ABSTRACT

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<u>SYNTHESIS OF A NEW SULFUR POLYMER</u>

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Thesis dated May 1977

A new sulfur polymer has been synthesized which may be related to 1,3,6,7-tetraphenylacenaphtho[5,6-cd]thiopyran. The structure of this heteropolymer was not elucidated. The polymer had a glass transition temperature of 348°.

SYNTHESIS OF A NEW SULFUR POLYMER

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R = iv   T = 40

ACKNOWLEDGEMENTS

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INTRODUCTION

A new class of tetravalent sulfur heterocycles has been
described which were synthesized from derivatives of naphtha-
lene.[1] 1,3,6,7-Tetraphenylacenaphtho[5,6-cd]thiopyran has
been prepared by the reaction of 1,4,5,8-tetrabenzoylnaphtha-
lene with phosphorus pentasulfide at 100° for two hours.[2]
This same synthetic scheme can be accomplished with pyrene
as the starting material.[3]

The aim of this research was to prepare a ladder polymer
by cycloaddition polymerization of 1,3,6,7-tetraphenylaceto-
naphtho[5,6-cd]thiopyran. Ladder polymers are defined as
those consisting of an uninterrupted series of rings connected
by links around which rotation can only occur by bond breaking.
For perfect ladder polymers, the chain can only be broken if
at least two bonds on the same ring are broken.[4] Thus, ladder
polymers should have far greater thermal stability. Dif-
ferential Scanning Calorimetry (DSC) was used to study this
interesting polymer system.

Pyrene as an Aromatic Hydrocarbon

A comprehensive review of pyrene and its derivatives has been outlined by Vollmann et al.[3] and Josephy and Radt.[5] Vollman, Becker, Correll and Steeck have outlined the method of synthesizing the derivatives of pyrene.[3] From these works, a schematic outline of the synthesis of 1,3,6,7-tetraphenyl-acenaphtho[5,6-cd]thiopyran, VII, from pyrene is given below:
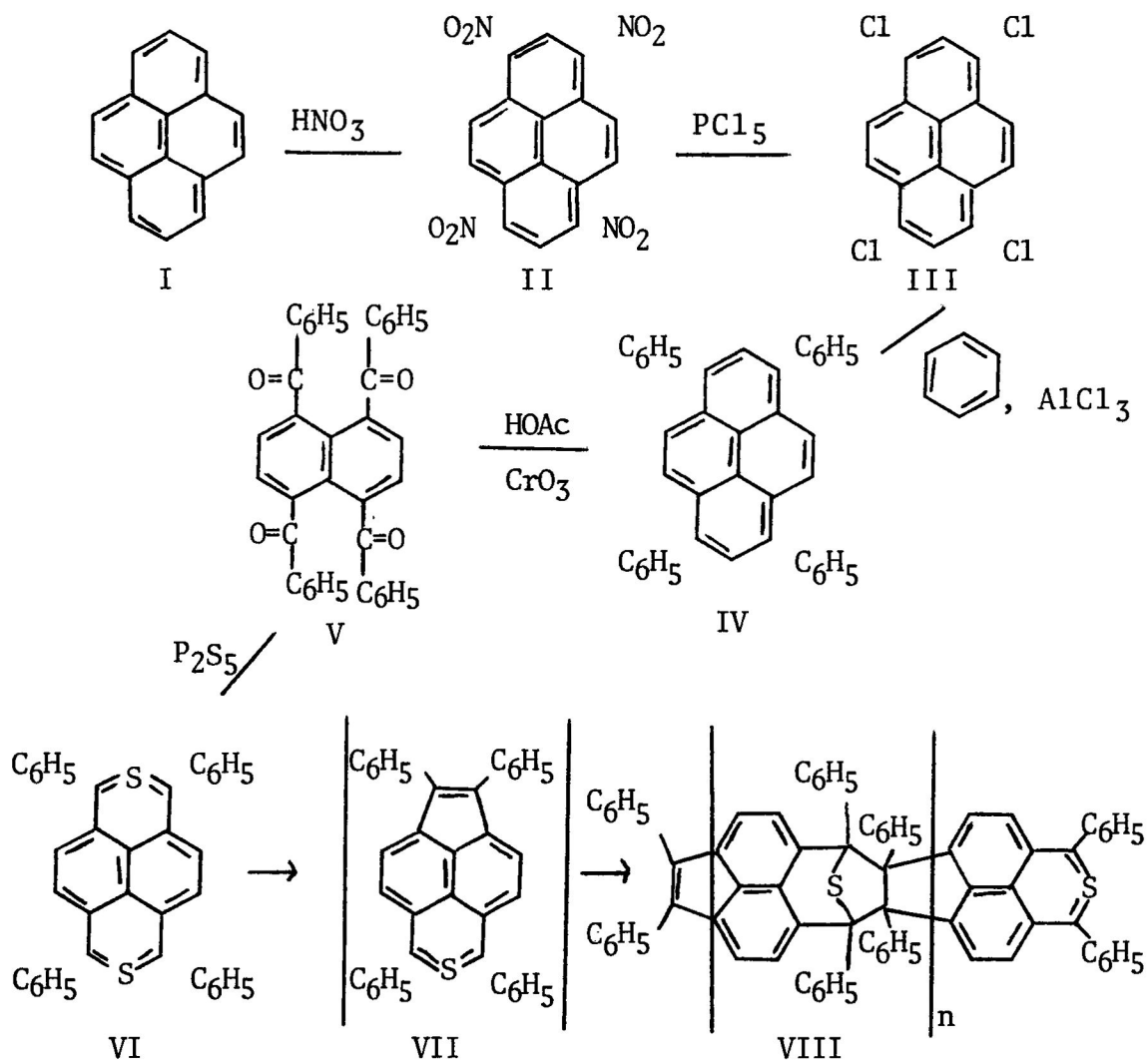
According to Perturbation Molecular Orbital (PMO) theory, pyrene is aromatic, though it contains 16 electrons (4n electrons). It can be seen that pyrene is an even ring system with (4n + 2) atoms in each ring. From the analysis given by Dewar,[6] all four rings are aromatic since each contains six atoms.

Dewar has also developed a speedier method that gives satisfactory results in predicting the position of substitution on an aromatic species. Here, he employs the coefficients of the non-bonding molecular orbital of the σ-complex, which works only for odd-alternant cations (and anions).[7]

Reactivity numbers for substitution in alternant hydrocarbons in the pyrene system are given below.
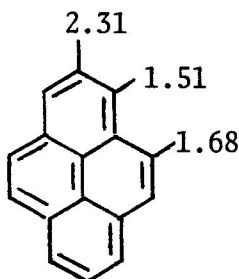
Predictions made from data agree qualitatively with experiment in all cases, in the sense that substitution always occurs preferentially at the position where the reactivity number is least.[7]

Earlier, Dewar et al. had calculated the partial rate

factors for interaction at various positions in different hydrocarbons. From those calculations, pyrene can be easily nitrated at position one with a partial rate factor of 17,000.[8]

From the above review, pyrene seems to be a good starting material for the preparation of the polymer as indicated in the synthetic outline.

The Tetravalency of Sulfur

In this treatment, use is made of the simple and more pictorial valence-bond resonance description of the structure and properties of 1,3,6,7-tetraphenylacenaphtho[5,6-cd]thiopyran (IX) which shows a structural similarity to thiophene.

IX
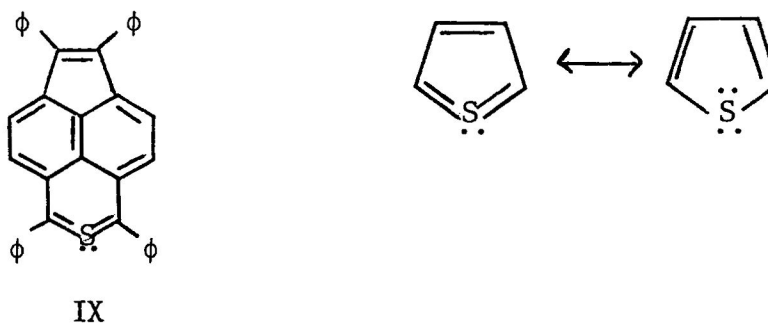
With thiophenes, one can envisage contributions from canonical forms, as indicated below.[9]
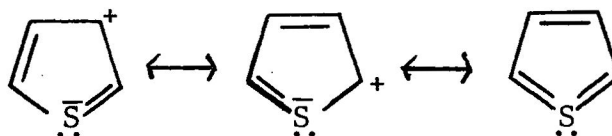
The stability of these tetravalent sulfur heterocycles can be attributed to several factors:

(1) Sulfur has a larger bonding radius which allows C-C-C bond angles to widen a little, thus allowing some gain in stability by losing a little angle-compression strain.

(2) Trivalent sulfur tolerates a positive change better than analogous ether oxygen in furan, so that polarized canonical forms contribute more to the resonance hybrid, with a corresponding increase in resonance stabilization energy.

(3) Sulfur, being a second-row element, can use the 3d orbitals for bonding, which means that in bond-resonance terms, one can envisage contributions from the canonical forms as indicated with thiophene.

Since the 3d orbitals in sulfur are unoccupied, the bonding electrons must come from the 2p orbitals on the attached C, O, or other atom to the vacant 3d orbital on sulfur. A 2p-3d π bond is then formed as indicated in Figure 1. The formation of this π bond has been suggested to explain conjugative effects attributed to many sulfur compounds.[10]

Conjugative Effects

Chemical and physical evidence clearly support the concept that sulfide sulfur, unlike analogous ether oxygen, can readily and effectively participate in the resonance stabilization of

A 2p-2p π bond

A 2p-3p π bond

A 2p-3d π bond
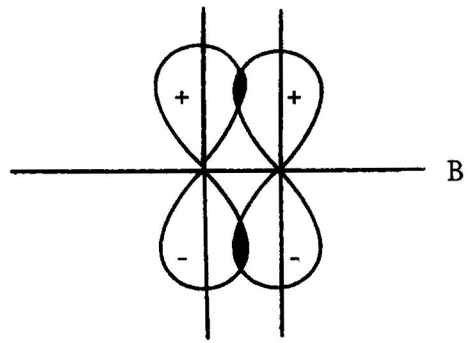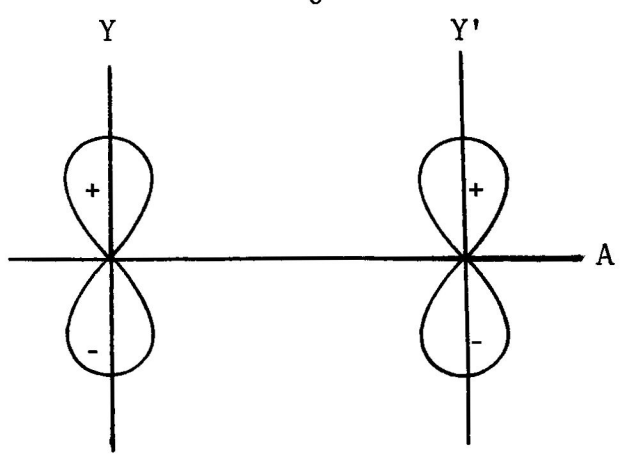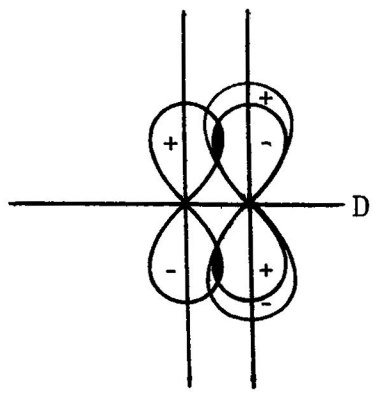
Fig. 1. π Bond overlap.

electron-deficient centers (such as carbonium ions), free
radical centers with an odd unshared electron, and electron
rich centers (such as carbanions).[11] The three major types
of resonance stabilization are:

$$-\overset{+}{\underset{|}{C}}-\overset{..}{\underset{..}{S}}- \quad \longleftrightarrow \quad -\underset{|}{C}=\overset{+}{\underset{..}{S}}- \qquad \begin{array}{l}\text{Carbonium Ion}\\ \quad\text{Electron-releasing}\end{array}$$

$$-\overset{.}{\underset{|}{C}}-\overset{..}{\underset{..}{S}}- \quad \longleftrightarrow \quad -\underset{|}{C}=\overset{.}{\underset{..}{S}}- \qquad \begin{array}{l}\text{Carbon Free Radical}\\ \quad\text{Electron-pairing}\end{array}$$
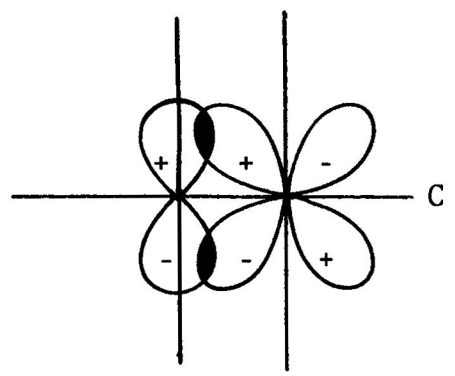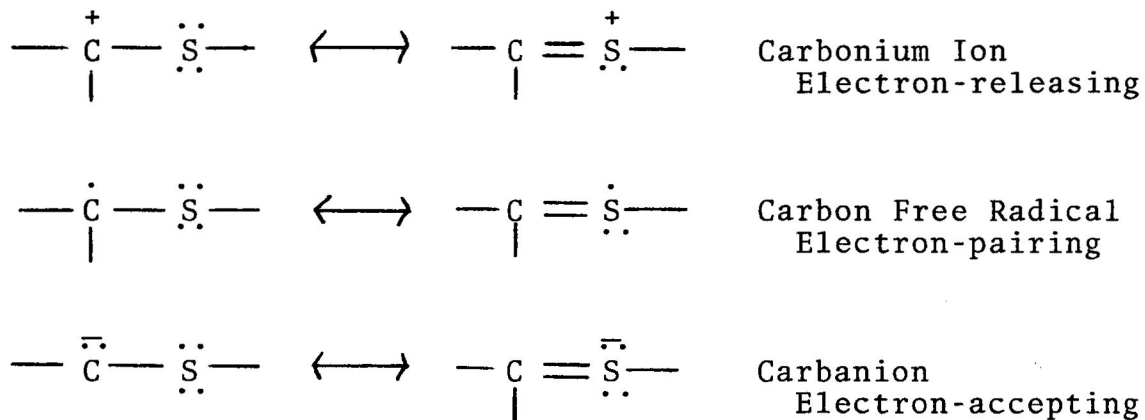
$$-\overset{\bar{.}}{\underset{..}{C}}-\overset{..}{S}- \quad \longleftrightarrow \quad -\underset{|}{C}=\overset{\bar{.}}{\underset{..}{S}}- \qquad \begin{array}{l}\text{Carbanion}\\ \quad\text{Electron-accepting}\end{array}$$

The last two contributions are involved in the expansion of
the sulfur valence shell. In the structure contributing to
the stabilization of the free radical and to the carbanion,
the sulfur atom has expanded the number of electrons in the
outer valence shell from eight to nine and ten respectively.

Sulfur atoms not only display electron-releasing but also
electron-accepting conjugative effects because of the vacant
3d orbitals on sulfur. In the cases of furan and thiophene,
their observed interatomic distances are C-O = 1.41 Å and
C-S = 1.74 Å as against the sums of single covalent radii,
i.e., C-O = 1.44 Å, C-S = 1.81 Å. These correspond, with

consideration of the electric charge effect, to about 8% total

contribution of the structures X and XI for furan and 28% for

thiophene.[11]
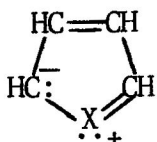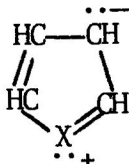
X   XI   XII

Thermochemical data for furan and thiophene also give the

values 19 or 23 kcal/mole and 29 or 31 kcal/mole, respectively,

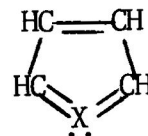for the resonance energy of these two heterocycles. This data

favors stronger conjugation of sulfur in the thiophene ring

than that of oxygen in the furan ring.[11] Thus, in thiophene,

not only the structures of X and XI contribute by the electron-

pair-releasing conjugation of sulfur, but also structures of

the type illustrated by XII. Here the sulfur atom expands its

valence shell from an octet to a decet. A similar phenomenon

occurs in 1,3,6,7-tetraphenylacenaphtho[5,6-cd]thiopyran.

Diels-Alder Polymerization

A polymerization reaction which utilizes a Diels-Alder

propagation to produce a high molecular weight polymer can pro-

ceed either by the reaction of a dienophile with a diene or

by self-reaction of a molecule which contains both a diene portion and a dienophile portion.[15] This is a cycloaddition reaction that involves the combination of two π systems to form a molecule containing at least one more ring, two more σ bonds, and two fewer π bonds than the original arrangement.[16]
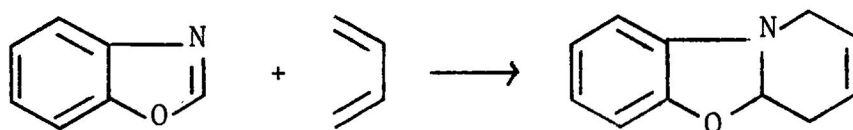
XIII
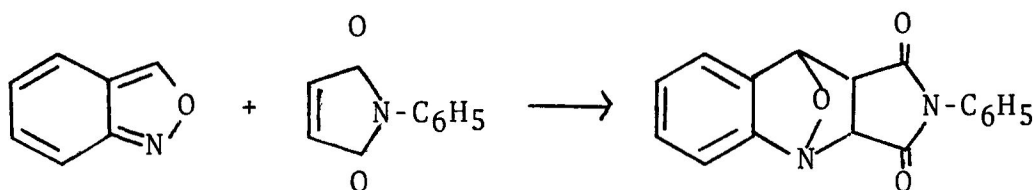
XIV

Such a polymerization reaction is catalyzed neither by ion nor by radical sources, has propagation kinetics and mechanisms which are characteristic of condensation polymerization, but yields structures which cannot be considered characteristic of condensation polymers.[17]

The reaction of a substituted cyclopentadienone with a bis-maleimide produces an adduct which loses carbon monoxide at elevated temperatures to yield a diene-dienophile monomer, XV, which is not isolated, but immediately polymerizes to form

a high molecular weight polymer, XVII.[14]
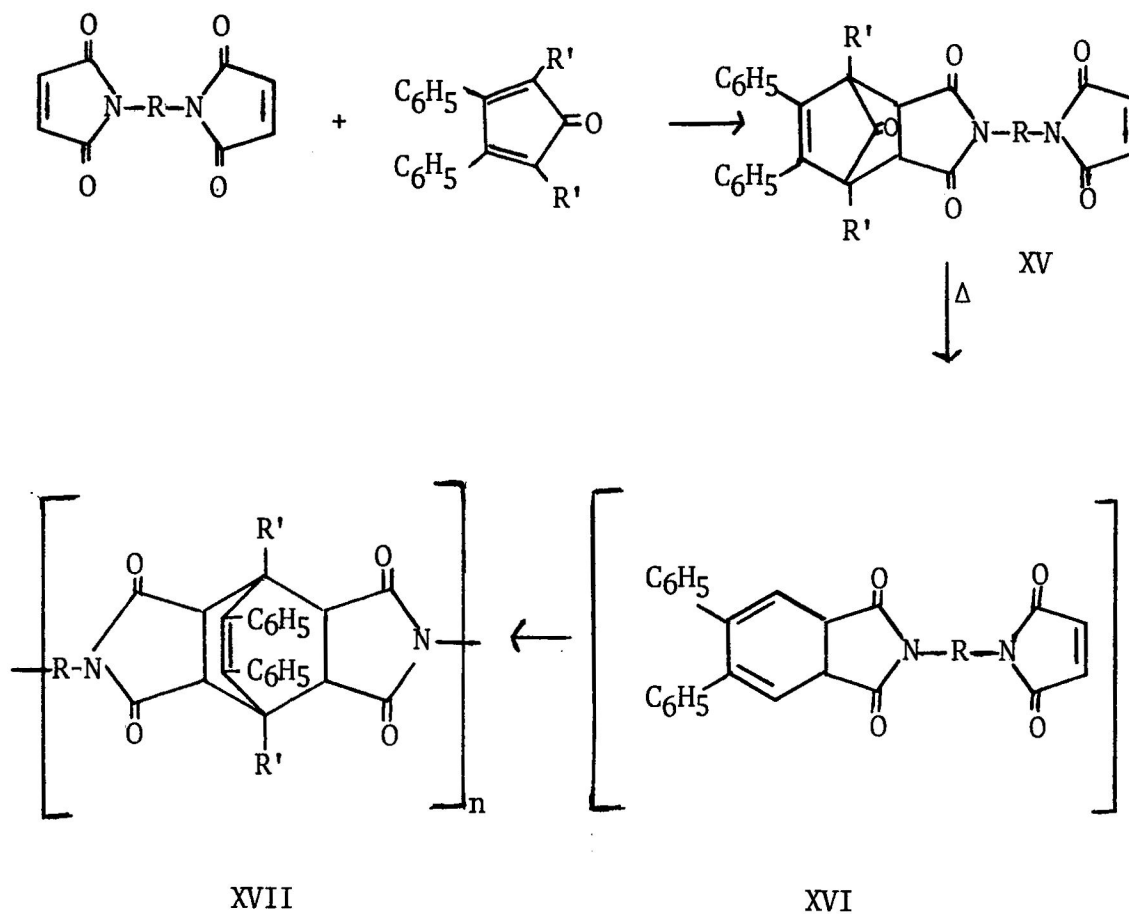
The reaction of 6,7-dibromo-1,3-diphenylacenaphtho[5,6-cd]-thiopyran (XVIII) with N-phenylmaleimide in degassed benzene solution at 80° gave rise to an adduct, XIX, in 70% yield.[1b]
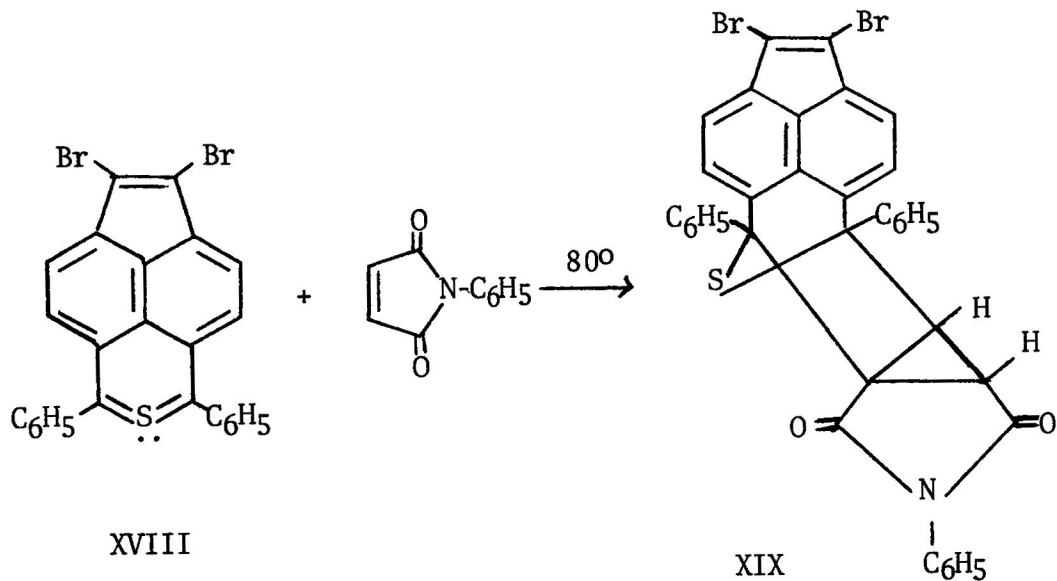
Here the sulfur heterocycle is the diene. It has also been noted that when 6,7-dibromo-1,3-diphenylacenaphtho[5,6-cd]-thiopyran was heated above its melting point (130°), a polymer was obtained.

This tetravalent sulfur heterocycle (XVIII), a diene-dieno-phile monomer, is related to 1,3,6,7-tetraphenylacenaphtho[5,6-cd]thiopyran (XX).
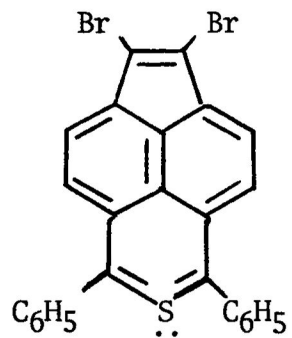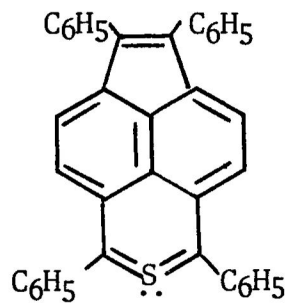
XVIII   XX

We, therefore, proposed to demonstrate the polymerization of 1,3,6,7-tetraphenylacenaphtho[5,6-cd]thiopyran by 1,3-cyclo-addition polymerization.

A classical method of synthesizing thiophenes is the reaction of 1,4-dicarbonyl compounds with inorganic sulfides.[15] Hoffman and Schlessinger[2] have shown that when the peri-substituted diketone, 1,8-dibenzoylnaphthalene (XXI), is treated with phosphorus pentasulfide, 1,2-diphenylacenaphthylene (XXIV) is formed in high yield. This reaction was thought to proceed through the reactive tetravalent sulfur heterocycle, 1,3-diphenylnaphtho[1,8-cd]thiopyran (XXII), which was known to undergo facile thermal extrusion of sulfur to give XXIV.

| XXI | XXII | XXIII | XXIV |
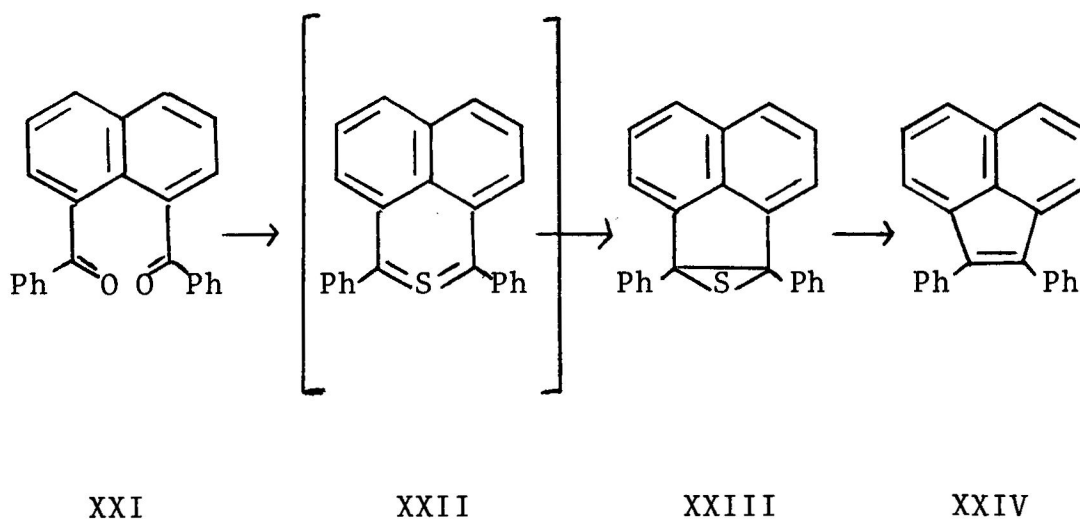
The preparation of 1,3,6,7-tetraphenylacenaphtho[5,6-cd]-thiophran (VII) appears to proceed through the initial formation of 1,3,6,8-tetraphenyl-2,7-dithiopyrene. Facile thermal extrusion of one sulfur atom from VI gives VII. Structures VI and VII contain (4n + 2) π electrons which may be delocal-

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ized in a number of resonance forms. The favorable electronic configurations account for their stability.

$$V \qquad\qquad VI \qquad\qquad VII$$
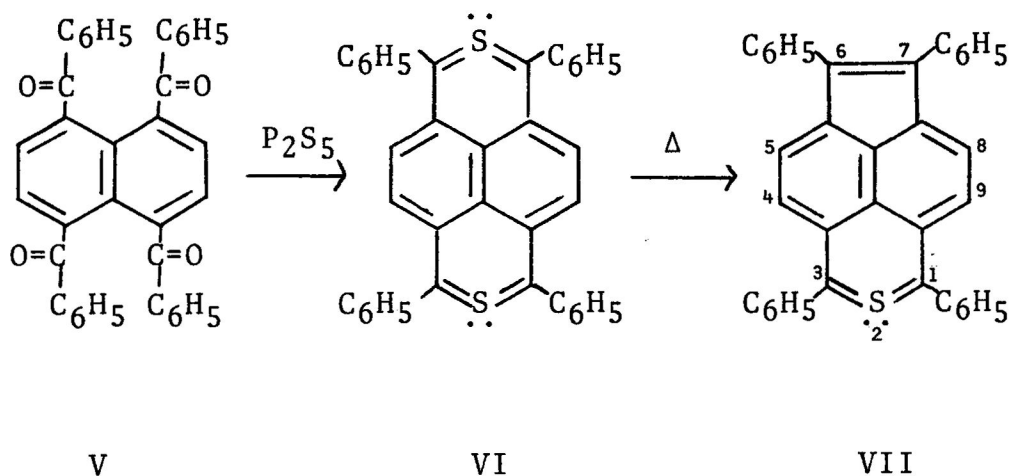
The mass spectrum of the product of the reaction of 1,4,5,8-tetrabenzoylnaphthalene with P_2S_5 gave the molecular ion peak m/e 544 which corresponds to the molecular weight of 1,3,6,8-tetraphenyl-2,7-dithiopyrene (VI). A characteristic cluster of ions at m/e 76, 77 and 78 may be attributed to phenyl cleavage. The stability of 1,3,6,8-tetraphenyl-2,7-dithiopyrene (VI) is reflected by the m/e 236 peak which is characteristic of the 2,7-dithiopyrene ion. The infrared spectrum of the product also showed the C=S band at 1100 cm^{-1}.

The mechanism of the formation of the hetero-polymer from 1,3,6,8-tetraphenyl-2,7-dithiopyrene (VI) would be expected to involve the intermediacy of 1,3,6,7-tetraphenylacenaphtho-[5,6-cd]thiopyran (VII).

$$C_6H_5 \overset{\cdot\cdot}{\underset{}{S}} C_6H_5$$

m/e 544

+ e⁻ →

+ 2e⁻

m/e 121

-CS·

m/e 44

m/e 77
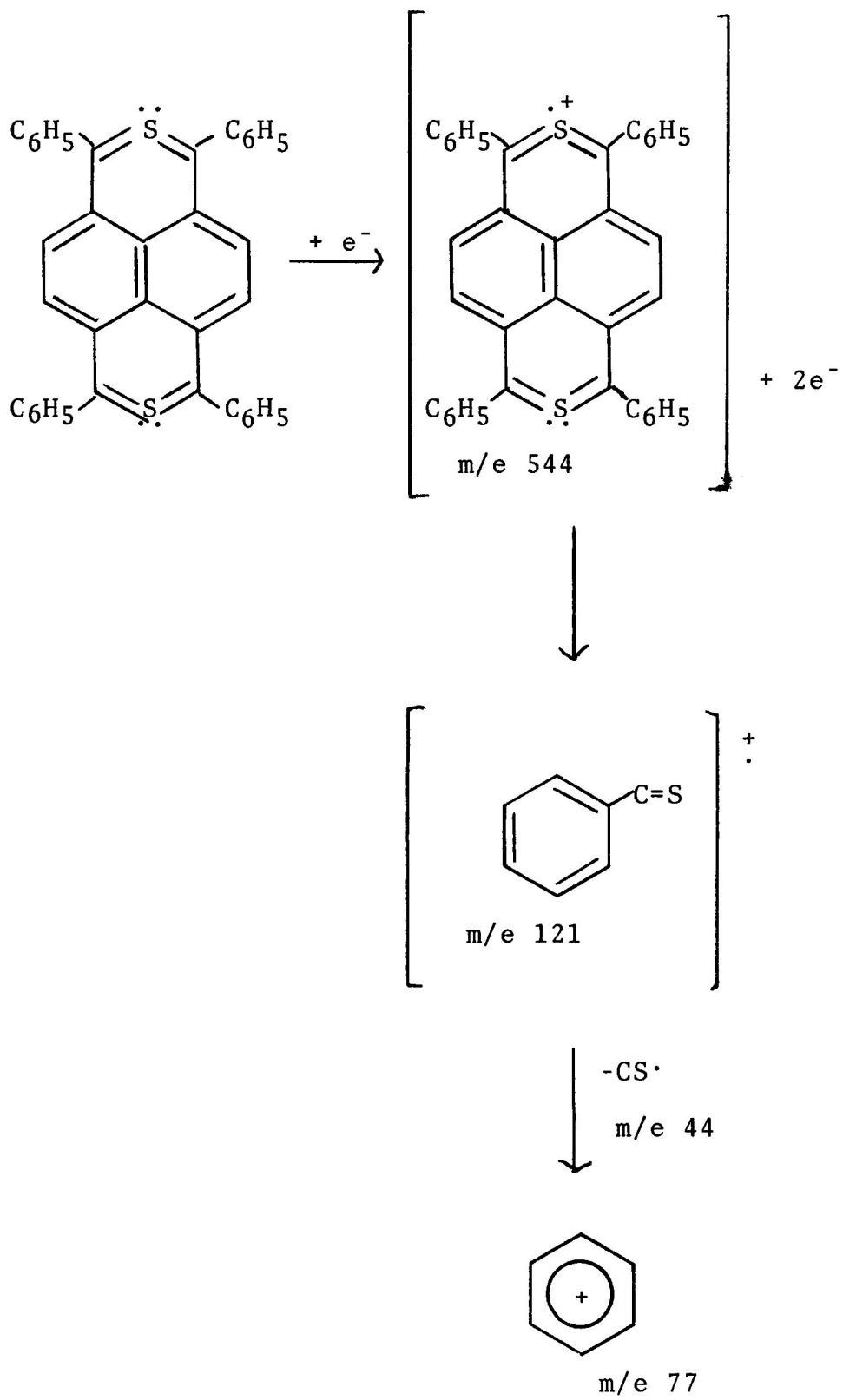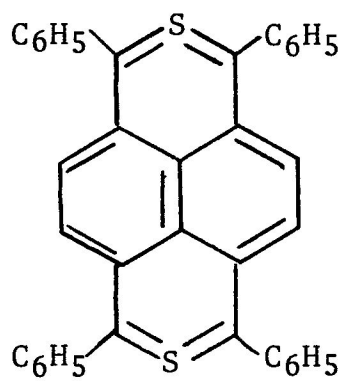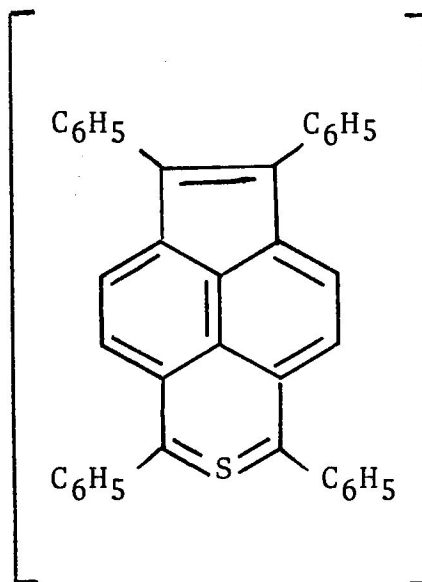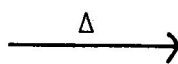
VI   VII
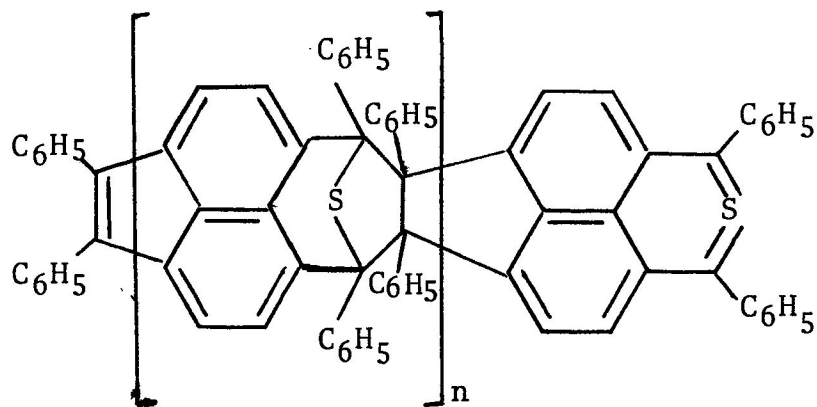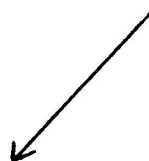
VIII

The heterocycle VII is a diene-dienophile intermediate which may polymerize to VIII. Similar polymers have been prepared by Ponticello and Schlessinger[1] but were not characterized. This heteropolymer had an infrared spectrum with a C-S absorption band at 605 cm^{-1}.

The disappearance of the C=S bands at 1100 and 1025 cm^{-1} in the infrared spectrum of the polymer and subsequent appearance of the C-S band at 605 cm^{-1} indicates the formation of a polymer which may be related to the polymer of the thiopyran derivative. The infrared spectrum of tetrahydrothiopyran shows the C-S peak at 665 cm^{-1}.[16]

The polymer was examined by differential scanning calorimetry. The thermogram of the amorphous polymer is shown in Figure 2. The physical transition represented here is the glass transition. This involves the motion of the short-chain segments in the amorphous region and is related to the brittleness of the polymer. The deflection near 345° represents the glass transition temperature of the polymer. A similar thermogram had been obtained for poly(ethylene terephthalate)[17] as indicated in Figure 3.

1,3,6,7-Tetraphenylacenaphtho[5,6-cd]thiopyran (VII) is a diene-dienphile monomer that can polymerize by 1,3-cyclo-addition. Huisgen has proposed a concerted mechanism for such reactions as the addition of diphenyldiazomethane to ethyl acrylate in dimethylformamide.[18] According to Molecular Orbital (MO) theory, the 1,3 dipolar intermediates contain

Fig. 2. The thermogram of the polymer of 1,3,6,8-tetra-
phenyl-2,7-dithiopyrene (glass transition tem-
perature, 348°).
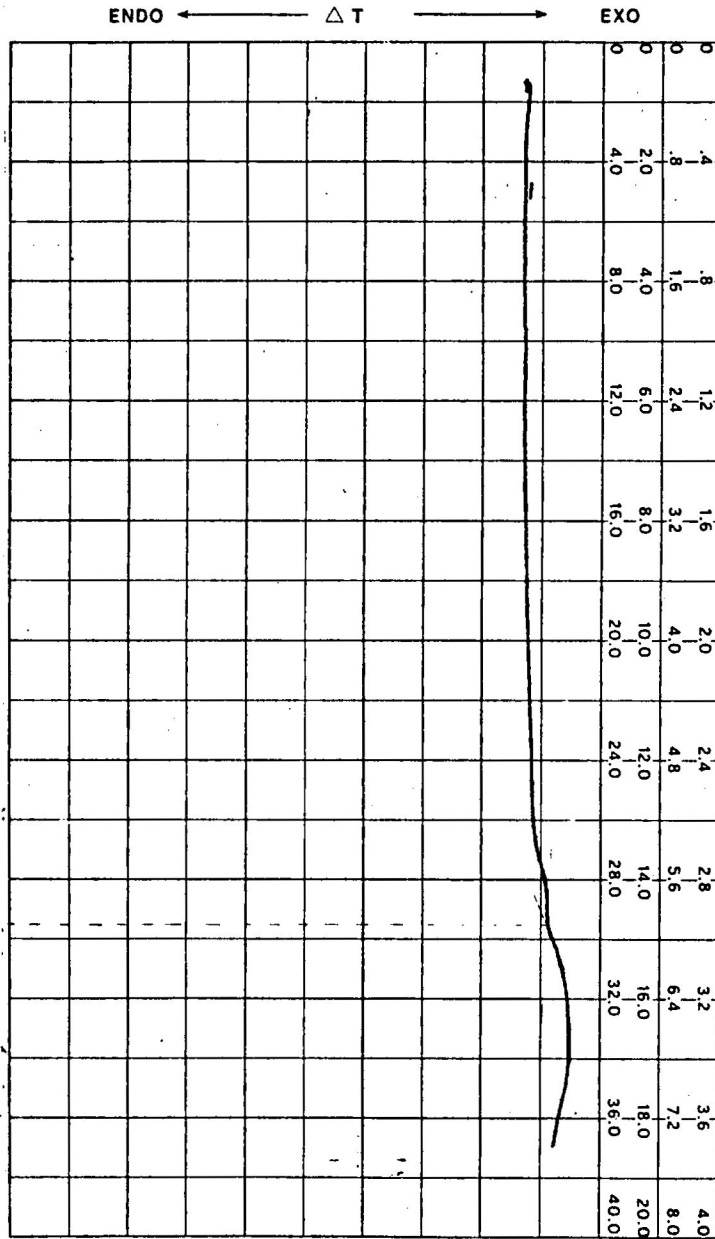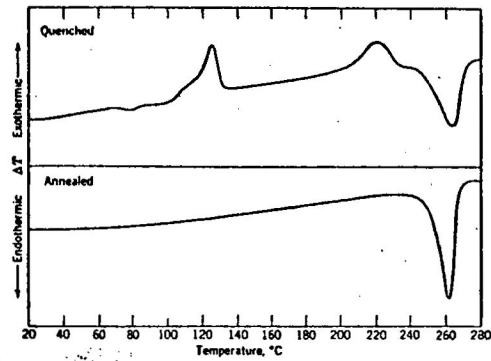
Thermograms of poly(ethylene terephthalate) (9).
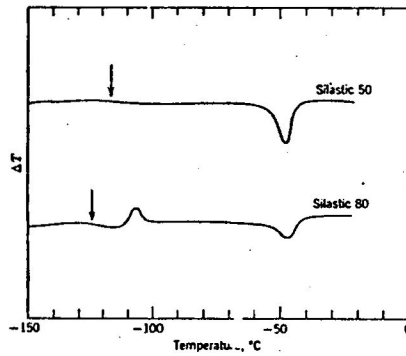
Thermograms of commercial polysiloxanes (30).

Fig. 3. The thermogram for the quenched poly(ethylene terephthalate) (glass transition temperature, 70°), compared to commercial polysiloxanes.[17]

four π electrons in three parallel p orbitals. As in the
iso-electronic allyl anion, the four electrons occupy pair-
wise the two lowest molecular orbitals. Figure 4 illustrates
this for one dipole of each class (with and without a double
bond in the 1,3 sextet structure). This allyl anion-like
structure is responsible for the ability of the 1,3 dipole
to undergo (4 + 2) π cycloadditions.

The "two-planes" orientation complex of Figure 5 indicates
that (4 + 2) π electrons are involved in the cycloaddition
process exactly as in the Diels-Alder reaction. The symmetry
considerations with the correlation diagrams reveal that the
concerted thermal cycloaddition is allowed.

The polymerization of 1,3,6,7-tetraphenylacenaphtho[5,6-cd]-
thiopyran should follow a similar mechanistic pathway as
described for the addition of diphenyldiazomethane to ethyl
acrylate. It should be a 1,3 cycloaddition that follows the
pattern shown in Figure 5.

4 π electrons

4 π

C₆H₅

N—methyl—C—phenylnitrone

(a)

(b)
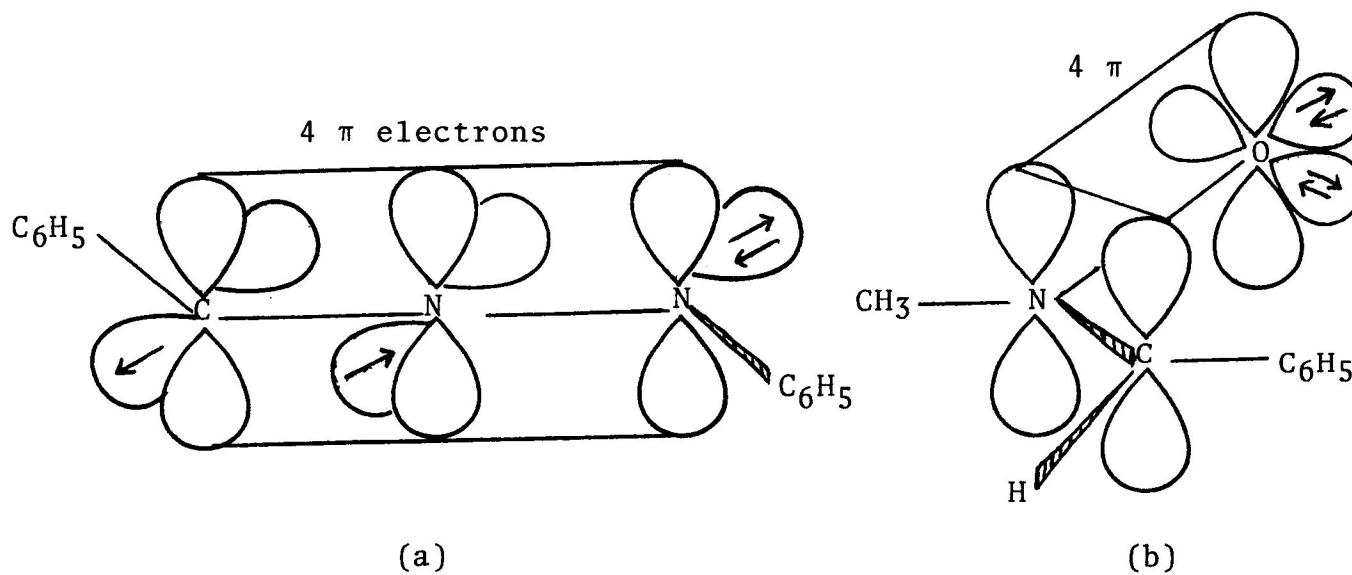
Fig. 4. 4 π Electron system in 1,3 sextet structure in (a) diphenylnitrilimine, and (b) N-methyl-C-phenylnitrone.
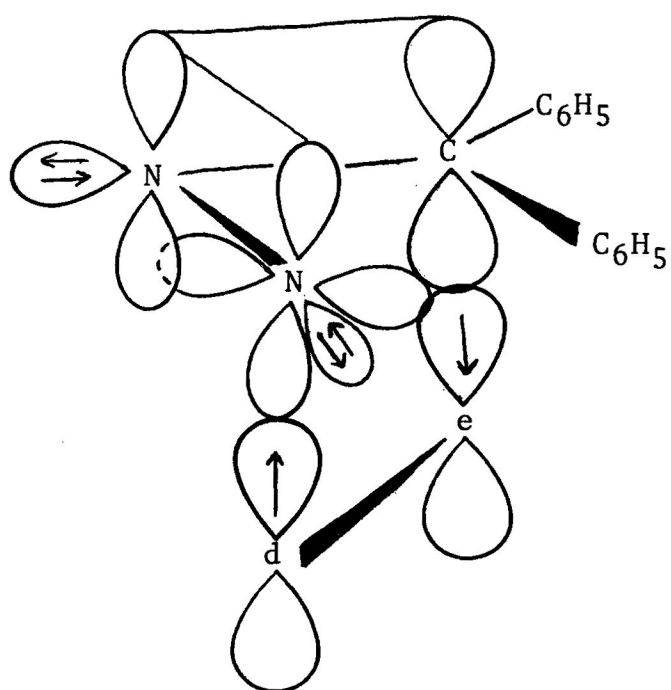
Fig. 5. Electronic pathway of 1,3-dipolar cycloaddition of diphenyldiazomethane to a dipolarophile (d-e).

EXPERIMENTAL

A Beckman Infrared 4240 Spectrophotometer was used to record infrared (ir) spectra. All spectra were obtained on potassium bromide (KBr) pellets. Only the most important absorption bands in the spectrum are listed. Standard infrared texts were used in the interpretation of the spectra.[19] The following abbreviations are used for ir spectra: s = strong, b = broad, w = weak and m = medium.

Melting points were determined using a Thomas-Hoover melting point apparatus and are uncorrected.

Ultraviolet (uv) spectra were measured using a Cary 17 Spectrophotometer. Mass spectra were run with a DuPont 21-490 Mass Spectrometer.

The DuPont 900 Differential Scanning Calorimeter (DSC) was used to study the enthalpy changes associated with the polymer system.

3,5,8,10-Tetranitropyrene (II).--The method followed was that described by Vollmann et al.[3] Pyrene from Eastman Kodak, Rochester was used. To 500 ml of concentrated nitric acid (specific gravity 1.5) were gradually added, while stirring under reflux, 150 g (0.74 m) of powdered pyrene. The reaction was allowed to continue for 2 hr. After cooling to room temperature, the yellow amorphous crystals were filtered by

suction, washed thoroughly 2 times with glacial acetic acid, and then 2 times with ethyl alcohol. The crystals were allowed to dry for 2 days at room temperature. The 3,5,8,10-tetranitropyrene melted at $310-315^\circ$ (lit.[3] mp 332°). The yield was 82.2 g (54.8%) of the crude product. The major ir peaks appeared at 3100 (m), 1600 (s), 1525 (s), 1350 (b,s) and 850 (s) cm^{-1}.

3,5,8,10-Tetrachloropyrene (III).--The method described by Vollmann et al.[3] was followed. Pulverized 3,5,8,10-tetranitropyrene (170.8 g, 0.447 m) was refluxed with 93.1 g (0.446 m) of phosphorus pentachloride for 2 hr in trichlorobenzene. The reaction was exothermic. The yellow amorphous crystals were collected and dried for 2 days at room temperature. The melting point of 3,5,8,10-tetrachloropyrene was $225-230^\circ$ (lit.[3] mp 226°). The yield was 133.2 g (78%) of the crude product. The major ir peaks were observed at 3020 (s), 1590 (m), 750 (s), and 710 (s) cm^{-1}.

3,5,8,10-Tetraphenylpyrene (IV).--The procedure employed here was that of Vollmann et al.[3], and modified as described by Thomas et al.[20] A fine suspension of 85 g (0.25 m) of pulverized 3,5,8,10-tetrachloropyrene was added to 1 liter of benzene (dried over calcium chloride) in a 3-liter 3-necked flask fitted with a stirrer and a reflux condenser. Another drying tube was placed at the top of the reflux condenser to exclude moisture. While stirring under reflux, 208 g (1.558 m)

of powdered anhydrous aluminum chloride were gradually added through a glass funnel. The glass funnel was removed and immediately the flask was corked with a rubber stopper carrying a thermometer.

To complete the reaction, the mixture was stirred for 1.5 hr at 70-75°. At 60°, the complex assumed a deep blue-black color. Purification of the complex to obtain the 3,5,8,10-tetraphenylpyrene was accomplished as follows: The complex was decomposed with water. There was no separation of excess benzene layer from the rest of the mixture when the complex was thus decomposed. The blue-black solid was washed with hot water. It was left to dry in a desiccator-drying tower overnight. The melting point of the crude product was 306-311° (lit.[3] mp 229-300°).

Attempts to crystallize purer crystals of 3,5,8,10-tetraphenylpyrene from chlorobenzene failed. The crude product was then used in the preparation of 1,4,5,8-tetrabenzoylnaphthalene. The ir spectrum of the crude 3,5,8,10-tetraphenylpyrene gave peaks at 3080 (m), 1595 (s), 1520 (s), and 1450 (w) cm^{-1}.

1,4,5,8-Tetrabenzoylnaphthalene (V).--The method described by Vollmann et al.[3] was followed. A 500 ml 3-neck round-bottomed flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel was supported on a heating mantle. In the flask was placed 1.0 g of 3,5,8,10-tetraphenylpyrene,

previously ground to a coarse powder, in 25 ml glacial acetic acid. The suspension was heated to 100° while stirring vigorously. At this temperature, a mixture of 3 g of chromic acid anhydride in 2.5 ml of warm water was added carefully to the reaction mixture from the dropping funnel. After a period of about 10-15 min, the 3,5,8,10-tetraphenylpyrene began to dissolve, the solution darkened and the temperature started to rise above 100°. Heating and stirring were continued throughout the addition of chromic acid anhydride until all the 3,5,8,10-tetraphenylpyrene dissolved. After a prolonged period of stirring, the oxidation product began to crystallize out. After 2.5 hr of stirring, the precipitate which separated was first washed with glacial acetic acid and then with ethyl alcohol. Crude product (0.53 g) melted above 300° (lit.[3] mp 373°). The yield was 50%. The ir spectrum showed peaks at 3060 (s), 1670 (s, b), and 1595 (s) cm^{-1}.

Attempted Synthesis of 1,3,6,7-Tetraphenylacenaphtho[5,6-cd]thiopyran (VI).--Attempts to prepare this sulfur heterocycle from 1,4,5,8-tetrabenzoylnaphthalene in a similar manner described by Fitton and Smalley,[21] and by Robinson and Todd[22] were unsuccessful. The procedure followed was evolved from the methods of Farrar and Levine,[23] and Smith.[24] Equimolar fractions of 1,4,5,8-tetrabenzoylnaphthalene and phosphorus pentasulfide were used in this preparation. To 1.0 g of 1,4,5,8-tetrabenzoylnaphthalene contained in a 500 ml 3-neck

round-bottomed flask, fitted with a reflux condenser and a
mechanical stirrer, was carefully added 10 ml of dry pyridine
from an addition funnel. Phosphorus pentasulfide (0.82 g)
was then added to the reaction mixture. The mixture was then
heated under reflux with vigorous stirring at 150-155° for
2.5 hr until some blue-black amorphous crystals were formed.
When the mixture cooled to room temperature, the contents of
the flask were rinsed with ether and the washings added to the
rest of the reaction product. The mixture was then extracted
several times with ether. The combined extracts were dried
($MgSO_4$), and the ether evaporated. The crude product melted
at 225-230°. The major ir peaks occurred at 3060 (w), 1600
and 1450 (m), and 1100 and 1025 (m) as illustrated in Figure
6. The mass spectrum, as indicated in the line diagram of
Figure 7, showed the following mass peaks:

Mass	% Relative to Base Peak
33	9.5
44	80.5
64	48
75	60
76	75
77	80.5
78	76
79	55
89	60
91	100

Fig. 6. Infrared spectra of product of attempted synthe-
         sis of 1,3,6,7-tetraphenylacenaphtho[5,6-cd]thio-
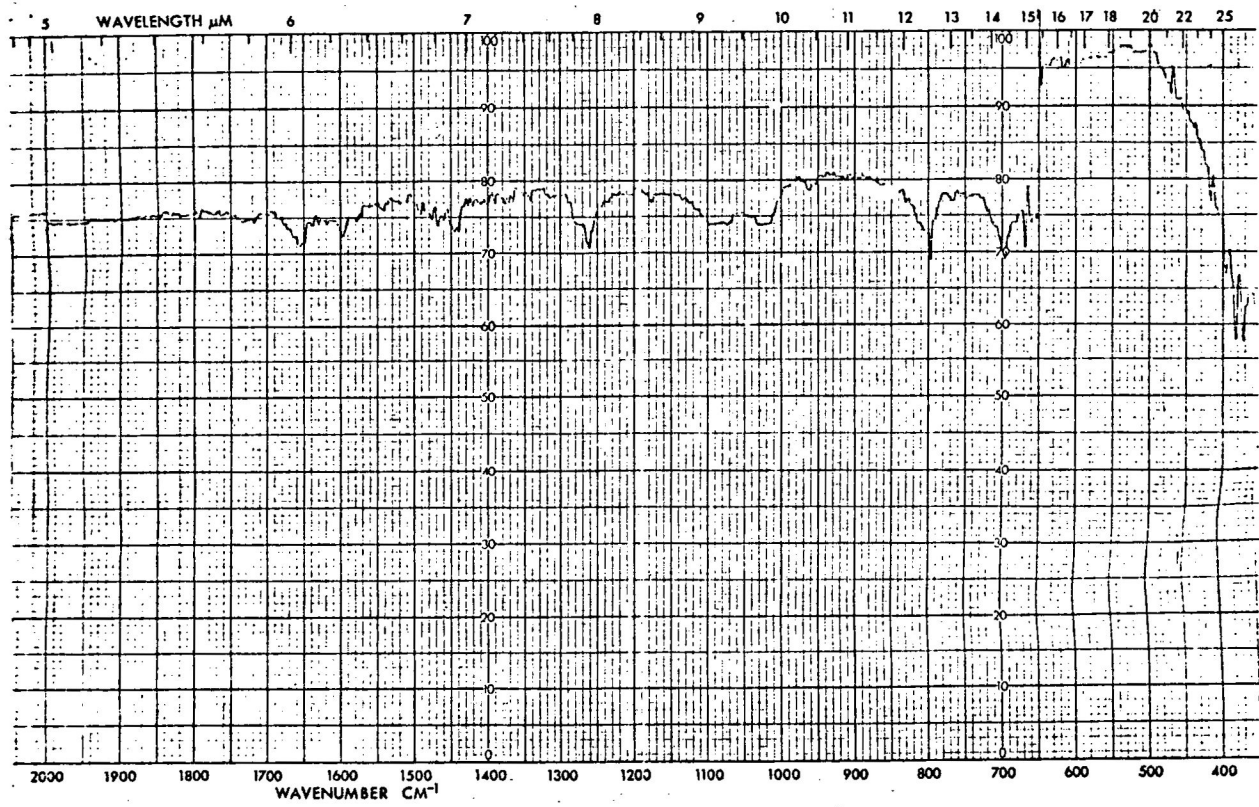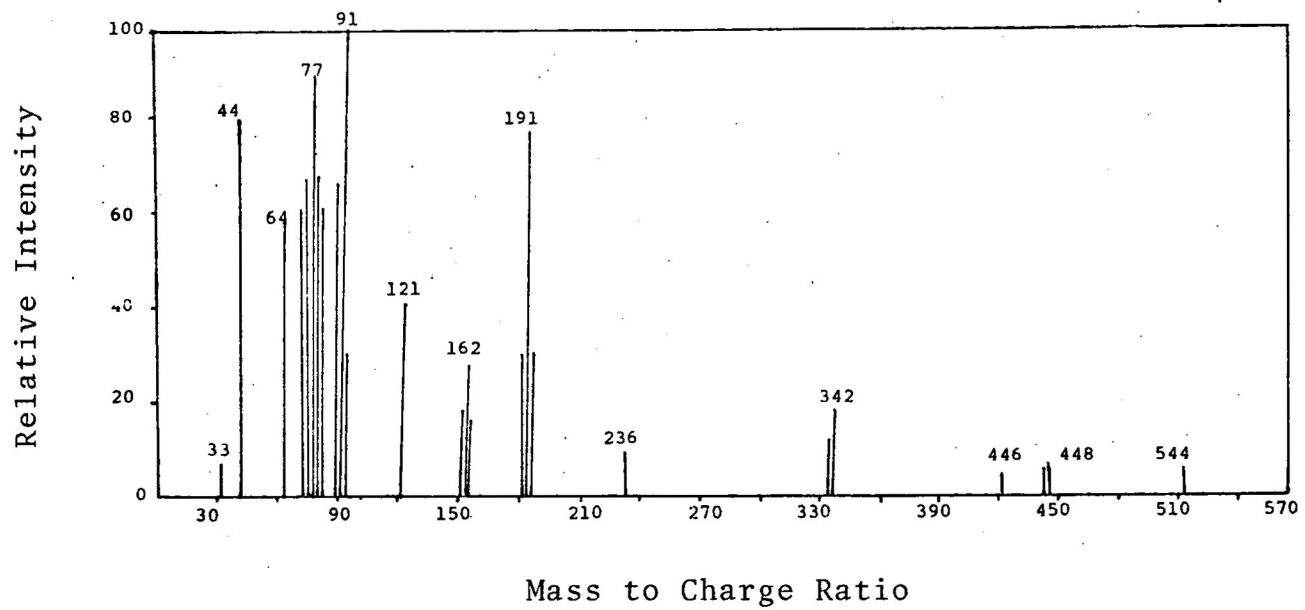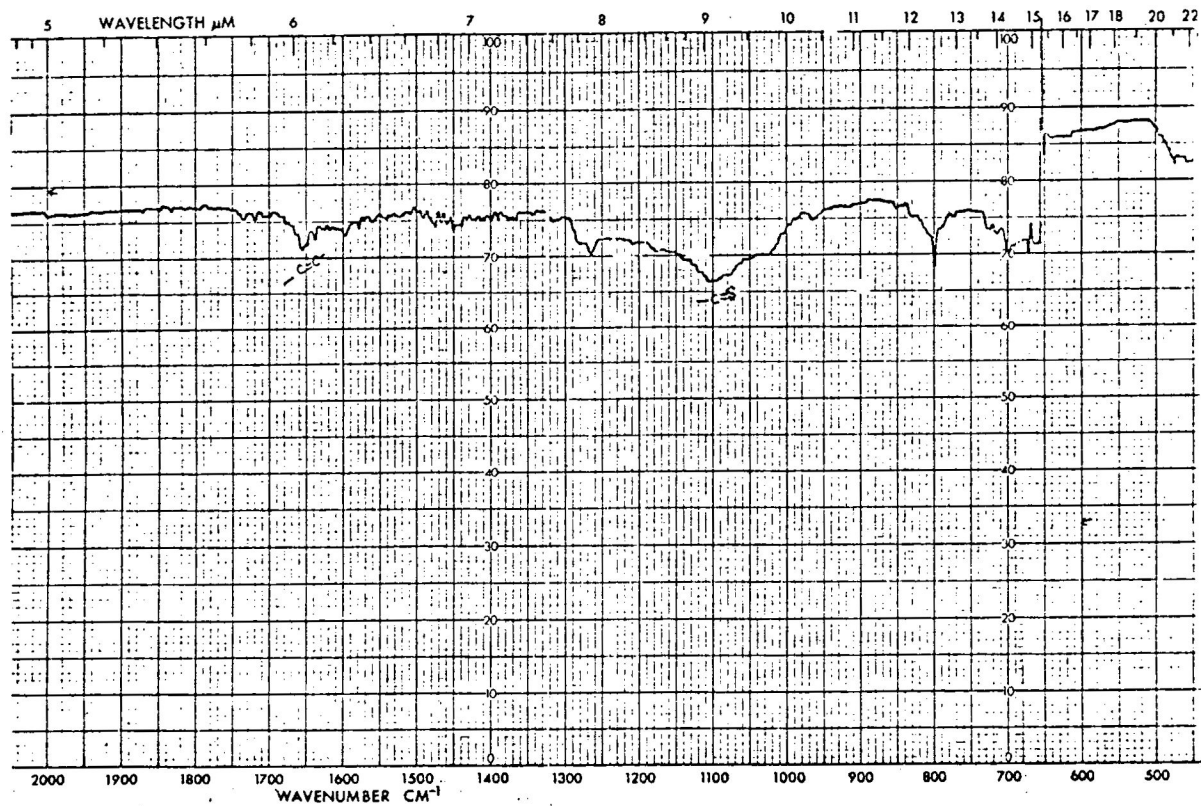   pyran.

WAVELENGTH μM

WAVENUMBER CM⁻¹

30

Fig. 7. Line diagram showing normalized relative abun-

dance of ions in the mass spectrum of product of

attempted synthesis of 1,3,6,7-tetraphenylacenaph-

tho[5,6-cd]thiopyran, m/e 91=100 units.

Mass	% Relative to Base Peak
121	20
191	85
236	5
351	12
346	5
448	5
544	4

The crude product thus prepared was purified as follows:
Crude product was dissolved in ether and then precipitated by
petroleum ether cooled in a Dry Ice-acetone mixture. Blue-
black crystals of the heterocycle separated out. The crystals
were collected by suction filtration. The purified crystals
melted at 275-278^0 (lit.[3] mp 280-282^0). The heterocycle was
then heated in a test tube with a Bunsen flame. The blue-
black color changed to black and vapors were given off. The
final product melted at 295-300^0. The overall yield was 4%
from pyrene. The ir spectrum (see Fig. 8) showed major peaks
at 3050 (w), 1650 (s), 1265 (s) and 1100 (b, s) cm^{-1}. The uv
of this heterocycle in methylene chloride showed λ max (ε)
at 222 nm (ε 3307), 290 (6944), 310 (6217), 330 (5225), and
420 (1521), with tailing from 600 nm. The lit.[2] λ max (ε)
for 1,3,6,7-tetraphenylacehaphtho 5,6-cd thiopyran were at
256 nm (ε 26400), 273 (25300), 301 (20200), 415 (71800), 565
(3930), 610 (3450) and 665 (2330) with tailing to 775 nm.

Fig. 8. Infrared spectrum of compound obtained when pro-
        duct of attempted synthesis of 1,3,6,7-tetra-
        phenylacenaphtho[5,6-cd]thiopyran is heated.

WAVELENGTH µM
WAVENUMBER CM⁻¹

Formation of the polymer.--Ponticello and Schlessinger[1] have indicated that when a compound analogous to 1,3,6,7-tetraphenyl-acenaphtho[5,6-cd]thiopyran, the 6,7-dibromo-1,3-diphenylace-naphtho[5,6-cd]thiopyran, was heated above its melting point (130°), only a polymer was formed. The synthesis of the polymer was accomplished by heating the heterocycle above its melting point (295-300°). The ir spectrum of the polymer showed major peaks at 3080 (w)(-CH=CH-); 1635 (s)(C=C); 985 (s, b)(CH=CH$_2$); and 605 (m)(C-S) cm^{-1}, as illustrated in Figure 9. The glass transition temperature of the polymer was 348°.

Fig. 9.   Infrared spectra of the polymer.

WAVELENGTH μM

| 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 20 | 22 | 25 |

-C-S-

WAVENUMBER CM⁻¹

| 2000 | 1900 | 1800 | 1700 | 1600 | 1500 | 1400 | 1300 | 1200 | 1100 | 1000 | 900 | 800 | 700 | 600 | 500 | 400 |
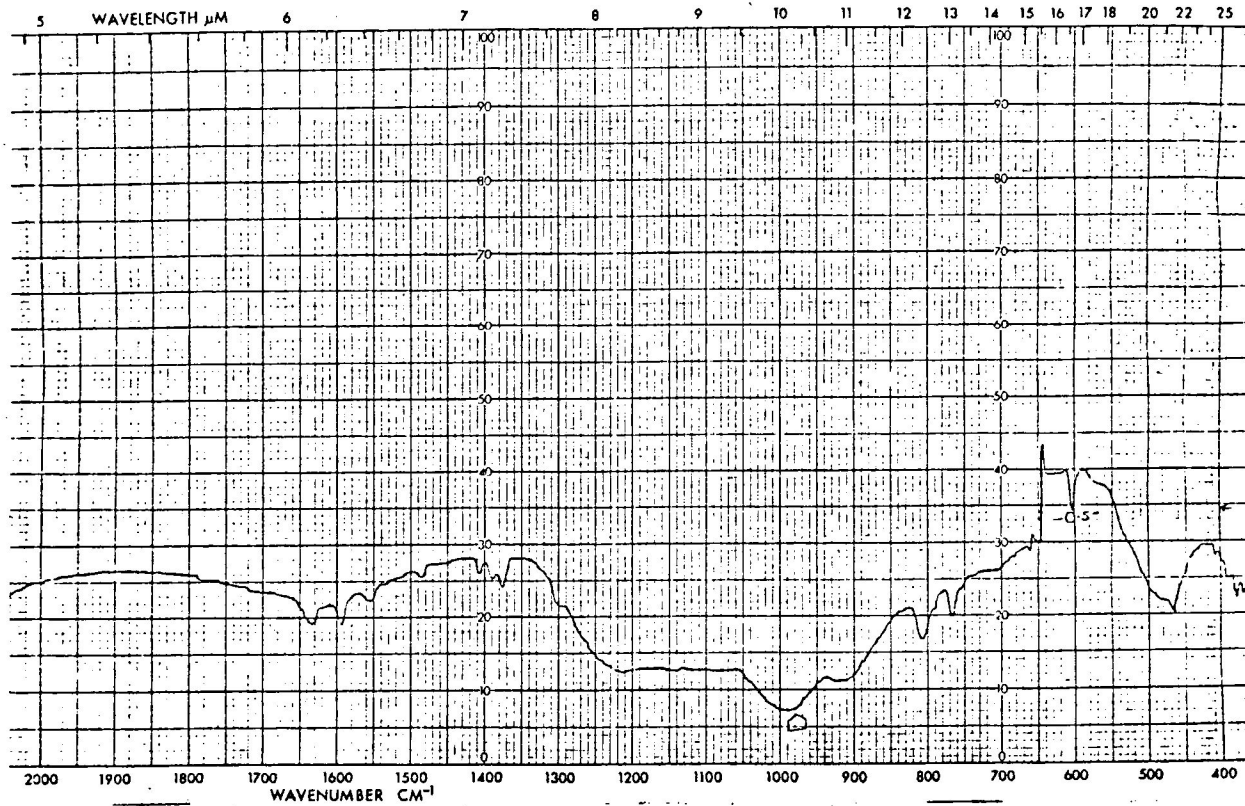
CONCLUSION

The structure of 1,3,6,7-tetraphenylacenaphtho[5,6-cd]thio-
pyran clearly shows that one end of the molecule exists as a
1,3 dipolarophile because of the multiple-bond system that
includes the hetero-atom. Conjugation increases the polariza-
bility of the π bond of the dipolarophile. A similar hetero-
cyclic compound, the 6,7-dibromo-1,3-diphenylacenaphtho[5,6-cd]-
thiopyran underwent self-polymerization, but the polymer was
not characterized. The polymerization of an uncharacterized
material which is assumed to be related to 1,3,6,7-tetraphenyl-
acenaphtho[5,6-cd]thiopyran was therefore accomplished on
heating.

REFERENCES

1. (a) R. H. Schlessinger and A. G. Schultz, J. Am. Chem. Soc., 90, 1676 (1968); (b) I. S. Ponticello and R. H. Schlessinger, ibid., 90, 4190 (1968).

2. J. M. Hoffman, Jr. and R. H. Schlessinger, ibid., 91, 3953 (1969).

3. H. Vollmann, H. Becker, M. Correll, and H. Steeck, Ann., 531, 1 (1937).

4. F. W. Billmayer, Jr., "Textbook of Polymer Science," 2nd Ed., Wiley-Interscience, New York, N. Y., 1970, pp. 459-460.

5. E. Josephy and F. Radt, "Elsevier's Encyclopedia of Organic Chemistry," Vol. 14, Series III, Elsevier Pub. Co,, New York, N.Y., 1940, pp. 376-395.

6. M. J. S. Dewar and R. C. Dougherty, "The Perturbation Molecular Orbital (PMO) Theory of Organic Chemistry," Plenum, New York, N.Y., 1975, pp. 100-101.

7. M. J. S. Dewar, Rec. Chem. Progr., 19, 1 (1958).

8. M. J. S. Dewar, T. Mole, E. W. T. Warford, J. Chem. Soc., 3581 (1956).

9. J. A. Joule and G. F. Smith, "Heterocyclic Chemistry," D. van Nostrand, London, U.K., 1972, p. 11.

10. M. Polk, Ph.D. Thesis, University of Pennsylvania, Philadelphia, Pa., 1964.

11. C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N.Y., 1962, pp. 4-6.

12. J. Hammer, "1,4-Cycloaddition Reactions. The Diels-Alder Reaction in Heterocyclic Synthesis," Academic, New York, N. Y., 1976, pp. 5-6.

13. J. A. Hirsch, "Concepts in Theoretical Organic Chemistry," Allyn and Bacon, Boston, Ma., 1974, pp. 70-73.

14. J. K. Stille, "Introduction to Polymer Chemistry," Wiley, New York, N.Y., 1962, pp. 142-143.

15. M. H. Palmer, "The Structure and Reactions of Heterocyclic Compounds," Edward Arnold Ltd., London, U.K., 1967, p. 259.

16. C. J. Pouchert, "The Aldrich Library of Infrared Spectra," 2nd Ed., Aldrich Chemical Co., Milwaukee, Wi., 1975, p. 143A.

17. N. M. Bikales, "Characterization of Polymers," Wiley-Interscience, New York, N.Y., 1971, p. 206.

18. R. Huisgen, J. Org. Chem., 33, 2291 (1968).

19. The standard texts used were: (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., New York, N.Y., 1959; (b) J. F. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N.J., 1965; (c) R. M. Silverstein, G. Bassler, C. Morrill, "Spectroscopic Identification of Organic Compounds," Wiley, New York, N.Y., 1974.

20. C. A. Thomas, M. B. Moshier, H. E. Morris and R. W. Moshier, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Pub. Co., New York, N.Y., 1941, pp. 78-81.

21. A. O. Fitton and R. K. Smalley, "Practical Heterocyclic Chemistry," Academic, New York, N.Y., 1968, p. 5.

22. Sir R. Robinson and W. M. Todd, J. Chem. Soc., 1743 (1939).

23. M. W. Farrer and R. Levine, J. Am. Chem. Soc., 72, 4433 (1950).

24. A. Smith, J. Chem. Soc., 57, 643 (1890).