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STEREOCHEMISTRY OF STYRYLPYRIDINE PHOTODIMERS

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STEREOCHEMISTRY OF STYRYLPYRIDINE PHOTODIMERS

BY

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The author would like to dedicate this manuscript to his wife Joyce and to his mother and father for their love, encouragement and gentle persuasion.

Stephen E Burkle

TABLE OF CONTENTS

LIST OF TABLES

HISTORICAL

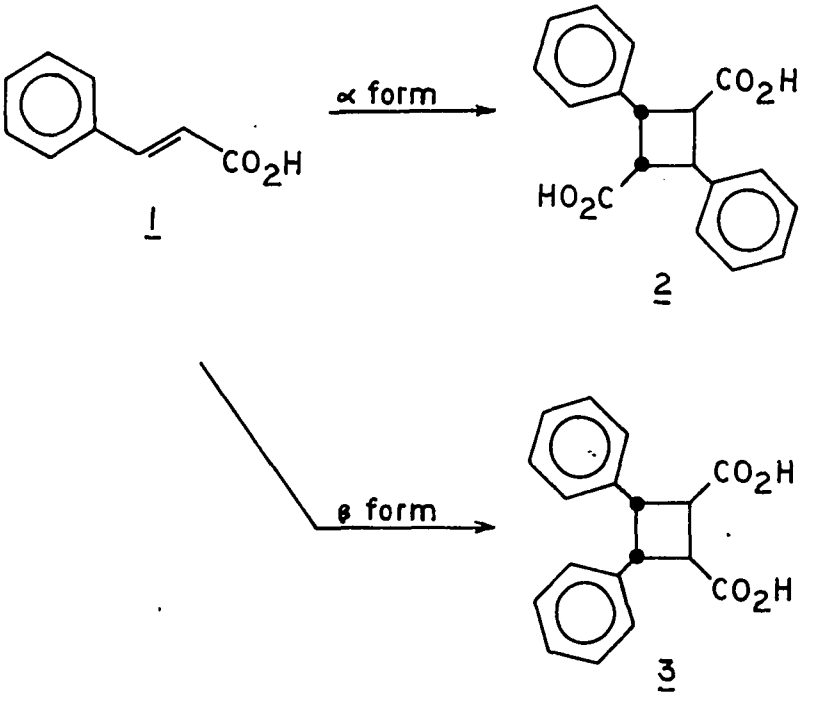
Considerable refinements in the area of photodimerization reactions have accumulated since Fritzsche[1] spent several months in 1867 precipitating dianthracene under sunlight from a benzene solution of anthracene. Yet, even after working for a short time in the field, one realizes that much definitive work remains to be done.

The information grouped under photodimerization reactions is extensive.[1-5] Even when one's attention is focused exclusively on dimerizations between carbon-carbon double bonds to form cyclobutane rings (2+2 cycloadditions), the theoretical possibilities are staggering. One must consider dimerization of the ethylenic group in both conjugated and non-conjugated systems both intermolecularly and intramolecularly.

The advent of mass-produced, photochemical reactors brought the practicing chemist in out of the sun. Now he could look at the mechanics of dimerization under more controlled conditions. Two obvious areas of investigation are the method of dimerization and the product structure. The former involves the energetics of the system and mechanistic pathways while the latter relates the structure of the monomer to that of the product.

A superficial view of these problems can be realized by reference to the familiar photodimerization of trans-cinnamic acid (1). Head-to-head and head-to-tail joining of two cinnamic acid units, assuming prior trans-cis isomerization, theoretically can generate eleven diastereomers. Experimentally only two isomers, α-truxillic

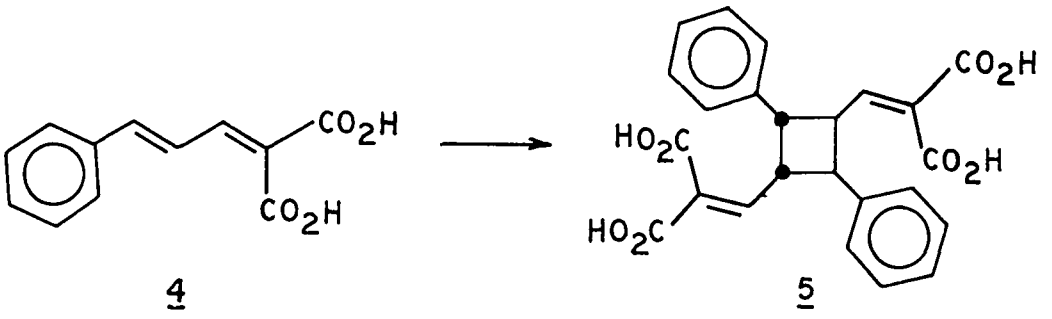
acid (2) and β-truxinic acid (3), were formed by irradiation of crystalline cinnamic acid. It was found that solid state dimerizations are directed by the orientation of the monomer in the crystal lattice, reaction occurring when adjacent double bonds lie within about four angstroms of each other. Thus a stable α form of 1 yields 2 while a metastable β form produces 3. Atypically, solution photolysis of 1 does not produce dimerization.



In the crystal lattice there tends to be a minimum of movement during reaction of trans monomers, reflected in dimer products which

retain a trans arrangement. Dimers of solid cis-cinnamic acids, however, also have a trans arrangement indicating an initial isomerization step.[6]

In solid state dimerizations it is often dangerous to make predictions of product structure even with closely related compounds. For example, in the dimerizations of dienic acids 4 and 6, products 5 and 7 arise.[7]



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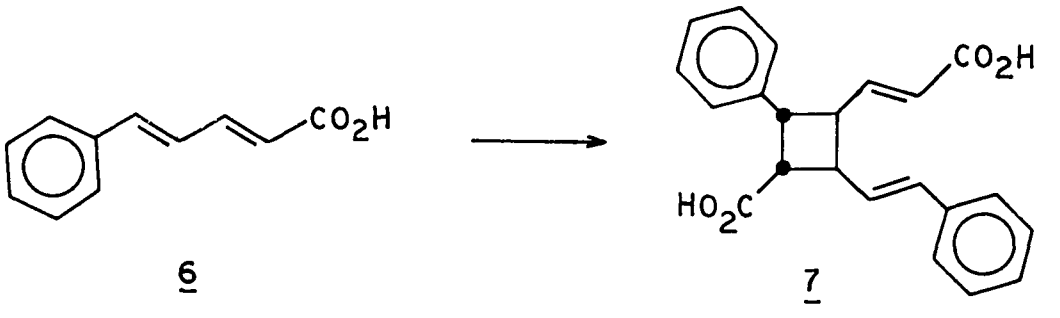
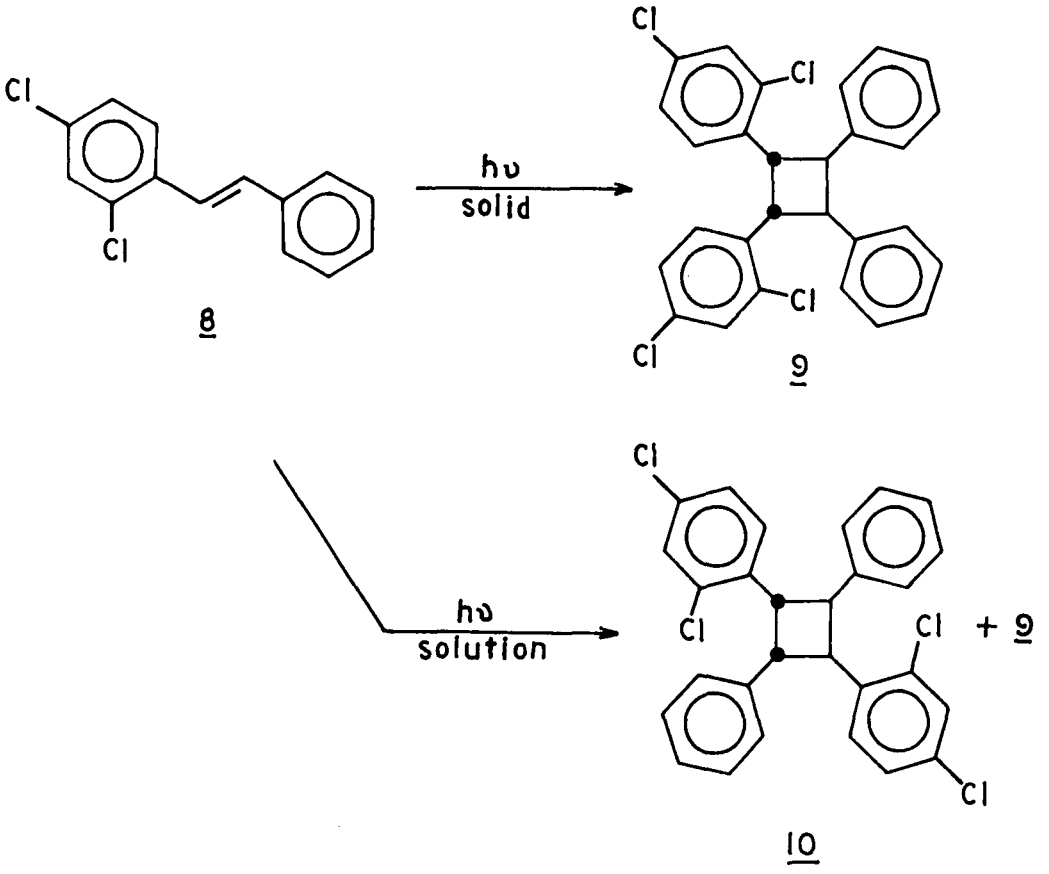


6 7

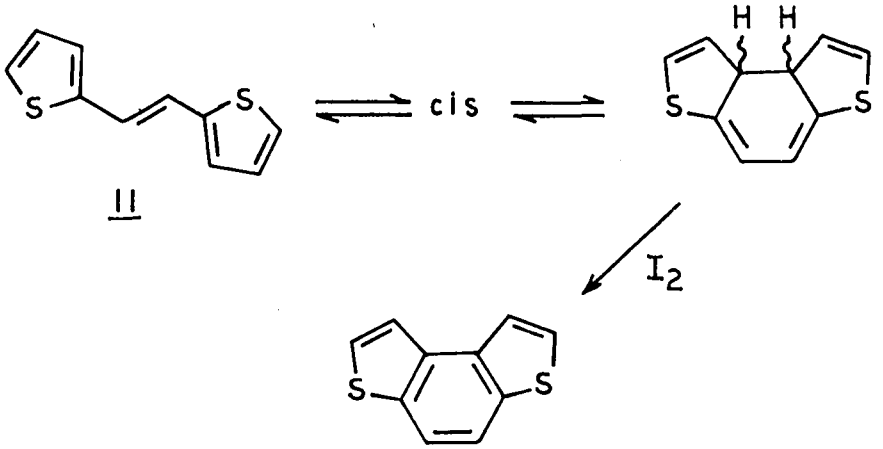
Dimerization of a compound in solution generally leads to a greater number of products than those formed from the solid state, yet the number is still remarkably low considering the isomer possibilities. For example, dimerization of the crystalline trans-stilbene (8) gave dimer 9, yet reaction of the same compound in solution gave only two dimers, 9 and 10 in about a 1:1 ratio.[8] The disadvantages of ultraviolet irradiation in creating a variety of pathways can be overcome by a careful selection of reaction conditions.



8 9 10

Two other major reactions of stilbene-like molecules to be considered in solution photochemistry are cis-trans isomerization[9] and cyclization.[10] Dimerization appears to occur only through the trans isomer. Thus although isomerization is a definite side reaction, it does not contribute to dimers containing the cis arrangement. The dimerization of stilbene is claimed to proceed only through the trans form because the cis molecule spends too little time in the first excited singlet state.[11]

Cyclization, being an intramolecular process, is aided by a dilute solution, while dimerization proceeds better in concentrated solution. Cyclization also requires an oxidizing medium to aromatize the dihydro intermediate. Usually iodine is employed. For example, a 90% yield of benzo (1,2-b:4,3-b') dithiophene (12) was realized from the irradiation of a dilute benzene solution of trans-1,2-di(2-thienyl) ethane (11).[12] Thus, cyclization can be effectively eliminated from competition with dimerization by a proper choice of reaction conditions.



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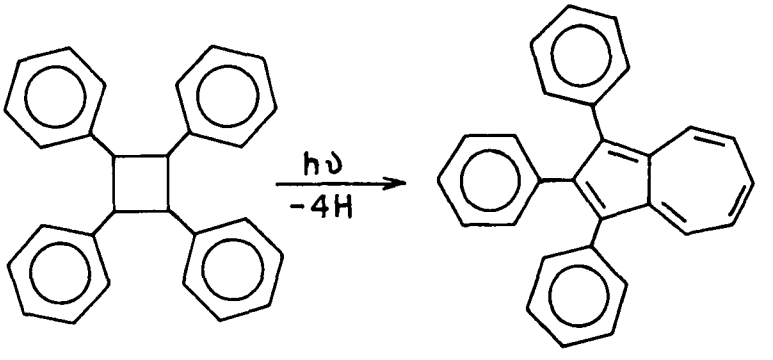
12

Aside from cis-trans isomerization, which can lead to cyclized products under oxidizing conditions, dimerization reactions produce at most small amounts of side products. A closer inspection of these products has uncovered some unusual rearrangements.

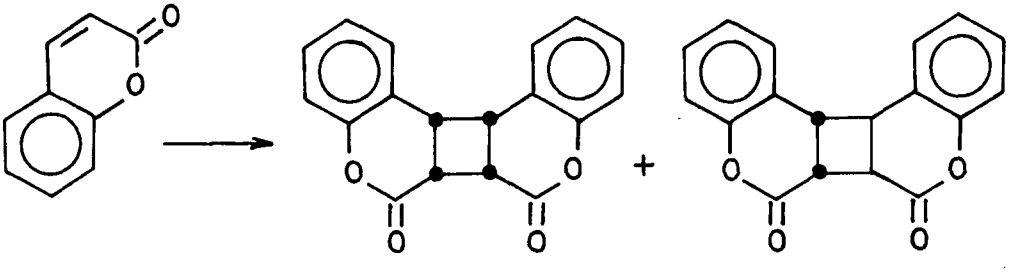
Very recently a stilbene dimer (13) was found to undergo further photoreaction in dilute cyclohexane solution to a triphenylazulene (14) in a 9.6% yield.[13]



13 14

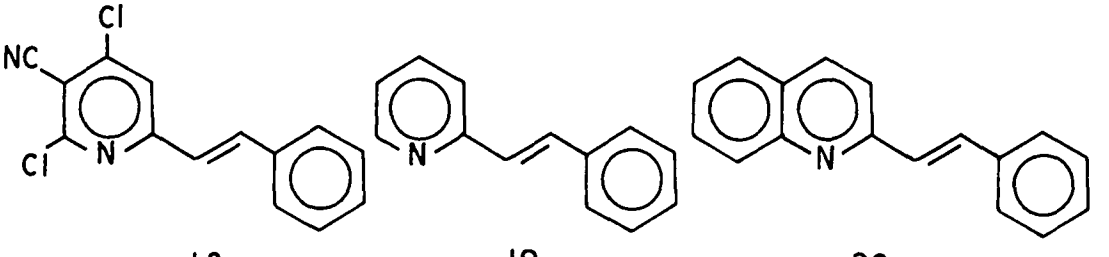
Recent studies indicate that the mechanics of dimerization in solution are complex and not well understood. For instance, the major products from the photodimerization of coumarin (15) are the syn and anti head-to-head dimers 16 and 17. Extensive investigation of this system has led to the following conclusions.[14] Formation of 16 proceeds through a singlet eximer (^{1}CC*) and is favored by high solvent polarity, while the anti dimer 17 is formed by reaction of a triplet monomer with a ground state molecule and is unusually favored in carbon

tetrachloride. The nature of these intermediates is still a matter of conjecture, however. Since many dimerizations are found to proceed in benzene, which cuts out high energy radiation, the energy required for reaction must be fairly low.



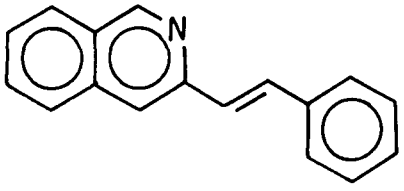
15 16 17

Historically, dimerization of compounds to cyclobutane derivatives containing hetero-aromatic groups dates back to 1927 when Koller reported that sunlight couples 2,4-dichloro-3-cyano-6-styrylpyridine (18).[15] Interestingly, attempts to dimerize 2-styrylpyridine (19) itself failed.[16]



18 19 20

Other compounds included here which were found to give dimers of yet unknown structure are 2-styrylquinoline (20)[16], 3-styrylisoquinoline (21)[17], and a series of N-methyl-4(vinylaryl)quinolinium chlorides (22).[18] A number of aryl acrylic acids ($ArCH{=}CHCO_2H$) were found to photodimerize in the solid state to give dimers of structure 24.[19] This series is represented by reaction of 2-(3-pyridyl)acrylic acid (23). In contrast, 1-2'-furyl-2-nitroethylene (25) produced an unstable compound which was thought to have a head-to-tail arrangement 26.[19]



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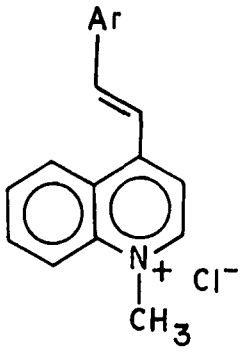

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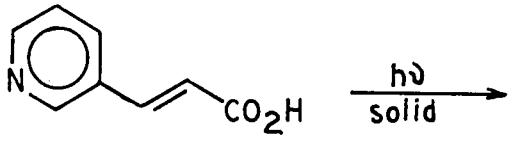

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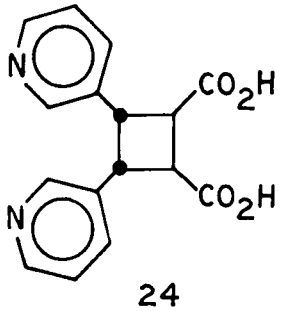

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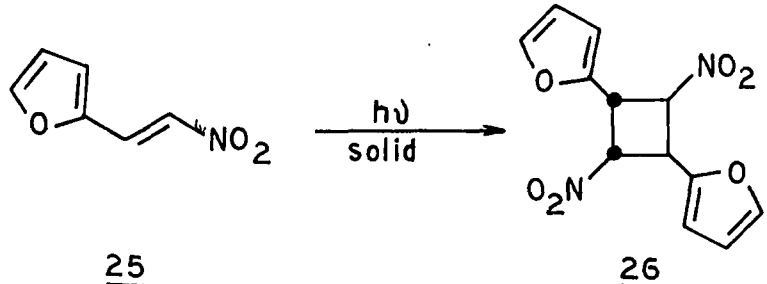
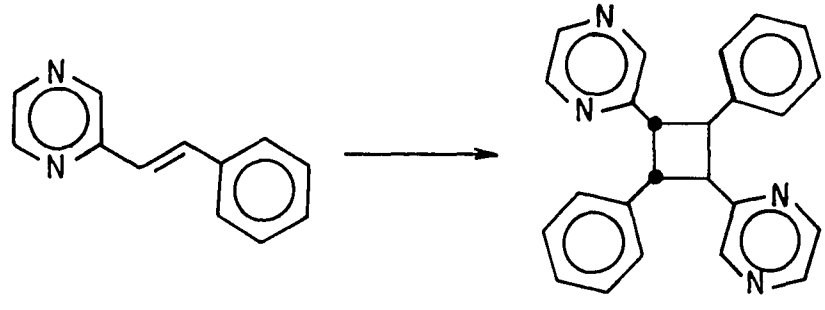


25 26

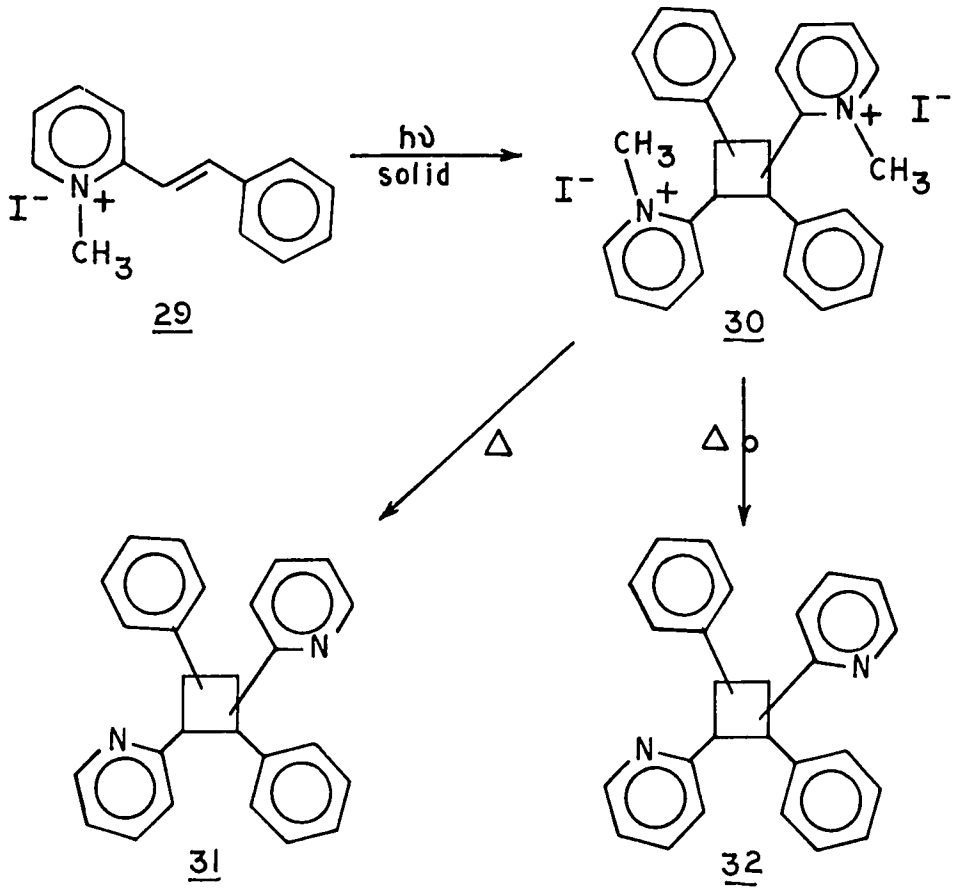
Very recently a dimer of 2-styryl-1,4-diazine (27) was produced as a by-product of a cyclization reaction, and was thought to possess the stereochemistry of 28.[20]

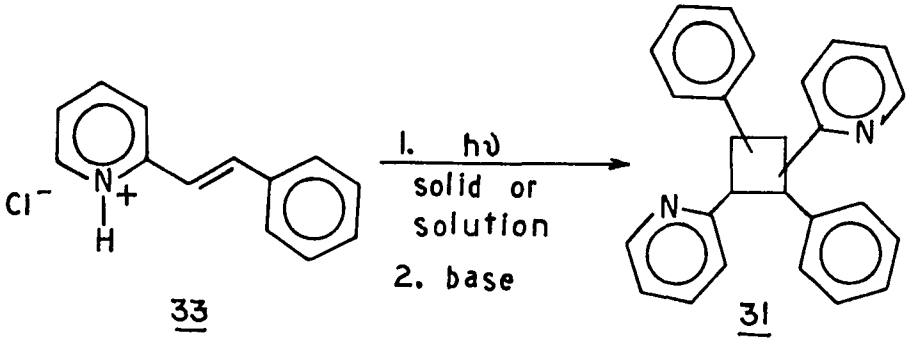


27 28

It is the work of Williams and co-workers[21,22], however, which directly affects this thesis. They discovered that salts of trans 2-styrylpyridine could be photodimerized as the solids and in solution. The methiodide 29 gave a single dimer 30 which upon vacuum pyrolysis gave two dimer bases. The higher melting isomer, 31, was found to be

the one formed initially while the lower melting compound, 32, was formed by isomerization during the pyrolysis step. The dimer 31 also could be formed by irradiation of the crystalline hydrochloride of 2-styrylpyridine (33). It was the purpose of this thesis to investigate the structure including the stereochemistry of Williams' products and to extend his work by including a number of photodimers of substituted 2- and 4-styrylpyridines.

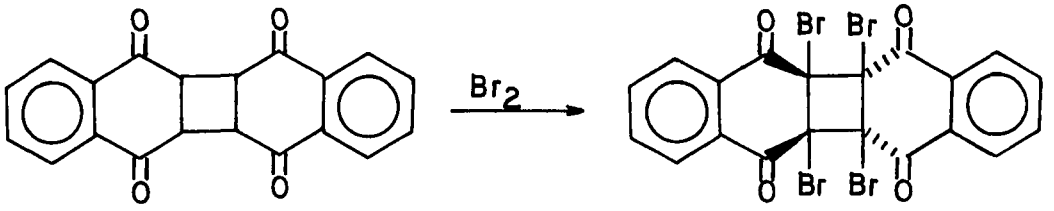




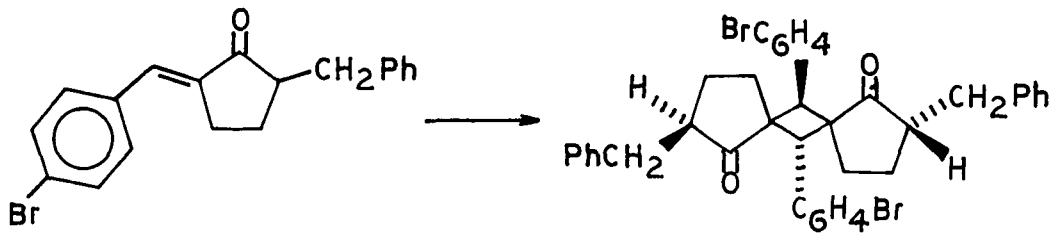
33 31

The question of dimer structure is an intriguing one and often difficult to resolve. Interpretation of nmr[23] mass spectral or X-ray data, or chemical conversion to dimers of known structure have provided the basis of structural assignments. Of these methods an X-ray study should give the most convincing answer to the spacial arrangement of a compound.

Recent X-ray analyses were made on the bromination product 35 of the 1,4-naphthoquinone dimer (34)[24] and on the photodimer (37) of trans-2-benzyl-5-p-bromo-benzylidene-cyclopentanone (36).[25] Compound 35 was confirmed to have the anti configuration. Dimer 37 was shown to be centrosymmetric.



34 35



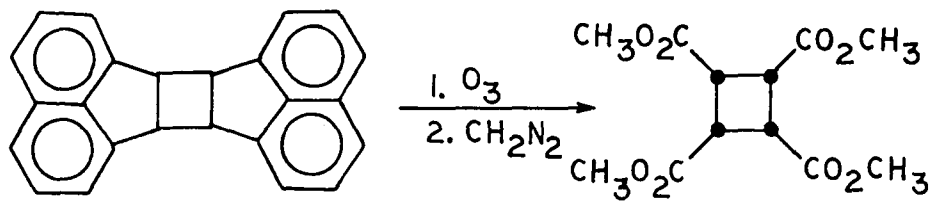
36 37

Unfortunately, a complete X-ray determination is still a laborious process and the capabilities are beyond the reach of most chemists.

Mass spectral data can be used to solve the question of head-to-head or head-to-tail arrangement. The fragmentation pattern of a head-to-head dimer can be expected to show three ions from cleavage of the cyclobutane ring, $(RCH{=}CHR)_2^{+}$, $(RCH{=}CHR')\cdot^{+}$, and $(R'CH{=}CHR')\cdot^{+}$, while only one of these ions $(RCH{=}CHR')\cdot^{+}$ can be found in the spectrum of a head-to-tail dimer. This method was used for the study of several substituted stilbene dimers.[8,26]

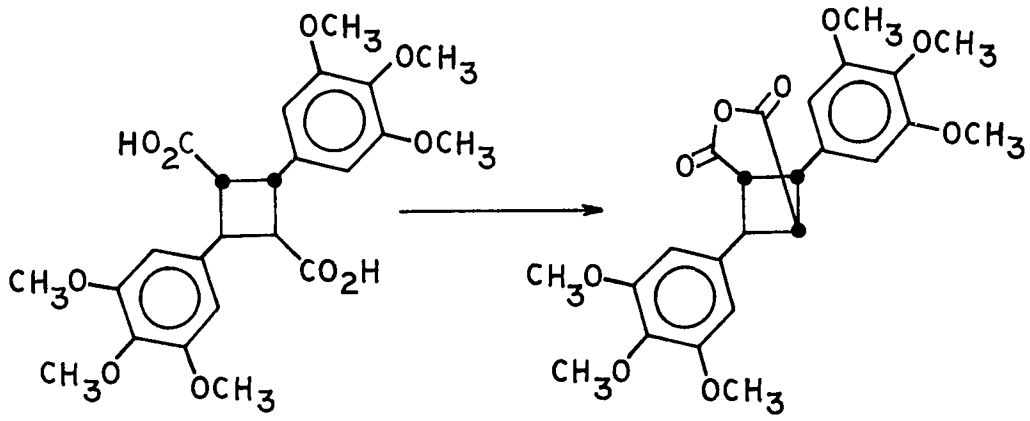
The nmr spectra of cyclobutane systems were reviewed in 1967.[27] Data of this kind can be helpful in structural determinations but does not lead to unequivocal answers. Lastly, a dipole moment study[28] has indicated the structures of some N,N-dimethyluracil dimers.

Chemical solutions to the problem of dimer structure most frequently take the route of interconversion to compounds of known structure. An aryl or ethylenic group can be degraded by ozonolysis to the carboxylic acid function without altering the stereochemistry of the cyclobutane ring. Thus, the lower melting dimer of acenaphthalene (38) was determined to have the cis configuration by conversion to the tetraester 39 in low yield.[29]



38 39

Reactions of this type are limited to those having a previously demonstrated effect on the stereochemistry of cyclobutane ring. Epimerization, for example, occurs in the α-truxillic acid series under certain conditions. The γ-truxillic anhydride (41) was formed on treatment of dimer 40 with acetic anhydride and p-toluenesulfonic acid.[30]



40 41

Chemical conversions are limited also by the relatively small number of known structures, such as the truxillic acids and the tetracarboxycyclobutanes, with which to compare an unknown.

This section is intended to provide an introduction to the facts and problems involved and should not be construed as a complete survey of the literature.

DISCUSSION

Preparation and Structure of Styrylpyridines

In general the styrylpyridines used for dimerization were produced either by the condensation of 2- or 4-picoline with various benzaldehydes in refluxing acetic anhydride or by the coupling of the corresponding picolinium methyl halide salt with a benzaldehyde in refluxing methanol. In the latter case, vacuum pyrolysis converted the styrylpyridinium salt to the free base. For an optimum yield, the method chosen depended upon the ring substituents.[31]

The styrylpyridinium compounds isolated have been shown to display a trans ring arrangement. This was evident in the infrared spectra of the newly prepared compounds where a strong absorption in the 950-1000 cm^{-1} region was noted.

Sheinkman and co-workers[32] identified 4-(α-methyl)styrylpyridine (48) as having trans rings. It seems likely that 4-(β-methyl)styryl-pyridine (49) must also possess this orientation.

Dimerization of Diarylethylenes

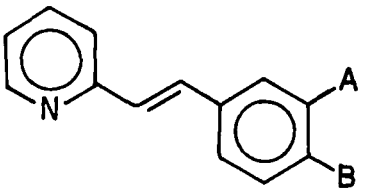
Various solid or dissolved trans aryl substituted ethylenes were irradiated using several power sources. It was found that dimerization could be effected by relatively long wavelength radiation. This was demonstrated by reaction in benzene, which absorbs below 2000 angstroms and by reaction using an ordinary incandescent light source.

The fact that dimerization indeed occurred was shown by the following observations: loss of the ethylenic absorption in the ultraviolet and infrared spectra, correct elemental analysis,

Table 1

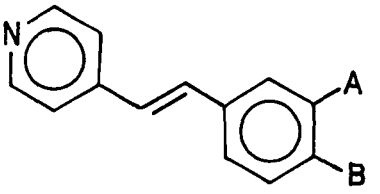
Diaryethylenes

No.	A	B
19	H	H
42	H	Cl



19, 42

No.	A	B
43	H	H
44	H	Br
45	H	Cl
46	OCH_3	$O\overset{O}{\overset{\|\|}{C}}CH_3$
47	$-OCH_2-$	



43 – 47

No.	X	Y	X'	Y'	R	R'
48	C	N	C	C	CH_3	H
49	C	N	C	C	H	CH_3
50	N	C	N	C	H	H
51	C	N	C	N	H	H

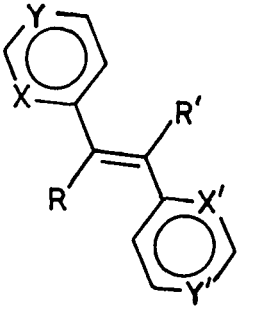


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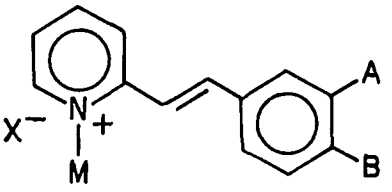
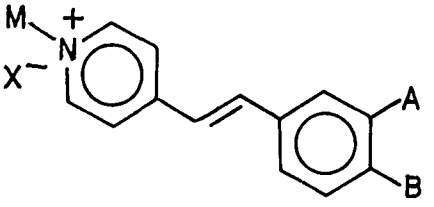
Table 2

Diarylethylene Salts



No.	A	B	M	X
29	H	H	CH_3	I
52	H	H	O	-
53	H	Br	CH_3	I
54	H	Cl	CH_3	I
55	H	Cl	H	Cl
56	$-OCH_2O-$		O	-



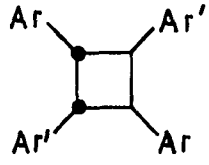
No.	A	B	M	X
57	H	H	CH_3	I
58	H	Br	CH_3	I
59	OCH_3	$OCCH_3$ (O above)	CH_3	I
60	OCH_3	OH	CH_3	Br
61	OCH_3	OH	CH_3	I

Table 3

Physical Properties of Dimers

Dimer	Ar	Ar'	mp.°C	Cyclobutane Protons* (τ)
(32)	2-Pyridyl,	Phenyl	114-115	4.7-6.1 (m., 4H)
(31)	2-Pyridyl,	Phenyl	192-193	5.20 (m., 4H)
(62)	2-Pyridyl,	p-BrC_6H_4	234-235	5.25 (m., 4H)
(63)	2-Pyridyl,	p-ClC_6H_4	212-213	5.22 (m., 4H)
(64)	2-Pyridyl,	2-Pyridyl	190-191	4.88 (s., 4H)
(65)	4-Pyridyl,	Phenyl	157-159	5.52 (s., 4H)
(66)	4-Pyridyl,	p-BrC_6H_4	223-225	5.97 (s., 4H)
(67)	4-Pyridyl,	p-ClC_6H_4	200-202	5.97 (s., 4H)
(68)	4-Pyridyl,	4-Pyridyl	234-236	5.52 (s., 4H)
(69)	4-Pyridyl-α-CH_3 ,	Phenyl	143-145	5.50 (s., 2H)
(70)	4-Pyridyl-β-CH_3 ,	Phenyl	211-213	5.48 (s., 2H)

*Measured in $DCCl_3$ relative to internal tetramethylsilane.



appearance of the appropriate parent peak in several of the mass spectra, and physical properties in accordance with those dimers described in the literature.

In the cases where dimerization did occur, conversion yields were excellent and the crude product mixtures were remarkably uncomplex. This latter observation is especially interesting when considering the number of products possible in solution photolysis.

Photo-inertness in solution probably resulted from factors more electronic than steric in nature. Photo-inertness in the solid state was attributed to an unfavorable arrangement in the crystal structure.

It is interesting to note that it has been reported that substitution of electron donating groups containing oxygen in the stilbene series enhanced dimerization[26] while this effect was reversed in the present study.

Dehalogenation of Styrylpyridine Dimers

Aromatic halogen atoms can be removed catalytically under mild conditions. This technique has been used several times on halogenated stilbene dimers to give the unsubstituted parent compounds with retention of configuration.[34]

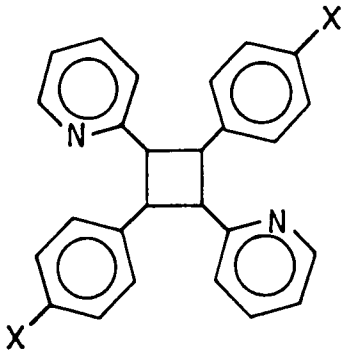
Debromination and dechlorination of four styrylpyridine dimers were accomplished in basic methanol with palladium on charcoal. The reaction went to completion under a slight positive hydrogen pressure. In each case no epimerization occurred. The dehalogenated products were shown by mixture melting points and infrared spectra to be identical with the analogous unsubstituted dimers (see Table 4).

Preliminary Stereochemical Conclusions

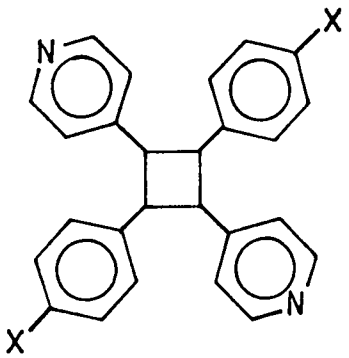
Cleavage of the cyclobutane rings of the unsubstituted dimers 31 and 65 in the mass spectrometer did not produce fragments of sufficient m/e difference to allow a distinction between head-to-head and head-to-tail arrangements. The mass spectra (figures 12 and 14) of the chlorinated dimers 63 and 67, however, indicated that they were head-to-tail. This assignment was based on the appearance of the 100% peak at 215 m/e, which is appropriate for the 4'-chlorostyryl-pyridine fragments. No indication in either spectrum of a 4,4'-dichloro-stilbene fragment at 249 m/e was found.

Further evidence of a head-to-tail arrangement in the 2-pyridyl dimer (31) was provided by heating the compound in a sealed tube. This treatment converted 31 into 2-styrylpyridine only.

The information obtained from the dehalogenations showed that dimers 31, 62, and 63 have identical stereochemistries. The same is true for dimers 65, 66, and 67. Thus, a partial structural assignment could be made for the six dimers.

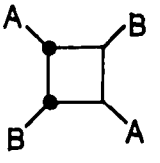


X= H 31
Br 62
Cl 63

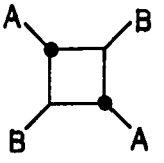


X= H 65
Br 66
Cl 67

From the evidence presented the six head-to-head isomers probably can be eliminated from the eleven possible disastereomers. The all cis isomer and the two cis-cis-trans isomers probably can be discarded by steric arguments, for these forms have not been found in similar stilbene dimerizations. The only remaining possibilities are the cis-trans-cis isomer 71 and the all trans isomer 72. Thus, the six dimers on page 20 should have the orientation of either 71 or 72. A cursory examination of the nmr spectra and other physical properties does not allow a distinction between these two forms.



71



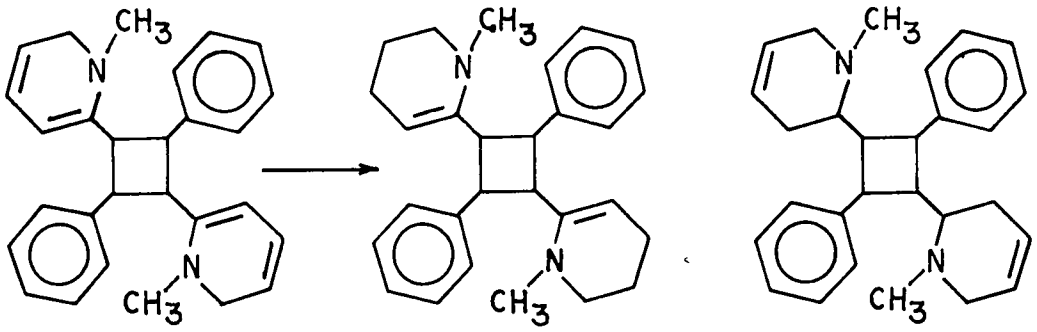
72

The mass spectra of the α and β-methyl dimers 69 and 70, indicated that they had head-to-tail orientations. For example, the mass spectrum of 70 (figure 15) has the 100% peak positioned at m/e 195 which is consistent for the β-methyl-4-styrylpyridine fragment, while an α,β-dimethylstilbene fragment at m/e 208 is absent.

Reduction of 2-Styrylpyridine Methiodide Dimer (30) with Sodium Borohydride

Treatment of 30 in aqueous methanol with sodium borohydride afforded a product which gave the correct analysis for a tetrahydropyridine. The expected product from the reduction of a 1-methyl 2-alkylpyridinium halide was the 1,2,3,6-tetrahydro derivative 75.[35] Since borohydride reductions are influenced by steric interactions[36], however, it was not too surprising to find that the nmr spectrum (figure 6) favored the 1,4,5,6-tetrahydro structure 74.

Initial attack by hydride ion at the 6-position would proceed normally but subsequent attack on the resulting dieneamine system 73 would be altered by the bulky cyclobutane ring.



73 74 75

The Attempted Degradation of Styrylpyridine Dimers

In order to determine the exact stereochemistry of the dimers, attempts were made to convert them to cyclobutanes of known configuration.

Oxidation

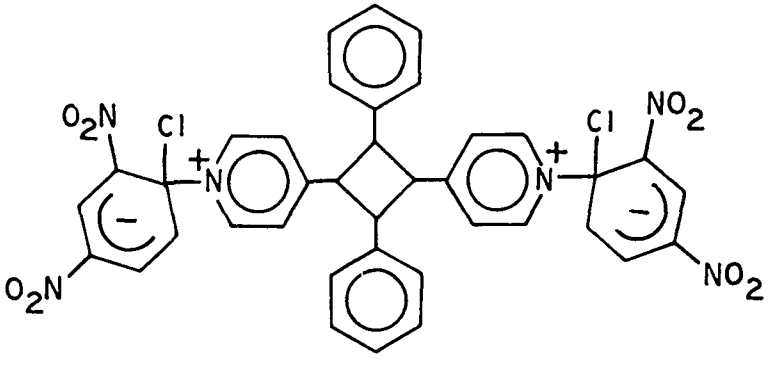
Experiments directed toward the cleavage and oxidation of the

aryl substituents into carboxylic acids were performed.

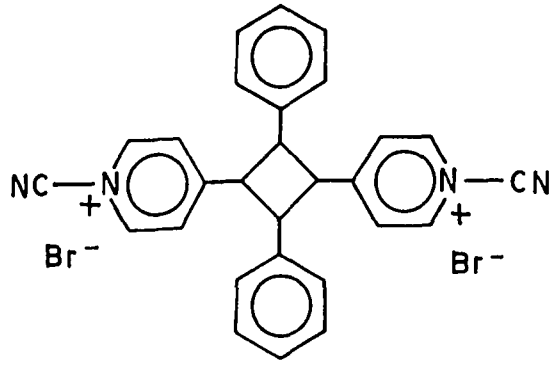
Oxidation at the benzylic positions of an indene dimer was shown to occur with sodium dichromate in refluxing glacial acetic acid.[37] Sodium dichromate in aqueous sulfuric acid, however, provided conditions that were too strenuous for the oxidation of dimer 74. Benzoic acid, resulting from the destruction of the cyclobutane ring, was recovered.

Salt Formation

Certain pyridinium salts are susceptible to hydrolytic cleavage.[38] In an attempt to make one such compound, the N-(2,4-dinitrophenyl)pyridinium chloride, the 2-styrylpyridine dimer (31) and the 4-styrylpyridine dimer (65) were treated with 2,4-dinotrochlorobenzene. This reagent and dimer 31 in refluxing acetone did not react. Dimer 65 reacted neat to give a dark purple acetone soluble material which became colorless in an acetic solution and returned to a purple color in base. This product appeared to be the Meisenheimer complex 76[39] and was unsuitable for further reaction.



76



77

A second salt that is susceptible to ring cleavage is the cyanogen bromide derivative 77. This product was made from dimer 65 in acetone as a yellow precipitate which turned brown on removal of the solvent. Treatment of this residue with aniline in dry ethanol gave an expected bright red solution. However, a tan solid which appeared to be 77 remained in suspension, was insoluble in organic solvents, and unreactive to base. Only aniline could be recovered from the red filtrate.

Ozonolysis

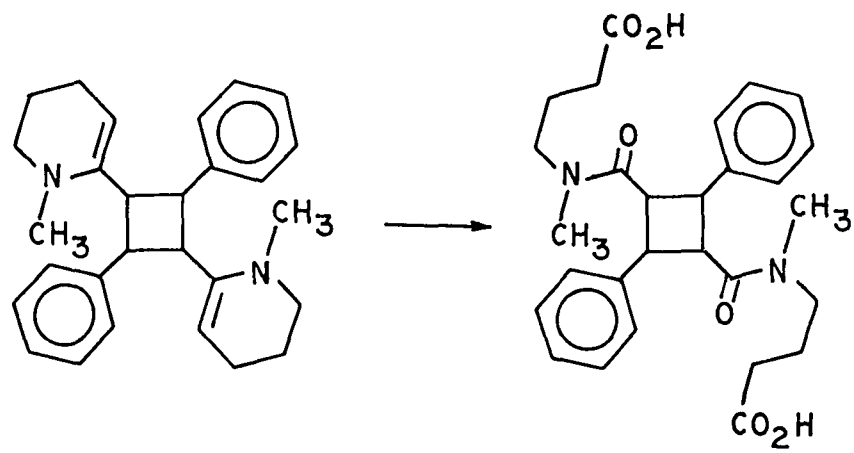
The preferred method for the cleavage of phenyl and fused phenyl substituents from cyclobutane rings has been ozonolysis.[29,40,42,43] Pyridines, although somewhat more resistant to ozonolysis than benzene rings, also can be degraded.[44,45,46]

Unfortunately, treatment of dimer 65 with ozone gave an unidentified material which still contained nitrogen, although the

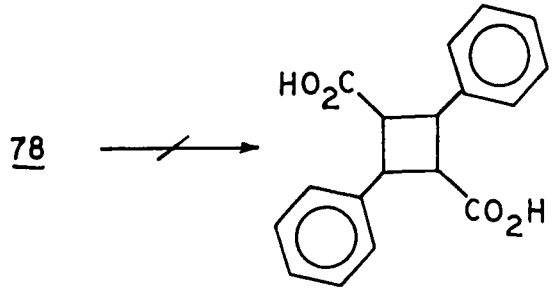
phenyl groups appeared to have been oxidized.

It was hoped that the ozonolysis of the tetrahydro dimer 74 would be more successful, since reaction of the isolated double bonds should occur at lower temperatures, while leaving the phenyl rings intact. Subsequent hydrolysis of the amide 78 would give the desired acid 79.

The ozonolysis product mixture gave indications in the infrared spectrum that the desired reaction had occurred. However, the product could not be purified and all attempts to hydrolyze it failed.



74 78



79

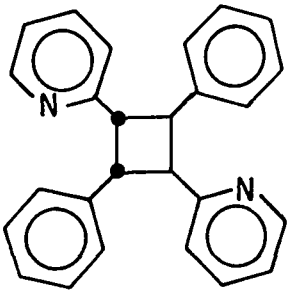
Williams' Dimers

As mentioned earlier, Williams obtained two dimers from the pyrolysis of a single dimer methiodide (see page 10). The higher melting isomer 31 has either C2 symmetry 71 of C2v symmetry 72. The lower melting point and unsymmetrical nmr splitting pattern of the rearranged isomer 32 suggested that it has one of the two possible cis-cis-trans forms.

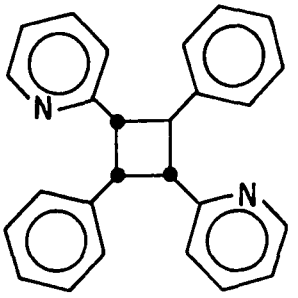
The exact structure of 31 was deduced after a computer analysis of the nmr spectrum (figure 7) by Highet in conjunction with this study, and simultaneously by Abernethy and Cavallito.[47] A computer simulated spectrum of the expanded cyclobutane proton region by Highet yielded the following coupling constants: $J_{12}=J_{34}= -0.09$, $J_{13}=J_{24}= 7.17$, $J_{23}=J_{24}= 10.12$. A negative number for J_{12} has been shown to result from a trans arrangement.[48] Abernethy and Cavallito reported J = -0.6, 6.8, and 9.7 respectively. These data can result only from a cis-trans-cis orientation for 31.

The structure of 32 was gained by Highet from an examination of the ^{13}C spectrum (figure 9). ^{13}C Spectroscopy, which utilizes the natural abundance of ^{13}C in a compound, is particularly suited to a

problem of this kind because of its ability to distinguish carbon atoms in different chemical environments.



31



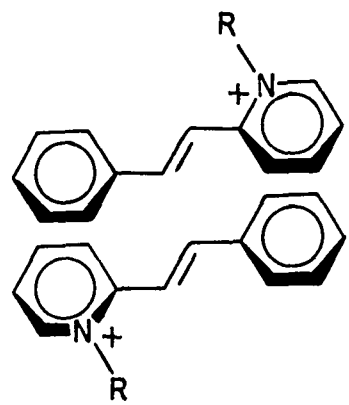
32

The spectrum showed identical pyridyl rings but nonidentical phenyl rings. Two identical and two nonidentical cyclobutane carbons also were evident. Only the cis-cis-trans form of 32 fits this data.

It appears, therefore, that isomerization during pyrolysis occurred at the pyridyl position, although the mechanism is not certain. As mentioned earlier, 31 dedimerized to 2-styrylpyridine on heating. This would suggest that at least one of the methiodide linkages was still present in the species undergoing isomerization. In addition, pyrolysis of the methiodide of 32 indicated that the reaction is reversible. This equilibrium might proceed through an open chain diradical although this and other interesting aspects of the isomerization remain to be solved.

Final Stereochemical Assignments

The preference of the solid methiodide 29 to dimerize in a cis-trans-cis arrangement must reflect, in a crude way, the packing of the monomer units in the crystal. However, the preference of a solution of the hydrochloride 33 to dimerize in the same cis-trans-cis orientation is not as easy to comprehend. Abernethy and Cavallito[47] proposed a model similar to 19a to show that when styrylpyridinium salts approach each other in solution, the rings align due to their attractive forces resulting in a cis-trans-cis arrangement in the dimer.



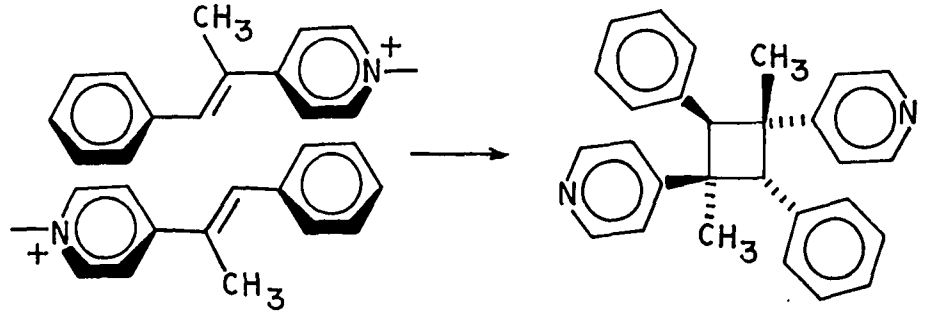
19a

Unlike the 2-pyridyl dimers, the 4-pyridyl dimers fortuitously display a singlet for the cyclobutane protons in the nmr spectra and, thus, cannot be analyzed. It was felt, however, that the position of the cyclobutane protons (5.57 τ) and phenyl protons (2.93 τ) of the 4-pyridyl dimer (65) so closely matched those of the cis-trans-cis stilbene dimer (5.60 τ and 2.95 τ) as compared to the all trans stilbene dimer (6.37 τ and 2.79 τ) that an assignment could be made.[47]

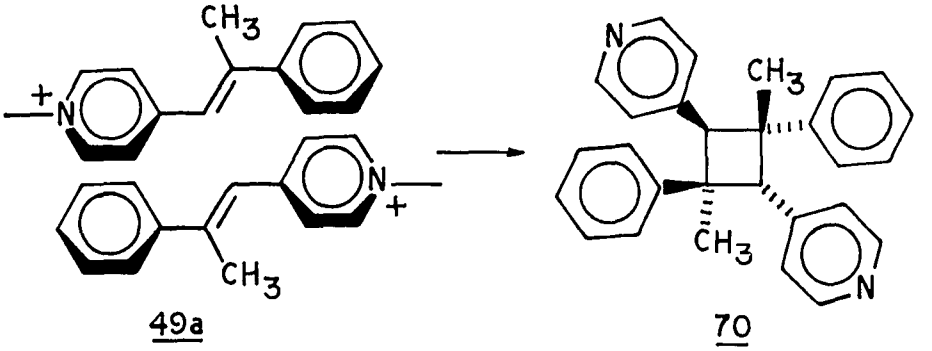
Although the evidence for a cis-trans cis arrangement is less substantial for 65 than for 31, it is reasonable to suspect that Cavallito's model holds for both dimerizations. The results of the dehalogenation tests showed that the halogenated dimers 62, 63, 66, and 67 were analogous to 31 and 65. Therefore, they must have the cis-trans-cis orientation.

It was also reasonable to predict that the two C-methyl dimers 69 and 70, and the two tetrapyridyl dimers 64 and 68 have the cis-trans-cis form. This was indicated in Table 3 where the similarity between the chemical shifts of the aliphatic protons of the dimers was noted. These values can be compared to those of the two stilbene dimers mentioned previously.

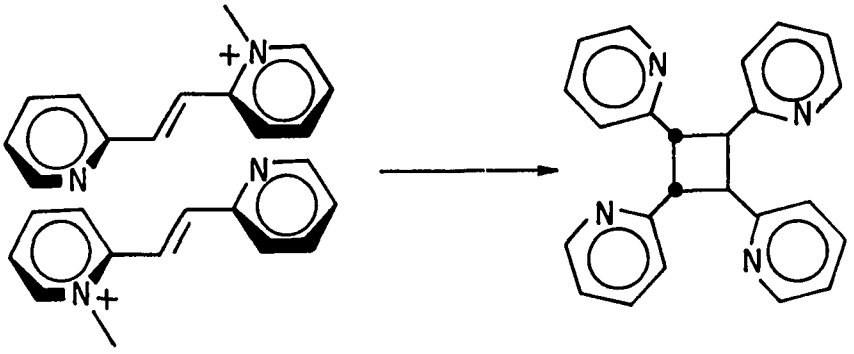
Hence, the molecular complex model can be expanded to include the following examples:



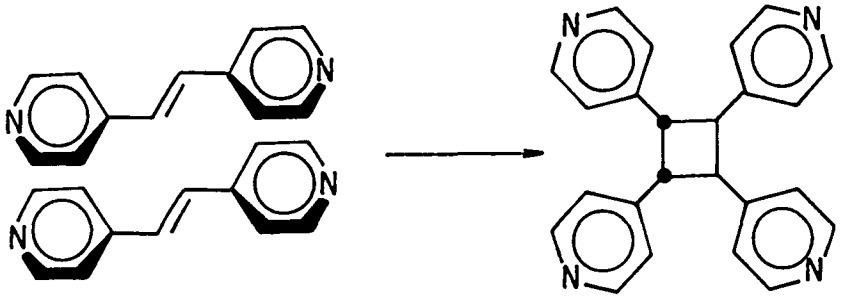
48a 69



49a 70



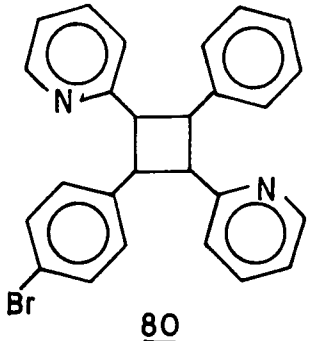
50a 64



51a 68

Mixed Dimerizations

An attempt to co-dimerize the solid methiodides of 2-styryl-pyridine and 4'-bromo-2-styrylpyridine failed to give the desired mixed product 80 after pyrolysis.



80

Pyrolysis of the crude product resulted in a complex mixture (probably a mixture of the possible dimers). The only pure product, which was separated by recrystallization, was the dibromo dimer 62.

Photo-inert Monomers

Several hypotheses have been forwarded to explain the photo-inertness of a particular compound. Some of these reasons have been discussed here, such as the wrong crystal structure, steric repulsions or unfavorable electronic properties. It is beyond the scope of this report to investigate the inability of a material to dimerize, although such an investigation would be of importance where it is advantageous for a compound to remain monomeric.

However, it is interesting to speculate on the reasons for unreactivity in the remaining attempted dimerizations. Those monomers which failed to react in the solid state probably had exceeded the 4 Å limit in the crystal structure. It might be possible to evoke Cavallito's model to explain the photo-inertness of 4-vinylpyridine (81) and 4-(3',4'-methylenedioxy)styrylpyridine (47) in solution.

In the case of 4-vinylpyridine (81) the absence of the phenyl ring produced too weak a complex, and thus retarded dimerization. The unreactivity of 4-(3',4'-methylenedioxy)styrylpyridine (47) was particularly surprising in view of previous work.[33] It is possible that this compound formed too strong a complex in solution and was resistant to further reaction.

EXPERIMENTAL

General

Melting Points. Melting points below 250° were determined using a Hoover capillary melting point apparatus and are corrected. Melting points above 250° were determined using a "Mel-Temp" capillary melting point apparatus and are not corrected.

Infrared Absorption Spectra. Infrared spectra were obtained as suspensions in potassium bromide using a Perkin-Elmer Model 337 grating spectrophotometer. Absorption bands are recorded in wave numbers (cm^{-1}), calibrated against polystyrene, and intensities are strong except those indicated as medium (m).

Ultraviolet Absorption Spectra. Ultraviolet spectra were determined using a Cary Model 15 spectrophotometer. Wavelengths are recorded in nanometers (nm) and intensities are reported as molar absorptivities (ε).

Nuclear Magnetic Resonance Spectra. Proton magnetic spectra were determined using a Varian Model A-60 spectrometer. The chemical shifts are given in parts per million (ppm) relative to the signal for internal tetramethylsilane (TMS).

Mass Spectra. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 80 volts.

Microanalyses. Microanalyses were determined using an F & M Model 180 carbon, hydrogen and nitrogen analyzer.

Ozonolysis. Ozone was produced by a PSI Corona Generator, Model LOA-2.

Irradiation Apparatus. Four basic units were used and are designated W, X, Y and Z.

W. A cobalt source providing gamma rays.

X. A water-cooled 1000 watt high pressure mercury lamp with Pyrex filter.

Y. A water-cooled 200 watt mercury Hanovia lamp with quartz filter.

Z. A Pyrex round bottom flask surrounded by five 200 watt incandescent bulbs.

EXPERIMENTAL

4-Picoline Methobromide (82). A solution of 14.0 g (0.15 mole) of 4-picoline in 150 ml of acetone was cooled in an ice bath with stirring. About one mole of methyl bromide was bubbled into the solution, and stirring was continued for 3.0 hr. The precipitate was removed by filtration to yield 18.5 g (67%) of 82 as white delequesent crystals.[49]

4-Picoline Methiodide (83). A procedure described by Fieser and Fieser[50] was used. To a solution of 17.7 g (0.19 mole) of 4-picoline in 40 ml of absolute ethanol initially heated to boiling was added 36.1 g (0.254 mole) of methyl iodide at a rate to maintain reflux. After 0.5 hr, the mixture was cooled, and 210 ml of ether were added. The precipitate was removed by filtration, washed with ether, and air dried to yield 43.3 g (97%) of 83 as light yellowish-white crystals, mp 150-152°, lit.[51] mp 149-150°.

2-Picoline Methiodide (84). The above procedure was followed to produce an 86% yield of 84 as white crystals, mp 229-230°, lit.[51] mp 226-228°.

4-Vinylpyridinium Methiodide (85). Addition of 4-vinylpyridine to an excess of methyl iodide caused the precipitation of a quantitative yield of the quaternary salt 85 as pinkish-tan crystals, mp 270° dec. Salt formation in a solvent such as ether leads to polymerization.[52]

2-Styrylpyridinium Methiodide (29). A solution of 20.5 g

(0.193 mole) of benzaldehyde, 31.8 g (0.135 mole) of 2-picoline methiodide (84) and 6.5 ml of piperidine in 160 ml of methanol was heated under reflux on a steam bath for 3 hr and allowed to stand overnight. After the precipitate (30.6 g) was removed and the filtrate was heated under reflux for 2 hr. After cooling the mixture in an ice bath, an additional 6.3 g of crystals was recovered. Two recrystalizations from methanol yielded 25.3 g (58%) of 29 as yellow needles, mp 227-229°, lit.[53] mp 230-231°.

2-Styrylpyridine (19). Vacuum pyrolysis of the methiodide 29 at 210° produced 19, mp 90-91°, lit.[31] mp 91.5-93.0°, in 98% yield.

2-Styrylpyridine N-oxide (52). The N-oxide of 2-styrylpyridine (19) was prepared by standard techniques[54] to give a white solid, mp 158-160°, lit.[54] mp 160°.

Dimerization of 2-Styrylpyridinium Methiodide (29). Following a procedure similar to that described by Williams[22], 6.0 g of 2-styrylpyridinium methiodide (29) was ground under benzene in a morter for 15 minutes. The resulting suspension in 600 ml of benzene was irradiated (apparatus X) for 6 hr with stirring, and the solid was recrystallized from boiling water to give 4.3 g (72%) of the dimer 30 as light yellow crystals, mp 318° dec., lit.[22] mp 310-312°.

Pyrolysis of 2-Styrylpyridinium Methiodide Dimer (30)[22]. Vacuum pyrolysis of 4.3 g of the dimer salt at 0.1 mm in a flame-heated air bath at 220° for 2 hr and 270-280° for 2 hr gave 2.0 g of a mixture of free bases. Separation of the products on 60 g of silica gel gave 0.1 g of 2-styrylpyridine, mp 88-90°, lit.[31] mp 91.5-93.0°

(10% chloroform-benzene eluant); 0.5 g of dimer 31, mp 192-193°; lit.[22] mp 189-190° (chloroform eluant); and 0.6 g of thermally rearranged dimer 32, mp 114-115°; lit.[22] mp 114-115° (acetone eluant).

NMR Spectrum of (32): See figure 1.

NMR Spectrum of (31): See table 3.

Mass Spectrum of (32): See figure 10.

Mass Spectrum of (31): See figure 11.

^{13}C Spectrum of (32): See figure 9.

^{13}C Spectrum of (31): See figure 8.

4'-Bromo-2-Styrylpyridinium Methiodide (53). This compound was made by the procedure of Phillips[55] and recrystallized from methanol to give a 65% yield of 53 as yellow needles, mp 203-205°; lit.[56] mp 205°.

Dimerization of 4'-Bromo-2-Styrylpyridinium Methiodide (53). Irradiation (apparatus Z) of 10.0 g of 53 as a fine suspension in benzene was continued until the uv spectrum showed no monomer absorption. The product, white needles from hot water, mp 235° dec., was removed by filtration and vacuum pyrolyzed. The residue was recrystallized from acetone with Norite treatment to give an 87% yield of the dimer base 62 as white needles, mp 234-235°.

Anal. Calcd. for $C_{26}H_{20}Br_2N_2$: C, 60.00; H, 3.88; N, 5.39. Found: C, 59.86; H, 3.89; N, 5.12.

NMR Spectrum: See table 3.

4'-Chloro-2-Styrylpyridinium Methiodide (54). Following the procedure of Phillips[55], this compound was made and recrystallized from methanol to give a 76% yield of 54 as yellow crystals, mp 213-215°.

Anal. Calcd. for $C_{14}H_{13}ClIN$: C, 47.02; H, 3.66; N, 3.92. Found: C, 46.88; H, 3.52; H, 3.84.

4'-Chloro-2-Styrylpyridine (42). Vacuum pyrolysis of the methiodide 54 gave an excellent yield of the base 42, which on recrystallization from benzene-hexane gave white needles, mp 82-84°; lit.[57] mp 83-84°.

Dimerization of 4'-Chloro-2-Styrylpyridine (42). Irradiation (apparatus Y) of a fine suspension of 42 as its hydrochloride 55, mp 191-193°; lit.[57] mp 193-195°, in hexane showed nearly complete reaction after 4 hr, as determined by tlc (silica gel). The product was removed by filtration, stirred in aqueous sodium carbonate, and extracted into chloroform; and the solvent was evaporated. Recrystallization of the residue from acetone gave the dimer 63 as white needles, mp 212-213°.

Anal. Calcd. for $C_{26}H_{20}Cl_2N_2$: C, 72.38; H, 4.68; N, 6.50. Found: C, 72.78; H, 4.64; N, 6.49.

NMR Spectrum: See figure 2.

Mass Spectrum: See figure 12.

4-Styrylpyridine (43). Following the procedure of Williams[31], 37.2 g (0.40 mole) of 4-picoline and 42.5 g of (0.40 mole) of benzaldehyde were heated under reflux for 16 hr in 65 ml of acetic anhydride. The solution was poured onto ice and made basic with 40%

aqueous sodium hydroxide. The crude product was removed by filtration, washed with water, and recrystallized from 95% ethanol to yield 40 g (55%) of 43 as yellow crystals, mp 129-130°; lit.[57] 130-130.5°.

Dimerization of 4-Styrylpyridine (43). Irradiation (apparatus X) of a warm solution of 25.0 g of 43 and 14 ml of hydrochloric acid in 600 ml of water for 6 hr showed nearly complete dimerization by tlc (silica gel). The crude product was precipitated by the addition of sodium carbonate solution. The solid was removed by filtration, washed with water, and recrystallized from 30% benzene-hexane to yield 22 g (88%) of 65 as white crystals, mp 157-159°.

Anal. Calcd. for $C_{26}H_{22}N_2$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.11; H, 6.02; N, 7.58.

NMR Spectrum: See table 3.

Mass Spectrum: See figure 13.

4-Styrylpyridine Methiodide (57). Following Phillips' procedure[55], 57 was prepared and crystallized from methanol as white crystals, mp 219-221°; lit.[55] 220-221°, in 78% yield.

4'-Bromo-4-Styrylpyridine (44). Following Williams' procedure[31], 30.0 g (0.158 mole) of 4-bromo-benzaldehyde (prepared by Rett Southwick) and 15.0 g (0.158 mole) of 4-picoline were heated under reflux for 16 hr in 30 ml of acetic anhydride. Work-up with sodium carbonate solution and recrystallization from 95% ethanol gave 14.7 g (35%) of 44 as light tan flakes, mp 150-152°. An analytical sample recrystallized from 30% benzene-hexane gave 44 as light tan crystals, mp 157-158°.

Anal. Calcd. for $C_{13}H_{10}BrN$: C, 60.00; H, 3.88; N, 5.39. Found: C, 60.13; H, 3.94; N, 5.16.

IR Spectrum: 1580, 1470 m, 1400 m, 1065, 1010, 990 m, 970, 865 m, 820.

Dimerization of 4'-Bromo-4-Styrylpyridine (44). Irradiation (apparatus X) of a warm solution of 7.0 g of 44 and 3.0 ml of hydrochloric acid in 600 ml water for 8 hr showed nearly complete dimerization by tlc (silica gel). The dimer was precipitated with sodium carbonate solution and extracted several times into chloroform. Evaporation of the chloroform followed by two recrystallizations of the solid from acetone gave an 82% yield of 66 as colorless crystals, mp 223-225°.

Anal. Calcd. for $C_{26}H_{20}Br_2N_2$: C, 60.00; H, 3.88; N, 5.39. Found: C, 59.82; H, 3.87; N, 5.46.

NMR Spectrum: See figure 4.

4'-Chloro-4-Styrylpyridine (45). Following Williams' procedure[31], 45 was prepared and recrystallized from 95% ethanol in 58% yield as white crystals, mp 109-111°; lit.[57] mp 110°.

Dimerization of 4'-Chloro-4-Styrylpyridine (45). Irradiation (apparatus X) of a hot solution of 12.0 g of 45 and 5.5 ml of hydrochloric acid in 600 ml of water for 9 hr gave, after work-up and recrystallization from acetone, 9.1 g (76%) of the dimer 67 as colorless crystals, mp 200-202°.

Anal. Calcd. for $C_{26}H_{20}Cl_2N_2$: C, 72.38; H, 4.68; N, 6.50. Found: C, 72.71; H, 4.86; N, 6.50.

NMR Spectrum: See table 3.

Mass Spectrum: See figure 14.

2-(3',4'-Methylenedioxy)Styrylpyridine N-oxide (56). Following the procedure of Pentimalli[58] for the preparation of 2-(4'-dimethylamino)styrylpyridine N-oxide, a mixture of 4.4 g (0.04 mole) of 2-picoline N-oxide, 8.4 g (0.056 mole) of piperonal, 2.0 g of potassium hydroxide and 12 ml of pyridine was heated under reflux for 6 hr. The mixture was stirred for 5 minutes in 200 ml of water, and the resulting precipitate was recrystallized twice from 95% ethanol to give 2.5 g (26%) of 56 as light yellow needles, mp 202-203°.

Anal. Calcd. for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.87; H, 4.48; N, 5.63.

IR Spectrum: 1625 m, 1600, 1510, 1450, 1440, 1280, 1250, 1230 m, 1045, 975, 840 m, 805 m, 790 m, 750.

UV Spectrum: (CH_3OH): 352 (28,900), 253 (19,850).

4'-Bromo-4-Styrylpyridinium Methiodide (58). Following the procedure of Phillips[55], the methiodide 58 was prepared and recrystallized from methanol to give a 52% yield of yellow crystals, mp 266-268°; lit.[59] mp 260-263°.

3'-Methoxy-4'-acetoxy-4-styrylpyridine (46). A solution of 12.2 g (0.131 mole) of 4-picoline, 20.0 g (0.131 mole) of vanillin and 50 ml of acetic anhydride was heated under reflux for 16 hr. The reaction mixture was poured onto ice and made basic with 40% sodium hydroxide solution. The resulting viscous oil was stirred in ice

water until it crystallized and then was triturated in a morter with ether. The crude solid was extracted further with ether in a Soxlet apparatus. The ether was evaporated to give 10.8 g (30%) of 46 as a yellow residual powder, mp 130-133°. An analytical sample of 46, crystallized and recrystallized from a concentrated acetone solution was a light tan powder, mp 132-134°.

Anal. Calcd. for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.36; H, 5.60; N, 4.98.

IR Spectrum: 1760, 1600, 1505, 1410 m, 1360 m, 1300, 1270, 1200, 1155, 1120 m, 1030 m, 972 m, 905 m, 855 m, 827 m, 807 m.

UV Spectrum: (CH_3OH): 318 (27,400), 307 (27,800).

3'-Methoxy-4'-acetoxy-4-styrylpyridinium Methiodide (59). A solution of 1.0 g of 46 and 0.8 g of methyl iodide in 15 ml of ethanol was stirred overnight at room temperature. The solid was removed by filtration to give 1.2 g (80%) of 59 as a bright yellow powder, mp 245° dec. Recrystallization of the solid from methanol gave 59 as yellow crystals, mp 248-249° dec.

Anal. Calcd. for $C_{17}H_{18}INO_3$: C, 49.65; H, 4.41; N, 3.41. Found: C, 49.72; H, 4.43; N, 3.37.

IR Spectrum: 1730, 1600, 1560 m, 1320 m, 1280 m, 1245, 1180, 1160, 1120, 1020 m, 975 m, 905 m, 870 m, 825 m.

UV Spectrum: (CH_3OH): 361 (25,000).

3'-Methoxy-4'-hydroxy-4-styrylpyridinium Methobromide (60). Following the procedure of Phillips[55], a solution of 36.5 g (0.24 mole) of vanillin, 32.0 g (0.17 mole) of 4-picoline methobromide 82 and 7.0 ml of piperidine in 200 ml of methanol was heated under reflux on a steam bath for 4 hr. After 45 minutes part of the product was removed by filtration to prevent excessive bumping. After 4 hr the reaction mixture was cooled in an ice bath and the remaining precipitate was collected. Recrystallization of the product from methanol gave 32.3 g (59%) of 60 as an orange-yellow powder, mp 292-294°.

Anal. Calcd. for $C_{15}H_{16}BrNO_2$: C, 55.91; H, 5.01; N, 4.35. Found: C, 56.13; H, 5.08; N, 4.10.

IR Spectrum: 3000, 1610, 1580, 1520, 1470, 1420, 1370, 1290, 1240, 1180, 1165, 1120, 1030, 980 m, 875 m, 825 m, 805 m.

UV Spectrum: (CH_3OH): 405 (31,300), 273 sh (8,000), 261 (10,000).

3'-Methoxy-4'-hydroxy-4-styrylpyridinium Methiodide (61). Following the procedure of Phillips[55], a solution of 29.4 g (0.193 mole) of vanillin, 31.8 g (0.135 mole) of 4-picoline methiodide (83) and 6.5 ml of piperidine in 160 ml of piperidine in 160 ml of methanol was heated under reflux on a steam bath for 4 hr. After cooling the mixture in an ice bath, the precipitate was collected and recrystallized from methanol to yield 32.2 g (65%) of 61 as gold needles, mp 276-277° dec.; lit.[55] mp 275-276°.

4-(3',4'-Methylenedioxy)styrylpyridine (47). A mixture of 25.0 g (0.167 mole) of piperonal, 15.5 g (0.167 mole) of 4-picoline and 30 ml of acetic anhydride was heated under reflux for 7 hr and allowed to stand at room temperature overnight. The precipitate was collected and stirred for 15 minutes in sodium carbonate solution, collected again, washed with water, and recrystallized from benzene to give 16 g (43%) of 47 as orange-brown crystals, mp 95-100°. An analytical sample of 47 was prepared by recrystallization from acetone, after stirring the solution with a small amount of neutral alumina. This procedure yielded 47 as yellow crystals, mp 107-109°.

Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 74.67; H, 4.89; N, 6.23. Found: C, 74.99; H, 4.78; N, 6.32.

IR Spectrum: 1580, 1480, 1430, 1405, 1350 m, 1330 m, 1285 m, 1230, 1090 m, 1040, 980, 925, 825, 815.

UV Spectrum: (CH_3OH): 337 (27,300), 304 (15,500), 252 sh (10,000), 238 (12,000).

4-(α-Methyl)styrylpyridine (48). Following a reported procedure[60], a mixture of 42.8 g (0.40 mole) of 4-ethylpyridine, 43.2 g (0.40 mole) of benzaldehyde and 160 ml of acetic anhydride was heated under reflux for 24 hr. After work-up the crude product was recrystallized from methanol to yield 31 g (40%) of 48 as colorless crystals, mp 69-71°; lit.[60] mp 74°.

Dimerization of 4-(α-Methyl)styrylpyridine (48). Irradiation (apparatus X) of 10 g of 48 as a suspension of its hydrochloride salt in water was carried out with a Pyrex filter. After 7 hr the solid was found to have gone into solution. Tlc (silica gel) showed dimerization to be nearly complete. The product was precipitated with aqueous sodium carbonate and crystallized twice from benzene-hexane to give the dimer 69 as colorless crystals, mp 143-145°.

Anal. Calcd. for $C_{28}H_{26}N_2$: C, 86.16; H, 6.67; N, 7.18. Found: C, 85.92; H, 6.78; N, 6.97.

NMR Spectrum: See Table 3.

4-(2-Hydroxy-2-phenyl)propylpyridine (86)[61]. A solution of 18.6 g (0.20 mole) of 4-picoline in 140 ml of anhydrous tetrahydrofuran under nitrogen was stirred and cooled in ice water while a solution of 0.22 moles of phenyl lithium in 150 ml of anhydrous ether was added over 30 minutes. The mixture was stirred 30 additional minutes at room temperature and a solution of 24 g (0.20 mole) of acetophenone in 110 ml of tetrahydrofuran was added over a period of 1 hr at 0°. The mixture was stirred overnight at room temperature. After addition of 100 ml of water, the nonaqueous layer was extracted with four 50 ml portions of 6N. hydrochloric acid; the extracts were washed with ether and made basic with cold ammonium hydroxide. The resulting oil was collected and crystallized and recrystallized from 10% benzene-hexane to give 24.3 g (57%) of 86 as colorless crystals, mp 83-85°; lit.[61] mp 83-85°.

4-(β-Methyl)styrylpyridine (49)[61]. A solution of 24 g of the alcohol 86 in 50 ml of 40% sulfuric acid was warmed on a steam bath for 45 minutes. After basicifying the solution with cold ammonium hydroxide, the resulting oil was crystallized and recrystallized from hexane yielding 13 g (33% based on 4-picoline) of 49 as colorless crystals, mp 53.5-54.5°; lit.[61] mp 51-54.5°.

Dimerization of 4-(β-Methyl)styrylpyridine (49). Treatment of 5.0 g of 49 with 40 ml of warm dilute hydrochloric acid gave a suspension of the salt on cooling. After irradiation (apparatus X) for 5 hr using a Pyrex filter, the crystalline suspension was converted to a thick oil. Basicifying the reaction mixture with aqueous sodium carbonate and extracting with ether gave an oil which showed nearly complete dimerization by tlc (silica gel). Recrystallization of the oil from 30% benzene-hexane yielded 4.2 g (85%) of the dimer 70 as colorless crystals, mp 211-213°.

Anal. Calcd. for $C_{28}H_{26}N_2$: C, 86.16; H, 6.67; N, 7.18. Found: C, 86.28; H, 6.72; N, 7.03.

NMR Spectrum: See figure 5.

Mass Spectrum: See figure 15.

Dimerization of 1,2-Bis-(4-pyridyl)ethylene (51). A solution of 9.5 g of 51 (Aldrich) in 50 ml of methanol was irradiated (apparatus X) for 10 hr with Pyrex filter. Tlc (silica gel) showed dimerization to be partially complete. The product was recrystallized twice from acetone to give 6.5 g (68%) of the dimer 68 as colorless rods, mp 234-236°.

Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.23; H, 5.51; N, 15.26.

NMR Spectrum: See Table 3.

Dimerization of 1,2-Bis-(2-pyridyl)ethylene (50). A solution of 6.5 g (0.036 mole) of 50 (Aldrich), 1.3 ml (0.016 mole) of hydrochloric acid and 150 ml of water was irradiated (apparatus Y) for 4.5 hr. Work-up with sodium carbonate solution and extraction with three 50 ml portions of chloroform was followed by treatment with charcoal. Filtration and evaporation of the solvent gave a residue which was crystallized and recrystallized from acetone to give 4.7 g (73%) of the dimer 64 as colorless rods, mp 190-191°.

Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.04; H, 5.54; N, 15.14.

NMR Spectrum: See figure 3.

Attempted Mixed Dimerization of 2-Styrylpyridine Methiodide (29) and 4'-Bromo-2-styrylpyridine Methiodide (53). Equimolar amounts of 29 and 53 were ground together in a morter and co-melted at 220°. The fused mixture was ground again and irradiated (apparatus Z) for 48 hr as a fine suspension in benzene. The uv spectrum showed an absence of monomer. The product was pyrolysed under vacuum and recrystallized from acetone. The only dimer isolated was a small amount of the dibromo compound 62, mp 229-231°; authentic sample of 62, mp 234-235°; mmp 232-233°. The remaining solid product was shown by tlc (silica gel) to be a mixture of 62 and a few unidentified materials. These could not be separated by fractional crystallization.

Attempted Dimerization of 4-Vinylpyridine (81). Only unreacted 4-vinylpyridine was recovered from the following attempted dimerizations using apparatus X:

A. Irradiation for 5 hr of a suspension of copper dichloride di-4-vinylpyridine[62] in water, both with and without a Pyrex filter, gave only unreacted starting material after work-up with sodium sulfide.

B. Irradiation for 6.5 hr of a saturated methanolic solution of nickel dichloride di-4-vinylpyridine, prepared like the copper complex, without filter, gave unreacted starting material after work-up with sodium sulfide.

C. Unfiltered irradiation for 5.3 hr of a water solution of 4-vinylpyridinium hydrochloride gave only 4-vinylpyridine after work-up with sodium carbonate solution.

D. Irradiation for 4 hr of a suspension of 4-vinylpyridinium hydrochloride (prepared in dry benzene, mp 250° dec.; lit.[63] mp 238°) in benzene gave only 4-vinylpyridine after work-up with sodium carbonate solution.

Dehalogenation of Dimers. General Procedure. To a solution of 0.26 g of the dimer, 0.2 g of potassium hydroxide and 12 ml of methanol was added 0.1 g of 5% palladium on carbon (0.2 g of catalyst for dechlorination). The suspension was stirred at room temperature under hydrogen at atmospheric pressure, the hydrogen uptake being measured by a buret. After the reaction had gone to completion, the catalyst was removed by filtration. The excess base was neutralized with dilute sulfuric acid. After evaporation of the methanol, the residue was stirred with aqueous sodium carbonate and extracted with

chloroform. The chloroform layer was washed with water and evaporated. The product was crystallized in good yield from benzene-hexane.

In all cases a second run, omitting the catalyst and hydrogen, showed no isomerization by base.

The results of four dehalogenations are tabulated in Table 4 along with mixture melting point comparisons with the analogous unsubstituted dimers. The corresponding infrared spectra in each case were identical.

Reduction of Dimer 30 with Sodium Borohydride. A suspension of 2.0 g of the dimer 30 in 15 ml of 30% aqueous methanol was covered with 30 ml of ether. To this was added a solution of 0.35 g of sodium borohydride in 5 ml of water with stirring. When the solid had disappeared, the ether layer was separated, and the aqueous layer was extracted with 15 ml of ether. The combined fractions were dried over anhydrous potassium carbonate and evaporated to give 1.0 g (81%) of a viscous yellow oil. Recrystallization of the oil from acetone gave 74 as colorless crystals, mp 170-172°.

Anal. Calcd. for $C_{28}H_{34}N_2$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.36; H, 8.65; N, 7.01.

IR Spectrum: 3050, 3020, 2920, 2830, 2780, 1650 m, 1610, 1500, 1460, 1440, 1390 m, 1370 m, 1350 m, 1330 m, 1270 m, 1210 m, 1115, 1090 m, 1030 m, 900 m, 880 m, 865 m, 770 m, 755, 705, 660, 642.

NMR Spectrum: See figure 6.

Table 4

Dimer	Dehalogenation Product mp.	Mixture Melting Points	
		Dimer (31) mp 190-192°	Dimer (65) mp 157-158°
(62)	188-189°	189-191°	
(63)	191-192°	191-192°	
(66)	155-157°		155-157°
(67)	155-156°		155-157°

Thermal Dedimerization of Dimer 31. A sample of the higher melting 2-styrylpyridine dimer 31 was sealed under vacuum in a soft glass tube and heated at 260° for 24 hrs. The product, which was crystallized from hexane as colorless needles, mp 89-91°, in nearly quantitative yield, was identical to 2-styrylpyridine by mixture melting point.

Pyrolysis of the Methiodide Salt of Dimer 32. A solution of 0.2 g of the lower melting 2-styrylpyridine dimer (32), 0.5 ml of methyl iodide and 3.0 ml of acetone was allowed to stand at room temperature overnight. A 98% yield of the salt, mp 250-260° dec., was removed by filtration and subjected to vacuum pyrolysis at 170-190°. Reaction was complete after 30 minutes. The crude product displayed spots on tlc (silica gel) corresponding to dimer 32 and a somewhat lesser amount of the higher melting 2-styrylpyridine dimer (31) plus some 2-styrylpyridine.

Ozonolysis of Dimer 74. No acidic compounds could be isolated by extraction with base from the crude products afforded by the following methods. Also all attempts failed to hydrolyse any amides formed.

Method A. A solution of 1.8 g of the partially reduced dimer 74 in 60 ml of methanol was treated with approximately 6 g of ozone over 3 hrs at 0°. The reaction mixture was allowed to stand for 2 days at room temperature with 10 ml of 30% hydrogen peroxide and 25 ml of water. Excess peroxide was destroyed with 5% palladium on charcoal. The solution was filtered and evaporated to dryness. The product mixture, although soluble in water, was insoluble in aqueous acid or base. The infrared spectrum displayed strong absorptions at 1730, 1680, 750, and 700 cm^{-1}.

Method B. A solution of 1.0 g of 74 in 30 ml of methylene chloride at -70° was treated with ozone until the solution became faintly blue. A solution of 5.0 g of periodic acid in 30 ml of water and 50 ml of acetic acid were added. The mixture was stirred at room temperature for 24 hrs, extracted with chloroform, and the extracts were evaporated. The crude product was essentially the same as that described in method A.

Ozonolysis of Dimer 31. Following a reported procedure[42], a solution of 1.0 g of 31 in 50 ml of 90% acetic acid at room temperature was treated with about 16 g of ozone over 8 hrs. The reaction mixture was allowed to stand for 2 days with 10 ml of 30% hydrogen peroxide and 26 ml of water. Excess peroxide was destroyed with 5% palladium on charcoal. The solution was filtered and evaporated to 5 ml. On standing, about 0.1 g of a white solid, mp 270° dec., precipitated. The infrared spectrum indicated the presence of an acetate salt and the absence of the phenyl ring. Elemental analysis, though inaccurate due to incomplete combustion, gave the following results: C, 47.3; H, 4.65; N, 6.90.

Attempted Ring Opening of Dimer 65. A solution of 1.0 g (0.0028 mole) of 65 and 0.6 g (0.0057 mole) of cyanogen bromide in 10 ml of dry acetone was allowed to stand overnight at room temperature. The yellow solid which precipitated appeared to be very hydroscopic. After removing the acetone by evaporation under reduced pressure, the brown residue was treated with 1.0 g of aniline in 10 ml of dry ethanol. The solution immediately turned bright red. About 0.6 g of a reddish-tan solid, mp 240 dec., which remained unreactive toward aniline, was

removed by filtration. The solid appeared to be the initial salt that was formed (strong infrared absorption at 2200 cm^{-1}) but it was not hydroscopic. The salt was soluble only in warm dimethylsulfoxide and was not affected by hot 4N sodium hydroxide or cold 4N hydrochloric acid. Only aniline could be recovered from the red filtrate.

Oxidation of Dimer 74. Treatment of 74 with an aqueous solution of sodium dichromate and sulfuric acid following a standard procedure[64] produced a good yield of benzoic acid.

Attempted Salt Formation with 2,4-Dinitrochlorobenzene.

A. Reaction with Dimer 31. A solution of 0.5 g (0.0014 mole) of 31 and 0.6 g (0.0030 mole) of 2,4-dinitrochlorobenzene in 15 ml of acetone resulted in no salt formation after 24 hr of heating under reflux.

B. Reaction with Dimer 65. A solution of 0.5 g (0.0014 mole) of 65 and 0.6 g (0.0030 mole) of 2,4-dinitrochlorobenzene rapidly turned a dark purple color but gave no precipitate. After evaporation to dryness, the residue was found to produce a purple solution in aqueous base and a colorless solution in aqueous acid.

Table 5

Photoinert Monomers

Monomer	Irradiation Conditions	Apparatus	Results
(19)	A. Two hr at 270-290°.	None	Several unidentified tlc spots.
	B. Solid for 24 hr.	W	Unchanged.
(52)	Suspension in benzene for 4 hr.	X	Unchanged.
(54)	Suspension in benzene for 5.5 hr.	Y	Unchanged.
(56)	Suspension in water for 4 hr.	X	Slight m.p. lowering.
(57)	Suspension in benzene for 11.5 hr.	X	Unchanged. Vacuum pyrolysis gave 4-styrylpyridine, mp 129-130°; mmp 129-130°.
(85)	Suspension in benzene for 6 hr.	X	Unchanged.
(58)	A. Suspension in benzene for 6 hr.	X	Unchanged in both cases.
	B. Hot concentrated methanolic solution for 5 hr.	X	
(47)	A. Benzene solution for 24 hr.	Z	Only monomer recovered in all cases.
	B. Water solution of the hydrochloride for 48 hr.	Z	
	C. Benzene suspension of the hydrochloride for 8 hr.	Y	
(46)	Solution in dilute hydrochloric acid for 10 hr.	X	Unchanged except for acid hydrolysis of the acetyl group.
(60)	Suspension in benzene for 4 hr.	X	Unchanged.
(61)	Suspension in benzene for 6 hr.	X	Slight infrared changes. Decomposition upon vacuum pyrolysis.

Appendix I

Nuclear Magnetic Resonance Spectra

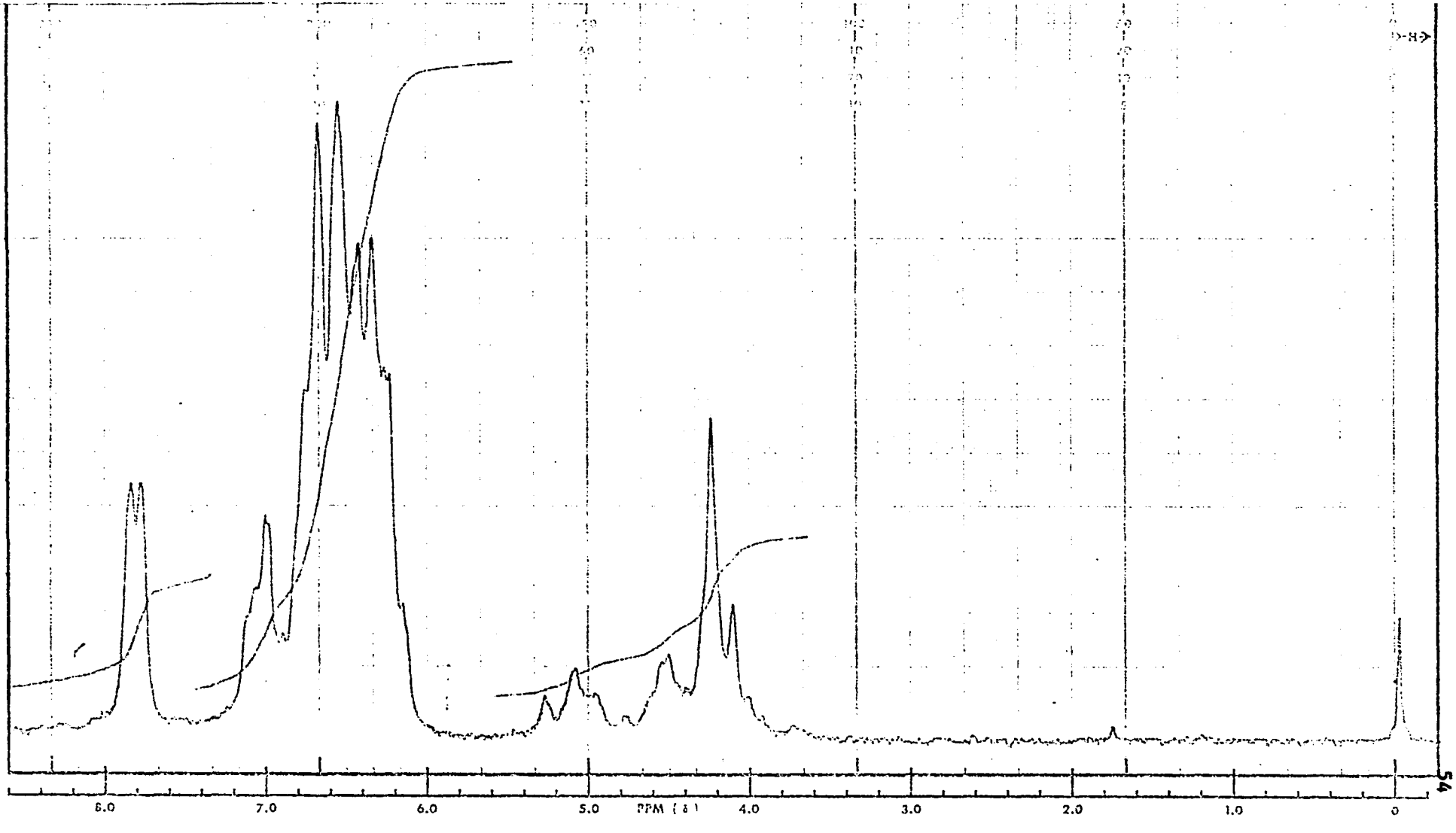


Fig. 1 NMR Spectrum of cis-cis-trans-1,3-di-2-pyridyl-2,4-diphenylcyclobutane (32).

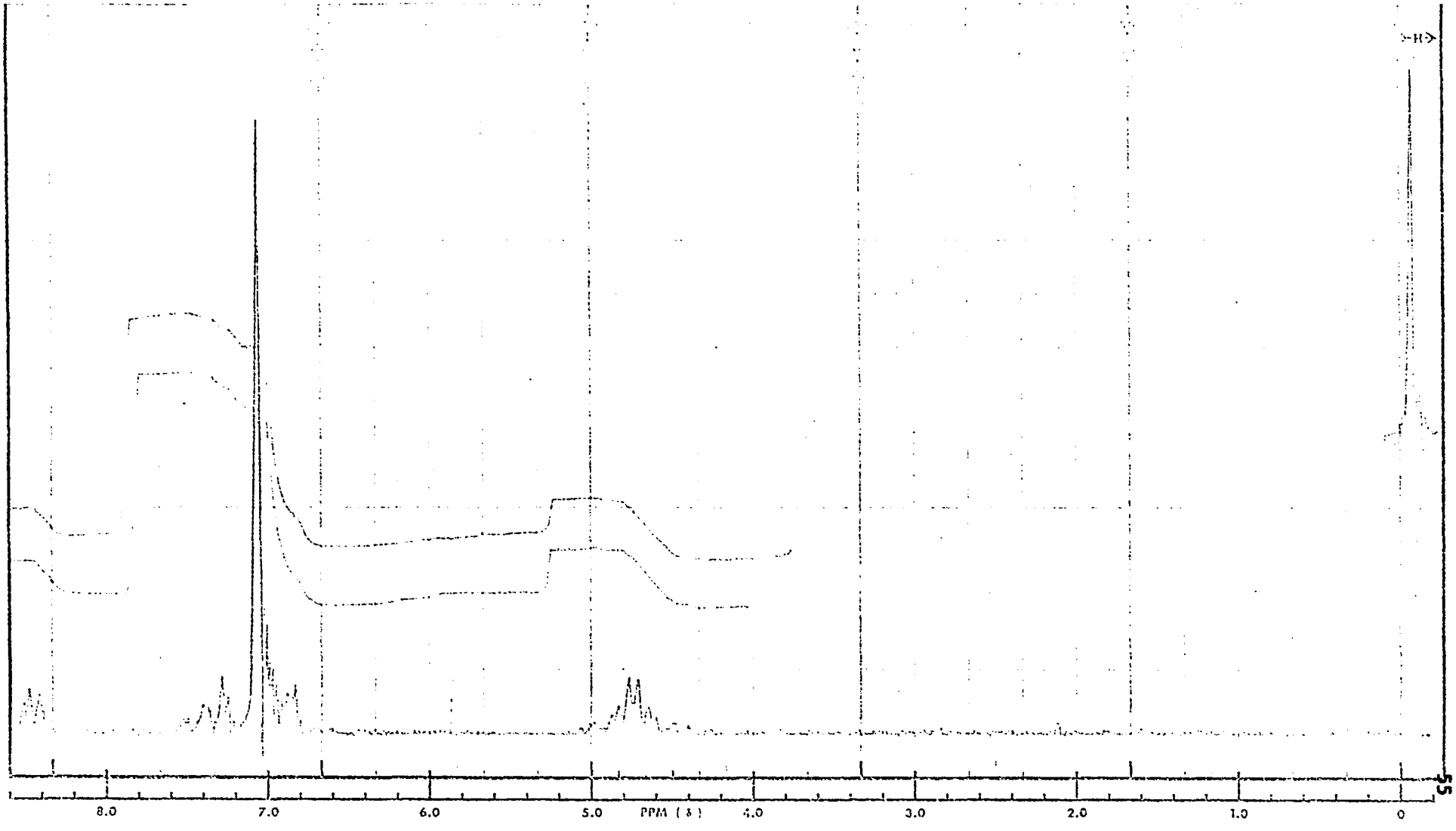


Fig. 2 NMR Spectrum of cis-trans-cis-1,3-di-2-pyridyl-2,4-di-4-chlorophenylcyclobutane (63).

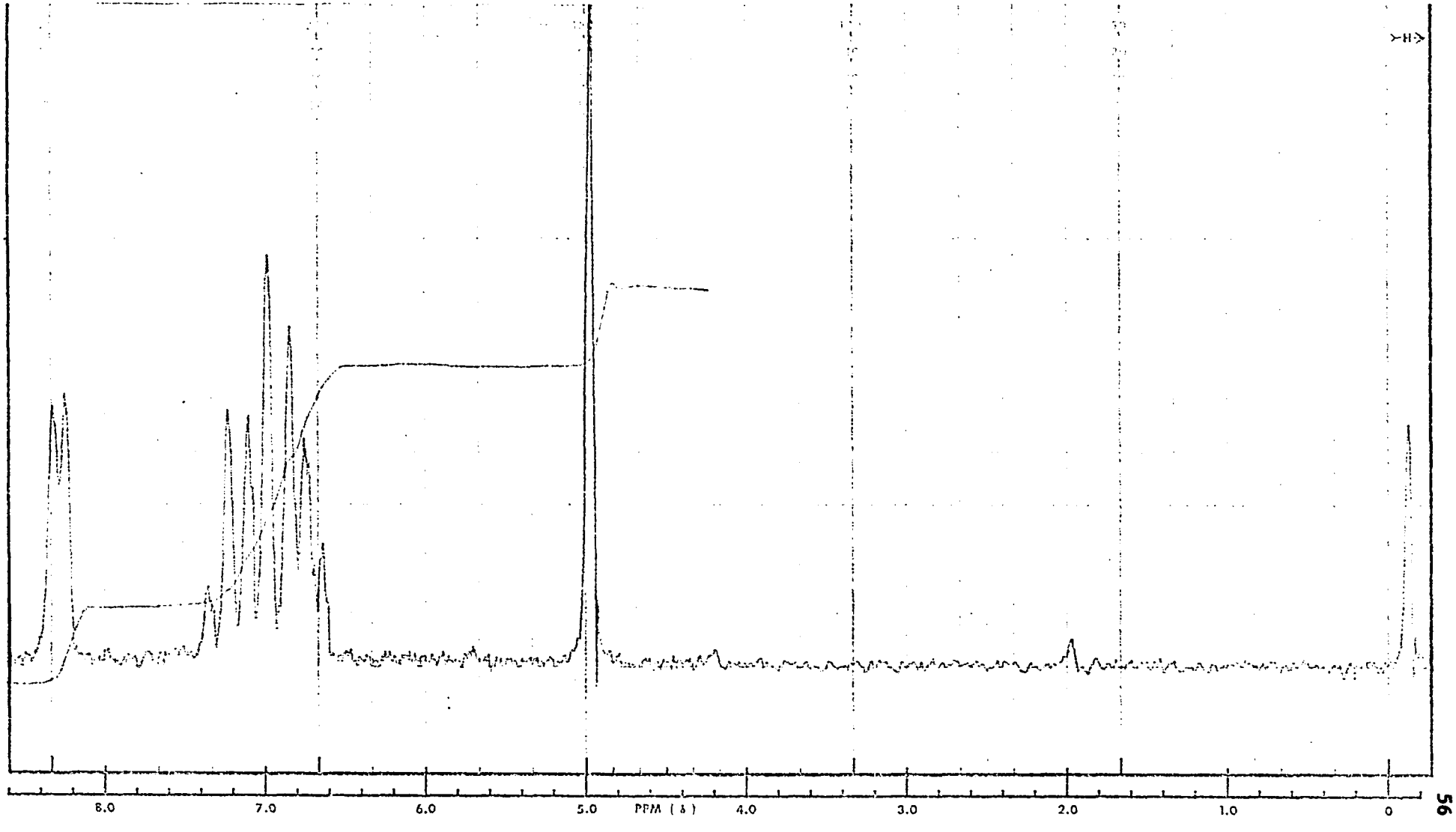


Fig. 3 NMR Spectrum of cis-trans-cis-1,2,3,4-tetra-2-pyridylcyclobutane (64).

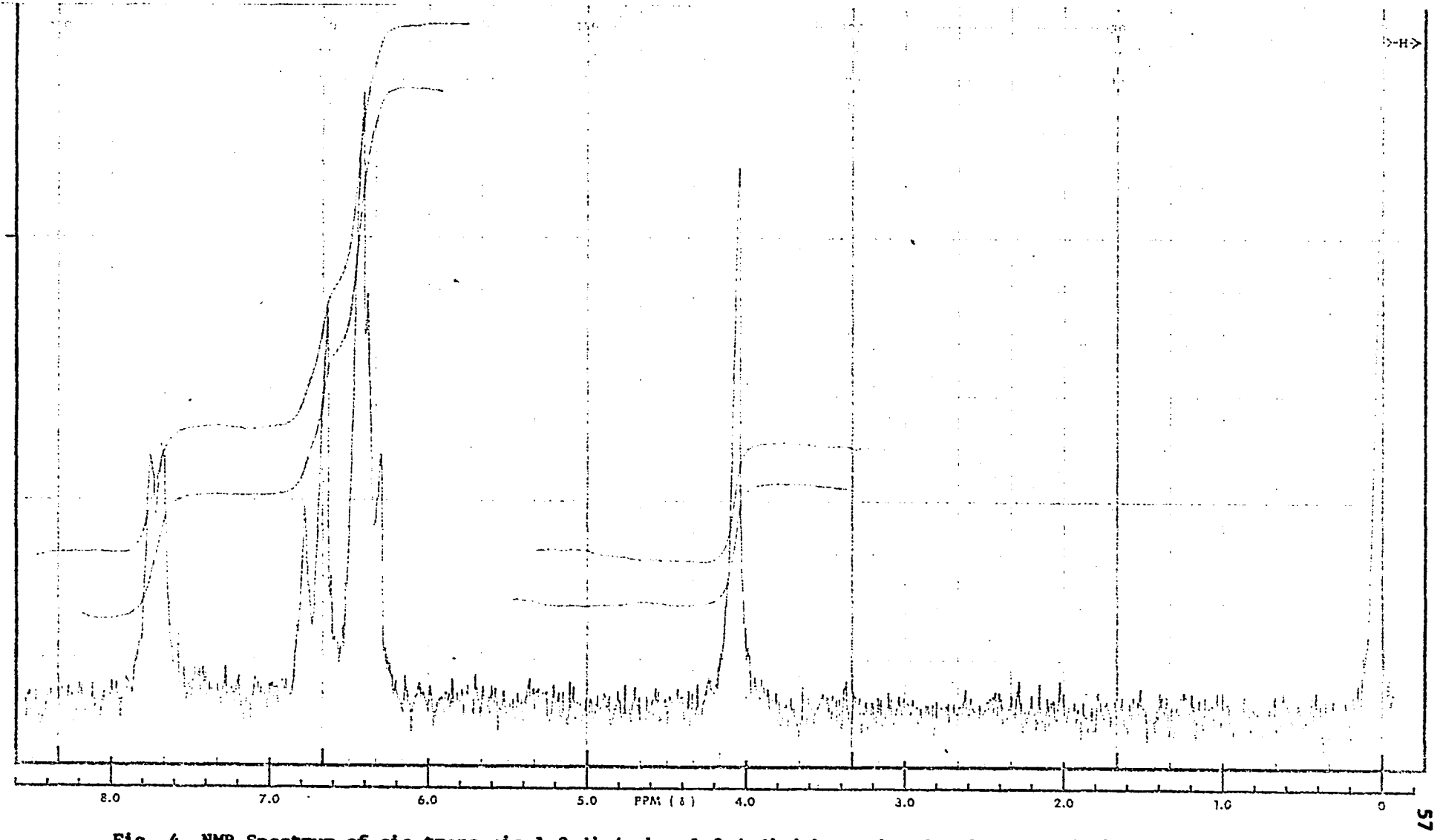


Fig. 4 NMR Spectrum of cis-trans-cis-1,3-di-4-phenyl-2,4-di-4-bromophenylcyclobutane (66).

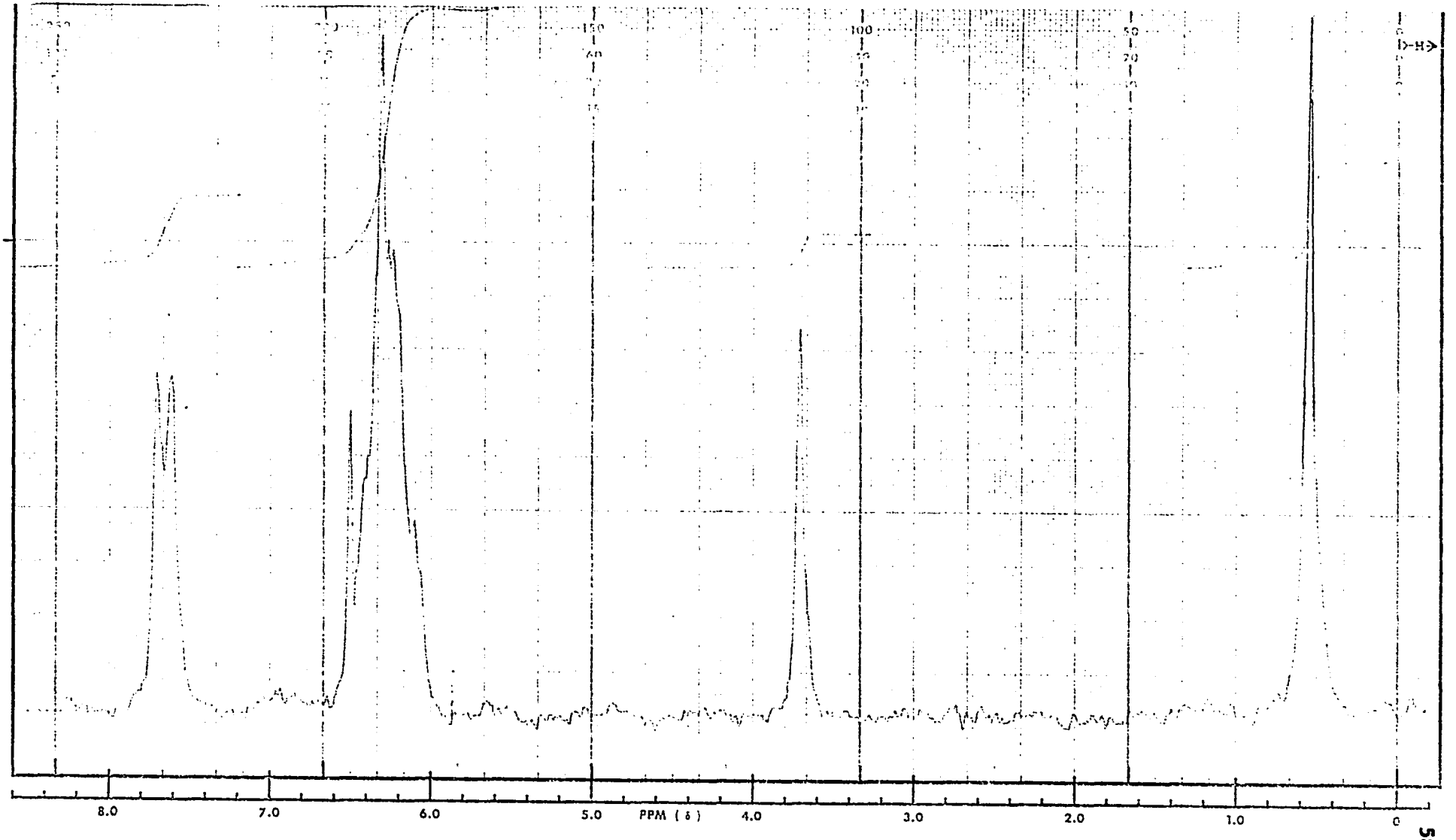


Fig. 5 NMR Spectrum of cis-trans-cis-1,3-di-4-pyridyl-2,4-diphenyl-2,4-dimethylcyclobutane (70).

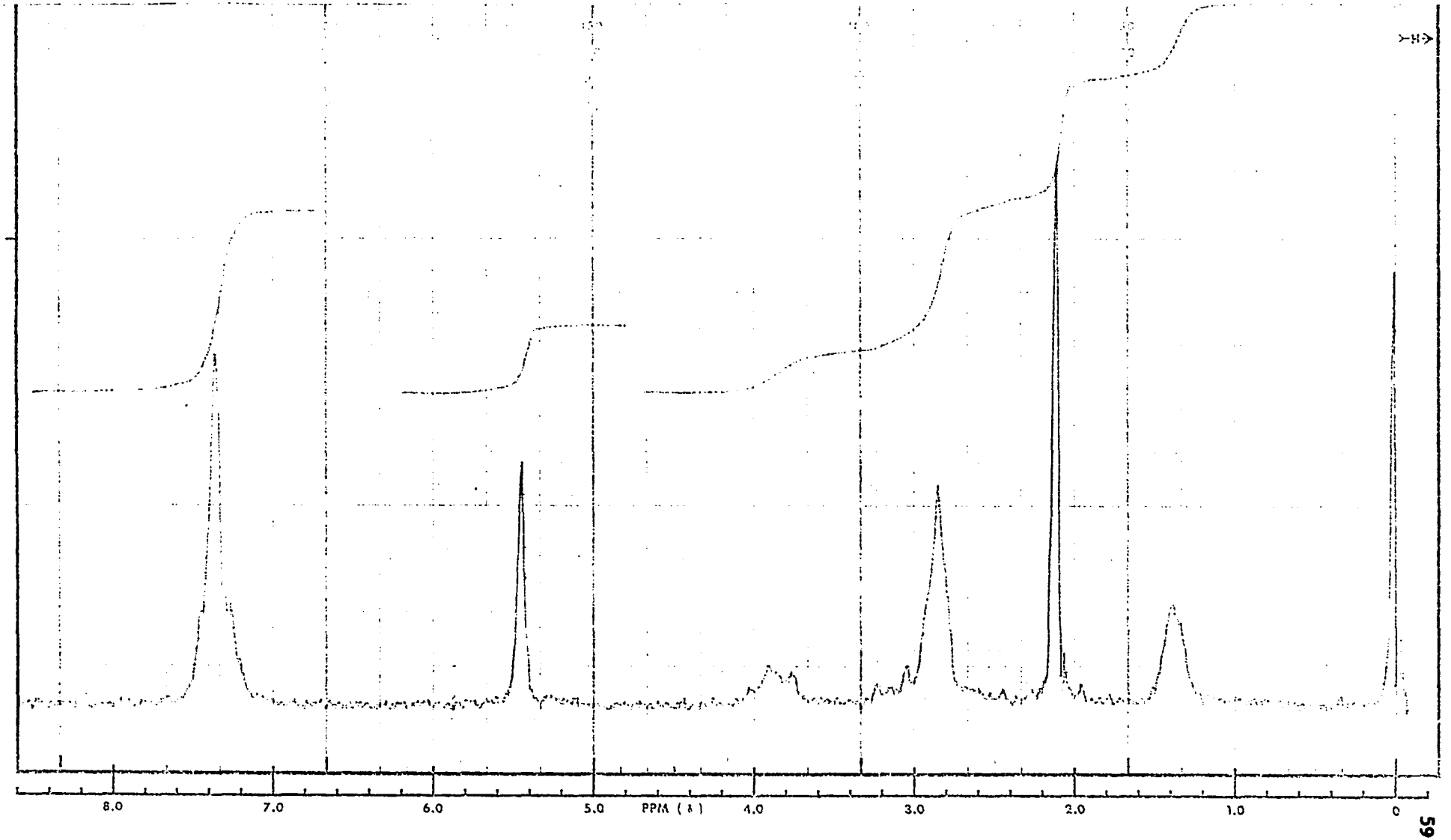


Fig. 6 NMR Spectrum of cis-trans-cis-1,3-di-2-(1-methyl-1,4,5,6-tetrahydropyridyl)-2,4-diphenylcyclobutane (74).

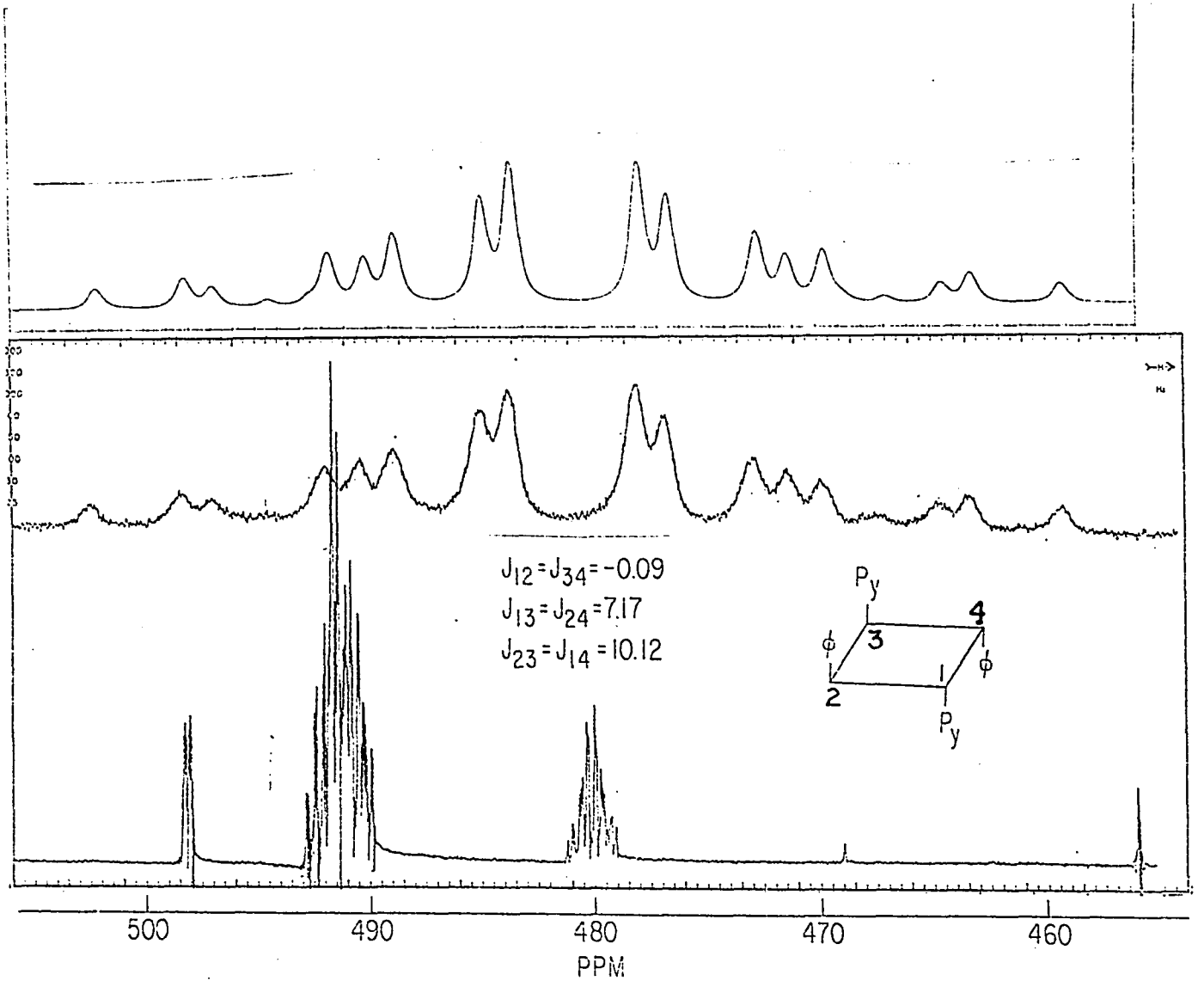


Fig. 7 NMR Spectrum and Computer Simulation of 2-Styrylpyridine Dimer (31).

Appendix II

^{13}C Spectra

The ^{13}C spectra of Williams' dimers 31 and 32 along with the tabulized data are reproduced on the following pages.

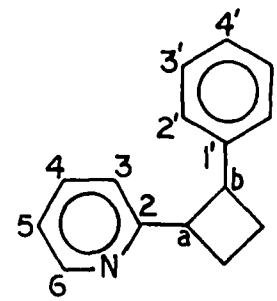
The data for the higher melting isomer 31 showed that the pyridyl rings were identical (a single value for each 2,3,4,5 and 6 position) and the phenyl rings were identical (a single value for each 1', 2', 3' and 4' position). Also there were two kinds of cyclobutane carbons. However, more than one structure can be drawn to satisfy this evidence.

The data for the lower melting isomer 32 showed identical pyridyl rings but nonidentical phenyl rings (two separate 1', 2', 3' and 4' positions). Two identical and two nonidentical aliphatic carbons also were evident. Only cis-cis-trans-1,3-di-2-pyridyl-2,4-diphenylcyclobutane satisfies these requirements.

Table 6

^{13}C Chemical Shifts of Dimers 31 and 32.[a]

Position[b]	31	33	2-Picoline[33]	Toluene[41]
2	160.4	159.8	C-2 159.9	
6	149.1	149.0	C-6 149.8	
1'		144.1		
	140.8	138.1*		C-1 137.4
4	135.6	135.5	C-4 137.2	
3'		130.0		
	128.3**	128.4		C-3 128.6
2'	128.0**	127.1		C-2 127.8
		127.0		
4'		126.3*		
	126.0	125.4*		C-4 125.6
3	123.6	122.4	C-3 123.4	
5	121.0	120.7	C-5 122.0	
a	49.0	49.6		
b		49.4*		
	45.8	43.4*		



a) PPM downfield from TMS; all peaks represent two carbon atoms except *one and **four.

b) Refer to figure at lower right.

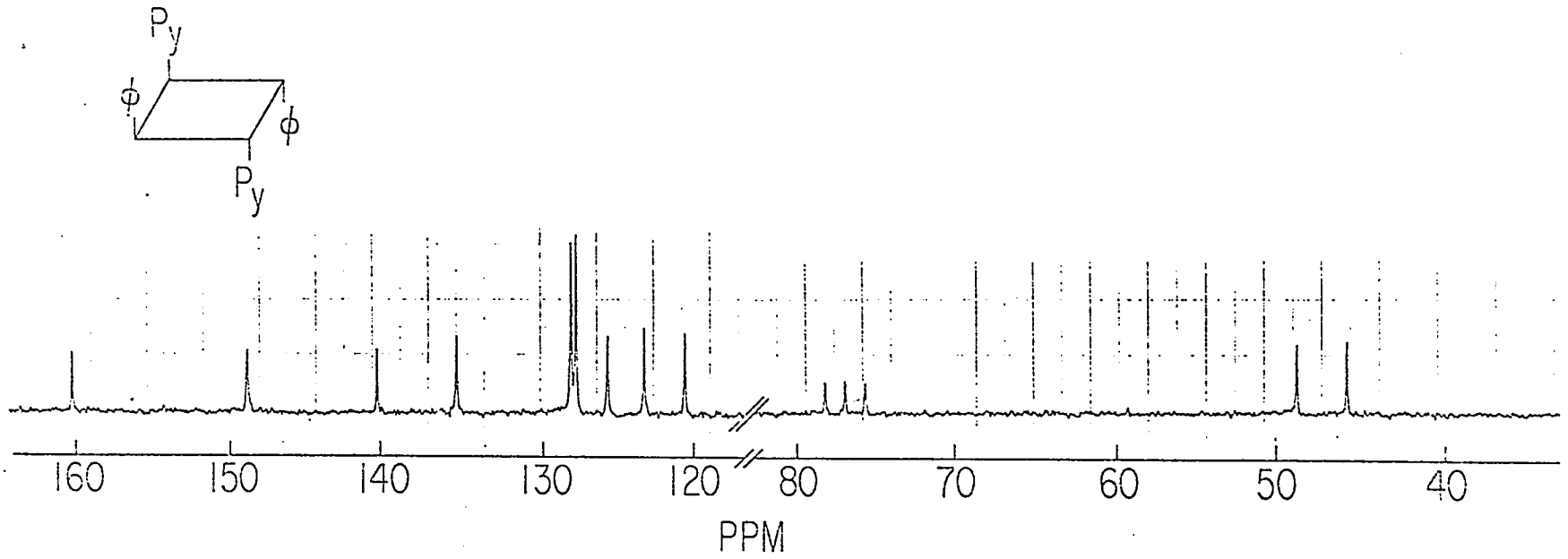
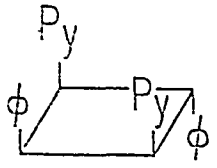


Fig. 8 ^{13}C **Spectrum of 2-Styrylpyridine Dimer (31).**



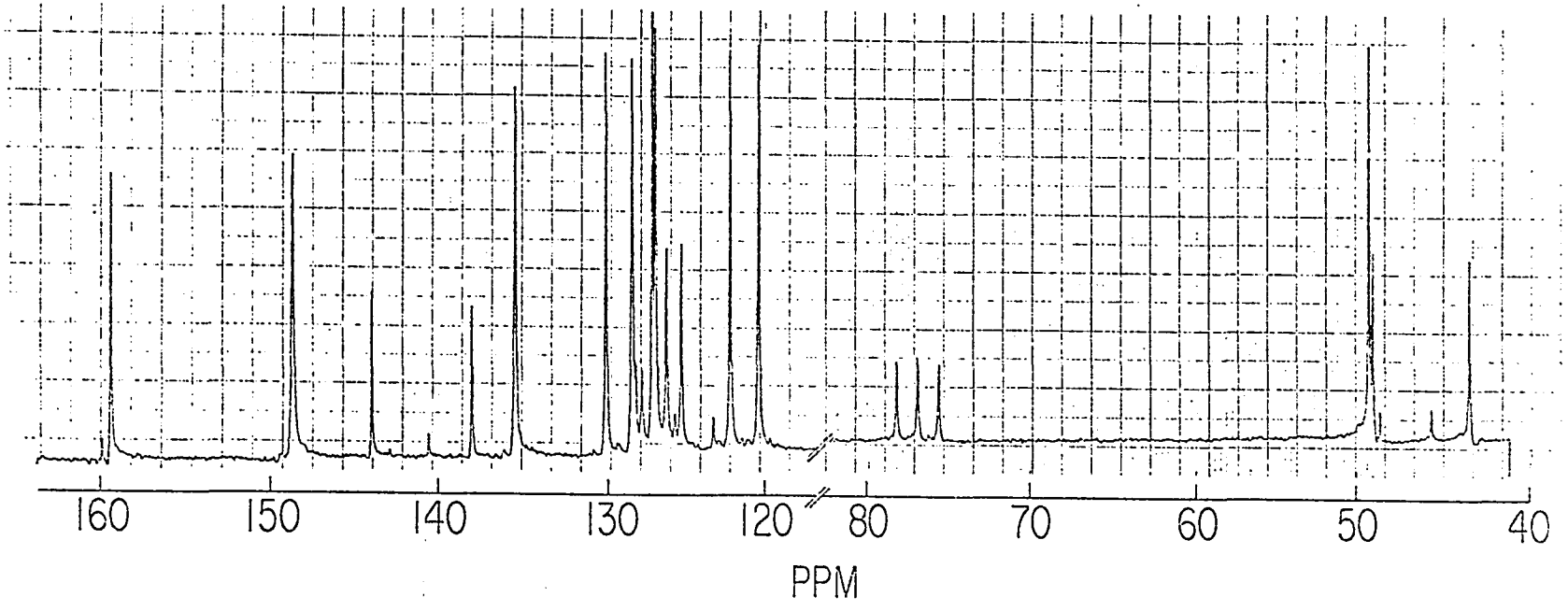


Fig. 9 ^{13}C **Spectrum of 2-Styrylpyridine Dimer (32).**

Appendix III

Mass Spectra

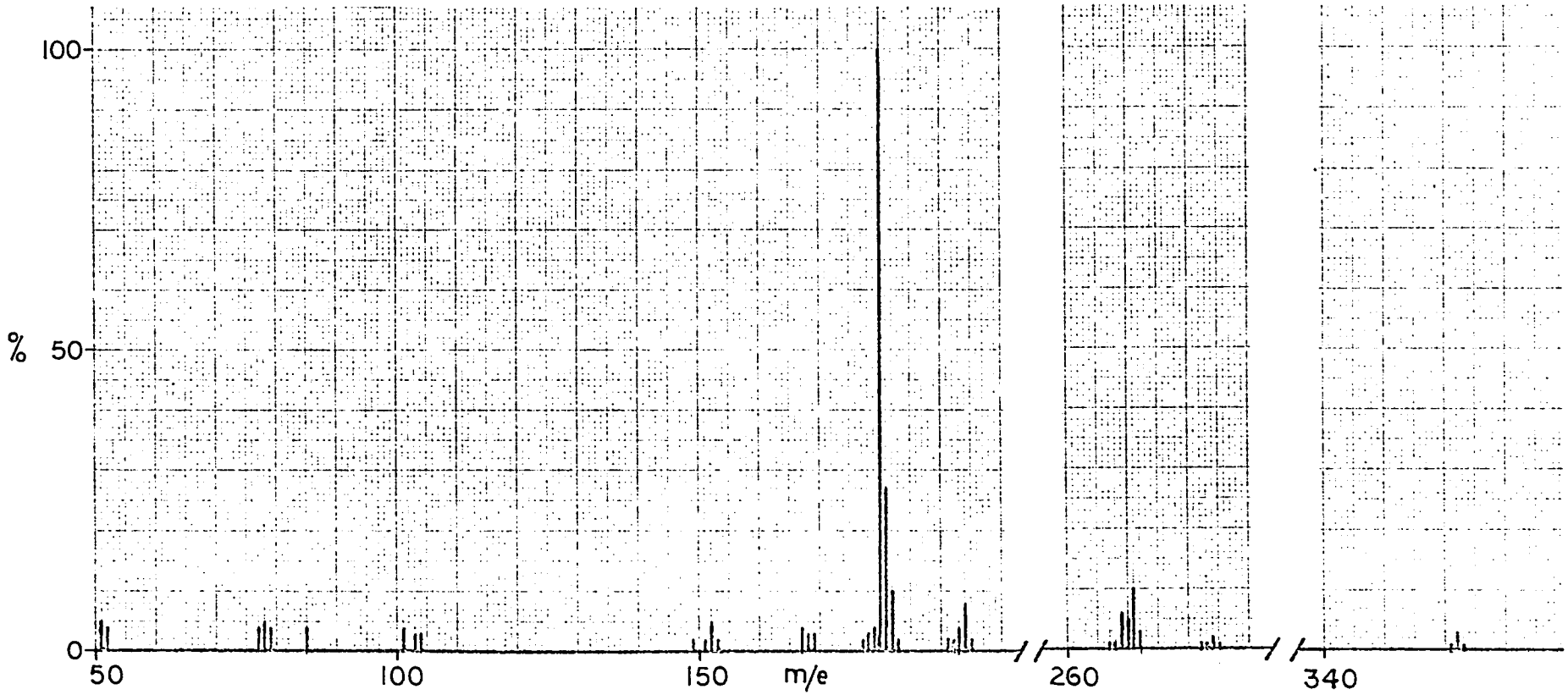


Fig. 10 Mass Spectrum of 2-Styrylpyridine Dimer (32).

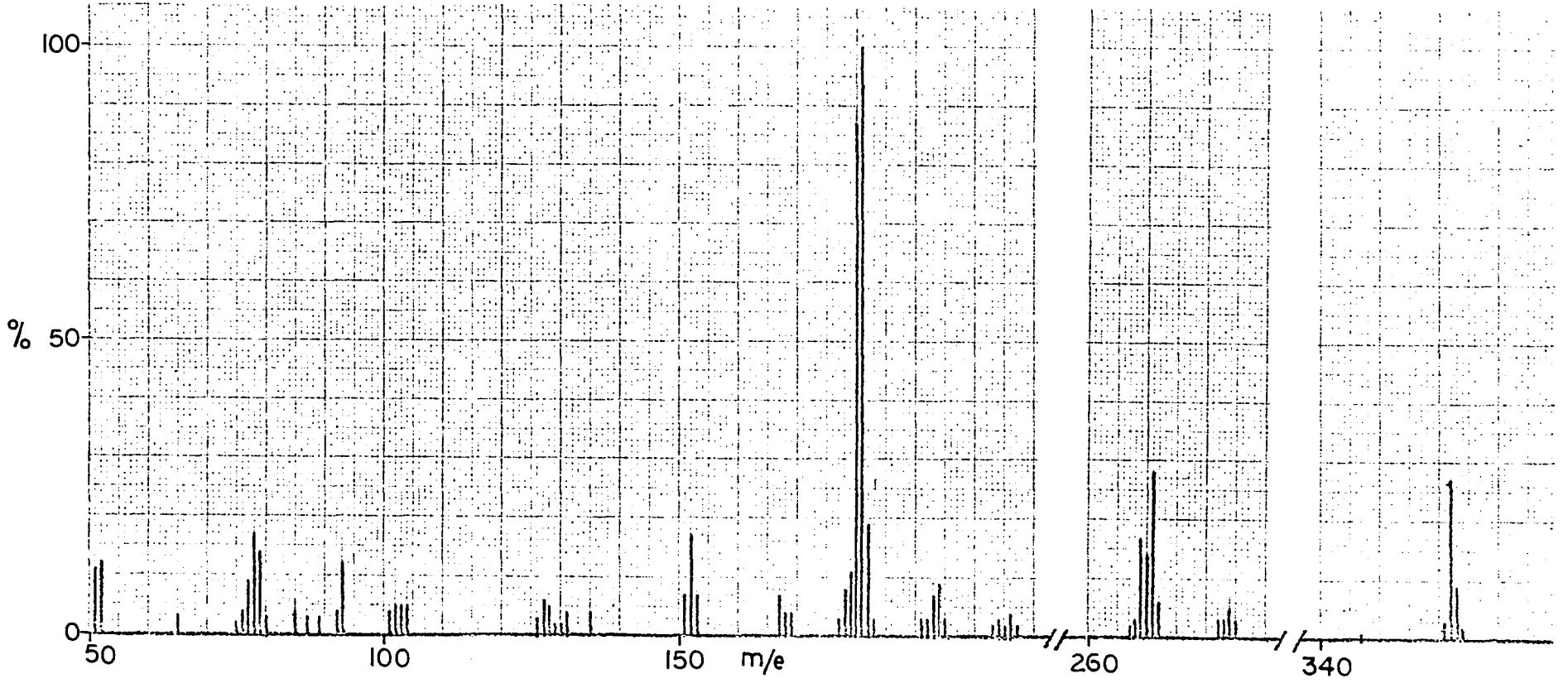


Fig. 11 Mass Spectrum of 2-Styrylpyridine Dimer (31).

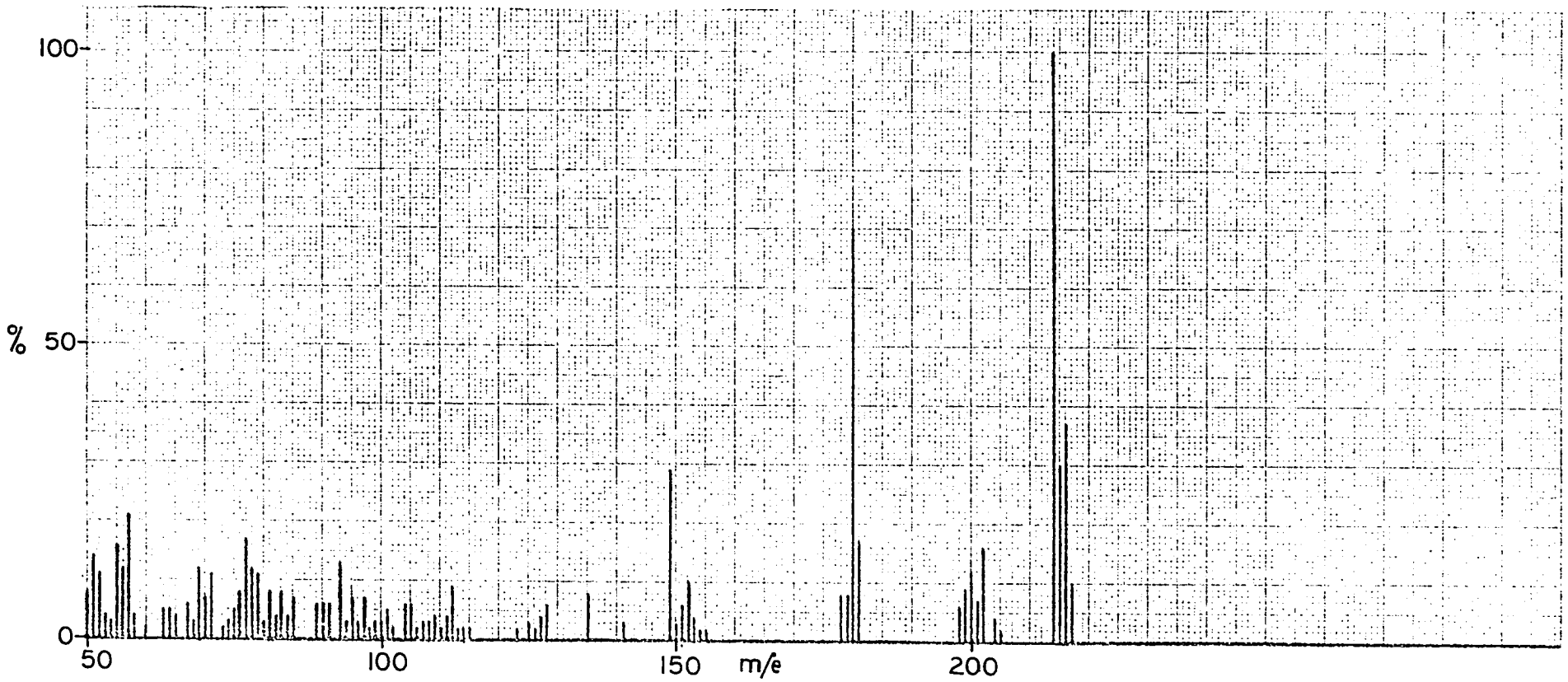


Fig. 12 Mass Spectrum of Dimer 63.

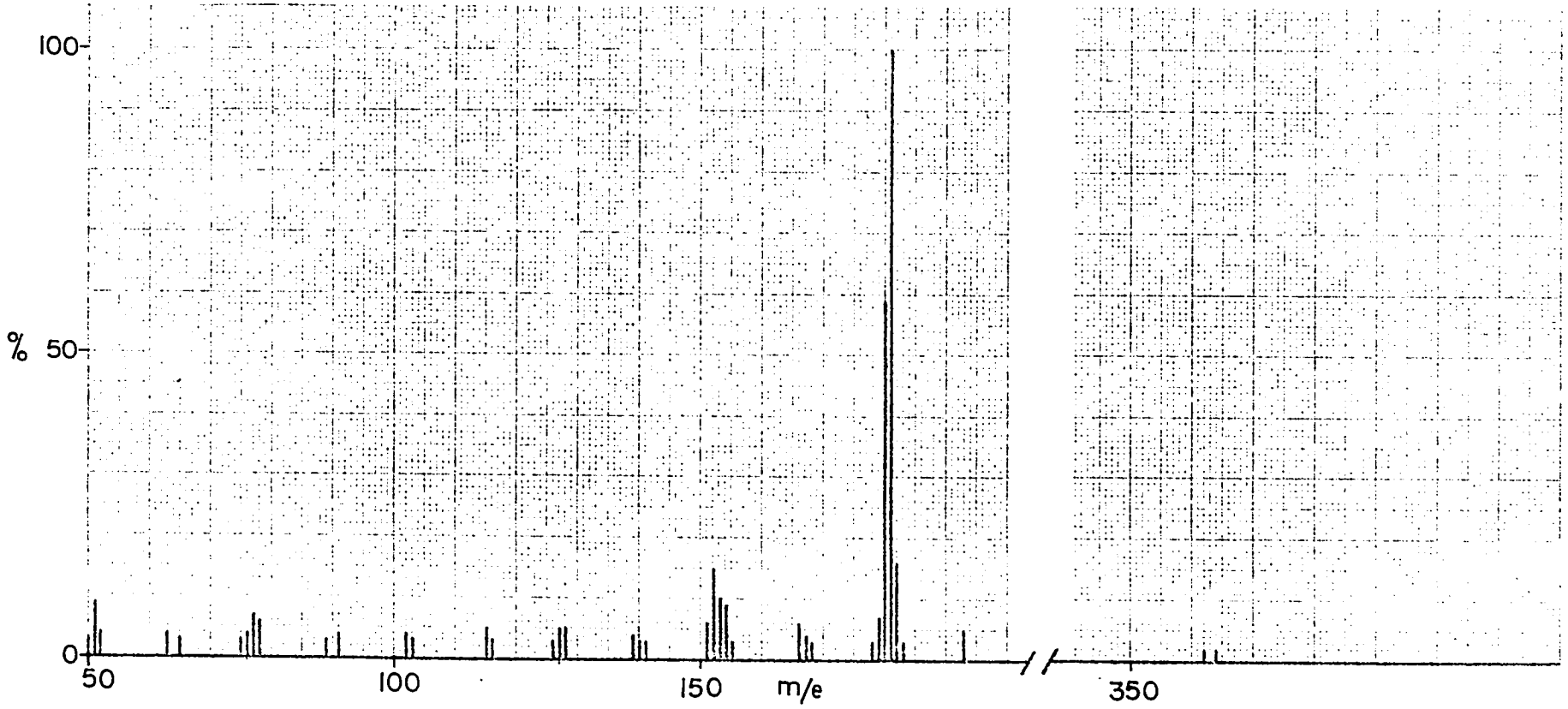


Fig. 13 Mass Spectrum of Dimer 65.

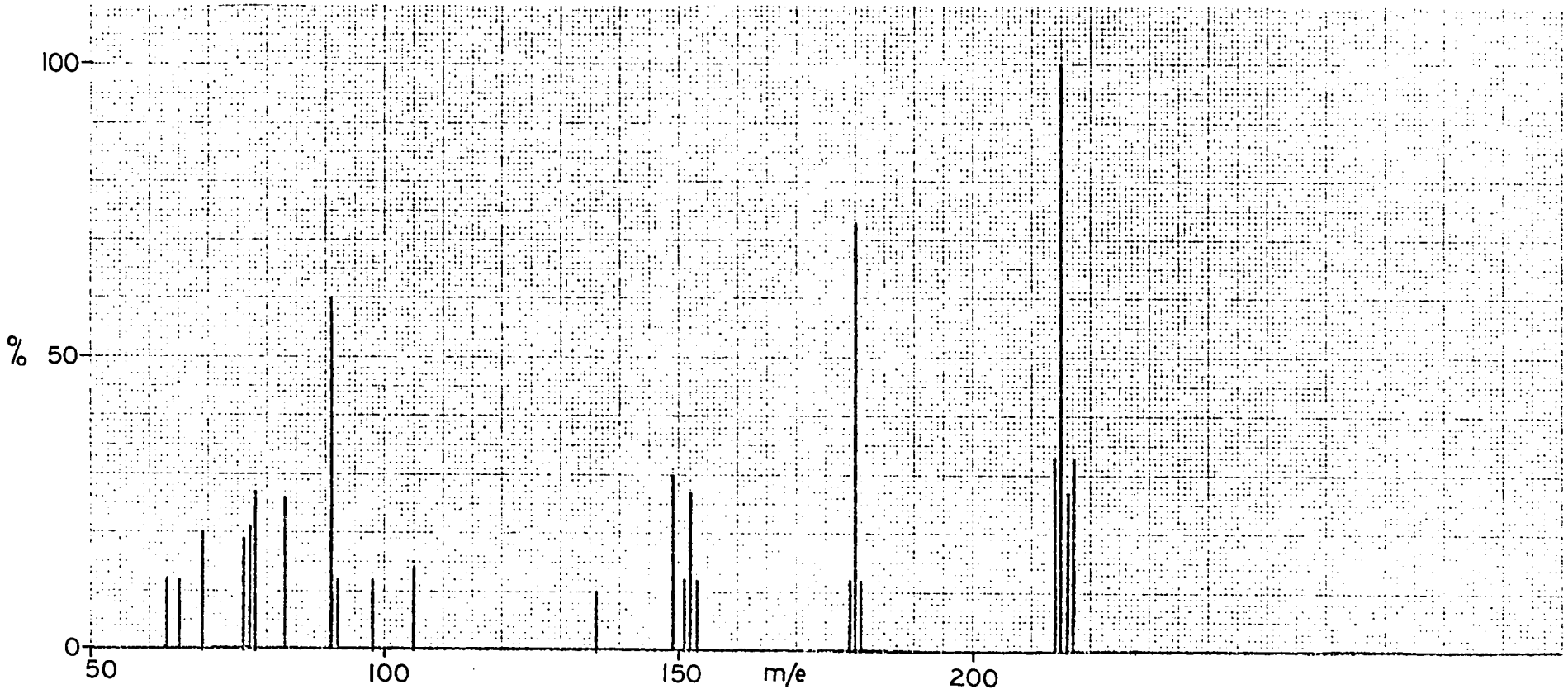


Fig. 14 Mass Spectrum of Dimer 67.

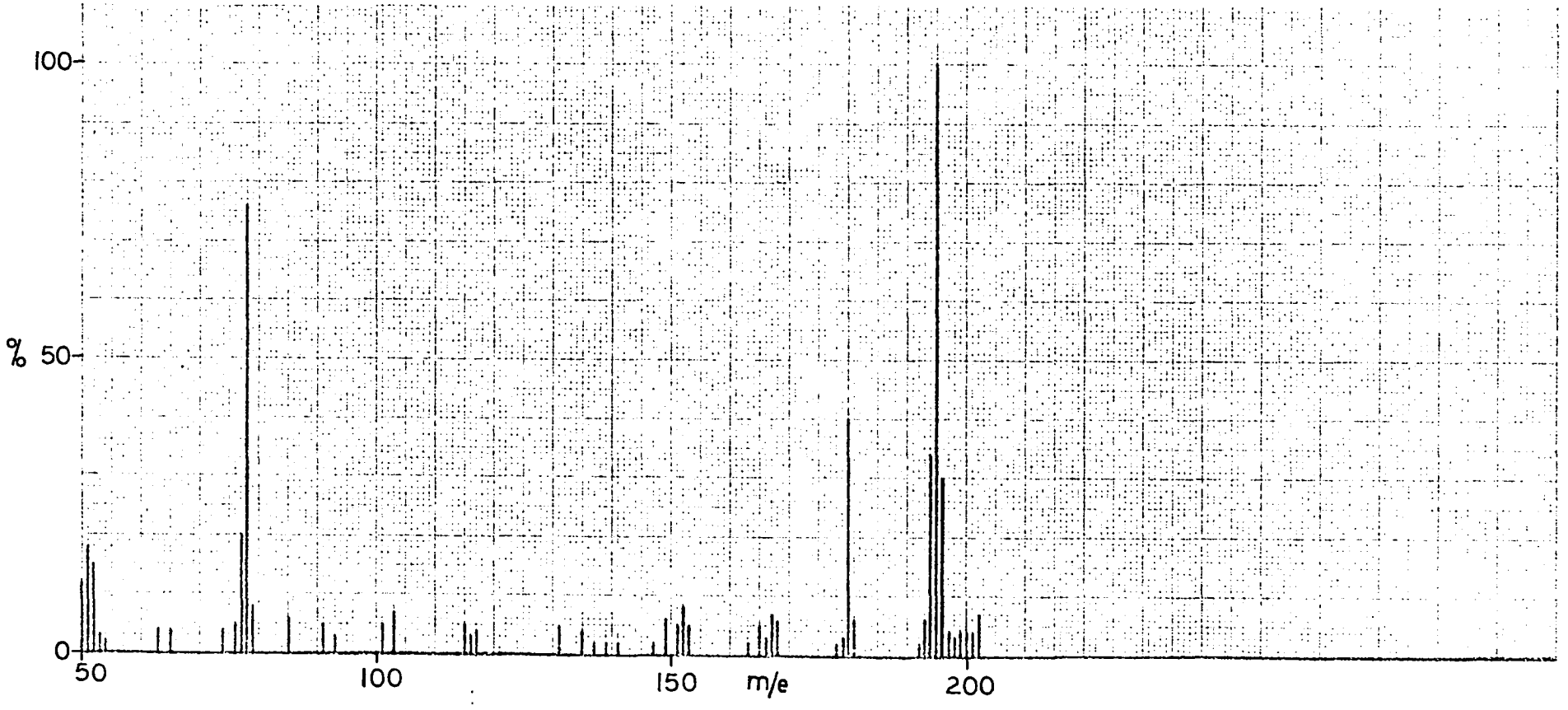
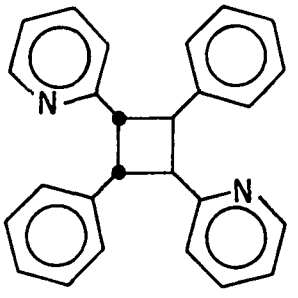


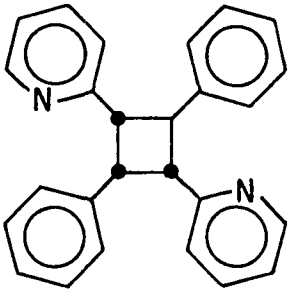
Fig. 15 Mass Spectrum of Dimer 70.

SUMMARY

The cyclobutane dimer derived from the solid state photolysis and subsequent pyrolysis of 2-styrylpyridinium methiodide (29) was shown by a computer aided examination of the nmr spectrum to be cis-trans-cis-1,3-di-2-pyridyl-2,4-diphenylcyclobutane (31). The pyrolysis step caused isomerization to a second dimer, present in about a 1:1 ratio with 31. This product was shown by an analysis of the ^{13}C spectrum to be cis-cis-trans-1,3-di-2-pyridyl-2,4-diphenylcyclobutane (32).



31



32

An indication of 31 among the products obtained from the pyrolysis of the methiodide of 32 showed that this step was reversible. Chemical evidence of the head-to-tail arrangement of 31 was gained by the recovery of only 2-styrylpyridine after heating.

A series of 2- and 4-styrylpyridines, 1,2-bis-(2-pyridyl) ethylene (50), and 1,2-bis-(4-pyridyl)ethylene (51) were dimerized using a variety of photolysis conditions. In each case the product was shown to have the head-to-tail and cis-trans-cis orientation of 31,

as indicated by the mass spectra and nmr spectra.

The product specificity was explained by the molecular complex model of Abernethy and Cavallito which relies on the attractive forces between aromatic rings to orient the monomer units prior to dimerization. This model was advanced as a possible explanation for the resistance of some compounds toward photodimerization.

Various chemical methods failed to convert the dimers to dicarboxydiphenylcyclobutanes. These methods concentrated on the opening and the oxidative cleavage of the pyridyl ring.

All of the dimers produced were stable, crystalline, easily workable materials. The 2-styrylpyridine dimers displayed a multiplet for the cyclobutane protons in the nmr spectra at approximately 5.2 τ and could be analyzed. The 4-styrylpyridine dimers, however, displayed only a singlet for the cyclobutane protons at a somewhat higher τ value. The mass spectrum of every dimer showed a fragmentation pattern typical of a cyclobutane system.

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