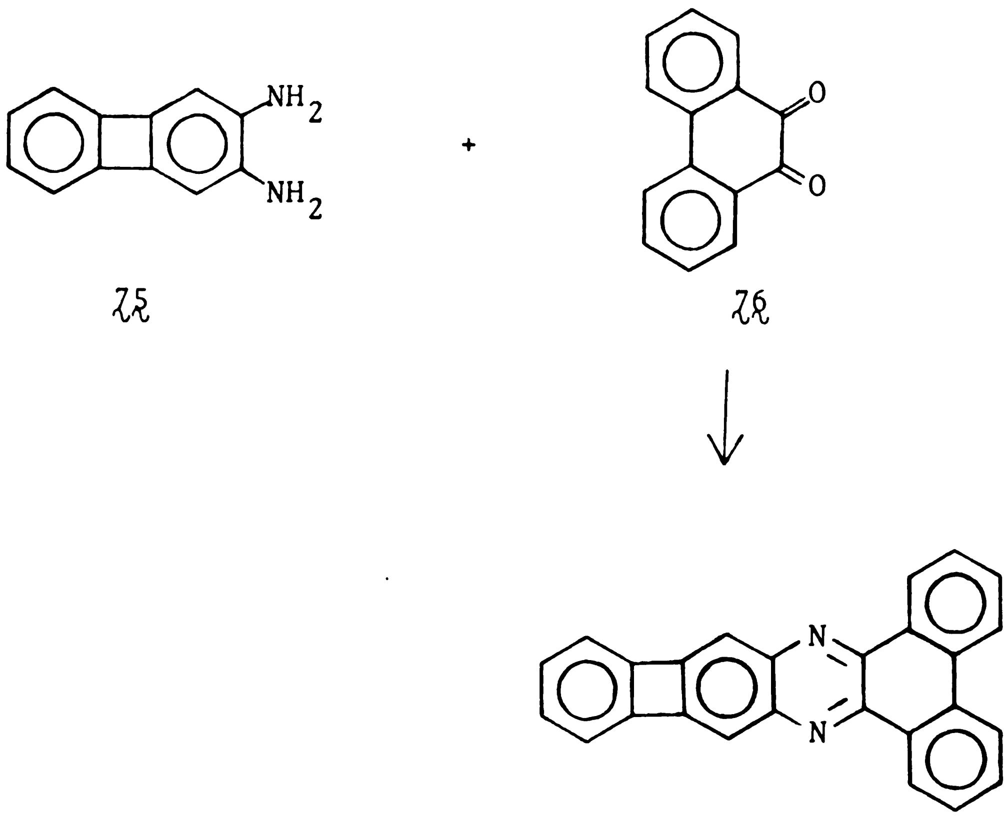


74

This structure is also consistent with the nmr and infrared spectral data.

Preparation of Quinoxaline Derivatives

During the course of this research the opportunity presented itself to synthesize some interesting biphenylene compounds. The reaction of 2,3-diaminobiphenylene 75 with an α-diketone leads to a biphenyleno quinoxaline. Barton and coworkers have prepared the quinoxaline with phenanthrene-9,10-quinone **76** for characterization of the easily oxidized aromatic *ortho* diamine **75**,[40] but reported



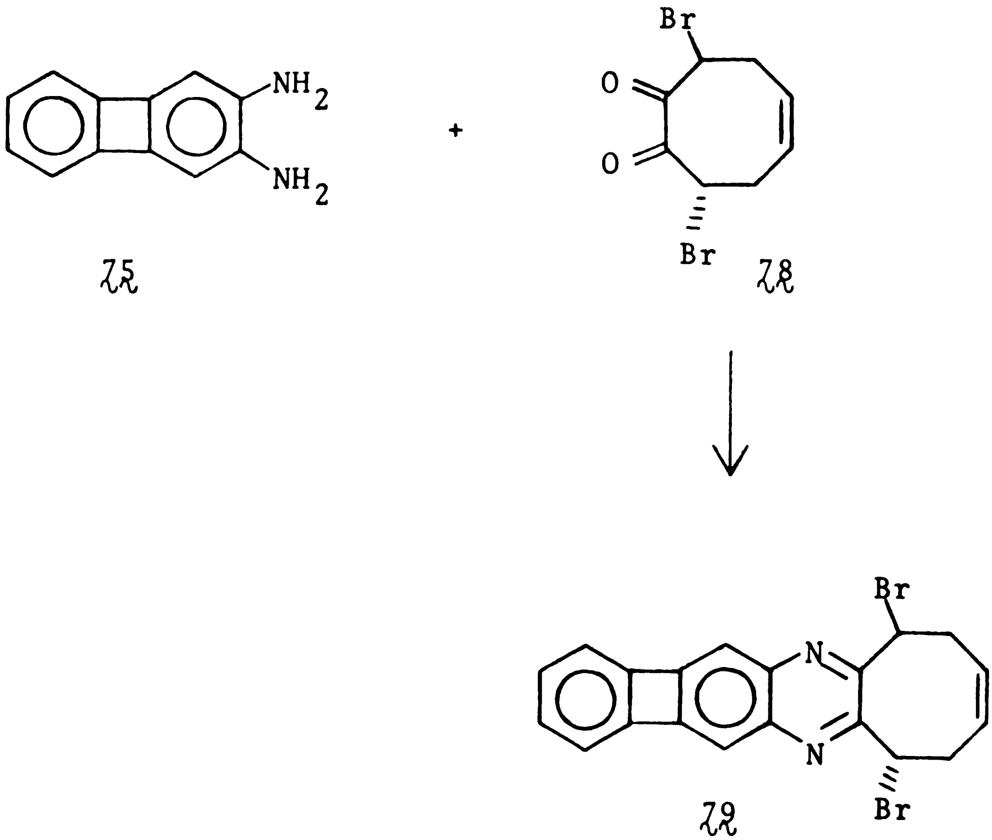
75 **76**

77

only the melting point of this derivative **77**.

It was thought that aside from being novel compounds the quinoxalines would be valuable model systems in this project. They are extended biphenylene systems and should be somewhat analogous to hydrocarbons **4** and **5**, but with less constraints due to unfavorable resonance forms.

The first quinoxaline prepared was that from *trans*-3,8 –dibromo-5-cycloöctene-1,2-dione **78**.[48] It was intended that this system would simply extend the biphenylene *via* the



1,4-diazadiene moiety, and the properties of this new biphenylene 79 could be observed.

The quinoxaline 79 was prepared either by stirring the reactants 75 and 78 in methanol catalyzed by acetic acid or by using glacial acetic acid as a solvent. Workup involved chromatography to purify the final product, and it was noted that decomposition of the product takes place on either alumina or silica.

Consequently, the chromatography was carried out rapidly and was followed by recrystallization from benzene/cyclohexane to yield 79 as pure yellow needles, mp > 300°. The pure compound also darkened slightly on exposure to air and in solution.

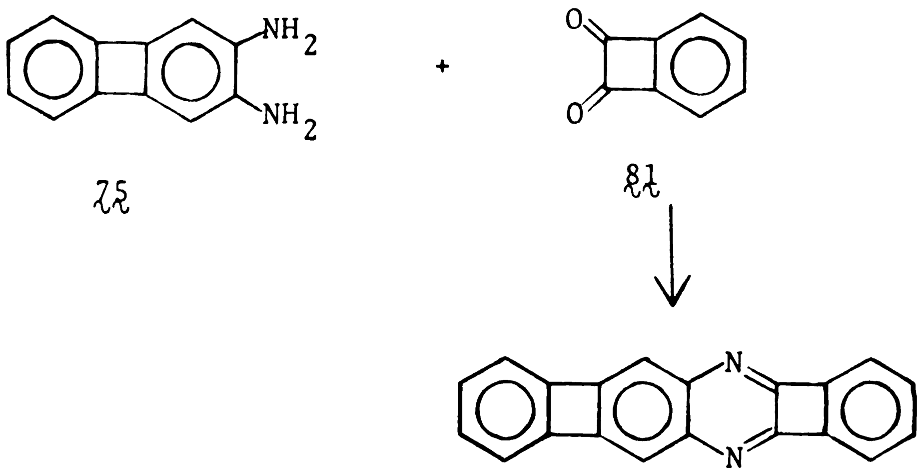
The structure of quinoxaline 78 was confirmed by spectral characteristics. The nmr spectrum showed an unsymmetrical doublet at δ 7.16 whose integration was consistent with six biphenylene hydrogens. The two methine hydrogens appear as a triplet (J=10 Hz) centered at δ 5.81, and the two vinylic hydrogens also give rise to a triplet (J=4 Hz) at δ 5.55, which slightly overlaps the methine triplet. Finally, the allylic hydrogens occur as a pair of doublets (J=10 Hz and J=4 Hz) at δ 3.20 and integrate correctly for four hydrogens.

The parent peak region of the mass spectrum is a three line pattern at m/e 444, 442, and 440, relative intensity ratio 98.8/191/100, denoting a compound containing two bromine atoms. In addition, the P-Br peak is a two line pattern at m/e 362 and 360 (relative intensity ratio 97.5/100) and the P-2Br peak occurs at m/e 281.

The mass spectrum also confirmed the molecular formula of $C_{20}H_{14}N_2Br_2$ and this was substantiated by the correct elemental analysis.

The uv spectrum of quinoxaline 78 was similar to that of a benzo[b]biphenylene, showing three distinct band systems. A typical bipheylene absorption band occurs between 250 and 275 nm, followed by a weaker, triple absorption band at 290, 297 and 302 nm. Finally, the long wavelength biphenylene absorption occurs as a four absorbance band at 358, 377, 389 and 400 nm.

Another quinoxaline 80 was prepared from 1,2-benzo-



75 81 80

cyclobutadienequinone 81.[48] This fully, conjugated, 22 π-electron system is one with two four membered rings in it, thus introducing an extended biphenylene system with the type of strain expected in 4 and 5. The diamine 75 and quinone 81 were stirred in methanol catalyzed by acetic acid, and quinoxaline 80 was isolated (after recrystallization) as light orange needles, mp 339° (dec).

The nmr spectrum of 80 consisted of two singlets at δ 7.30 and δ 6.93. These were of equal area, but the nondeuterated chloroform present in the solvent was included in the low field signal. It was expected that the low-field resonance corresponded to the four aromatic hydrogens on the benzene ring of the original quinone, and the high-field signal represented the six biphenylene hydrogens. This was substantiated by the addition of tris(dipivaloylmethanato)europium(III) to the sample. The shift reagent caused no change in position or intensity of the low-field singlet but the high-field biphenylene resonance separated into two peaks. The singlet at δ 6.93 decreased in intensity and a new singlet appeared at downfield at δ 7.06. These two biphenylene singlets integrated in a ratio of 4 to 2 respectively. These results are as expected; the shift reagent complexing to the quinoxaline nitrogens and shifting the two closest hydrogens downfield, while the eight peripheral hydrogens are too far removed from the complexation site to be affected.

Quinoxaline **80** exhibited a uv spectrum comparable to quinoxaline **79** except that the short-wavelength bands coalesced to a single, broad, intense band with maxima at 268, 275, and 287 nm. The long-wavelength system was shifted bathochromically by 40-45 nm and increased slightly in intensity, as expected for this extended quinoxaline system.

The mass spectrum of quinoxaline **80** revealed a parent peak at m/e 278 and, together with the elemental analysis, confirmed the molecular formula of $C_{20}H_{10}N_2$.

Conclusion

It is evident from the trapping experiments that biphenylyne **24**, generated from the diazonium carboxylate **57** is a true aryne, undergoing Diels-Alder reactions. Based on the quinoxaline experiments it also seems that extended biphenylene systems, including those which contain more four membered rings are amenable to preparation. However, under conditions generally favorable for aryne dimerization, **24** either does not undergo aryne coupling (i.e. dimerization or crossing) or does so in such a myriad of concomitant reactions that hydrocarbons **4** or **5** are not isolable.

Reasons for this reluctance toward coupling may include the fact that products **4** or **5** are prohibitively high in energy, or that the aryne **24** needs to be generated under different conditions or even from an alternate precursor in order to react in the desired fashion.

Regardless of this, biphenylyne **24** is in itself an interesting intermediate warranting further synthetic and theoretical investigation.

EXPERIMENTAL

General Procedures

All melting points, determined on a Thomas Hoover melting point apparatus, are uncorrected.

Ultraviolet spectra were recorded on a Unicam Model SP-800B; samples were contained in 1 cm quartz cells. Infrared spectra were obtained using a Perkin-Elmer Model 237B spectrophotometer. A Varian T-60 spectrometer was used to record nmr spectra and unless indicated all spectra are recorded as δ values in ppm downfield from an internal standard of tetramethylsilane. Mass spectra were obtained by Mrs. L. Guile on a Hitachi Perkin Elmer RMU-6 mass spectrometer.

Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

2-Nitrobiphenylene (30).

To a cooled solution of 13.0 g (8.55×10^{-2} mol) of biphenylene 1[22] in 400 ml of methylene chloride was added dropwise concentrated nitric acid (69-71%) until thin layer chromatography (alumina/pentane-benzene) revealed exhaustion of starting material. The mixture was immediately washed with three 200 ml portions of water and the methylene chloride layer dried and evaporated to 25-50 ml. This deep red solution was chromatographed on neutral alumina, eluting with benzene. The initial yellow fraction collected yielded 4.5 g (26.7%) of **30** as a bright orange solid: mp 99-101° (lit[30] 105-106.5°).

This material was used directly in subsequent reactions.

2-Aminobiphenylene (**31**)

Following Bavin's procedure[31b] for reduction of nitro-compounds, 0.7 g (3.5×10^{-3} mol) of 2-nitrobiphenylene **30** were suspended in 15 ml of 95% ethanol and the mixture warmed to 50-60°. Addition of 0.1 g of 10% palladium-on-charcoal was followed by dropwise addition of 0.5 ml of hydrazine hydrate (99-100%). Evolution of nitrogen occurred. Another small portion of catalyst was added and the mixture refluxed until all of the nitrobiphenylene had dissolved and the orange color of the supernatant liquid had disappeared.

The catalyst was filtered off and after washing the residue with 95% ethanol, the filtrate was poured onto water. The precipitate was collected and dried yielding 0.4 g (67%) of **31** as yellow-greenish solid: mp 121-123° (lit[30] 123-124°).

This material was used directly in subsequent reactions.

<u>2-Ethyl-3-nitrobiphenylene (36)</u>

A solution of 1.1 g (6.1 x 10^{-3} mol) of 2-ethylbiphenylene (35) in 200 ml of methylene chloride was cooled in an ice bath and stirred. Concentrated nitric acid (69-71%) was added dropwise and the reaction was followed by thin layer chromatography (silica/pentane).

The reaction was sluggish and an excess of nitric acid developed in the reaction flask. After 1/2 hr the cooling bath was removed, the mixture slowly warmed to room temperature and the reaction continued for another 1/2 hr; still containing unreacted nitric acid.

The mixture was then washed well with water and the methylene chloride layer dried and evaporated to dryness. The residue was chromatographed on neutral alumina eluting with pentane/benzene. The first fraction yielded 0.25 g (23%) of unreacted starting material; the second yielded 0.25 g (19%) of 2-ethyl-3-nitrobiphenylene 36 as an orange solid: mp 92-95° (lit[34] 95-97°).

This material was used directly in subsequent reactions.

<u>2-Acetylbiphenylene Oxime (42)</u>

A mixture of 5.83 g (3.0 x 10^{-2} mol) of 2-acetylbiphenylene 34, 2.6 g (3.75 x 10^{-2} mol) of hydroxylamine hydrochloride and 4.9 g (6.0 x 10^{-2} mol) of anhydrous sodium acetate in 125 ml of 95% ethanol was heated to 70° for 2 hr.

The solvent was evaporated under vacuum and the residue dissolved in methylene chloride. This solution was washed with water, dried and evaporated to dryness yielding a solid which was recrystallized from aqueous ethanol yielding 4.2 g (67%) of **42** as yellow needles: mp 175-176° (lit[33] 176°).

This material was used directly in subsequent reactions.

<u>2-Acetamidobiphenylene (**38**)</u>

Following the procedure of Smith and Dice,[37a,b] to a solution of 7.3 g (3.75×10^{-2} mol) of 2-acetylbiphenylene **34** in 55 g of molten trichloroacetic acid (bath temperature = 65°) was added 3.6 g (5.5×10^{-2} mol) of sodium azide. The dark, thick mixture was slowly stirred at 65° and evolved large quantities of nitrogen. During the 11 hr reaction period further portions of sodium azide (0.9 g at 5 hr and 0.5 g at 9 hr) were added. (Note - smaller scale preparations may not require as much time.)

After cooling, the black mixture was poured, with stirring, onto ice/water and allowed to stand. A black solid formed which was filtered, dried and chromatographed over neutral alumina. The material was applied to the column was dissolved in chloroform, but the eluent immediately changed to benzene or benzene/pentane.

Following an impurity fraction, a fraction was collected which yielded 7.0 g (89%) of slightly impure **38** as a yellow solid: mp 144-145° (lit[33] 146-147°).

This material was used in subsequent reactions.

2-Acetamido-3-cyanobiphenylene (**40**)

Following the method of Dewar and Grisdale[39] a mixture of 3.6 g (1.25×10^{-2} mol) of 2-acetamido-3-bromobiphenylene **39**, 1.15 g (1.27×10^{-2} mol) of cuprous cyanide and 6 drops of pyridine in 125 ml of dimethylformamide was heated to 140° for 6 1/2 hr.

After cooling, the black reaction mixture was poured onto a mixture of 100 ml of concentrated ammonium hydroxide and 60 grams of ice.

The precipitate was filtered, washed with water, dried and recrystallized (with hot filtration) from chloroform/ benzene yielding 1.6 g (55%) of **40** as fluffy yellow needles: mp 244-245°; ir (Nujol) 3275 (weak, NH), 2220 (weak, sharp, CN), and 1700 cm^{-1} (C = O); nmr ($CDCl_3$) δ 7.80 (s, 1, aromatic), δ 7.55 (br s, 1, NH), δ 6.9-6.6 (m, 5, aromatic), δ 2.22 (s, 3, NHC$\underline{CH_3}$); uv max (95% EtOH) 247 sh (ε 37,000), 264 (ε 69,600), 327 sh (ε 2600), 346 (ε 4770) and 365 nm (ε 7160); mass spectrum (70 eV) m/e 234 (parent).

(Note: purification was also accomplished by chromatography (alumina/chloroform-acetone) of a filtered chloroform solution of the crude material.)

Anal. Calcd. for $C_{15}H_{10}N_2O$: C, 76.90; H, 4.31. Found: C, 76.60; H, 4.42.

3-Acetamidobiphenylene-2-carboxylic Acid (41)

A suspension of 0.37 g (1.57 a 10^{-3} mol) of 2-acetamido-3-cyanobiphenylene 40 in 50 ml of concentrated hydrochloric acid was heated to 85° for 1 1/2 hr. After cooling, the yellow solid was filtered, washed well with water and dried.

The 0.36 g (87%) of 41 as a yellow solid showed one spot on TLC and was used in subsequent reactions.

Recrystallization from 95% ethanol yielded analytically pure 41 as yellow needles: mp 240-241°; ir (Nujol) 3700 (weak, NH), 1675 and 1660 (C = O), and 1520 cm^{-1} (NH bend, Amide II); nmr (CF_3CO_2H/TMS) δ 7.4-6.7 (m, aromatic + NH), δ 2.96 (s, $-NH\overset{O}{\overset{\|}{C}}\underline{CH_3}$), δ 2.42 (s, CH_3 in a decomposition product); nmr (D_2O/DSS/NaOH) δ 7.42 (s), δ 7.02 (s) and δ 7.0-6.5 (m) [total 7, aromatic + NH], δ 2.07 (s, 3, $NH\overset{O}{\overset{\|}{C}}\underline{CH_3}$), uv max (95% EtOH) 263 sh (ε 54,400), 268 (ε 62,500), 330 sh (ε 3070), 346 (ε 6130) and 365 nm (ε 8050); mass spectrum (70 eV) m/e 253 (parent), 235 ($P-H_2O$).

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.13; H, 4.39. Found: C, 71.09; H, 4.38.

<u>3-Aminobiphenylene-2-carboxylic Acid (25)</u>

A solution of 0.612 g (2.41×10^{-1} mol) of 3-acetamidobiphenylene-2-carboxylic acid 41 in a mixture of 25 ml of 20% aqueous sodium hydroxide and 25 ml of 95% ethanol was refluxed for 3 hr, cooled, and water was added.

The reaction was neutralized with dilute hydrochloric acid to pH slightly below 7 and allowed to stand for several hours.

The precipitate was collected, washed with water, and dried yielding 0.480 g (94%) of 25 as a bright yellow solid which showed one spot on TLC and was used in subsequent reactions.

Sublimation yielded analytically pure 25 as a yellow solid: mp 193° (dec); ir (Nujol) 3475 (NH), 3340 (sharp, NH), 1675, 1660, 1640 (C = O) and 1225 cm^{-1} (C-O); nmr (D_2O/DSS/NaOH) δ 7.03 (s, 1, aromatic), δ 6.80 (sp. s, 4, aromatic), δ 6.35 (s, 1, aromatic); nmr (acetone-d_6/TMS) δ 7.19 (s), δ 6.93 (m), δ 6.49 (s) 3.45 (br s); nmr (trifluoroacetic acid/TMS) δ 8.0-6.0 (m); uv max (95% EtOH) 259 (ε 38,400), 266 (ε 50,700), 328 (ε 4230), 345 (ε 8450) and 363 nm (ε 13,700); mass spectrum (70 eV) m/e 211 (parent), 193 (P-H_2O).

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.91; H, 4.30. Found: C, 73.86; H, 4.25.

3-Biphenylenediazonium-2-carboxylate (57)

For use in the aryne dimerization and crossing reactions, the inner salt 57 was prepared following Friedman's method.[22]

To a cooled solution of 0.106 g (5.0×10^{-4} mol) of 3-aminobiphenylene-2-carboxylic acid 25 in 15 ml of tetrahydrofuran was added a trace of trichloroacetic acid as catalyst. Then 0.1 g (8.5×10^{-4} mol) of isoamyl nitrite dissolved in 2 ml tetrahydrofuran was added dropwise over a period of 1 min.

The mixture immediately turned dark green and was removed from the cooling bath after 10 min. It was stirred for 3 hr during which time a light precipitate formed and the green solution color gave way to brown or reddish brown.

The mixture was then cooled in an ice bath and filtered with precautions not to allow drying of the filter cake. The solid was washed with tetrahydrofuran then with the solvent to be used in generation of the bipheneylene 24.

(Note: the benzenediazonium-2-carboxylate 15 used for crossing experiments was generated by Friedman's method.[22])

Generation and Attempted Reactions of 2,3-Dehydrobiphenylene (Biphenylyne **24**)

In the dimerization and crossing experiments the aryne **24** was generated by adding a suspension of the 3-biphenylene-diazonium-2-carboxylate **57** (or **57** + benzene-diazonium-2-carboxylate **15**) in the chosen solvent to a beaker of the same solvent at reflux. Heating was continued for 10-20 min, depending on solvent.

For a run such as that described above (p. 62) the inner salt **57** was suspended in 10 ml of solvent and added to 25 ml of the refluxing solvent.

Attempted Dimerization of Biphenylyne **24** in 1,2-Dichloroethane

As described above (pp. 62-63) biphenylyne **24** was generated *in situ* by diazotization of 0.211 g (1.0×10^{-3} mol) of 3-aminobiphenylene-2-carboxylic acid **25** to yield the inner salt **57**.

The salt was filtered (with precautions taken to avoid aspirating to dryness), suspended in 20 ml of 1,2-dichloroethane and added to 30 ml of gently refluxing 1,2-dichloroethane. The mixture was refluxed for 10 min then cooled to room temperature and the solvent allowed to evaporate under a hood.

The dark residue was chromatographed on a column of neutral alumina. The first fraction (pentane elution) was rechromatographed on a Brinkman Silica Gel F-254 thick layer plate, eluting twice with pentane.

The first and major band yielded 16.2 mg (8.7%) of 2-chlorobiphenylene **58** as an off-white solid: mp 69-70 (lit[30] 67.5-68.5); mass spectrum (70 eV) m/e 188, 186 (parent), 151 (P-Cl). The fourth fraction eluted from the column (methylene chloride) was also rechromatographed on a thick layer plate, and yielded 2.8 mg (1.6%) of coumarin **60** as a bright yellow solid: mp *ca.* 300° (dec); ir ($CHCl_3$) 1715 cm^{-1}; uv max (ether) (not quantitative) 245, 250, 259, 269, 280, 292, 368, 383, 430 and 456 nm; mass spectrum (70 eV) m/e 368 (impurity), 344 (parent).

Attempted Dimerization of Biphenylene **24** in Benzene

As described above (pp. 62-63) biphenylyne **24** was generated *in situ* by diazotization of 0.211 g (1.0 x 10^{-3} mol) of 3-aminobiphenylene-2-carboxylic acid **25** to yield the inner salt **57**.

The salt was filtered (with precautions taken to avoid aspirating to dryness), suspended in 20 ml of dry benzene and added to 30 ml of a gently refluxing solution of dry benzene. The mixture was refluxed for 15 min, then cooled to room temperature and the solvent allowed to evaporate under a hood.

The dark residue was chromatographed on a column of neutral alumina, eluting with benzene. The first fraction was rechromatographed on a Brinkman Silica Gel F-254 thick layer plate, eluting with benzene/pentane.

The first and major band yielded 3.0 mg (1.3%) of biphenylenobarrelene **69** as a light yellow solid: mp 156-158°, nmr ($CDCl_3$) δ 7.2-6.3 (m, 10, aromatic + olefinic), δ 5.0-4.7 (m, 2, bridgehead); mass spectrum (70 eV) m/e 228 (parent), 202 ($P-C_2H_2$).

<u>1,2,3,4-Tetraphenylbenzo[b]biphenylene (Adduct **72**)</u>

To a refluxing solution of 0.154 g (4.0×10^{-4} mol) of tetraphenylcyclopentadienone **71** in 20 ml of 1,2-dimethoxyethane were added simultaneously over a period of 30 min solutions of 0.158 g (7.5×10^{-4} mol) of 3-aminobiphenylene-2-carboxylic acid **25** in 20 ml of 1,2-dimethoxyethane and 0.15 g (1.3×10^{-3} mol) of isoamyl nitrite in 5 ml of 1,2-dimethoxyethane. The reaction was then stirred at reflux for 45 min.

After cooling, the solvent was evaporated and the residue chromatographed on neutral alumina, eluting with pentane. The first reaction yielded 0.038 g (10%) of **72** as a white solid.

Recrystallization from cyclohexane yielded **72** as white needles: mp 316-317.5°; ir ($CHCl_3$) 1600, 1490, 1435, 1410 and 1150 cm^{-1} (resembles biphenylene spectrum); nmr ($CDCl_3$) δ 7.15 (s, 10, phenyls on C-1 and C-4) δ 6.80 (s) and δ 6.76 (s) [16, phenyls on C-2 and C-3 plus biphenylene hydrogens]; uv max (cyclohexane) 251 (ε 27,500), 274 (ε 50,700), 282 (ε 66,700), 296 (ε 42,800), 309 (ε 55,100), 341 (ε 7250), 353 (ε 5070), 373 (ε 6520) and 394 nm (ε 6520); mass spectrum (70 eV) m/e 506 (parent).

Anal. Calcd. for $C_{40}H_{26}$: C, 94.82; H, 5.18.
Found: C, 94.69; H, 5.14.

Attempted Crossed Coupling of Biphenylyne **24** with Benzyne **12**

A portion of 3-biphenylenediazonium-2-carboxylate **57** was prepared as described on p. 62 by diazotization of 0.317 g (1.5×10^{-3} mol) of the amino acid precursor **25**.

A portion of benzenediazonium-2-carboxylate **15** was prepared using Friedman's method[22] by diazotization of 0.55 g (4.0×10^{-3} mol) of anthranilic acid **14**.

After filtration of both inner salts, they were both suspended the same 20 ml portion of 1,2-dichloroethane and this suspension was added to 30 ml of gently refluxing 1,2-dichloroethane, the mixture was refluxed for 15 min, cooled and the solvent evaporated under a hood.

Chromatography of the dark residue on neutral alumina (benzene elution) yielded a fraction which was rechromatographed on a Brinkman Silica Gel-254 thick layer plate, eluting twice with benzene/pentane.

The initial, major band yielded 81 mg (*ca.* 25%) of biphenylene contaminated slightly by 2-chlorobiphenylene (as noted in the mass spectrum): mp 68-110° (lit[22] 109-112°); mass spectrum (70 eV) m/e 188, 186 (2-chlorobiphenylene, parent), 152 (biphenylene, parent), 151 (P-Cl in 2-chloro-biphenylene).

A later bright yellow band yielded a yellow solid which showed an ir carbonyl absorption at 1725 cm^{-1} and only aromatic nmr resonances, but was impure. The solid was rechromatographed on a thick layer plate yielding 16 mg (*ca.* 4%) of a yellow solid speculated to be impure phenyl ester 74: mp 138-155°; mass spectrum (70 eV) high molecular weight impurities, major peak at m/e 272 (parent), 179 (P-O-), 151 (P-C(=O)-O-).

2,7-Dibromo-10,11-biphenyleno-9,12-diazabicyclo[6.4.0]-4,8,10,12-dodecatetraene (Quinoxaline 79)

A mixture of 0.188 g (1.03×10^{-3} mol) of 2,3-diaminobiphenylene 75[40] and 0.296 g (1.0×10^{-3} mol) of 3,8-dibromo-5-cycloöctene-1,2-dione 78 in 20 ml of glacial acetic acid was stirred at room temperature for 36 hours.

The mixture was then poured onto water and the precipitate collected, dried, and chromatographed over neutral alumina, eluting with chloroform.

The first fraction collected yielded 0.218 g (50%) of 79 as a yellow solid.

Recrystallization from benzene/cyclohexane yielded analytically pure 79 as light yellow needles: mp > 300° (dec at 250°); ir ($CHCl_3$) 1405, 1150 and 1100 cm^{-1} (resembles biphenylene spectrum); nmr ($CDCl_3$) δ 7.16 (m, 6, aromatic), δ 5.81 (t, 2, J=10Hz, -C<u>H</u>Br-), δ 5.55 (t, 2, J=4Hz, olefinic), δ 3.20 (m, 4, allylic); uv max (cyclohexane) 254 sh (ε 49,400), 262 sh (ε 55,700), 268 (ε 63,300), 290 (ε 20,300), 297 (ε 20,300), 302 (ε 23,400), 340 (ε 3800), 358 (ε 10,800), 377 (ε 27,800), 389 (ε 16,500) and 400 nm (ε 44,900); mass spectrum (70 eV) m/e 444, 442, 440 (parent), 362, 360 (P-Br), 281 (P-2Br).

Anal. Calcd. for $C_{20}H_{14}N_2Br_2$: C, 54.32; H, 3.20. Found: C, 54.41; H, 3.15.

(Note: the diaminobiphenylene is prepared by reduction of pure 2-amino-3-nitrobiphenylene and is used immediately as isolated. Further purification leads to decomposition of the diamine.)

7,8-Benzo-3,4-biphenyleno-2,5-diazabicyclo[4.2.0]-1,3,5,7-octatetraene (Quinoxaline **80**).

A solution of 0.087 g (4.77×10^{-4} mol) of freshly prepared 2,3-diaminobiphenylene **75**[40] and 0.066 g (5.0×10^{-4} mol) of benzocyclobutadienequinone **81** in 5 ml of methanol catalyzed by 2 drops of glacial acetic acid was stirred at room temperature for 12 hr.

The mixture was then poured onto water, and the precipitate filtered, dried, and chromatographed on neutral alumina, eluting with chloroform. The first fraction eluted yielded 0.054g (41%) of **80** as an orange solid.

This was recrystallized from benzene to yield analytically pure **80** as orange needles: mp 339° (dec), ir (Nujol) 1310, and 1090 cm^{-1} (resembles biphenylene spectrum); nmr ($CDCl_3$) δ 7.30 (s), δ 6.93 (s), integration is exactly equal, but δ 7.30 contains $CHCl_3$ from solvent; nmr ($CDCl_3$ + Eu(DPM)$_3$) δ 7.30 (s, 4, phenyl), δ 7.06 (s, 2, biphenylene, substituted ring), δ 6.93 (s, 4, biphenylene, unsubstituted ring), uv max (cyclohexane) 268 sh (ε 47,700), 275 (ε 58,000), 287 (ε 46,500), 337 (ε 7600), 397 (ε 12,200), 415 (ε 29,000), 432 (ε 25,600) and 445 nm (ε 50,600); mass spectrum (70 eV) m/e 278 (parent).

Anal. Calcd. for $C_{20}H_{10}N_2$: C, 86.30; H, 3.63. Found: C, 86.20; H, 3.57.

(Note: the diaminobiphenylene is prepared by reduction of pure 2-amino-3-nitrobiphenylene and is used immediately as isolated. Further purification leads to decomposition of the diamine.)

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48. Sample courtesy of Dr. Thomas Kowar.

APPENDIX

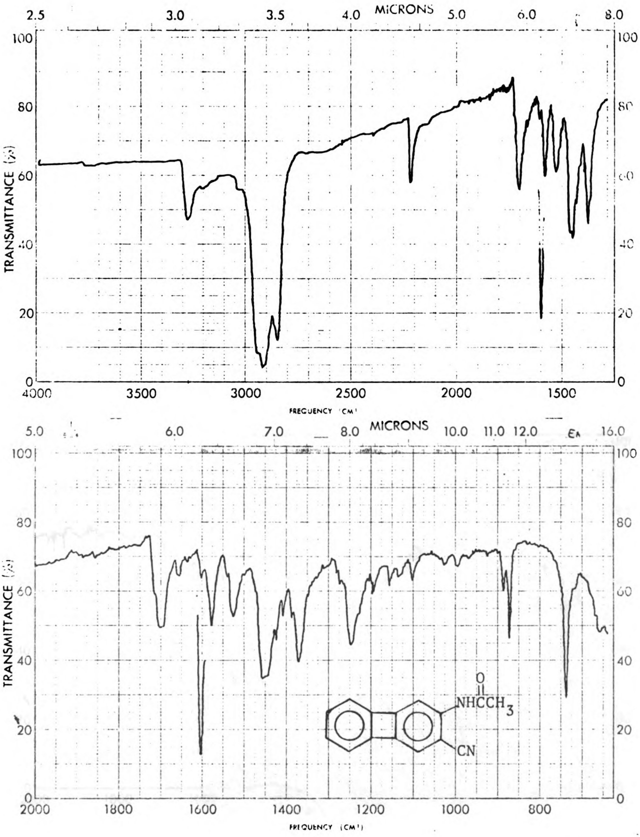

Figure 1. Infrared spectrum of 2-acetamido-3-cyanobiphenylene **40** (Nujol).

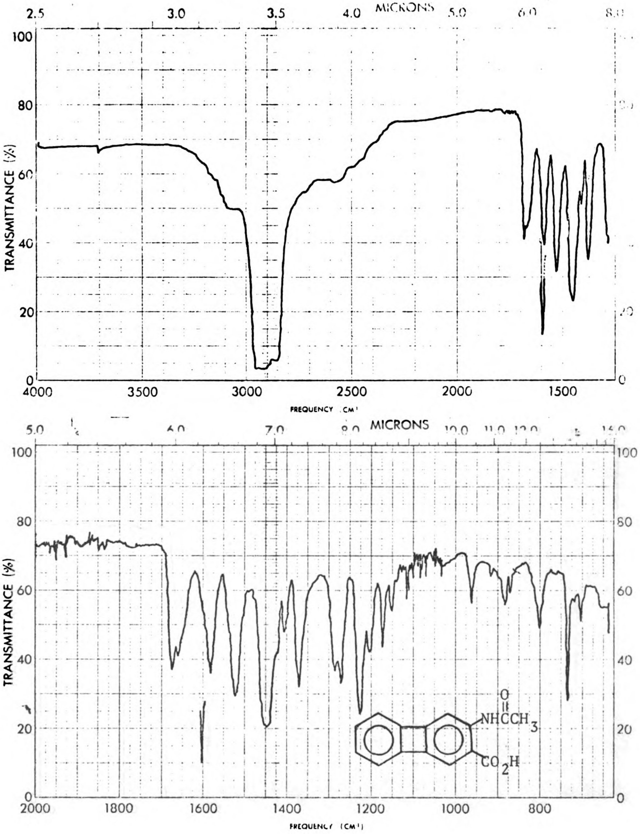

Figure 2. Infrared spectrum of 3-acetamidobiphenylene-2-carboxylic acid 41 (Nujol).

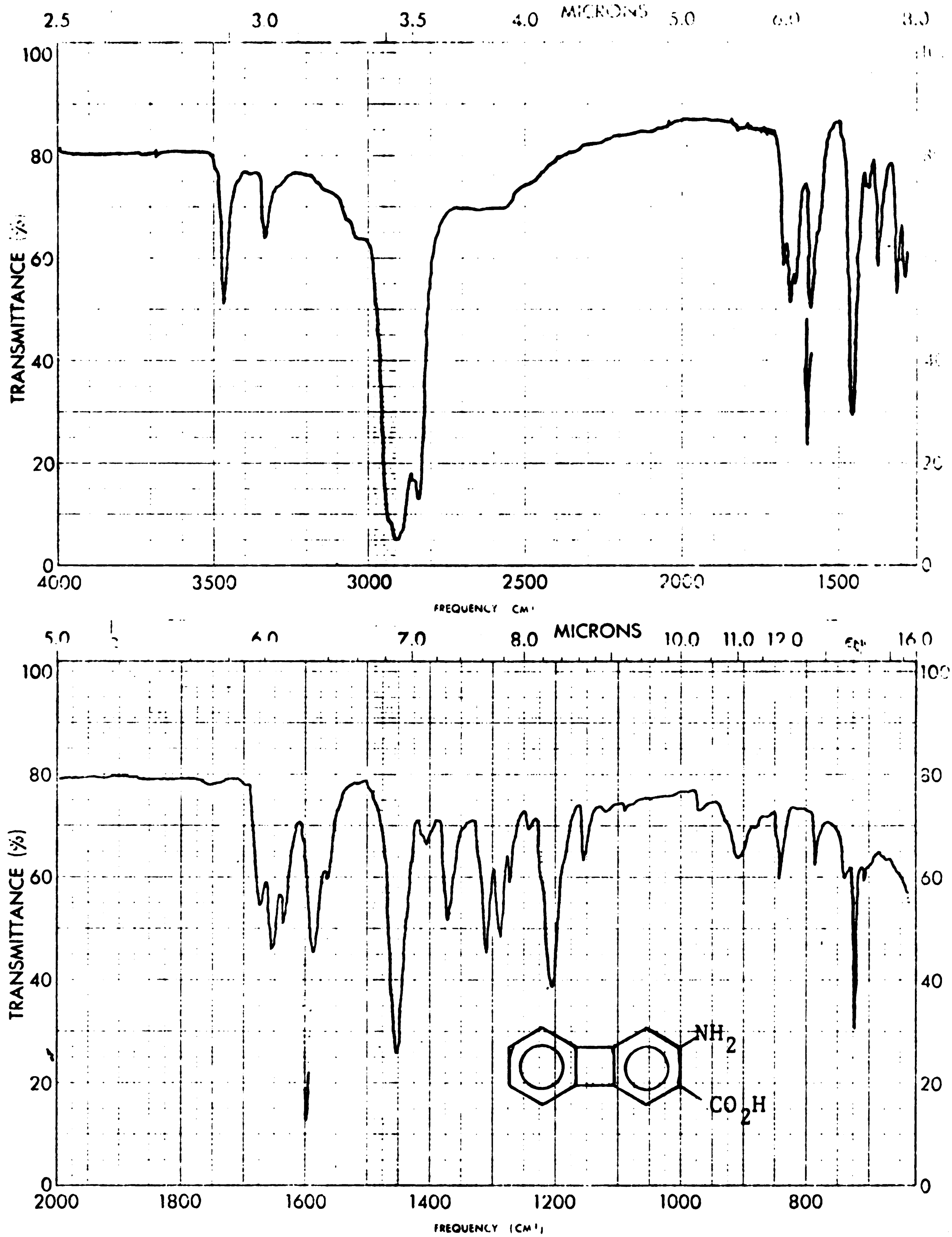

Figure 3. Infrared spectrum of 3-aminobiphenylene-2-carboxylic acid 25 (Nujol)

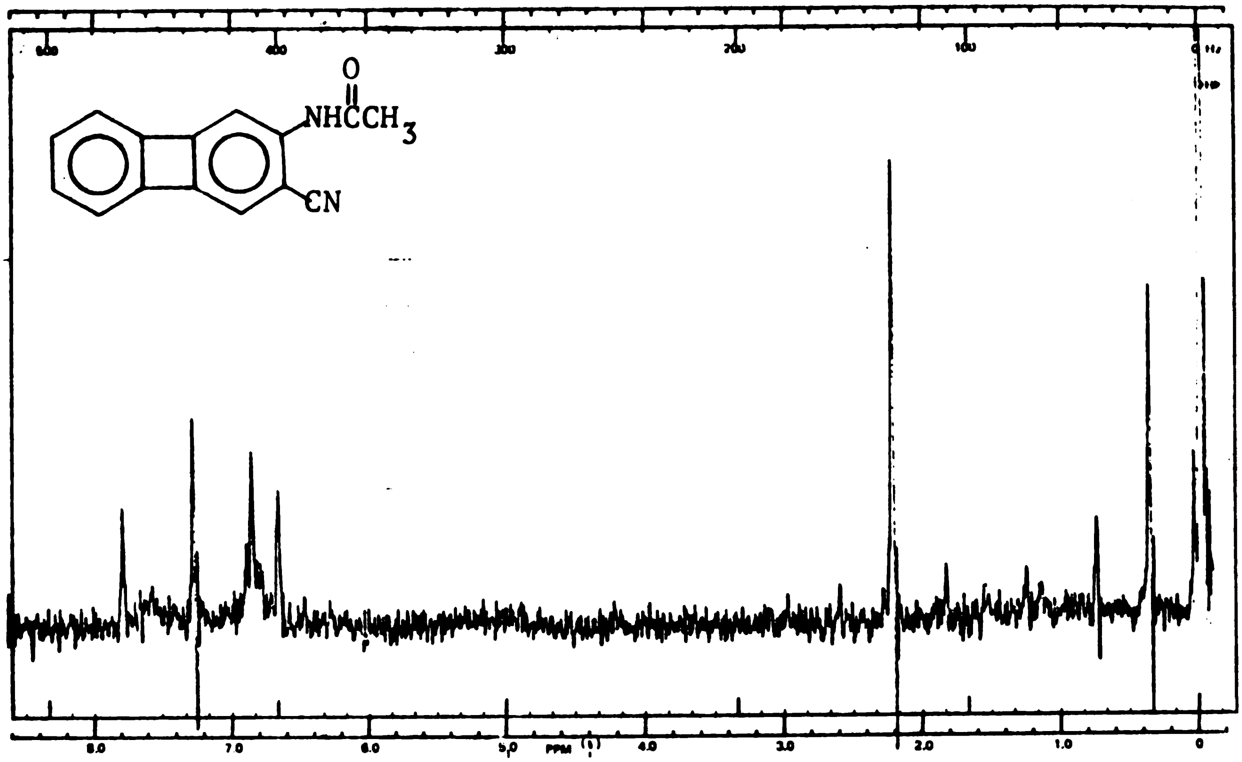

Figure 4. Nmr spectrum of 2-acetamido-3-cyanobiphenylene 40 ($CDCl_3$).

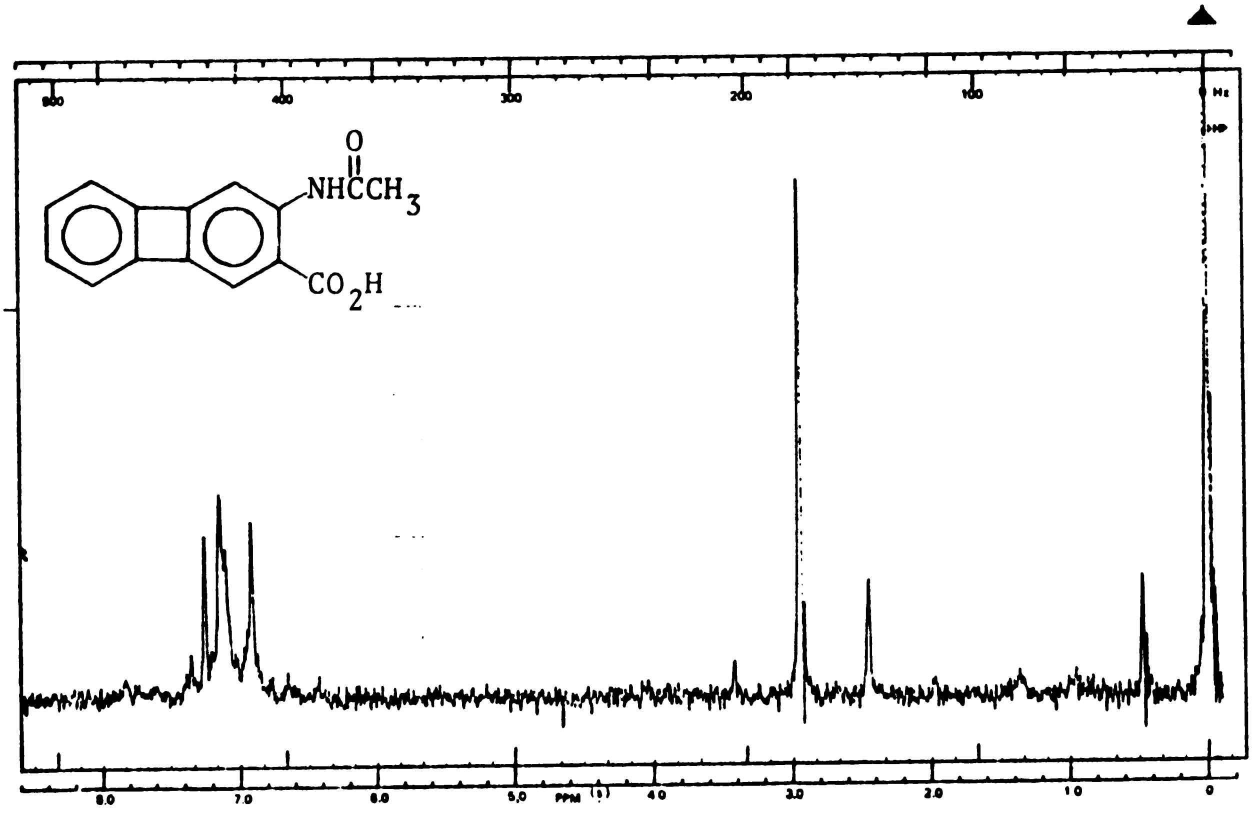

Figure 5. Nmr spectrum of 3-acetamidobiphenylene-2-carboxylic acid 41 (CF_3CO_2H/TMS).

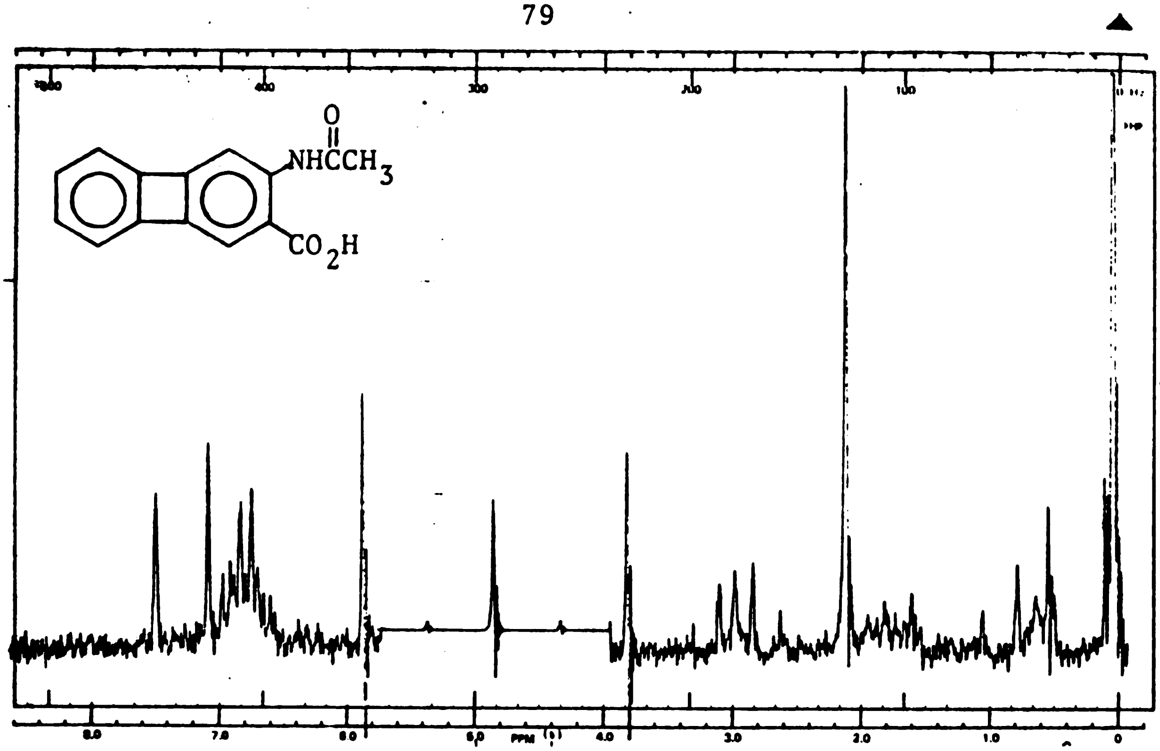

Figure 6. Nmr spectrum of 3-acetamidobiphenylene-2-carboxylic acid 41 (D_2O/DSS/NaOH).

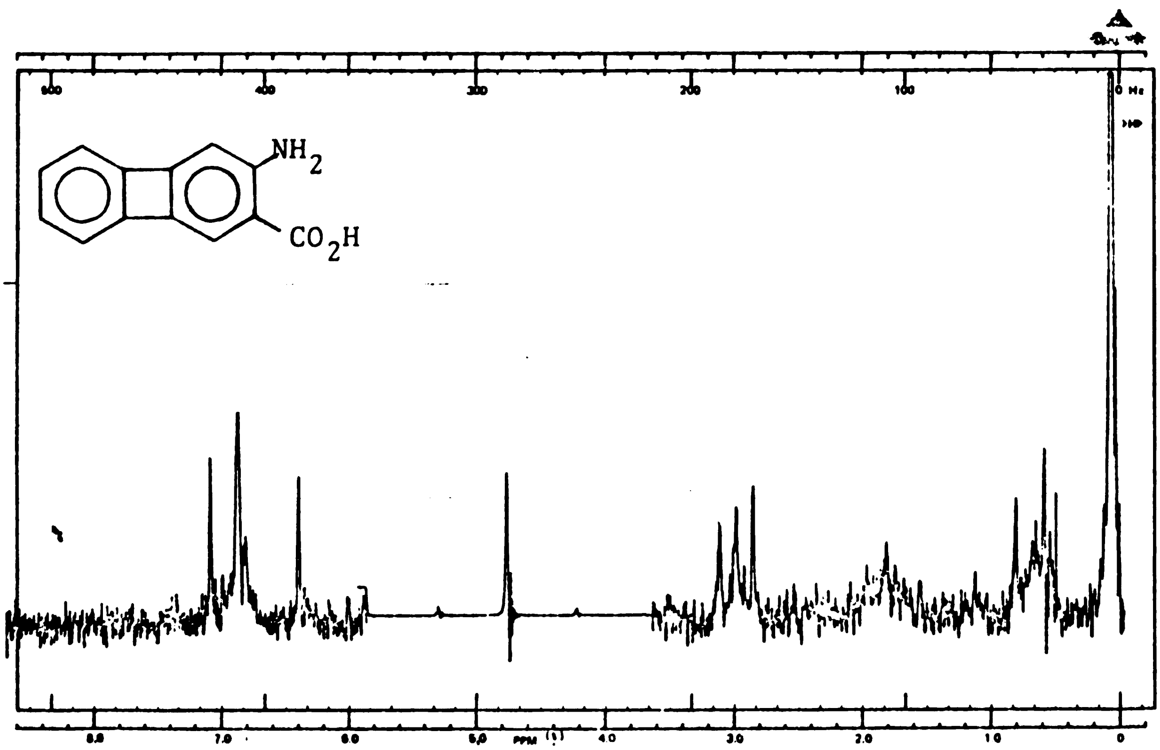

Figure 7. Nmr spectrum of 3-aminobiphenylene-2-carboxylic acid 25 (D_2O/DSS/NaOH).

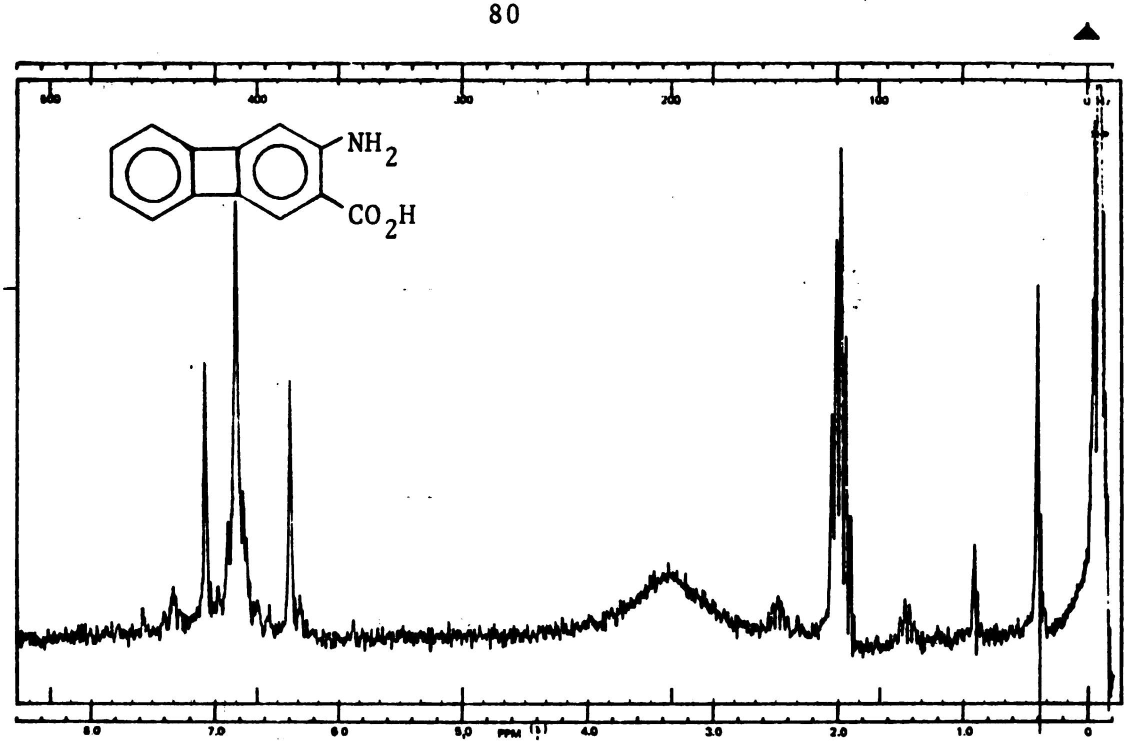

Figure 8. Nmr spectrum of 3-aminobiphenylene-2-carboxylic acid 25 (acetone-d_6/TMS).

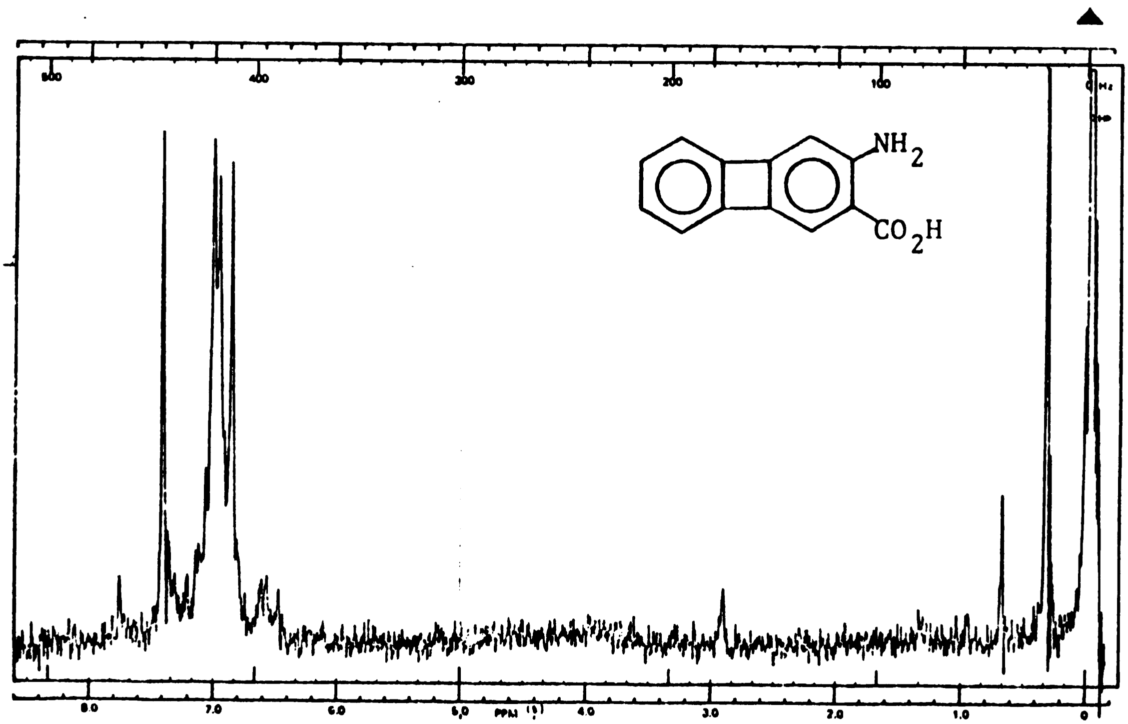

Figure 9. Nmr spectrum of 3-aminobiphenylene-2-carboxylic acid 25 (CF_3CO_2H/TMS).

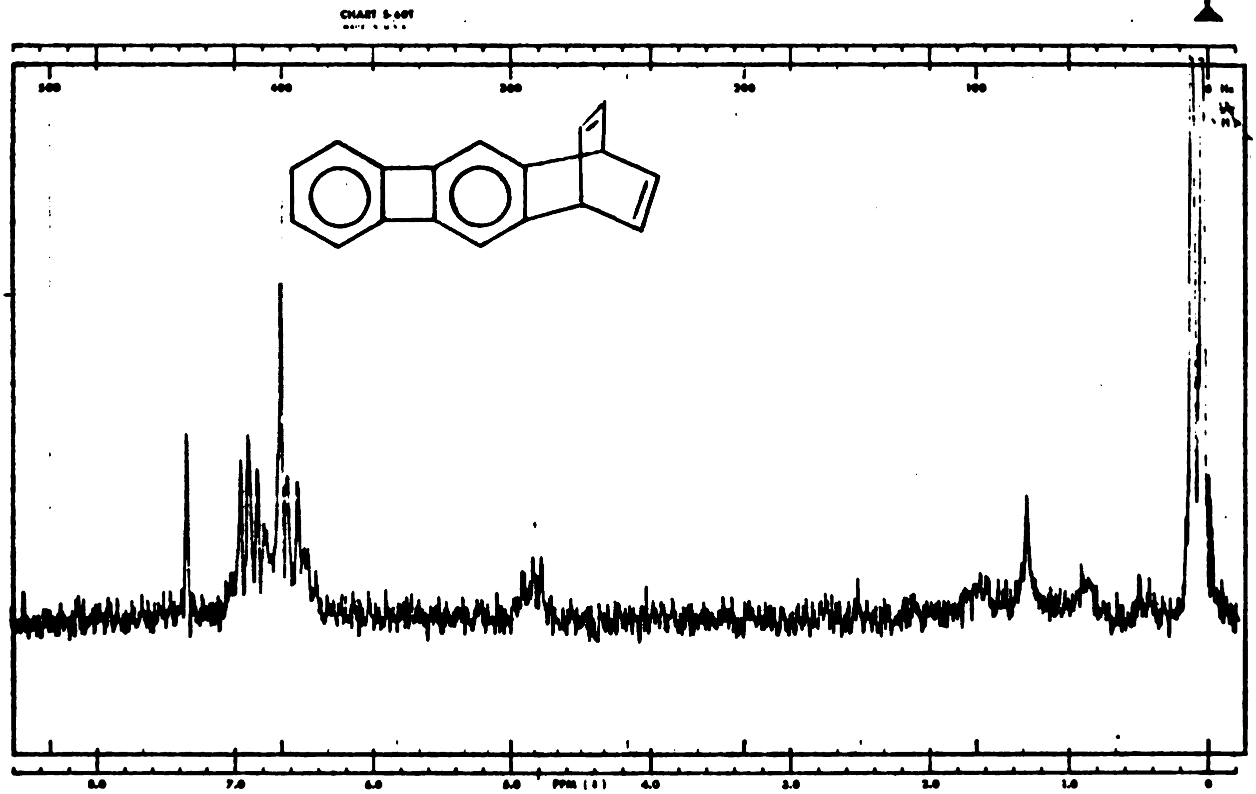

Figure 10. Nmr spectrum biphenylenobicyclo-[2.2.2]octatriene (69) ($CDCl_3$).

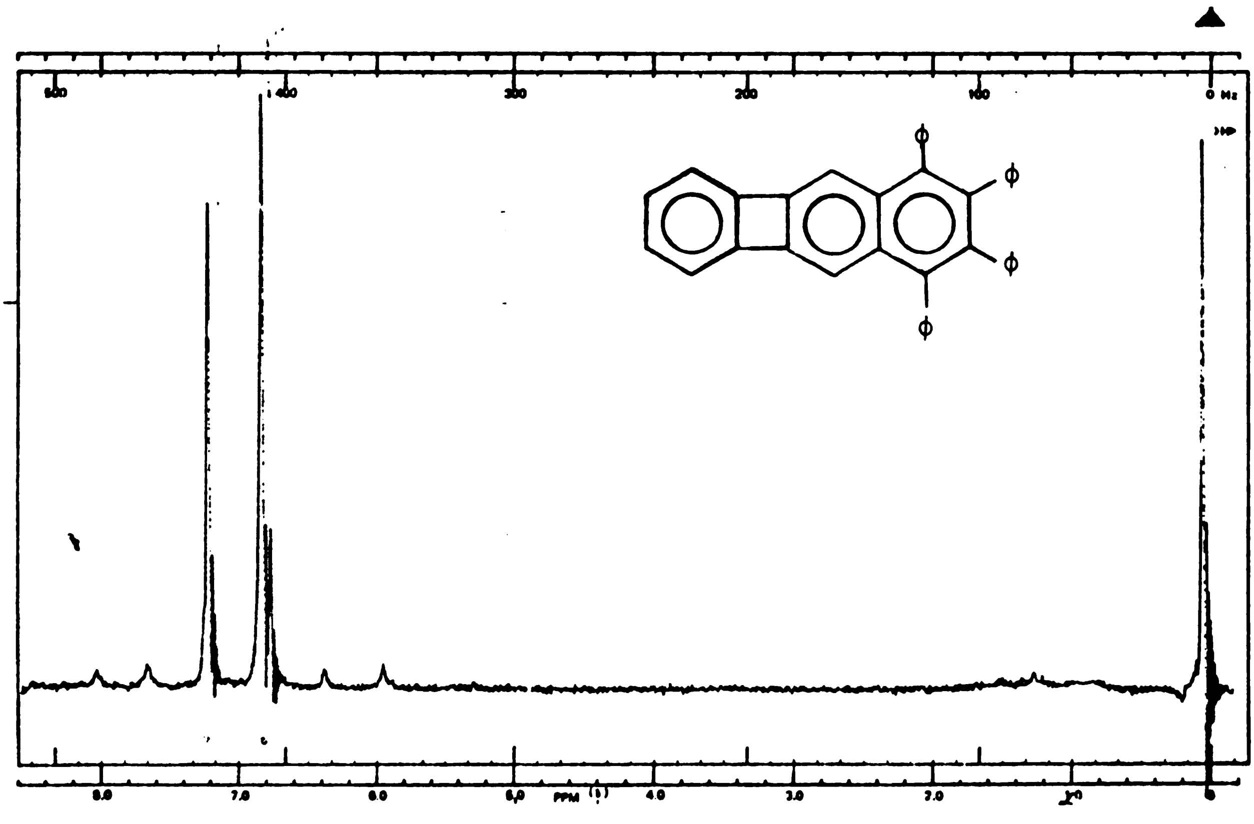

Figure 11. Nmr spectrum of 1,2,3,4-tetraphenylbenzo[b]biphenylene 72 ($CDCl_3$).

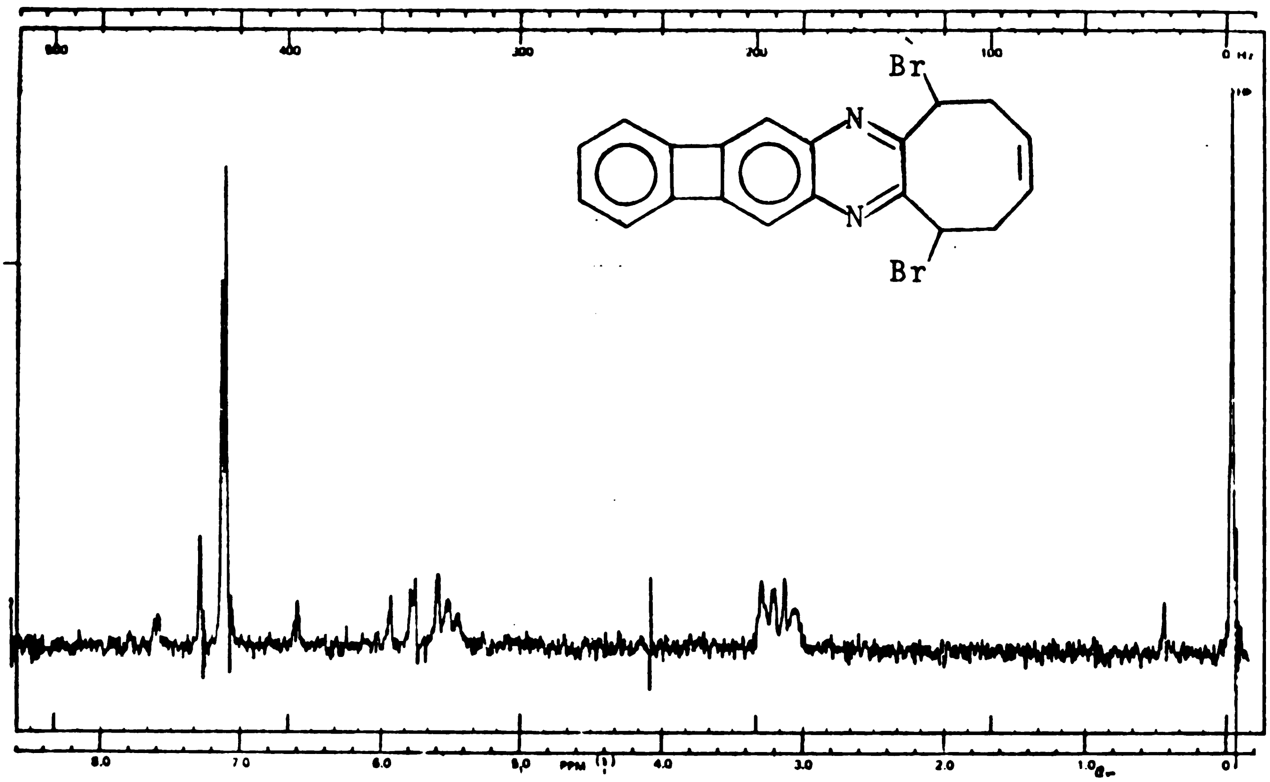

Figure 12. Nmr spectrum of 2,7-dibromo-10,11-biphenyleno-9,12-diazabicyclo[6.4.0]-4,8,10,12-dodecatetraene 79 ($CDCl_3$).

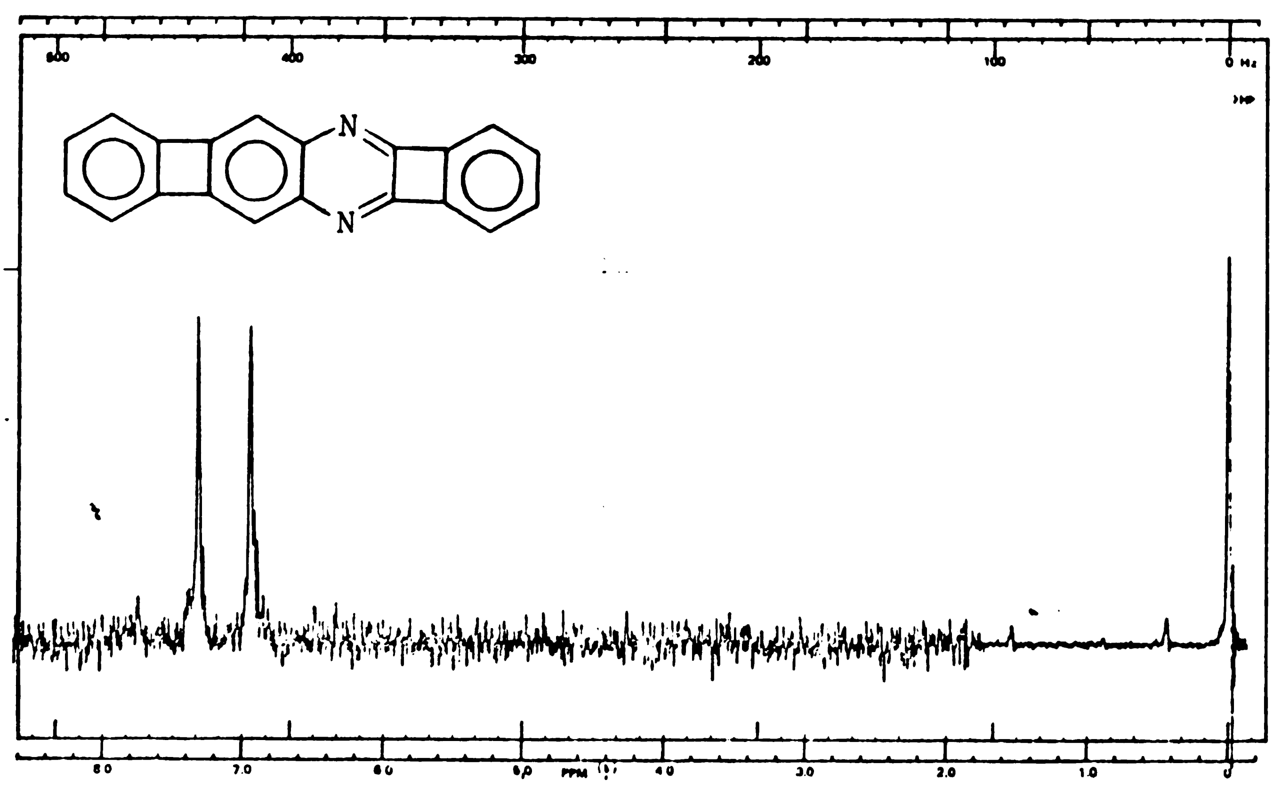

Figure 13. Nmr spectrum of 7,8-benzo-3,4-biphenyleno-2,5-diazabicyclo[4.2.0]-1,3,5,7-octatetraene 80 ($CDCl_3$).

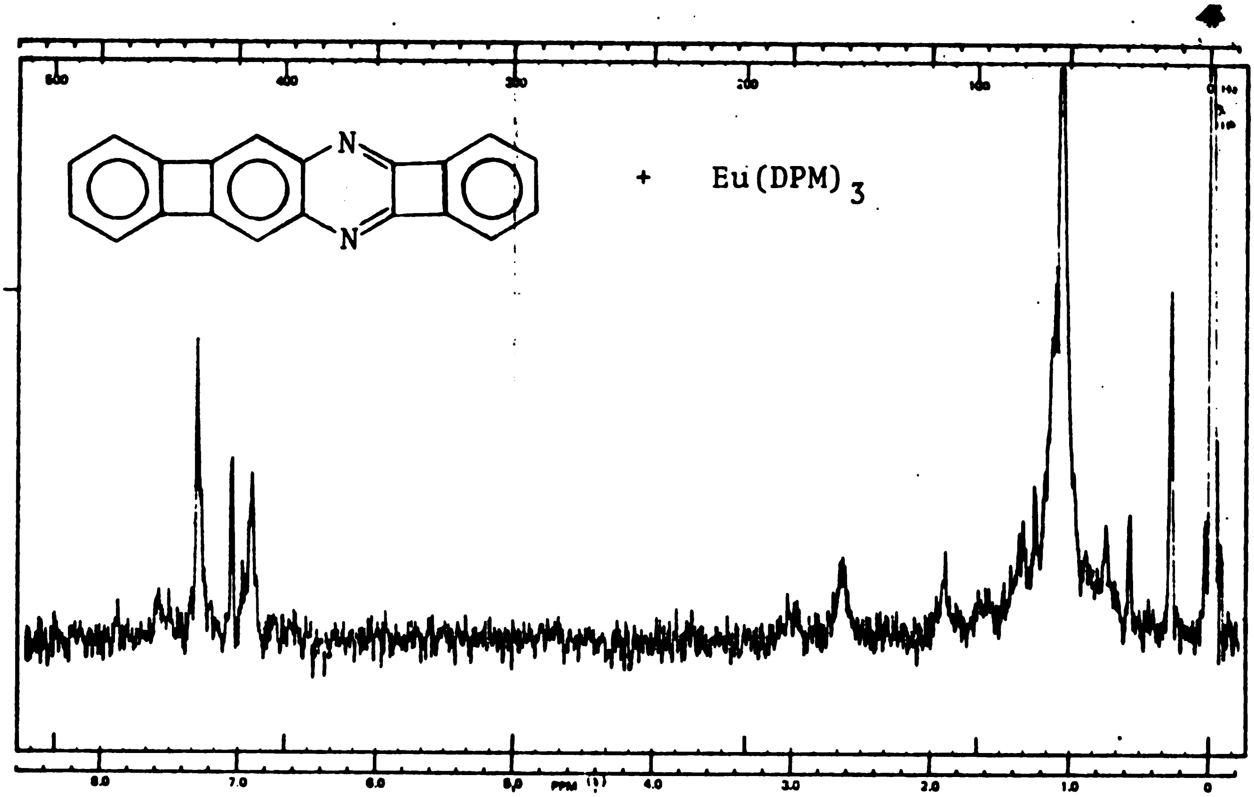

Figure 14. Nmr spectrum of 7,8-benzo-3,4-biphenyleno-2,5-diazobicyclo[4.2.0]-1,3,5,7-octatetraene 80 + Eu (DPM)$_3$ ($CDCl_3$).

Table 2. Mass Spectrum of 2-Acetamido-3-cyanobiphenylene 40

m/e	Rel. Intensity
236	0.4
235	2.5
234	14.1
194	1.1
193	15.3
192	100.0
191	4.7
166	1.3
165	6.8
164	18.1
163	2.2
140	1.1
139	2.2
138	6.5
137	3.4
114	1.4
113	1.4
112	1.1
111	1.1
88	2.2
87	2.5
86	1.6
76	1.1
75	1.4
74	1.6
63	3.4
62	1.6
51	1.1
50	1.4
43	15.8

Table 3. Mass Spectrum of 3-Acetamidobiphenylene-2-carboxylic Acid 41

m/e	Rel. Intensity	m/e	Rel. Intensity
255	100.0	114	2.4
254	5.1	113	2.4
253	29.6	112	2.4
		111	2.4
236	11.5	110	2.4
235	68.8		
220	4.0	99	2.4
		98	3.2
212	5.5	90	2.8
211	34.0	89	3.6
209	3.2	88	5.5
		87	4.0
194	11.5		
193	68.8	76	3.2
		75	5.1
167	7.5	74	5.1
166	6.3	63	6.3
165	31.2	62	4.3
164	32.2		
151	3.6	57	2.8
150	17.0	55	2.8
		51	2.4
140	3.2	50	3.2
139	15.8	44	4.0
138	19.8	43	24.1
137	7.5		

Table 4. Mass Spectrum of 3-Aminobiphenylene-2-carboxylic Acid 25

m/e	Rel. Intensity	m/e	Rel. Intensity
212	1.2	76	3.2
211	5.2	75	3.2
193	6.4	74	3.2
		73	3.2
168	13.6	71	2.4
167	100.0	70.5	4.0
166	16.9	70	3.2
165	4.0	69.5	5.2
164	4.0	69	4.0
		63	3.6
150	3.6		
149	2.4	57	4.8
148	3.6	56	2.4
141	2.8	55	3.2
140	10.8	51	2.4
139	27.7	50	2.4
138	3.6	44	2.8
		43	4.0
126	2.4	41	4.8
120	3.2	39	3.6
89	2.4		
88	4.0		
87	3.2		
84	2.4		
83.5	12.9		
83	2.4		
82.5	4.0		

Table 5. Mass Spectrum of 1,2,3,4-Tetraphenylbenzo[b]biphenylene **22**

m/e	Rel. Intensity	m/e	Rel. Intensity
508	9.9	238	4.6
507	44.3	237.5	4.6
506	100	237	6.9
505	4.6	236	4.6
		231.5	4.6
430	3.8	231	6.1
429	10.7	230.5	6.9
428	11.5	229.5	3.8
427	10.7	225	3.8
426	10.7	224.5	3.8
425	5.3	224	6.1
424	6.1		
		214	8.4
414	3.8	213.5	6.9
413	6.9	213	9.9
400	4.6	212.5	6.1
		212	9.2
352	8.4	211	4.6
351	6.1		
350	7.6	207	4.6
		206.5	9.9
242.5	3.8	206	6.1
243	4.6	203.5	6.9
243.5	4.6	200	5.3
244	3.8	199	4.6
245	3.8		
		131	7.6
		119	7.6
		84	5.3
		77	3.8
		69	79.4

Table 6. Mass Spectrum of 2,7-Dibromo-10,11-biphenyleno-9,12-diazabicyclo[6.4.0]-4,8,10,12-dodecatetraene 79

m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity
445	1.7	228	3.3	115	2.9
444	3.8	227	4.2	114	4.2
443	2.1	227	2.9	113.5	3.3
442	7.1			113	3.3
441	1.3	214	2.5	112	2.5
440	3.8	202	2.5	111	2.5
363	2.5	188	2.5	104	8.3
362	5.0	178	2.9	103	6.3
361	3.3	177	3.3	102	4.2
360	5.0	176	7.5	101	5.0
		175	5.4	100	5.8
284	4.2	164	4.2	99	4.2
283	20.4			98	3.3
282	71.3	153	2.5	91	3.3
281	100.0	152	4.2	89	3.3
280	29.2	151	7.5	88	4.2
279	23.8	150	13.3	87	4.6
278	2.9	149	5.4	82	24.2
		146	3.8	81	10.0
269	2.5	141.5	3.3	80	23.3
268	7.1	141	14.2	79	10.0
267	19.2	140.5	17.9	78	5.0
266	5.0	140	22.1	77	18.3
		139.5	10.8	76	8.3
256	6.7	139	5.0	75	8.3
255	29.2	135	2.5	74	6.3
254	40.4	134.5	5.0		
253	6.7	134	4.2	65	3.3
252	3.3			63	7.5
251	2.5	128	5.4	62	3.3
		127.5	10.0	58	2.5
243	2.5	126.5	3.3	57	2.5
242	7.9	126	7.9	56	2.5
241	7.1	125	3.3	54	2.5
240	3.3	124	2.5	53	5.0
		121	3.3	52	10.0
		120.5	2.9	51	5.8
		120	2.5		

Table 7. Mass Spectrum of 7,8-Benzo-3,4-biphenyleno-2,5-diazabicyclo[4.2.0]-1,3,5,7-octatetraene **80**

m/e	Rel. Intensity
281	1.0
280	7.7
279	60.6
278	75.0
277	6.3
276	4.3
251	4.3
250	3.4
249	3.4
203	3.4
202	3.4
179	3.6
178	6.7
152	4.3
151	57.0
150	100.0
149	19.0
148	2.9
139.5	11.1
139	48.8
138.5	7.0
128	6.7
126	6.7
125.5	16.6
125	7.7
124	11.1
123	8.4
122	5.0
112.5	4.8
111.5	3.4
111	10.3
110	5.3

m/e	Rel. Intensity
104	2.6
102	4.8
101	7.9
100	17.8
99	15.1
98	20.7
97	3.1
95	2.4
88	4.1
87	13.0
86	6.0
85	4.3
83	3.4
81	2.6
78	5.3
77	6.3
76	24.8
75	19.2
74	28.1
71	8.2
70	2.9
69	4.8
67	2.1
64	2.4
63	9.6
62	6.5
61	2.9
57	14.4
56	8.9
55	8.2