

Benzannelated Analogs of Phenanthro[1,2-*b*]- and [2,1-*b*]thiophene: Synthesis and Structural Characterization by Two-Dimensional NMR and X-Ray Techniques

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Syntheses of benzo[3,4]phenanthro[1,2-*b*]thiophene, benzo[3,4]phenanthro[2,1-*b*]thiophene and their 1-methyl analogs are reported as potential constituents of solvent refined coal liquids and for mutagenicity testing. The attempted synthesis of the 13-methyl analogs which gave the 11-methyl isomers is also described. Total assignments of the ¹H- and ¹³C-nmr spectra based on long range optimized heteronuclear proton-carbon two-dimensional chemical shift correlation are reported. Carbon assignments obtained for benzo[3,4]phenanthro[1,2-*b*]thiophene using this approach were confirmed with a 125 MHz ¹³C-¹³C INADEQUATE spectrum. X-Ray crystal structures were determined for benzo[3,4]phenanthro[1,2-*b*]thiophene and 1-methylbenzo[3,4]phenanthro[2,1-*b*]thiophene. Both molecules were helically distorted from planarity. Close intramolecular contacts between the bay region H1-H13 and C1Me-H13 of 2.03 and 2.28 Å, respectively, were responsible for the distortions. There were no close intermolecular contacts of <3.5 Å. Both molecules refined to an R value of <0.05.

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Introduction.

Considerable emphasis has been placed upon the characterization of the sulfur constituents of coal liquids in view of the pronounced mutagenicity which has been observed for several such compounds. Indeed, phenanthro[3,4-*b*]thiophene and benzo[2,3]phenanthro[4,5-*bcd*]thiophene have been shown to be potent mutagens [2,3]. Efforts in the synthesis and characterization of potential sulfur constituents of coal have been reviewed by Castle and co-workers [4]. In a continuation of these studies, we now wish to report the synthesis of the benzo[3,4]phenanthro[1,2-*b*]thiophene (**7**) and benzo[3,4]phenanthro[2,1-*b*]thiophene (**13**) parent ring systems and selected methyl analogs. Characterization and total assignment of the ¹H- and ¹³C-nmr spectra using two-dimensional nmr and X-ray diffraction is also reported.

Synthesis.

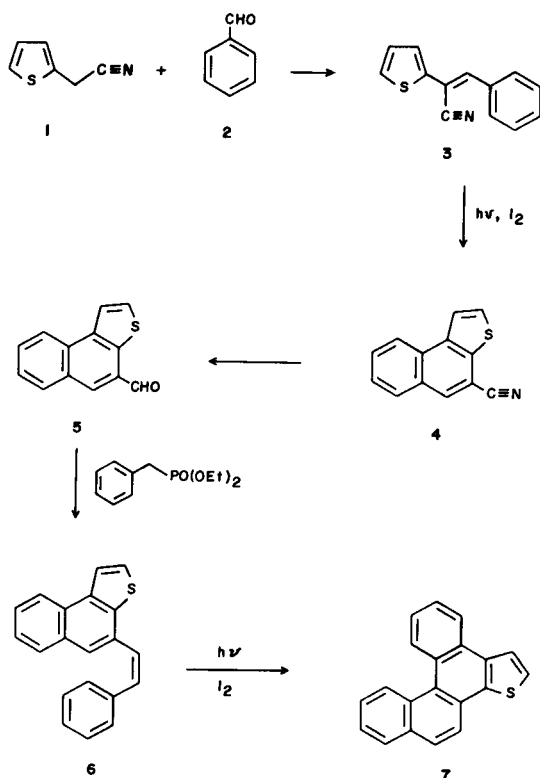
Synthetic elaboration of the benzannelated phenanthro[1,2-*b*]- and [2,1-*b*]thiophene ring systems was completed in high yield using the well established Wadsworth-Emmons

procedure [5-29]. Preparation of benzo[3,4]phenanthro[1,2-*b*]thiophene (**7**) was begun with the condensation of 2-thienylacetonitrile (**1**) with benzaldehyde (**2**) in the presence of sodium ethoxide affording 2-(2'-thienyl-3-phenylpropenenitrile) (**3**) in a 92% yield as shown in Scheme I.

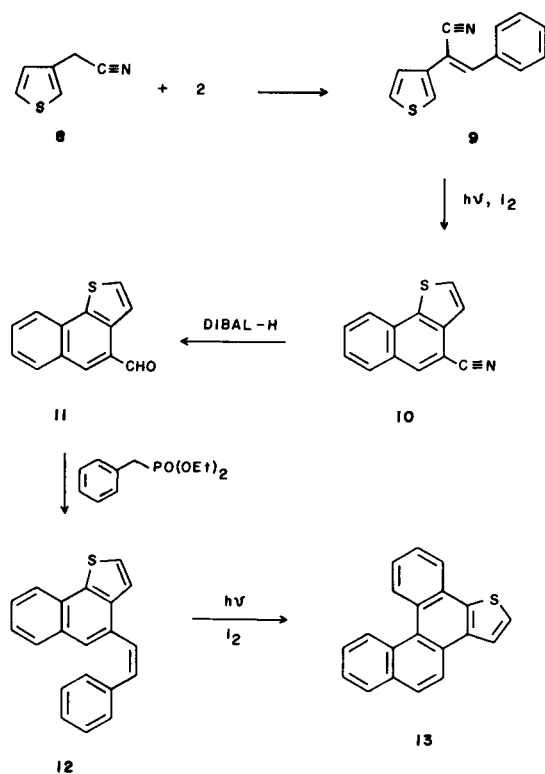
Photocyclization of **3** to afford 4-cyanonaphtho[2,1-*b*]thiophene (**4**) was completed in an 80% yield followed by reduction to the corresponding aldehyde, **5**, using diisobutylaluminum hydride (DIBAL-H) in a 65% yield. Condensation of **5** with diethyl benzylphosphonate under Wadsworth-Emmons conditions gave the styryl intermediate, **6**, in a 90% yield which was followed by photocyclization to afford benzo[3,4]phenanthro[1,2-*b*]thiophene (**7**) in an 88% yield giving an overall yield for the sequence of 38%. The preparation of the benzo[3,4]phenanthro[2,1-*b*]thiophene (**13**) was conducted in a nearly identical fashion as shown in Scheme II differing only in that it began with 3-thienylacetonitrile (**8**). The overall yield obtained in the synthesis of **13** was a comparable 43%.

Preparation of the 1-methyl isomers of **7** and **13** was ac-

Scheme 1

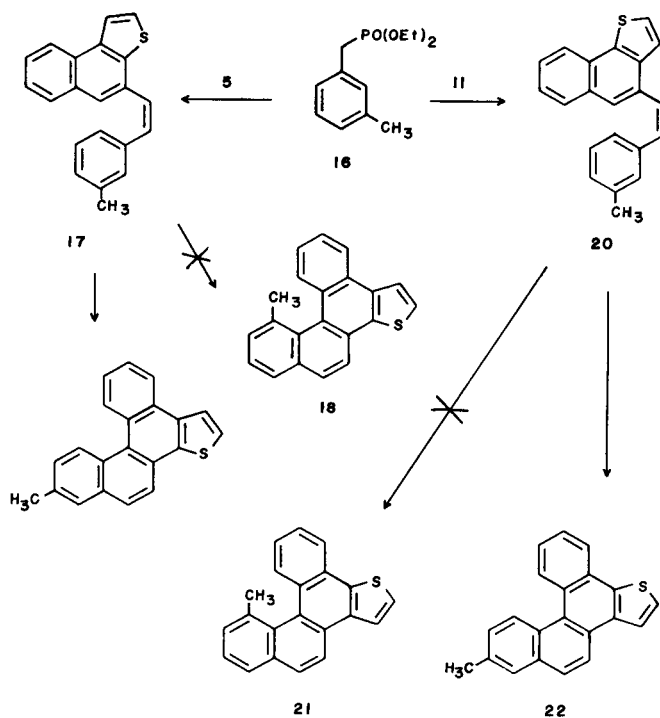


Scheme 2



complicated in a straightforward manner by substituting *o*-tolualdehyde in place of benzaldehyde in Schemes I and II. Thus, 1-methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (28) and 1-methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (33) were obtained in overall yields of 46 and 39%, respectively. In contrast, the attempted synthesis of the 13-methyl isomers of 7 and 13 failed to provide the desired methyl isomers. Synthetically, the approach to 18 and 21 began from the naphtho[*b*]thiophene carboxaldehydes 5 and 11, respectively, both of which were condensed with diethyl 3-methylbenzylphosphonate (16) to afford the corresponding styryl compounds 17 and 20, respectively, as shown in Scheme III. Rotational freedom of the tolyl species 17 and 20 would allow the methyl containing ring to be oriented such that condensation could afford either the desired 13-methyl isomers, 18 and 21, respectively, or the sterically less hindered 11-methyl analogs 19 and 22. As would be expected in such circumstances, the less hindered 11-methyl isomers, 19 and 22, were obtained from the tolylvinyl intermediates in isolated yields of 75% in both cases.

Scheme 3



The synthesis of 1-methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (28) was accomplished in the same fashion as outlined above. The overall yield of 28 from 1 and 23 was 46%. The reactions are outlined in Scheme IV.

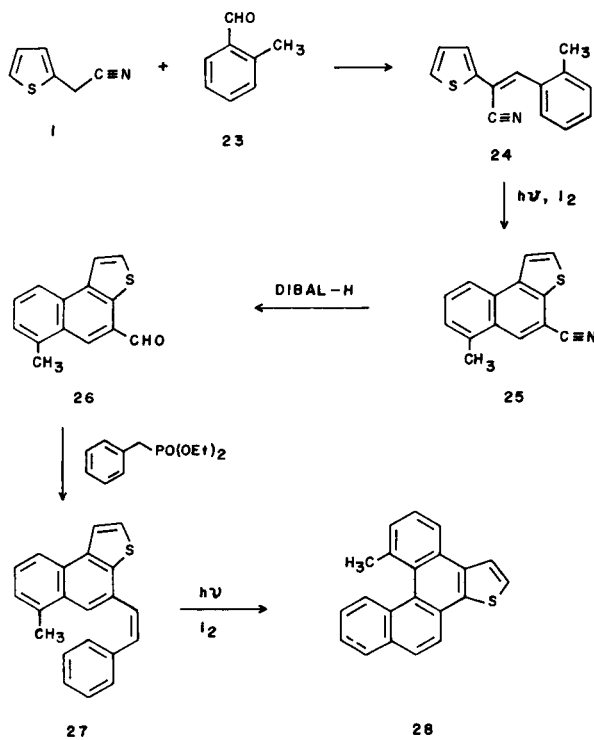
Table I

¹H- and ¹³C-NMR Chemical Shift Assignments of Benzo[3,4]phenanthro[1,2-*b*]thiophene (**7**), Benzo[3,4]phenanthro[2,1-*b*]thiophene (**13**), 1-Methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (**28**) and 1-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (**33**) in Deuteriochloroform at Observation Frequencies of 300.068 and 75.459 MHz and an Ambient Probe Temperature of 17°.

	7				13		28		33	
	δ ¹ H	δ ¹³ C (obs)	δ ¹³ C (calcd)		δ ¹ H	δ ¹³ C	δ ¹ H	δ ¹³ C	δ ¹ H	δ ¹³ C
			(a)	(b)						
1	9.10	128.96	127.6	127.6	9.10	129.27		121.74		131.61
2	7.48	124.99	125.8	125.8	7.60	126.50	7.45	128.66	7.48	129.00
3	7.50	126.26	125.5	125.5	7.65	125.40	7.59	126.29	7.61	126.56
4	8.21	124.02	128.2	128.2	8.25	124.31	8.19	120.88	8.08	121.22
4a		129.53	126.1	124.1		129.06		130.32		128.16
4b		135.09	138.3	138.8		136.85		136.12		137.64
5	7.77	122.84	124.0	124.7			7.90	123.12		
6	7.39	125.50	126.4	125.6	7.89	123.14	7.54	125.41	8.02	127.84
7					7.54	125.05			7.54	125.26
7a		136.86	137.8	137.8		135.17		135.72		137.08
7b		126.63	127.5	127.1		127.07		127.55		127.98
8	7.90	122.50	126.5	122.8	8.20	122.34	8.04	122.14	7.56	125.26
9	7.73	128.17	127.1	127.6	7.90	127.83	7.91	127.65	7.93	122.88
9a		133.19	130.5	131.7		132.92		135.79		134.84
10	7.82	128.58	128.2	128.7	8.05	128.42	7.92	128.10	8.05	129.99
11	7.44	125.43	125.5	127.8	7.64	125.34	7.48	125.18	7.53	125.16
12	7.50	126.25	125.8	126.0	7.70	126.07	7.51	125.49	7.98	127.54
13	8.90	127.97	127.6	122.9	9.05	128.05	7.98	129.88	8.29	121.91
13a		130.53	126.0	127.1		130.47		130.78		130.89
13b		125.08	126.1	130.7		125.65		124.95		125.59
13c		128.84	126.0	125.0		128.36		128.35		128.05
-CH ₃							2.30	25.00	2.30	25.06

[a] Calculated by incrementation for fusion of a thiophene moiety onto the 5,6 face of benzo[*c*]phenanthrene. [b] Calculated by incrementation for fusion of a benzo moiety onto the phenanthro[1,2-*b*]thiophene nucleus.

Scheme 4



Scheme 5

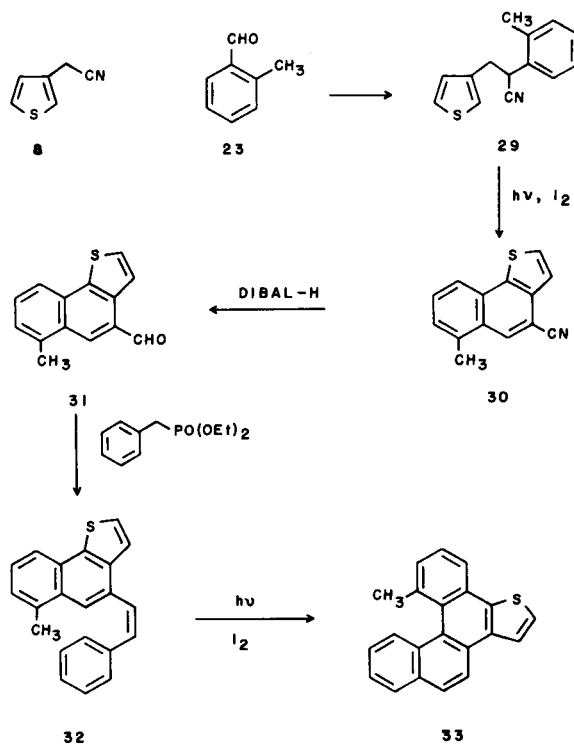


Table II

Positional and Thermal Parameters for
Benzo[3,4]phenanthro[1,2-*b*]thiophene (7)

Atom	X	Y	Z	U _{eq} , Uiso [a]
S(7)	.39702(6)	.62409(14)	.27968(2)	.0289(2)
C(1)	.9668(3)	.4457(5)	.39291(9)	.0270(8)
C(2)	1.0817(3)	.5943(6)	.38189(9)	.0302(8)
C(3)	1.0587(3)	.8061(5)	.35180(9)	.0296(8)
C(4)	.9202(3)	.8572(5)	.33054(9)	.0262(7)
C(4a)	.8012(2)	.7039(5)	.33995(8)	.0218(7)
C(4b)	.6613(2)	.7359(5)	.31244(8)	.0216(7)
C(5)	.6189(3)	.9147(5)	.27443(8)	.0259(8)
C(6)	.4809(3)	.8779(6)	.25424(8)	.0295(8)
C(7a)	.5516(2)	.5643(5)	.31951(8)	.0222(7)
C(7b)	.5638(2)	.3703(5)	.35588(7)	.0218(7)
C(8)	.4470(3)	.1993(5)	.36112(9)	.0258(8)
C(9)	.4602(3)	.0089(5)	.39414(9)	.0283(8)
C(9a)	.5861(3)	-.0070(5)	.42853(8)	.0259(7)
C(10)	.5931(3)	-.1930(5)	.46583(9)	.0321(8)
C(11)	.7025(3)	-.1900(6)	.50285(10)	.0357(9)
C(12)	.8058(3)	.0060(6)	.50505(9)	.0349(9)
C(13)	.8052(3)	.1844(5)	.46829(9)	.0288(8)
C(13a)	.7000(2)	.1754(4)	.42721(8)	.0223(7)
C(13b)	.6962(2)	.3496(5)	.38611(7)	.0212(7)
C(13c)	.8208(2)	.5015(5)	.37456(8)	.0217(7)
H(C1)	.987(2)	.293(5)	.4117(8)	.023(6)
H(C2)	1.177(3)	.549(5)	.3924(8)	.029(7)
H(C3)	1.139(3)	.914(5)	.3439(9)	.036(7)
H(C4)	.900(3)	1.000(6)	.3098(9)	.037(8)
H(C5)	.678(3)	1.045(5)	.2645(8)	.031(7)
H(C6)	.429(3)	.970(6)	.2287(9)	.044(8)
H(C8)	.361(3)	.230(5)	.3388(9)	.034(7)
H(C9)	.382(3)	-.120(5)	.3973(8)	.027(6)
H(C10)	.514(3)	-.316(5)	.4651(8)	.023(6)
H(C11)	.706(3)	-.307(6)	.5277(10)	.044(8)
H(C12)	.875(3)	.027(5)	.5317(10)	.040(8)
H(C13)	.876(2)	.325(5)	.4713(7)	.017(6)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j A_{ij}$$

Where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

Table III

Positional and Thermal Parameters for
1-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (33)

Atom	X	Y	Z	U _{eq} , Uiso [a]
S(5)	.11572(5)	.06326(6)	.43663(2)	.02845(12)
C(1)	.5396(2)	-.0061(2)	.27234(8)	.0217(4)
C(2)	.6275(2)	-.0615(2)	.33140(9)	.0262(5)
C(3)	.5726(2)	-.0954(2)	.39606(9)	.0293(5)
C(4)	.4297(2)	-.0604(2)	.40459(8)	.0257(4)
C(4a)	.3360(2)	-.0035(2)	.34637(8)	.0204(4)
C(4b)	.1932(2)	.0576(2)	.35645(8)	.0210(4)
C(6)	-.0317(2)	.1709(2)	.39837(10)	.0309(5)
C(7)	-.0227(2)	.2011(2)	.32846(9)	.0280(5)
C(7a)	.1064(2)	.1342(2)	.30285(8)	.0215(4)
C(7b)	.1462(2)	.1255(2)	.23068(8)	.0206(4)
C(8)	.0498(2)	.1868(2)	.17297(9)	.0250(5)
C(9)	.0776(2)	.1638(2)	.10433(9)	.0255(5)
C(9a)	.1954(2)	.0647(2)	.08773(8)	.0223(4)
C(10)	.2130(2)	.0214(2)	.01622(9)	.0274(5)
C(11)	.3161(2)	-.0873(2)	.00072(9)	.0308(5)
C(12)	.4030(2)	-.1628(2)	.05652(9)	.0276(5)
C(13)	.3904(2)	-.1213(2)	.12639(8)	.0228(4)
C(13a)	.2921(2)	-.0003(2)	.14424(8)	.0194(4)
C(13b)	.2770(2)	.0478(2)	.21696(7)	.0183(4)
C(13c)	.3857(2)	.0091(2)	.27703(8)	.0188(4)
C(14)	.6182(2)	.0558(3)	.21087(10)	.0294(5)
H(C2)	.726(2)	-.073(3)	.3265(11)	.038(6)
H(C3)	.635(2)	-.134(3)	.4350(11)	.037(6)
H(C4)	.393(2)	-.070(3)	.4505(11)	.036(6)
H(C6)	-.106(2)	.199(3)	.4277(11)	.040(6)
H(C7)	-.095(2)	.257(2)	.3016(10)	.030(5)
H(C8)	-.035(2)	.242(2)	.1837(10)	.029(5)
H(C9)	.016(2)	.212(2)	.0668(10)	.030(5)
H(C10)	.152(2)	.073(2)	-.0195(10)	.026(5)
H(C11)	.327(2)	-.114(3)	-.0473(12)	.040(6)
H(C12)	.471(2)	-.245(3)	.0471(10)	.031(5)
H(C13)	.447(2)	-.175(2)	.1642(9)	.023(5)
H(141)	.655(2)	-.026(3)	.1832(12)	.051(7)
H(142)	.556(2)	.124(3)	.1783(11)	.041(6)
H(143)	.689(2)	.119(3)	.2300(12)	.048(6)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j A_{ij}$$

where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

In like manner, 1-methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (**33**) was obtained in five steps from **8** and **23**. The overall yield of **33** was 39%. The reactions are outlined in Scheme V.

NMR Spectroscopy.

Previous work from these laboratories has detailed efforts directed towards the total proton and carbon nmr assignments of various polynuclear aromatic thiophene analogs, these efforts beginning with phenanthro[1,2-*b*]thiophene (**23**) [30] which was assigned using simple two-dimensional autocorrelated proton (COSY) [31-33] and heteronuclear proton-carbon chemical shift correlation [34-37] techniques. Although an effort was made to assign the quaternary carbon resonances in this study through

the use of the ¹³C-¹³C INADEQUATE [38-41] experiment, the assignment of these resonances was only partially successful at 50 MHz. More recently, we have reported the total assignment of the spectra of phenanthro[3,4-*b*]thiophene [43] which employed autocorrelated ¹³C-¹³C double quantum coherence [43-46]. Here the total assignment was successful at 75 MHz although this might not have been possible with only slightly more complicated systems. As an example, our efforts at 75 MHz in the total assignment of the spectra of phenanthro[4,3-*a*]dibenzothiophene using heteronuclear chemical shift correlation [34-37] and heteronuclear relayed coherence transfer [47-56] were only partially successful [53] requiring the subsequent acquisition of a 125 MHz ¹³C-¹³C double quantum spectrum to complete the assignments [46]. In contrast, most recently we

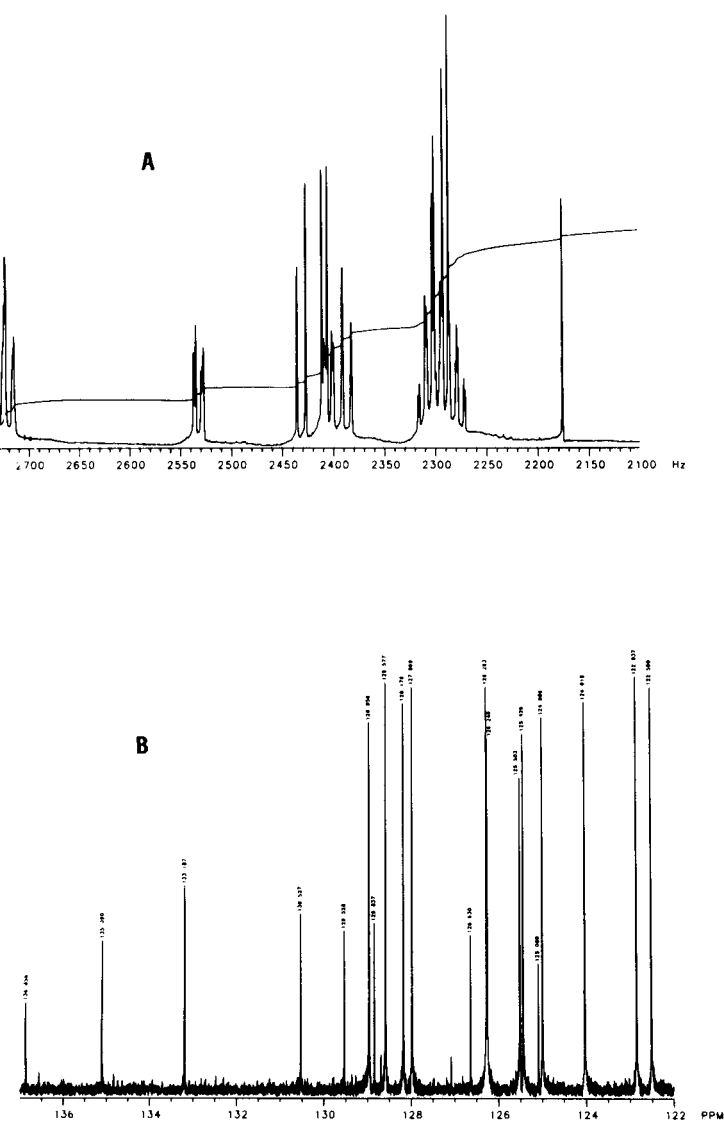


Figure 1. A) ^1H -nmr spectrum of benzo[3,4]phenanthro[1,2-*b*]thiophene (7) in deuteriochloroform recorded at 300 MHz; B) ^{13}C -nmr spectrum of benzo[3,4]phenanthro[1,2-*b*]thiophene (7) in deuteriochloroform at 75 MHz.

have reported the total assignment of the proton and carbon spectra of 9-methylphenanthro[4,3-*a*]dibenzothiophene [57] through the combined usage of heteronuclear chemical shift correlation with broadband homonuclear proton decoupling [58], heteronuclear relayed coherence transfer [47-56], and long range optimized proton-carbon heteronuclear chemical shift correlation [59-68]. Since this last study was completed entirely at observation frequencies of 300/75 MHz for $^1\text{H}/^{13}\text{C}$, we were thus quite interested in the extension of the approach to include the characterization of other systems of equal or greater complexity.

Since there is always a degree of uncertainty inherent in the extension of relatively new approaches to a problem to new and completely unrelated systems, we elected to utilize both long range optimized proton-carbon heteronuclear chemical shift correlation and 125 MHz ^{13}C - ^{13}C INADEQUATE in the characterization of benzo[3,4]phenanthro[1,2-*b*]thiophene (7) before proceeding with the assignment of the spectra for the remainder of the systems prepared in this study.

Benzo[3,4]phenanthro[1,2-*b*]thiophene (7).

Several alternative approaches are available for the empirical prediction of the ^{13}C -nmr chemical shifts of benzo[3,4]phenanthro[1,2-*b*]thiophene (7). Chemical shifts may be calculated for the fusion of an additional ring on the phenanthro[1,2-*b*]thiophene (23) which has been previously assigned by Martin and co-workers [30]. Alternatively, chemical shifts may be calculated for the fusion of the thiophene ring onto benzo[*c*]phenanthrene in a manner similar to that previously employed in the prediction of the chemical shifts of phenanthro[1,2-*b*]thiophene (23). However, regardless of which approach is employed, there are expected to be numerous opportunities for permutation of resonance assignments based on chemical shift arguments alone. Generally, however, this approach provides insight into one or two assignments which are largely unequivocal because of unique environments in the molecule, these often providing useful starting points for the assignments. Thus, calculated chemical shift assignments for 7 are presented in Table I and will be discussed as appropriate during the course of the spectral assignment.

The proton and carbon spectra of 7 recorded in deuteriochloroform at observation frequencies of 300.068 and 75.459 MHz, respectively, are shown in Figures 1A and B. Beginning with the proton spectrum, furthest downfield ($\delta = 9.08$) we observe two overlapped doublets which would clearly correspond to the bay region H1 and H13 resonances. Resonating somewhat upfield at $\delta = 8.45$ is a well resolved double doublet which intuitively might be assigned as the H8 resonance. Resonating within the range from $\delta = 8.13$ -7.93 are four very well resolved multiplets while the balance of the resonances of 7 all resonate as a complexly overlapped multiplet centered at $\delta = 7.63$.

The ^{13}C -nmr spectrum contained twenty resonances and although all were resolved, a number were in very close proximity to one another. The complete chemical shift range was from $\delta \sim 122$ -137. Protonated carbon resonances, which relax more efficiently by virtue of the r_{CH}^{-6} term of the expressions governing relaxation, appeared with about twice the resonance intensity of the partially saturated quaternary carbon resonances, the former reso-

Table IV

X-Ray Crystallographic Data and Refinement Summary for Benzo[3,4]phenanthro[1,2-*b*]thiophene (7) and
1-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (35)

	Crystal Data (163°K) [a]	
	7	33
a, Å	9.214(3)	9.1623(13)
b, Å	5.234(2)	8.3549(11)
c, Å	27.59(2)	18.821(4)
β , °	95.91(3)	95.474(12)
Volume, Å ³	1323.5(12)	1434.2(4)
d_{calc} , g/cc	1.43	1.38
crystal system	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /c
Z	4	4

Data Collection (163°K) [b]		
radiation, λ (Å)	MoK α , .71069	MoK α , .71069
mode	omega scan	omega scan
scan range	1° omega	1° omega
scan rate	2.5°	3.6°
max decay correction (on I)	2%	not applied
2 θ range, °	4-52	4-60
unique reflections measured	2603	4186
range of h,k,l	0-9, 0-17, -20-20	0-12, 0-11, -26-26
check reflections	0, -1, -4; 2, 0, -4; 0, 0, 8; 0, 1, -4	-4, 0, 0; 1, 2, -3; 3, 0, 2; 0, 0, 4
crystal dimensions, mm	.12 × .09 × .84	.26 × .33 × .38
absorption coefficient, cm ⁻¹	2.22	2.08
transmission factor range	.97-.98	.93-.95

Structure Refinement [c]		
ignorance factor	.04	.04
observed reflections, m, (F > 4 sigma _F)	1943	3223
number of variables, n	238	255
R, wR	0.42, .046	.042, .051
S, goodness of fit	1.31	1.56
max shift/esd	<.01	<.01
min, max peaks in diff map (e ⁻ /Å ³)	-.31, .24	-.21, .39

[a] Lattice parameters were obtained by least-squares refinement of the setting angles of 45 reflections with 2θ between 18.6° and 27.6° for I and between 23.9° and 30.0° for II. [b] Data were collected on a Syntex P2₁ diffractometer equipped with a syntex LT-1 low temperature delivery system. Data reduction was carried out as described in Riley and Davis [87]. Crystal and instrument stability were monitored by remeasurement of 4 check reflections every 96 reflections. These data were analyzed as described in Henslee and Davis [88]. [c] Relevant expressions are as follows, where in this footnote F_o and F_c represent the observed and calculated structure factor amplitudes, respectively.

Function Minimized: $\Sigma(w(F_o - F_c))^2$, where $w = 1/(\text{sigma}_F)^2$

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2]^{1/2}$

$S = [\Sigma w(F_o - F_c)^2 / \Sigma (m-n)]^{1/2}$

nating within the relatively narrow range from $\delta = 129$ -122.5.

Assignment of the nmr spectra of compounds such as 7 may be approached in a number of different ways. Generally, proton connectivities will be established first, the COSY [31-33] experiment used most frequently for this purpose. Alternatively, however, vicinal proton connectivities can be established using a combination of hetero-

nuclear proton-carbon chemical shift correlation [34-37] and heteronuclear relayed coherence transfer [47-56]. The latter approach is particularly useful when highly congested proton spectra must be dealt with such as in the case of phenanthro[4,3-*a*]dibenzothiophene [46,53] and its 9-methyl analog [57] both of which have recently been assigned. Unfortunately, the latter approach does not provide any information about long range inter-ring coupl-

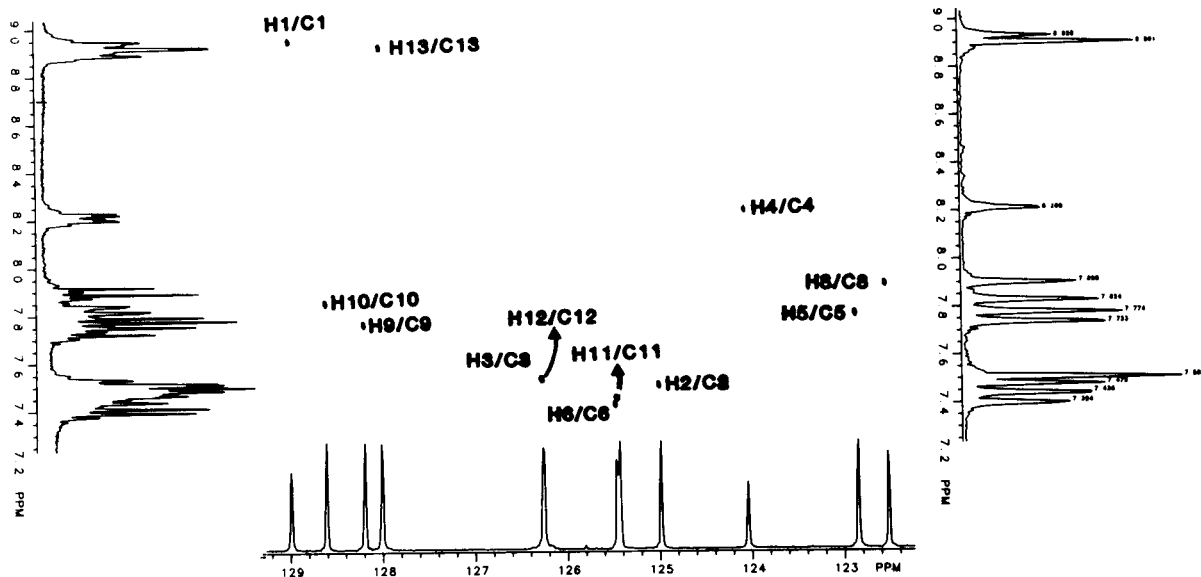


Figure 2. Two dimensional proton-carbon heteronuclear chemical shift correlation spectrum of benzo[3,4]phenanthro[1,2-*b*]thiophene (7) with broad band homonuclear proton decoupling.

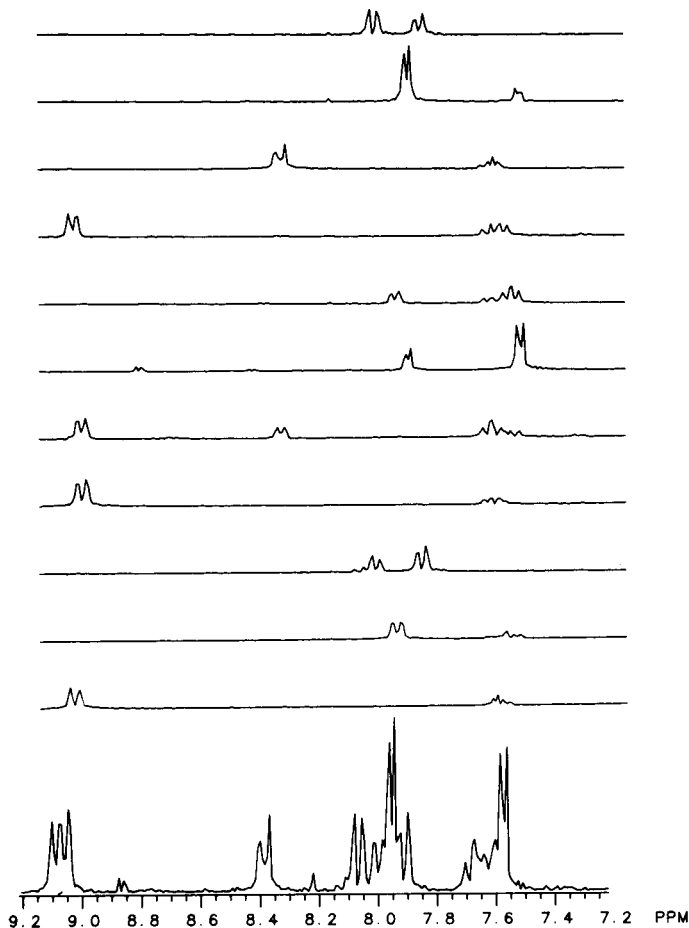


Figure 3. Two-dimensional heteronuclear relayed coherence transfer (RCT2D) nmr spectrum of benzo[3,4]phenanthro[1,2-*b*]thiophene (7).

ings which are very commonly encountered in polynuclear aromatic systems. Finally, a newly available alternative for the establishment of proton connectivities would be their indirect verification from long range optimized heteronuclear chemical shift correlation [57,59-68]. This last approach to the problem of establishing proton connectivities allows access to both vicinal and long range coupling information in an indirect fashion but has yet to be employed in this fashion.

Precise proton chemical shifts were first established using heteronuclear chemical shift correlation with broad-band homonuclear proton decoupling as described by Bax [58] (Figure 2). Accurate proton chemical shifts were obtained by extracting the appropriate interferograms and zero filling to 4K points prior to the second Fourier transform. As will be noted from the projection of the data matrix, singlets were obtained for eleven proton resonances, two of the protons having degenerate proton and nearly degenerate carbon chemical shifts (7.50 and 126.25/126.26 ppm). Next, the vicinal proton coupling network was established from the heteronuclear relayed coherence transfer (RCT2D) experiment [47-56] (Figure 3). Although this experiment does extend the proton/carbon network considerably, it does not have any provision for the orientation of the individual heteronuclear spin system relative to one another. The task of orienting the spin systems may be accomplished in any of several ways which were presented briefly above.

In terms of relative efficiency, the COSY experiment is undeniably the most sensitive and the least demanding in terms of quantities of material and spectrometer time.

Table V

Torsion Angles for the Non-Hydrogen Atoms of
Benzo[3,4]phenanthro[1,2-*b*]thiophene (7)

1	2	3	4	1-2-3-4
C(6)	S(7)	C(7A)	C(4B)	-.1(2)
C(6)	S(7)	C(7A)	C(7B)	178.0(2)
C(7A)	S(7)	C(6)	C(5)	.5(2)
C(2)	C(1)	C(13C)	C(4A)	6.5(4)
C(2)	C(1)	C(13C)	C(13B)	-179.1(2)
C(13C)	C(1)	C(2)	C(3)	-.4(4)
C(1)	C(2)	C(3)	C(4)	-4.0(4)
C(2)	C(3)	C(4)	C(4A)	2.0(4)
C(3)	C(4)	C(4A)	C(4B)	-171.0(2)
C(3)	C(4)	C(4A)	C(13C)	4.3(4)
C(4B)	C(4A)	C(13C)	C(1)	167.1(2)
C(4B)	C(4A)	C(13C)	C(13B)	-7.5(3)
C(13C)	C(4A)	C(4B)	C(5)	-176.4(2)
C(13C)	C(4A)	C(4B)	C(7A)	-1.9(3)
C(4)	C(4A)	C(4B)	C(5)	-1.0(4)
C(4)	C(4A)	C(4B)	C(7A)	173.5(2)
C(4)	C(4A)	C(13C)	C(1)	-8.3(3)
C(4)	C(4A)	C(13C)	C(13B)	177.1(2)
C(5)	C(4B)	C(7A)	S(7)	-.2(3)
C(5)	C(4B)	C(7A)	C(7B)	-178.4(2)
C(7A)	C(4B)	C(5)	C(6)	.6(3)
C(4A)	C(4B)	C(5)	C(6)	175.4(2)
C(4A)	C(4B)	C(7A)	S(7)	-175.7(2)
C(4A)	C(4B)	C(7A)	C(7B)	6.2(4)
C(4B)	C(5)	C(6)	S(7)	-.7(3)
S(7)	C(7A)	C(7B)	C(8)	2.4(3)
S(7)	C(7A)	C(7B)	C(13B)	-178.7(2)
C(4B)	C(7A)	C(7B)	C(8)	-179.8(2)
C(4B)	C(7A)	C(7B)	C(13B)	-.8(4)
C(8)	C(7B)	C(13B)	C(13A)	-9.4(3)
C(8)	C(7B)	C(13B)	C(13C)	170.3(2)
C(13B)	C(7B)	C(8)	C(9)	-1.7(4)
C(7A)	C(7B)	C(8)	C(9)	177.2(2)
C(7A)	C(7B)	C(13B)	C(13A)	171.6(2)
C(7A)	C(7B)	C(13B)	C(13C)	-8.6(3)
C(7B)	C(8)	C(9)	C(9A)	7.4(4)
C(8)	C(9)	C(9A)	C(10)	174.2(3)
C(8)	C(9)	C(9A)	C(13A)	-1.5(4)
C(10)	C(9A)	C(13A)	C(13)	-9.4(4)
C(10)	C(9A)	C(13A)	C(13B)	174.6(2)
C(13A)	C(9A)	C(10)	C(11)	4.8(4)
C(9)	C(9A)	C(10)	C(11)	-170.9(3)
C(9)	C(9A)	C(13A)	C(13)	166.3(2)
C(9)	C(9A)	C(13A)	C(13B)	-9.7(3)

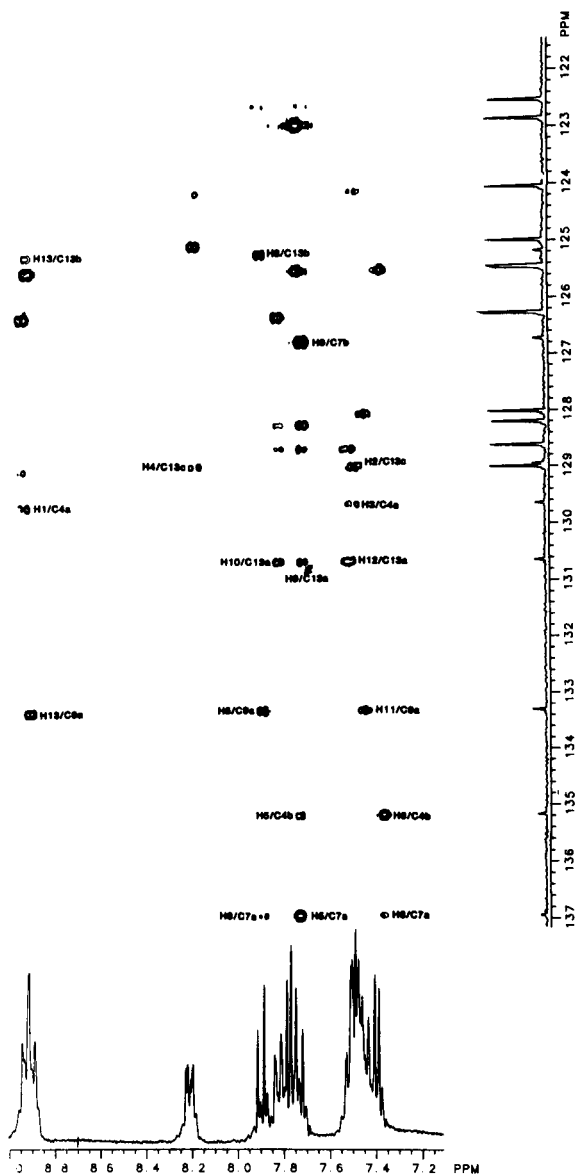


Figure 4. Long range optimized proton-carbon heteronuclear chemical shift correlation spectrum of benzo[3,4]phenanthro[1,2-*b*]thiophene (7) in deuteriochloroform. The experiment was performed with delays for magnetization transfer, Δ_1 and Δ_2 , optimized for 10 Hz at 50.0 and 33.3 msec respectively.

Subsequent acquisition of a heteronuclear chemical shift correlation experiment will then afford the protonated carbon resonance assignments. This approach has the disadvantage, unfortunately, of leaving the quaternary carbon resonances unassigned. In contrast, both long range optimized heteronuclear chemical shift correlation [57, 59-68] and ^{13}C - ^{13}C INADEQUATE [38-44] provide the means of making quaternary carbon resonance assignments. Based upon our previous experience with 9-methyl-

phenanthro[4,3-*a*]dibenzothiophene [57] we have found that the long range proton-carbon heteronuclear chemical shift correlation experiment can be performed with approximately thirty times the relative sensitivity of the ^{13}C - ^{13}C INADEQUATE experiment. However, since our previous study [57] represents the only application of this technique to complex polynuclear aromatic heterocycles to appear in the literature, we were concerned about the transportability of the experiment from the relatively well characterized phenanthro[4,3-*a*]dibenzothiophene [46,53] system to the completely unstudied benzo[3,4]phenanthro-

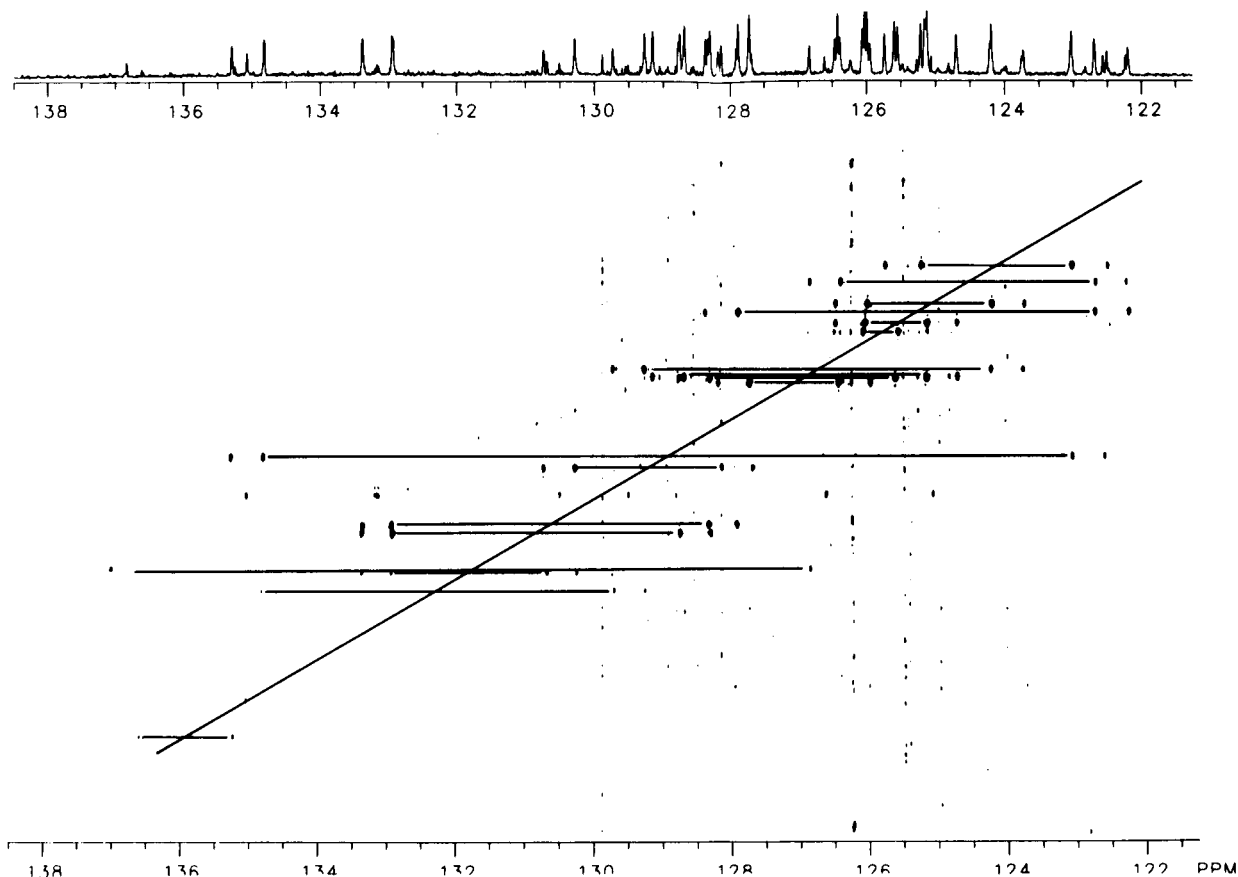
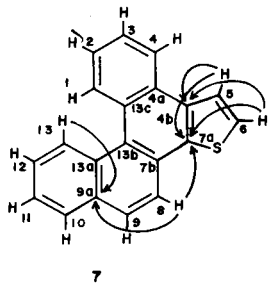


Figure 5. ^{13}C - ^{13}C double quantum INADEQUATE spectrum of benzo-[3,4]phenanthro[1,2-*b*]thiophene (**7**) in deuteriochloroform recorded at 125.762 MHz.

[1,2-*b*]thiophene (**7**) ring system. Thus, we elected to first perform the long range optimized heteronuclear chemical shift correlation experiment followed by the confirmation of the assignments with a 125 MHz ^{13}C - ^{13}C INADEQUATE spectrum.

Several key long range connectivities are critical to the assignment of the proton and carbon nmr spectra of **7**. Coupling of the bay region H13 proton to C9a and further coupling to H8 would be expected, effectively linking these two spin systems to one another as shown by **7**. Alternatively, should either of these couplings be unobservable for some reason, the connectivity could still be established through the anticipated five bond *epi* zig-zag coupling between H13-H9 which would be readily observable in the



7

COSY spectrum based upon past experience [30,43,69]. Once H8 has been tentatively identified, it would in turn be expected to be long range coupled to the C7a resonance which is readily assignable in the carbon spectrum, on the basis of its chemical shift and T_1 relaxation behavior, as the quaternary carbon resonating furthest downfield and possessing the longest relaxation time. Coupling between H5 and C7a should also be observed. Through this series of connectivities, H13 may be differentiated from H1 thus allowing an unequivocal assignment of the spectra to be obtained. In similar fashion, a strategy may be built up which completes the assignment and orientation of the remaining AB spin system on the thiophene moiety. Here, C4b would also be utilized as a key focal point in addition to C7a. Possible three bond coupling pathways for C4b would include coupling to H4 and H6 (**7**), the two bond coupling to H5 would also have to be considered since this is a prominent coupling in the proton coupled ^{13}C -nmr spectrum of thiophene [70].

Analysis of the long range optimized heteronuclear proton-carbon chemical shift correlation spectrum shown in Figure 4 shows that some of the expected coupling pathways are readily observed in addition to some which

Table VI

Torsional Angles for the Non-Hydrogen Atoms of
1-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene **33**

1	2	3	4	1-2-3-4
C(4B)	S(5)	C(6)	C(7)	-0.2(2)
C(6)	S(5)	C(4B)	C(4A)	173.2(2)
C(6)	S(5)	C(4B)	C(7A)	-0.82(13)
C(2)	C(1)	C(13C)	C(4A)	12.1(2)
C(2)	C(1)	C(13C)	C(13B)	-172.5(2)
C(13C)	C(1)	C(2)	C(3)	-3.2(3)
C(14)	C(1)	C(2)	C(3)	168.5(2)
C(14)	C(1)	C(13C)	C(4A)	-158.9(2)
C(14)	C(1)	C(13C)	C(13B)	16.5(3)
C(1)	C(2)	C(3)	C(4)	-5.8(3)
C(2)	C(3)	C(4)	C(4A)	5.4(3)
C(3)	C(4)	C(4A)	C(4B)	-170.1(2)
C(3)	C(4)	C(4A)	C(13C)	3.9(2)
C(4B)	C(4A)	C(13C)	C(1)	161.57(14)
C(4B)	C(4A)	C(13C)	C(13B)	-14.2(2)
C(13C)	C(4A)	C(4B)	S(5)	-176.68(12)
C(13C)	C(4A)	C(4B)	C(7A)	-3.2(2)
C(4)	C(4A)	C(4B)	S(5)	-2.5(2)
C(4)	C(4A)	C(4B)	C(7A)	170.9(2)
C(4)	C(4A)	C(13C)	C(1)	-12.6(2)
C(4)	C(4A)	C(13C)	C(13B)	171.66(15)
S(5)	C(4B)	C(7)	C(7)	1.4(2)
S(5)	C(4B)	C(7A)	C(7B)	-173.14(12)
C(4A)	C(4B)	C(7A)	C(7)	-172.86(15)
C(4A)	C(4B)	C(7A)	C(7B)	12.6(2)
S(5)	C(6)	C(7)	C(7A)	.8(2)
C(6)	C(7)	C(7A)	C(4B)	-1.4(2)
C(6)	C(7)	C(7A)	C(7B)	172.4(2)
C(4B)	C(7A)	C(7B)	C(8)	172.50(15)
C(4B)	C(7A)	C(7B)	C(13B)	-3.9(2)
C(7)	C(7A)	C(7B)	C(8)	-1.0(3)
C(7)	C(7A)	C(7B)	C(13B)	-177.4(2)
C(8)	C(7B)	C(13B)	C(13A)	-14.3(2)
C(8)	C(7B)	C(13B)	C(13C)	170.14(14)
C(13B)	C(7B)	C(8)	C(9)	3.7(2)
C(7A)	C(7B)	C(8)	C(9)	-172.6(2)
C(7A)	C(7B)	C(13B)	C(13A)	162.07(14)
C(7A)	C(7B)	C(13B)	C(13C)	-13.5(2)
C(7B)	C(8)	C(9)	C(9A)	6.3(3)
C(8)	C(9)	C(9A)	C(10)	170.9(2)
C(8)	C(9)	C(9A)	C(13A)	-5.2(2)
C(10)	C(9A)	C(13A)	C(13)	-7.7(2)
C(10)	C(9A)	C(13A)	C(13B)	178.09(15)
C(13A)	C(9A)	C(10)	C(11)	3.3(3)
C(9)	C(9A)	C(10)	C(11)	-172.8(2)
C(9)	C(9A)	C(13A)	C(13)	168.5(2)
C(9)	C(9A)	C(13A)	C(13B)	-5.7(2)
C(9A)	C(10)	C(11)	C(12)	2.5(3)
C(10)	C(11)	C(12)	C(13)	-3.7(3)
C(11)	C(12)	C(13)	C(13A)	-1.0(3)
C(12)	C(13)	C(13A)	C(9A)	6.7(2)
C(12)	C(13)	C(13A)	C(13B)	-179.3(2)
C(9A)	C(13A)	C(13B)	C(7B)	15.2(2)
C(9A)	C(13A)	C(13B)	C(13C)	-169.42(14)
C(13)	C(13A)	C(13B)	C(7B)	-158.66(15)
C(13)	C(13A)	C(13B)	C(13C)	16.7(2)
C(7B)	C(13B)	C(13C)	C(1)	-152.8(2)
C(7B)	C(13B)	C(13C)	C(4A)	22.6(2)
C(13A)	C(13B)	C(13C)	C(1)	31.9(2)
C(13A)	C(13B)	C(13C)	C(4A)	-152.72(15)

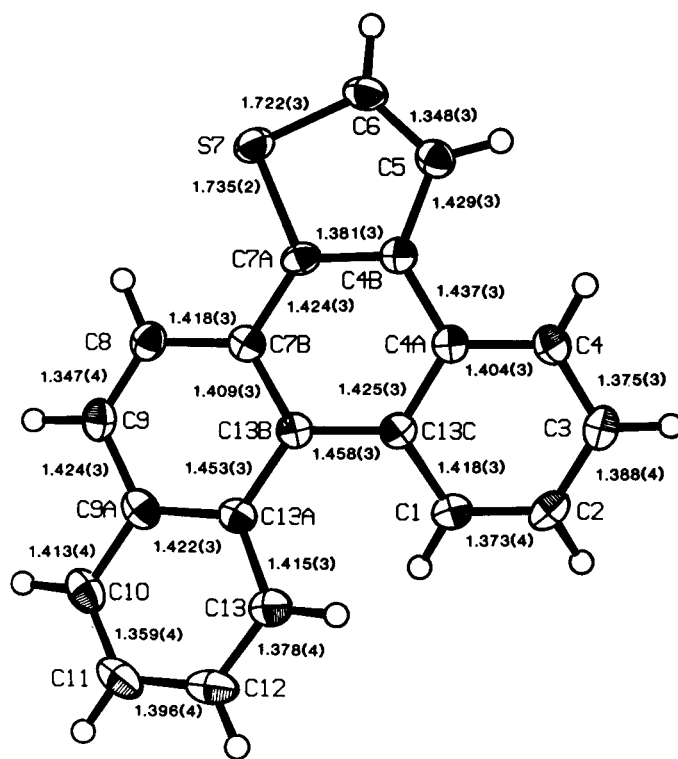
Figure 6. View of benzo[3,4]phenanthro[1,2-*b*]thiophene (**7**) showing the atom labelling scheme and bond distances.

Table VII

Bond Distances and Angles for the Hydrogen Atoms of
Benzo[3,4]phenanthro[1,2-*b*]thiophene (**7**)

1	2	3	1-2	1-2-3
H(C1)	C(1)	C(2)	.96(2)	118.5(14)
H(C1)	C(1)	C(13c)	.93(2)	119.4(14)
H(C2)	C(2)	C(3)	.93(2)	118.(2)
H(C2)	C(2)	C(1)	.97(3)	121.(2)
H(C3)	C(3)	C(4)	.97(3)	119.(2)
H(C3)	C(3)	C(2)	.95(3)	122.(2)
H(C4)	C(4)	C(4a)	.95(3)	117.(2)
H(C4)	C(4)	C(3)	.93(3)	122.(2)
H(C5)	C(5)	C(6)	.93(3)	122.5(14)
H(C5)	C(5)	C(4b)	.94(3)	124.9(14)
H(C6)	C(6)	S(7)	.94(3)	119(2)
H(C6)	C(6)	C(5)	.96(2)	128.(2)
H(C8)	C(8)	C(9)	.96(2)	125.(2)
H(C8)	C(8)	C(7b)	1.00(3)	114.(2)
H(C9)	C(9)	C(9a)	1.00(3)	116.8(13)
H(C9)	C(9)	C(8)	.97(2)	123.1(13)
H(C10)	C(10)	C(11)	.97(2)	121.4(13)
H(C10)	C(10)	C(9a)	.92(3)	117.6(13)
H(C11)	C(11)	C(12)	.92(3)	119.(2)
H(C11)	C(11)	C(10)	.93(3)	122.(2)
H(C12)	C(12)	C(13)	.93(3)	117.(2)
H(C12)	C(12)	C(11)	.98(2)	122.(2)
H(C13)	C(13)	C(13a)	.98(2)	119.2(12)
				119.6(12)

were not anticipated. Thus, in the case of the C7a resonance, the anticipated couplings to H8 and H5 were observed in addition to an unanticipated weak coupling to H6 which is probably through the heteroatom. Couplings to the C4b resonance included the expected two and three bond couplings to H5 and H6, respectively, but no coupling to H4 was observed. Based upon the analysis of the long range coupling information provided from Figure 4 and the vicinal proton-proton coupling information afforded by the RCT2D spectrum (Figure 3) it was possible to totally assign the proton and carbon spectra of **7** as collected in Table I.

Confirmation of the ^{13}C -resonance assignments of **7** obtained by the analysis of the long range optimized heteronuclear proton-carbon chemical shift correlation spectrum was also provided by the acquisition of a 125 MHz ^{13}C - ^{13}C INADEQUATE spectrum which is shown in Figure 5. Comparison of the spectra illustrated by Figures 4 and 5 allows some useful insight to be gained in terms of the relative sensitivities of the two experiments. First, both spectra were obtained using the same sealed sample. Second, Figure 4 was obtained using a 300 MHz spectrometer while Figure 5 was recorded on a 500 MHz instrument. Lastly, Figure 4 was obtained as an overnight run of 13 hours while the ^{13}C - ^{13}C INADEQUATE spectrum required a run of approximately 18 hours at 125 MHz. Hence, in those cases where insufficient quantities of material are available or where spectrometer time is limited, especially on lower field instruments such as a 300 MHz system, the

long range optimized heteronuclear chemical shift correlation experiment will become the one of choice. Doubtless, however, there will arise instances in which the data will not be amenable to analysis in this fashion in which case recourse to the ^{13}C - ^{13}C INADEQUATE experiment will become necessary.

Responses for some of the quaternary carbons in the 125 MHz ^{13}C - ^{13}C INADEQUATE spectrum of **7** were, unfortunately, rather weak because of the lengthy relaxation times of these carbons relative to the 2.7 second recycle time used in the performance of the experiment. Despite this shortcoming, connectivities were observed for all but one of the possible connectivities in the molecule, that one not observed because of the highly AB character of that particular ^{13}C - ^{13}C pairing.

While there is little point in a protracted discussion of all of the possible connectivities contained in the spectrum in Figure 5, it is useful to discuss connectivities which were critical to the assignment of the long range optimized proton-carbon heteronuclear chemical shift correlation experiment presented in Figure 4. Weakest of the responses in Figure 5 is that observed between C7a-C4b which resonate at 136.83 and 135.07 ppm, respectively. It will also be noted that there is a further connectivity between C7a and another quaternary carbon resonating upfield at

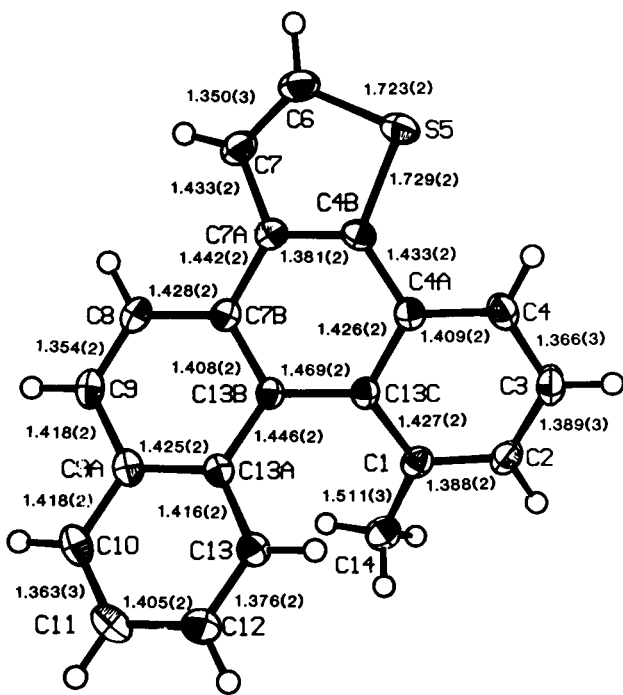


Figure 7. View of 1-methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (**33**) showing the atom labelling scheme and bond distances.

Table VIII

Bond Distances and Angles for the Hydrogen Atoms of 1-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene **33**

1	2	3	1-2	1-2-3
H(C2)	C(2)	C(3)	.92(2)	120.6(13)
H(C2)	C(2)	C(1)		116.8(13)
H(C3)	C(3)	C(4)	.94(2)	120.0(13)
H(C3)	C(3)	C(2)		120.5(13)
H(C4)	C(4)	C(4a)	.96(2)	119.1(12)
H(C4)	C(4)	C(3)		120.8(12)
H(C6)	C(6)	C(7)	.95(2)	129.4(12)
H(C6)	C(6)	S(5)		117.8(12)
H(C7)	C(7)	C(7a)	.92(2)	125.9(12)
H(C7)	C(7)	C(6)		121.5(12)
H(C8)	C(8)	C(9)	.94(2)	120.5(11)
H(C8)	C(8)	C(7b)		118.5(11)
H(C9)	C(8)	C(9a)	.95(2)	119.6(12)
H(C9)	C(9)	C(8)		119.7(12)
H(C10)	C(10)	C(11)	.94(2)	122.2(12)
H(C10)	C(10)	C(9a)		116.6(12)
H(C11)	C(11)	C(12)	.95(2)	120.1(13)
H(C11)	C(11)	C(10)		120.2(13)
H(C12)	C(12)	C(13)	.96(2)	118.3(11)
H(C12)	C(12)	C(11)		121.1(11)
H(C13)	C(13)	C(13a)	.95(2)	118.2(11)
H(C13)	C(13)	C(12)		120.4(11)
H(141)	C(14)	H(142)	.94(3)	107.(2)
H(141)	C(14)	H(143)		108.(2)
H(141)	C(14)	C(1)		113.(2)
H(142)	C(14)	H(143)	.98(2)	107.(2)
				113.0(13)
			-.95(2)	107.9(14)

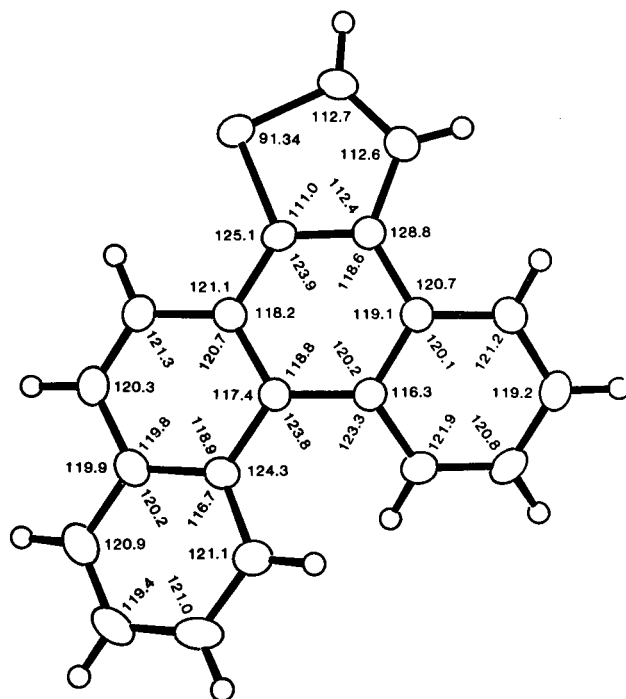


Figure 8. View of benzo[3,4]phenanthro[1,2-b]thiophene (7) showing bond angles of the non-hydrogen atoms (esd's are in the range 0.12-0.30°).

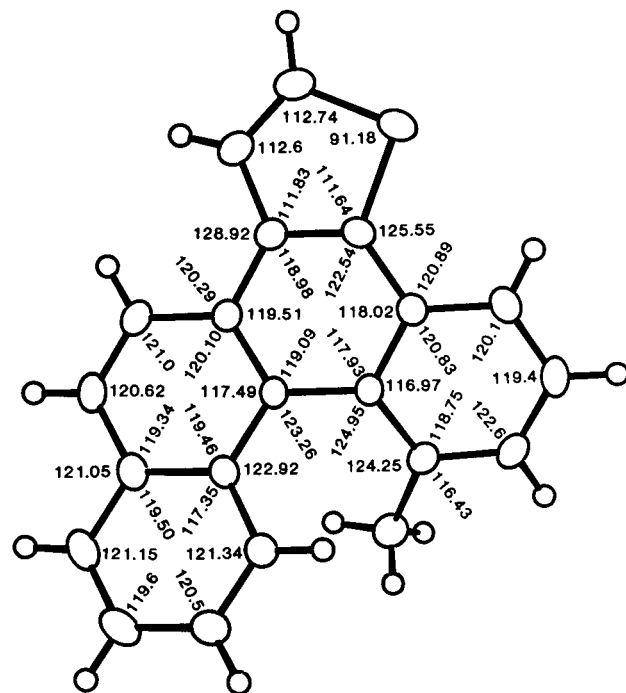


Figure 9. View of 1-methylbenzo[3,4]phenanthro[2,1-b]thiophene (33) showing bond angles for the non-hydrogen atoms (esd's are in the range 0.08-0.20°).

Table IX

Least-Squares Planes and Dihedral Angles for
Benzo[3,4]phenanthro[1,2-b]thiophene (7)

Plane 1

Equation of plane

$$-3.7869x + 3.23213y + 19.57181z - 5.98768 + 0$$

Distances of atoms from plane in Å.

$$S(7) -.0002(7) \text{ C}(4b) .001(2) \text{ C}(5) -.004(3) \text{ C}(6) .004(3) \text{ C}(7a) .001(2)$$

$$\chi^2 5.31$$

Plane 2

Equation of plane

$$1.98237x - 3.13632y - 21.77370z + 8.05755 = 0$$

Distances of atoms from plane

$$\text{C}(1) .021(3) \text{ C}(2) .023(3) \text{ C}(3) -.032(3) \text{ C}(4) -.004(3) \text{ C}(4a) .036(2) \text{ C}(13c) \\ -.044(2) \text{ H}(C1)^* .13(2) \text{ H}(C2)^* .13(2)$$

$$\chi^2 908.17$$

Plane 3

Equation of plane

$$3.30922x - 3.37145y - 19.55398z + 6.36080 = 0$$

Distances of atoms from plane

$$\text{C}(4a) -.008(2) \text{ C}(4b) -.041(2) \text{ C}(7a) .036(2) \text{ C}(7b) .019(2) \text{ C}(13b) -.064(2) \\ \text{C}(13c) .062(2)$$

$$\chi^2 2147.78$$

Plane 4

Equation of plane

$$4.30118x - 3.34615y - 18.09512z + 5.23371 = 0$$

Distances of atoms from plane

$$\text{C}(7b) -.020(2) \text{ C}(8) -.045(3) \text{ C}(9) .051(3) \text{ C}(9a) .024(3) \text{ C}(13a) -.073(2) \\ \text{C}(13b) .072(2) \text{ H}(C8)^* -.11(3) \text{ H}(C9)^* .09(2)$$

$$\chi^2 2844.05$$

Plane 5

Equation of plane

$$-5.68410x + 3.16861y + 15.55463z - 3.26694 = 0$$

Distances of atoms from plane

$$\text{C}(9a) -.045(3) \text{ C}(10) .004(3) \text{ C}(11) .040(3) \text{ C}(12) -.028(3) \text{ C}(13) -.025(3) \\ \text{C}(13a) .045(2) \text{ H}(C13)^* -.11(2) \text{ H}(C12)^* -.12(3)$$

$$\chi^2 1070.26$$

Dihedral Angles for Selected Planes

Planes	Angle
1 3	3.35(7)
2 3	10.25(9)
3 4	7.19(8)
4 5	10.79(9)
2 5	27.96(8)

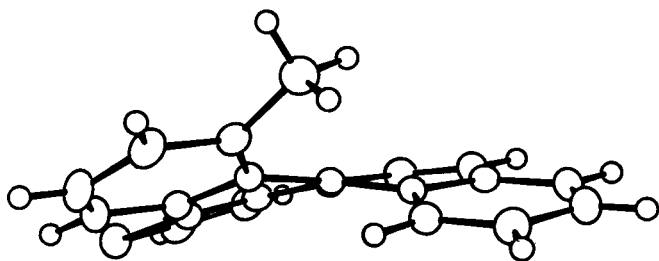


Figure 10. Edge view of 1-methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (**33**) showing the helical distortion of the 4-helicene nucleus.

126.61 ppm which must therefore be assigned as C7b. The latter assignment, although not discussed above, was identified by a prominent long range ^1H - ^{13}C connectivity between H9 and C7b, the two experiments thus in complete agreement. Continuing from the C4b response at 135.07 ppm, we observe two additional connectivities, one to a quaternary carbon resonating at 129.50 ppm which must be C4a, the other to protonated carbon resonating upfield at 122.81 ppm which is assigned as C5. Again, there is complete agreement between the long range proton-carbon and ^{13}C - ^{13}C INADEQUATE experiments. Overall, the ^{13}C - ^{13}C INADEQUATE spectrum shown in Figure 5 fully confirmed the assignments of **7** made using the long range optimized proton-carbon heteronuclear chemical shift correlation experiment shown in Figure 4.

Benzo[3,4]phenanthro[2,1-*b*]thiophene (**13**).

Assignment of the proton and carbon nmr spectra of benzo[3,4]phenanthro[2,1-*b*]thiophene (**13**) was accomplished in a fashion identical to that employed in the assignment of the spectra of **7** with the sole exception that the acquisition of the ^{13}C - ^{13}C INADEQUATE was omitted. Thus, proton-carbon chemical shift pairings were established with the heteronuclear chemical shift correlation experiment with broadband homonuclear proton decoupling [58] followed by the acquisition of a RCT2D spectrum [47-56] which established the vicinal proton coupling network. Finally, the total assignment was completed using the long range optimized heteronuclear chemical shift correlation experiment. Assignments for **13** are contained in Table I.

Assignment of the Spectra of the 1-Methyl Isomers.

Assignment of the proton and carbon spectra of the 1-methyl isomers was straightforwardly accomplished. Spectral assignments were made on the basis of COSY [31-33] and chemical shift correlation with broadband homonuclear decoupling [58] spectra taking into account empirical changes in quaternary carbon chemical shifts on the basis of methyl substituent additivities. Assignments

Table X

Least-Squares Planes and Dihedral Angles for 1-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene **33**

Plane 1

Equation of plane

$$4.28128x + 7.12420y + 3.53672z - 2.49071 = 0$$

Distances of atoms from plane in Å. (* indicates atom not used in plane calculation)

$$\text{S(5)} \text{ } -.0003(5) \text{ C(4b)} \text{ } .007(2) \text{ C(6)} \text{ } .000(2) \text{ C(7)} \text{ } .006(2) \text{ C(7a)} \text{ } -.008(2) \text{ H(C6)*} \text{ } .01(2) \text{ H(C7)*} \text{ } .00(2)$$

$$\chi^2 \text{ } 62.74$$

Plane 2

Equation of plane

$$1.69757x + 7.933386y + 4.40706z - 2.01920 = 0$$

Distances of atoms from plane

$$\text{C(1)} \text{ } .049(2) \text{ C(2)} \text{ } .019(2) \text{ C(3)} \text{ } -.058(2) \text{ C(4)} \text{ } .014(2) \text{ C(4a)} \text{ } .050(2) \text{ C(13c)} \text{ } -.0715(15) \text{ C(14)*} \text{ } .402(2) \text{ H(C2)*} \text{ } .08(2)$$

$$\chi^2 \text{ } 5508.21$$

Plane 3

Equation of plane

$$3.68864x + 7.55587y + 1.929287z + 1.92921z - 1.91114 = 0$$

Distances of atoms from plane

$$\text{C(4a)} \text{ } -.030(2) \text{ C(4b)} \text{ } -.076(2) \text{ C(7a)} \text{ } .079(2) \text{ C(7b)} \text{ } .021(2) \text{ C(13b)} \text{ } -.1096(15) \text{ C(13c)} \text{ } .1146(15)$$

$$\chi^2 \text{ } 16765.86$$

Plane 4

Equation of plane

$$5.03922x + 6.97346y - 1.53904z - 1.31038 = 0$$

Distances of atoms from plane

$$\text{C(7b)} \text{ } -.0536(15) \text{ C(8)} \text{ } -.023(2) \text{ C(9)} \text{ } .062(2) \text{ C(9a)} \text{ } -.010(2) \text{ C(13a)} \text{ } -.062(2) \text{ C(13b)} \text{ } .0850(15) \text{ H(C8)*} \text{ } -.09(2) \text{ H(C9)*} \text{ } .14(2)$$

$$\chi^2 \text{ } 7662.52$$

Plane 5

Equation of plane

$$6.30973x + 6.02943y - 2.55567z - 1.43220 = 0$$

Distances of atoms from plane

$$\text{C(9a)} \text{ } -.034(2) \text{ C(10)} \text{ } -.0001(2) \text{ C(11)} \text{ } .034(2) \text{ C(12)} \text{ } -.016(2) \text{ C(13)} \text{ } -.023(2) \text{ C(13a)} \text{ } .0410(15) \text{ H(C13)*} \text{ } -.09(2) \text{ H(C12)*} \text{ } -.06(2)$$

$$\chi^2 \text{ } 1749.93$$

Dihedral Angles for Selected Planes

Planes	Angle
1 3	7.10(5)
2 3	14.27(6)
3 4	13.57(5)
4 5	10.53(6)
2 5	37.34(5)

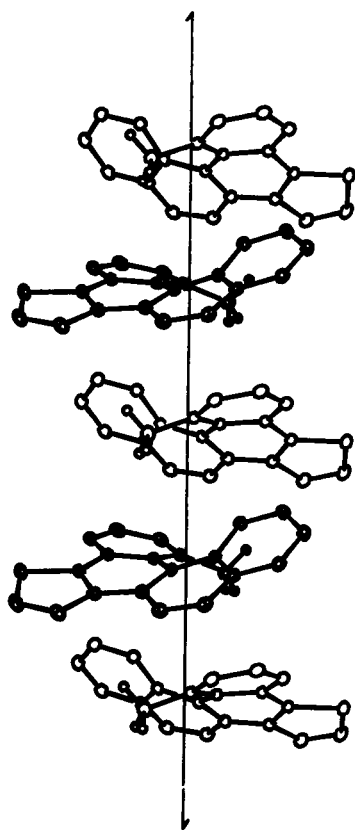


Figure 11. View showing the interleaving of homochiral molecules of 1-methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (**7**) along the screw axis. Molecules with shaded ellipsoids are related to those represented by open ellipsoids by the 2_1 screw operation.

for 1-methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (**28**) and 1-methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (**33**) are also summarized in Table I.

X-Ray Crystallography.

Crystals suitable for X-ray crystallographic study were obtained for two of the compounds studied, benzo[3,4]phenanthro[1,2-*b*]thiophene (**7**) and 1-methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (**33**), by slow evaporation of the deuteriochloroform solutions from the nmr investigations. Positional and thermal parameters are listed for **7** and **33** in Tables II and III, respectively. Views of the atom labeling scheme showing bond distances for **7** and **33** are shown in Figures 6 and 7, while the bond angles for **7** and **33** are shown in Figures 8 and 9, respectively.

Both molecules are non-planar and are twisted in a helical fashion. As a result, they are chiral. An edge-on view of **33** illustrating this twist is shown in Figure 10. Unlike many helicenes which are spontaneously resolved upon crystallization, **7** and **33** crystallize as enantiomeric pairs related by a center of symmetry. Presumably, like benzo[*c*]phenanthrene (4-helicene) [71], **7** and **33**

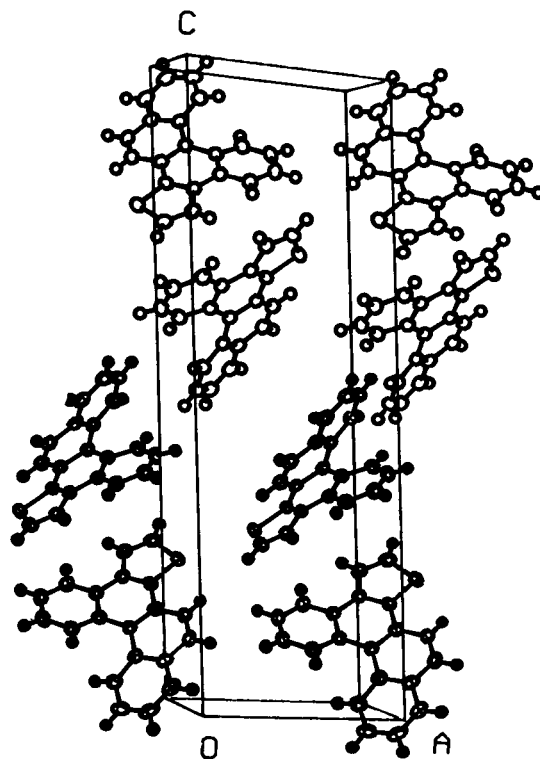


Figure 12. Packing diagram for benzo[3,4]phenanthro[1,2-*b*]thiophene (**7**) showing the alternating double layers of homochiral molecules along *c*. Molecules with shaded ellipsoids are of opposite chirality to those represented by open ellipsoids.

readily racemize. The crystallographic screw axes at $1/2, y, 1/4$ and $1/2, y, 3/4$ pass through the bay regions of the different enantiomorphs of **33** respectively, in a manner similar to that observed in 1-methylphenanthro[3,4-*b*]thiophene [72]. This packing mode results in the interleaving of columns of molecules of like chirality along the screw axes (Figure 11). The enantiomorphs are related by inversion so that columns of molecules of alternating chirality are observed along *c*. The closest intermolecular contacts are generally among atoms related by the twofold screw, although there are no non-H contacts closer than 3.5 \AA . Due to the relative shortness of the *b* axis in **7**, the interleaving of molecules related by a screw axis operation is not possible, and screw axes do not pass through the bay regions of **7**. Double layers of molecules of like chirality alternate in the *c* direction (see Figure 12). The closest intermolecular contacts are generally among atoms related by a *b* axis translation with the closest C...C contact being $3.274(4) \text{ \AA}$ between C7a and C9 (related by $x, 1+y, z$).

Close, intramolecular contacts in the bay regions are responsible for the non-planarity of **7** and **33**. While the thiophene rings are planar, the individual phenyl rings are not. In both **7** and **33**, the central phenyl rings show the

largest deviations from planarity. As would be expected due to the 1-methylation, the deviations from planarity are greater for **33**. The methyl carbon, C14, is forced out of the plane of the phenyl ring to which it is bound by 0.402(2) Å. The dihedral angles between the planes of the adjacent phenyl rings for **33**, which range from 10.53(6)° to 14.27(6)°, are intermediate between those observed in benzo[*c*]phenanthrene [71] and 1,12-dimethylbenzo[*c*]phenanthrene [73], while the dihedral angles for **7** which range from 7.19(8)° to 10.79(9)° are more similar to those found in benzo[*c*]phenanthrene. In addition to the distortion from planarity, the result of overcrowding can be seen in the sum of the exocyclic angles at the bridgehead carbon atoms of the bay regions which are 371.4° and 371.1° for **7** and **33**, respectively. A value of 360° is expected for an unstrained system. There are also large deviations from the ideal values of 0° or 180° for many of the torsional angles. A complete list of torsion angles is contained in Tables V and VI. Because the methyl group can rotate to minimize steric crowding, the closest H...H intramolecular contact in **33** (H141...H1 is 2.28(3) Å) is greater than that for in **7** (H1...H13, 2.03(3) Å) even though the closest C...C contact in **33** (C14...C1, 2.905(2) Å) is less than that of **7** (C13...C1, 3.009(4) Å).

The 4-helicene fragment of **7** shows some slight deviations from twofold symmetry (with the twofold axis lying along the C7b-C13b bond) as a result of the fusion of the thiophene ring. For example, a difference of 0.034 Å is observed between the bond lengths of C4b-C7b and C8-C9 and a difference of 2.6° is found between the bond angles of C4b-C7a-C7b and C7b-C8-C9. Additional deviations from twofold symmetry are observed for the 4-helicene fragment of **33** upon 1-methyl substitution.

The bond lengths and angles of the thiophene rings of both molecules are similar. The S to bridgehead carbon bonds are slightly longer than the S to tertiary carbon bonds in both compounds which is consistent with that observed for 1-methylphenanthro[3,4-*b*]thiophene [72]. The C4a and C7b bond is shorter than that between comparable atoms in 1-methylphenanthro[3,4-*b*]thiophene. There is a significant difference in bond lengths between C4a-C7a and C5-C6 in **7** and between C4a-C7a and C6-C7 in **33**. The variation in bond lengths and angles of the helicene fragments of **7** and **33** follows the pattern observed in other helicenes [74-80]. There are alternating long-short C-C bonds around the outside of the molecules, whereas the longest C-C bonds are between the inner atoms of the bay region. Away from the bay region and except for the effects related to the fusion of the thiophene ring, the angles at the C atoms are close to those normally observed for an aromatic system.

Conclusions.

Both possible orientations for thiophene ring [*b*]-fusion

to the 1,2-face of benzo[*c*]phenanthrene have been synthesized accompanied by their 1- and 11-methyl analogs. Despite moderately congested spectra even at 300 MHz (proton observation), it was possible to make total assignments of both the ¹H- and ¹³C-nmr spectra in all cases. Direct comparison of assignments made by both long range optimized proton-carbon heteronuclear chemical shift correlation and ¹³C-¹³C INADEQUATE experiments have shown the former to be highly reliable for both ordering proton spin systems relative to one another and in making quaternary carbon resonance assignments. In addition, the long range optimized experiment can also be performed in much more reasonable periods of time on moderate field superconducting spectrometers than can the ¹³C-¹³C INADEQUATE experiment, and hence the latter should be reserved for those cases in which assignments cannot be made using the former. Crystal structures of one of the parent systems, **7**, and the opposing 1-methyl analog, **33**, were obtained. Both molecules were found to be helically distorted from planarity and are therefore chiral. Deviations from planarity in the case of the phenyl rings in the 4-helicene fragment was noted in both cases, the methyl substitution, as expected, causing an increased deviation. Studies are at present underway using these unequivocally characterized compounds to determine if they are constituents of solvent refined coal liquids, the results of these studies to be communicated elsewhere.

EXPERIMENTAL

Melting points were determined in open capillary tubes using a Thomas-Hoover melting point apparatus. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Mass spectra were obtained on a Hewlett-Packard Model 5980A mass spectrometer which employed electron impact ionization at an ionizing energy of 70 eV. Samples were introduced using by direct probe insertion at an ionization chamber temperature of 250°. Photocyclization was performed using an apparatus comprised of the following components: a 450 Watt medium pressure mercury ultraviolet lamp; a 500 ml capacity jacket constructed especially for the insertion of the compound to be photocyclized in benzene; an immersion well with a quartz jacket through which cold water was circulated. The uv lamp was inserted into the open space between the regular glass and the quartz jacket. All of the components of the photocyclization apparatus were purchased from ACE Glass, Inc., New Jersey. Proton nmr spectra were recorded for reaction intermediates at 60 MHz using a Varian EM-360A spectrometer operating in the CW mode. Proton spectra of final products, carbon and two-dimensional nmr spectra were acquired using a Nicolet NT-300 wide bore spectrometer operating at observation frequencies of 300.068 and 75.459 MHz, respectively, for ¹H/¹³C observation. The instrument was controlled by a Model 293-C pulse programmer and was equipped with a 5 mm ¹H/¹³C dual tuned probe. Typical instrument parameters were as follows: the 90° pulse lengths were 15.5 and 17.5 μsec for ¹H and ¹³C respectively with attenuation of the pulse power amplifier by 4 dB, the pulse lengths calibrated using the procedure of Lawn and Jones [81]. Interpulse delays for normal proton spectra were the acquisition time plus 1 sec while an interpulse delay of 3 sec was typically used for ¹³C experiments. Typical sweep widths for proton were +/- 2000 Hz, digitized with 16 or 32K points prior to Fourier transformation, while carbon spectra were routinely acquired using a sweep width of +/- 9600 Hz digitized with 32K points prior to

Fourier transformation. Proton spectra were variously processed using either a 0.1 Hz exponential multiplication of a sinusoidal multiplication to provide resolution enhancement. Carbon spectra were routinely processed using either a 1 Hz exponential multiplication or were mildly resolution enhanced using a double exponential apodization where signal to noise ratios would permit. The two-dimensional nmr experiments employed in this study are discussed individually below.

Synthesis.

2-(2'-Thienyl)-3-phenylpropenenitrile (3).

2-Thienylacetonitrile (**1**) (10 g, 0.081 mole, Aldrich) in 140 ml of absolute ethanol was added to a solution of sodium ethoxide (prepared from 1.9 g, 0.0041 mole of sodium in 56 ml of absolute ethanol). Benzaldehyde (**2**) (11.8 g, 0.11 mole) was added dropwise over ten minutes with stirring. The mixture was then warmed on a steam bath for 2.5 hours. The product was extracted with chloroform, washed with water, dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue obtained was then chromatographed over neutral alumina using benzene:hexane (1:1) as the eluent gave 15.7 g (92% yield) of 2-(2'-thienyl)-3-phenylpropenenitrile (**3**), mp 80°; ¹H-nmr (deuteriochloroform): 60 MHz, δ 7.30-6.87 (m, aromatic-H, thiophene and alkene protons, 9H); ms: m/e 211 (M⁺, 100), 209 (24.9), 196 (22.7), 212 (M⁺, 20.2).

Anal. Calcd. for C₁₃H₉NS: C, 73.90; H, 4.29; N, 6.63; S, 15.18. Found: C, 74.09; H, 4.41; N, 6.76; S, 15.03.

4-Cyanonaphtho[2,1-b]thiophene (4).

A solution of 1.5 g (0.007 mole) of the nitrile **3** and 0.2 g (0.00078 mole) of iodine in 360 ml of benzene was irradiated for 6 hours with a 450 Watt Hanovia medium pressure mercury lamp. During the course of the reaction, a slow stream of air was passed through the solution. The solvent was removed *in vacuo* and the residue was chromatographed over neutral alumina using benzene:hexane (1:1) as the eluent giving 4-cyanonaphtho[2,1-b]thiophene (**4**), 1.17 g (80% yield), mp 126°; ¹H-nmr (deuteriochloroform): 60 MHz, δ 8.90-6.90 m, aromatic-H, thiophene protons, 7H; ms: m/e 209 (M⁺, 100), 210 (M⁺, 15.5), 211 (M⁺, 5.3), 169 (7.9).

Anal. Calcd. for C₁₃H₇NS: C, 74.61; H, 3.37; N, 6.70; S, 15.32. Found: C, 74.87; H, 3.51; N, 6.65; S, 15.47.

Naphtho[2,1-b]thiophene-4-carboxaldehyde (5).

A solution of 100 ml of dry benzene and 1.5 g (0.007 mole) of the nitrile, **4**, was stirred at room temperature under a nitrogen atmosphere while 25.9 ml (0.025 mole) of diisobutylaluminum hydride (DIBAL-H, 1M in hexane) was added slowly *via* a syringe. The reaction flask was cooled in an ice bath and 20 ml of cold 15% hydrochloric acid was carefully added dropwise. The organic layer was extracted with chloroform and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded a yellowish solid, 0.97 g (65% yield), mp 85°; ¹H-nmr (deuteriochloroform): 60 MHz δ 8.92-6.90 (m, aromatic-H, thiophene protons, 7H), 10.2 (aldehyde-H). This compound was not submitted for mass spectral or elemental analyses due to the instability of the aldehyde moiety, but rather was used directly in the next synthetic step.

4-Styrylnaphtho[2,1-b]thiophene (6).

Sodium hydride (50%, 1.5 g) was washed with hexanes to remove adhering hydrocarbon oils, then 50 ml of dry dimethoxyethane (DME) was added, and a current of dry nitrogen was passed through to exclude air and moisture. To the resultant slurry at 20° was added dropwise 1.14 g (0.005 mole) of diethylbenzylphosphonate with stirring. After the addition, the solution was stirred at room temperature for 20 minutes. To the pale solution at 20°, naphtho[2,1-b]thiophene-4-carboxaldehyde (**5**) (0.90 g, 0.004 mole) in 10 ml of DME was added dropwise. The solution was stirred at room temperature for three hours. A large excess of water was added, and the precipitated product was filtered and recrystallized from ethanol to give 4-styrylnaphtho[2,1-b]thiophene (**6**) 1.02 g (90% yield), mp 122°; ¹H-nmr (deuteriochloroform): 60 MHz δ 9.0-7.0 (m, aromatic-H, thiophene protons, 14H); ms: m/e 286 (M⁺, 100), 285 (71.3), 284 (25.4). Compound **6** was photocyclized directly without further purification.

Benzo[3,4]phenanthro[1,2-b]thiophene (7).

A solution of 1.5 g (0.005 mole) of 4-styrylnaphtho[2,1-b]thiophene (**6**) and 0.2 g (0.00078 mole) of iodine in 360 ml of benzene was irradiated for six hours with a 450 Watt Hanovia medium pressure mercury lamp. During the course of the reaction, a slow stream of air was passed through the solution. The solvent was removed *in vacuo* and the resulting product purified by chromatography over neutral alumina (benzene:hexane (1:1) as the eluent) giving benzo[3,4]phenanthro[1,2-b]thiophene (**7**), 1.31 g (88% yield), mp 101-102°; ¹H-nmr (deuteriochloroform): 300 MHz, see Table I; ¹³C-nmr (deuteriochloroform): 75 MHz, see Table I; ms: m/e 284 (M⁺, 100), 285 (23.5), 283 (40.6), 282 (32.3).

Anal. Calcd. for C₂₀H₁₂S: C, 84.50; H, 4.20; S, 11.27. Found: C, 84.37; H, 4.33; S, 11.12.

2-(3'-Thienyl)-3-phenylpropenenitrile (9).

2-(3'-Thienyl)-3-phenylpropenenitrile (**9**) was synthesized from 10.0 g (0.081 mole) of 3-thienylacetonitrile (**8**) (Aldrich), 0.90 g (0.041 g-atom) of metallic sodium and 11.8 g (0.11 mole) of benzaldehyde in a manner similar to the preparation of **3**. Colorless crystals, 16.06 g (94% yield) were obtained, mp 75°; ¹H-nmr (deuteriochloroform): 60 MHz δ 6.87-7.30 (m, aromatic-H, thiophene protons, alkene proton, 9H); ms: m/e 211 (M⁺, 100), 212 (20.5), 196 (21.6), 166 (2.3).

Anal. Calcd. for C₁₃H₉NS: C, 73.90; H, 4.29; N, 6.63; S, 15.18. Found: C, 74.01; H, 4.07; N, 6.78; S, 15.06.

4-Cyanonaphtho[1,2-b]thiophene (10).

4-Cyanonaphtho[1,2-b]thiophene (**10**) was synthesized from 1.5 g (0.007 mole) of **9** and 0.2 g (0.00078 mole) of iodine in 360 ml of benzene in a manner similar to the preparation of **4**. Colorless crystals, 1.30 g (88% yield) were obtained, mp 130°; ¹H-nmr (deuteriochloroform): 60 MHz δ 6.90-8.90 (m, aromatic-H, thiophene protons, 7H); ms: m/e 209 (M⁺, 100), 210 (15.2), 211 (4.8).

Anal. Calcd. for C₁₃H₇NS: C, 74.61; H, 3.37; N, 6.70; S, 15.32. Found: C, 74.79; H, 3.60; N, 6.81; S, 15.19.

Naphtho[1,2-b]thiophene-4-carboxaldehyde (11).

Naphtho[1,2-b]thiophene-4-carboxaldehyde (**11**) was synthesized in a manner similar to compound **5** from 2.0 g (0.01 mole) of **10** and 37 ml (0.037 mole) of DIBAL-H in 180 ml of dry benzene under nitrogen. The product was extracted with chloroform and dried over anhydrous sodium sulfate. Evaporation *in vacuo* gave **11** as a yellow solid, 1.48 g (70% yield), mp 80°; ¹H-nmr (deuteriochloroform): 60 MHz δ 6.90-8.92 (m, aromatic-H, thiophene protons, 7H), 10.2 (aldehyde-H). Compound **11** was used directly without further purification in the synthesis of **12** below.

4-Styrylnaphtho[1,2-b]thiophene (12).

Synthetic preparation of 4-styrylnaphtho[1,2-b]thiophene (**12**) was similar to that for **6**. Thus, 1.5 g (0.06 mole) of sodium hydride, 0.54 g (0.002 mole) of diethylbenzyl phosphonate and 0.5 g (0.002 mole) of **11** in 50 ml of dry DME were mixed and stirred under dry nitrogen at room temperature for three hours. The product, **12**, 0.52 g (92% yield), was obtained, mp 117-118°; ¹H-nmr (deuteriochloroform): 60 MHz δ 7.0-9.0 (m, aromatic-H, thiophene protons, 14H); ms: m/e 286 (M⁺, 100), 285 (25.0), 252 (24.0). This compound was used without further purification and was cyclized directly to the final product, **13**.

Benzo[3,4]phenanthro[2,1-b]thiophene (13).

The parent compound, benzo[3,4]phenanthro[2,1-b]thiophene (**13**) was prepared by photocyclization in a typical photolysis reaction. Thus, 1.5 g (0.005 mole) of **12** and 0.2 g (0.00078 mole) of iodine in 360 ml of dry benzene, through which a slow stream of air was passed, was irradiated for a period of four hours, giving 1.13 g of **13** (80% yield), mp 101.5°; ¹H-nmr (deuteriochloroform): 300 MHz, see Table I; ¹³C-nmr (deuteriochloroform): 75 MHz, see Table I; ms: m/e 284 (M⁺, 100), 285 (23.6), 283 (43.4).

Anal. Calcd. for C₂₀H₁₂S: C, 84.47; H, 4.25; S, 11.12. Found: C, 84.58; H, 4.46; S, 11.12.

4-(3'-Methylstyryl)naphtho[2,1-*b*]thiophene (17).

4-(3'-Methylstyryl)naphtho[2,1-*b*]thiophene (17) was prepared in a typical Wadsworth Emmons reaction from 0.50 g (0.002 mole) of naphtho[2,1-*b*]thiophene-4-carboxaldehyde (5), 0.484 g (0.002 mole) of diethyl-3-methylbenzyl phosphonate (16) and 0.50 g (0.02 mole) of sodium hydride in DME. The product was separated by filtration after excess distilled water was added. Compound 17 was recrystallized from ethanol to give 0.51 g (85% yield) of product, mp 90°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.30 (s, methyl, 3H), 7.35-8.85 (m, aromatic-H, thiophene protons, 13H); ms: m/e 300 (M⁺, 100), 299 (24.9), 285 (46.6), 284 (32.7), 301 (23.0), 302 (5.9).

Anal. Calcd. for C₂₁H₁₆S: C, 83.96; H, 5.37; S, 10.67. Found: C, 84.22; H, 5.53; S, 10.47.

11-Methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (19).

The synthesis of 11-methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (19) was conducted by reacting 0.48 g (0.002 mole) of 17 and 0.06 g (0.00026 mole) of iodine in 360 ml of dry benzene in a manner similar to the preparation of 13. Colorless crystals, 0.36 g (75% yield) were obtained, mp 135-136°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.31 (s, methyl, 3H), 7.32-9.00 (m, aromatic-H, thiophene protons, 11H); ms: m/e 298 (M⁺, 100), 299 (24.0), 282 (19.8), 297 (15.1), 300 (6.5).

Anal. Calcd. for C₂₁H₁₄S: C, 84.53; H, 4.73; S, 10.74. Found: C, 84.44; H, 4.75; S, 10.62.

13-Methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (18) was not detected in the above reaction mixture.

4-[3'-Methylstyryl]naphtho[1,2-*b*]thiophene (20).

4-[3'-Methylstyryl]naphtho[1,2-*b*]thiophene (20) was prepared in a typical Wadsworth-Emmons reaction from 0.50 g (0.002 mole) of naphtho[1,2-*b*]thiophene-4-carboxaldehyde (11), 0.484 g (0.02 mole) of diethyl-3-methylbenzyl phosphonate (16) and 0.50 g (0.02 mole) of sodium hydride in DME. The product was isolated by filtration after excess distilled water was added. Compound 20 was recrystallized from ethanol to give 0.54 g (90% yield), mp 80°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.31 (s, methyl, 3H), 7.35-8.85 (m, aromatic-H, thiophene protons, 13H).

Anal. Calcd. for C₂₁H₁₄S: C, 83.96; H, 5.37; S, 10.67. Found: C, 83.98; H, 5.52; S, 10.53.

11-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (22).

11-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (22) was synthesized from 0.80 g (0.002 mole) of 20 and 0.06 g (0.00026 mole) of iodine in 360 ml of dry benzene in a manner similar to the preparation of 13. Colorless crystals, 0.58 g (75% yield) were obtained after chromatography over neutral alumina using benzene:hexane (1:1) as the eluent, mp 115.5°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.32 (s, methyl, 3H), 7.35-8.80 (m, aromatic-H, thiophene protons, 11H); ms: m/e 298 (M⁺, 100), 299 (23.7), 282 (18.7), 183 (13.0), 300 (6.8).

Anal. Calcd. for C₂₁H₁₄S: C, 84.63; H, 4.73; S, 10.74. Found: C, 84.70; H, 4.82; S, 10.47.

13-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (21) was not detected in the above photocyclization mixture.

2-(2'-Thienyl)-3-(2''-tolyl)propenenitrile (24)

2-(2'-Thienyl)-3-(2''-tolyl)propenenitrile (24) was prepared in a similar fashion to that for 3 except that *o*-tolualdehyde (23) was used in place of benzaldehyde. Stoichiometric quantities of 2-thienylacetonitrile (5.0 g, 0.041 mole) and 23 in 70 ml of absolute ethanol were reacted to give 24 resulting in 8.67 g (94% yield), mp 84°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.32 (s, methyl, 3H), 6.90-7.95 (m, aromatic-H, thiophene protons, alkene protons, 8H); ms: m/e 225 (M⁺, 100), 226 (18.0), 224 (49.5), 210 (60.8), 227 (5.4).

Anal. Calcd. for C₁₄H₁₁NS: C, 74.63; H, 4.92; N, 6.22; S, 14.23. Found: C, 74.76; H, 4.88; N, 6.23; S, 14.26;

4-Cyano-6-methylnaphtho[2,1-*b*]thiophene (25).

4-Cyano-6-methylnaphtho[2,1-*b*]thiophene (25) was obtained in a manner similar to that employed in the synthesis of 4. Thus, 1.5 g, (0.007

mole) of 24 and 0.2 g (0.00078 mole) of iodine were dissolved in 360 ml of benzene. During the reaction, a slow stream of air was passed through the reaction medium. The reaction mixture was irradiated for four hours, after which 25 was obtained, 0.56 g (88% yield), mp 148°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.30 (s, methyl, 3H), 6.90-8.90 (m, aromatic-H, thiophene protons, 6H); ms: m/e 223 (M⁺, 100), 224 (18.9), 225 (5.8).

Anal. Calcd. for C₁₄H₉NS: C, 75.31; H, 4.06; N, 6.27; S, 14.36. Found: C, 75.50; H, 4.28; N, 6.40; S, 14.21.

6-Methylnaphtho[2,1-*b*]thiophene-4-carboxaldehyde (26).

The synthesis of 6-methylnaphtho[2,1-*b*]thiophene-4-carboxaldehyde (26) was conducted in a manner similar to that described for 4. Under a dry nitrogen atmosphere, 0.50 g (0.002 mole) of 4-cyano-6-methylnaphtho[2,1-*b*]thiophene (25) and 8 ml of DIBAL-H (0.008 mole) were mixed in 37 ml of dry benzene. The reaction mixture was irradiated for four hours affording 6-methylnaphtho[2,1-*b*]thiophene-4-carboxaldehyde (26) 0.32 g (72% yield) mp 160°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.31 (s, methyl, 3H), 6.90-8.50 (m, aromatic-H, thiophene protons, 6H), 10.2 (aldehyde, 1H). This compound was not further purified but rather was used directly in the next step in the synthesis.

6-Methyl-4-styrylnaphtho[2,1-*b*]thiophene (27).

A mixture of 6-methylnaphtho[2,1-*b*]thiophene-4-carboxaldehyde (26) 0.50 g (0.002 mole) and diethylbenzylphosphonate, 0.684 g (0.003 mole) together with sodium hydride 1.5 g (0.006 mole) in 50 ml of DME under dry nitrogen was allowed to stir at 20° for three hours. The product was collected by filtration after the addition of excess distilled water to the reaction mixture. The product, 27, was recrystallized from ethanol to give 0.575 g (96% yield), mp 108°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.32 (s, methyl, 3H), 6.95-9.15 (m, aromatic-H, thiophene protons, 13H); ms: m/e 300 (M⁺, 100), 301 (24.5), 285 (29.7), 302 (7.7), 252 (12.3).

Anal. Calcd. for C₁₂H₁₆S: C, 83.96; H, 5.37; S, 10.67. Found: C, 83.88; H, 5.37; S, 10.72.

1-Methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (28).

6-Methyl-4-styrylnaphtho[2,1-*b*]thiophene (27) was cyclized to afford 1-methylbenzo[3,4]phenanthro[1,2-*b*]thiophene (28) in a manner analogous to that employed in the preparation of 7. Thus, 1.5 g (0.005 mole) of 27 and 0.2 g (0.00078 mole) of iodine were dissolved in 360 ml of benzene and the solution subjected to photolysis. The reaction was complete after ten hours. Evaporation and chromatography on neutral alumina (benzene:hexane (1:1)) gave 1.19 g (80% yield) of 28, mp 139-140°; ¹H-nmr (deuteriochloroform): 300 MHz data is contained in Table I; ¹³C-nmr (deuteriochloroform): 75 MHz data is contained in Table I; ms: m/e 298 (M⁺, 100), 299 (24.7), 297 (54.1), 295 (28.7).

Anal. Calcd. for C₂₁H₁₄S: C, 84.53; H, 4.73; S, 10.74. Found: C, 84.62; H, 4.88; S, 10.61.

3-(3'-Thienyl)-2-(2''-tolyl)propenenitrile (29).

The synthesis of 3-(3'-thienyl)-2-(2''-tolyl)propenenitrile (29) was accomplished by reacting 5.0 g (0.041 mole) of 3-thienylacetonitrile in 70 ml of absolute ethanol with 0.930 g (0.041 mole) of metallic sodium in 28 ml of absolute ethanol and 4.9 g (0.041 mole) of *o*-tolualdehyde affording 29, 9.04 g (98% yield), mp 100°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.31 (s, methyl, 3H), 6.90-7.35 (m, aromatic-H, thiophene protons, 8H); ms: m/e 225 (M⁺, 53.6), 210 (100), 226 (9.9), 224 (31.5), 209 (21.0).

Anal. Calcd. for C₁₄H₁₁NS: C, 74.63; H, 4.92; N, 6.22; S, 14.23. Found: C, 74.86; H, 5.01; N, 6.27; S, 14.16.

4-Cyano-6-methylnaphtho[1,2-*b*]thiophene (30).

Photocyclization of 1.5 g (0.006 mole) of 29 with 0.2 g (0.00078 mole) of iodine in 360 ml of dry benzene in the presence of a slow stream of air gave 1.58 g (72% yield) of 30, mp 180°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.23 (s, methyl, 3H), 6.95-8.90 (m, aromatic-H, thiophene protons, 6H); ms: m/e 223 (M⁺, 100), 224 (18.9), 225 (5.8), 222 (61.1), 196 (11.0).

Anal. Calcd. for C₁₄H₉NS: C, 75.31; H, 4.06; N, 6.27; S, 14.36. Found:

C, 75.51; H, 4.00; N, 6.29; S, 14.39.

6-Methylnaphtho[1,2-*b*]thiophene-4-carboxaldehyde (**31**).

Conversion of the 4-cyano substituent of **30** into the corresponding 4-formyl group was achieved by treating 1.5 g (0.007 mole) of **30** with 24 ml of DIBAL-H in 100 ml of dry benzene under dry nitrogen, giving 1.14 g (75% yield) of **31** after a standard workup, mp 120°; ¹H-nmr (deuteriochloroform): 60 MHz δ 2.32 (s, methyl, 3H), 6.90-8.25 (m, aromatic-H, thiophene protons, 6H), 10.20 (aldehyde, 1H). This compound was not further purified but was used directly in the next reaction described below.

6-Methyl-4-styrylnaphtho[1,2-*b*]thiophene (**32**).

The preparation of 6-methyl-4-styrylnaphtho[1,2-*b*]thiophene (**32**) was conducted under typical Wadsworth-Emmons reaction conditions using 1.0 g (0.004 mole) of **31** and 1.15 g (0.005 mole) of diethyl benzylphosphonate in a slurry with 1.0 g of sodium hydride in 50 ml of DME under dry nitrogen. After three hours, the reaction mixture was worked up and the product recrystallized from ethanol to give 1.08 g (91% yield) of **32**, mp 130-130.5°.

Anal. Calcd. for C₂₁H₁₆S: C, 83.96; H, 5.37; S, 10.67. Found: C, 83.71; H, 5.54; S, 10.51.

1-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (**33**).

1-Methylbenzo[3,4]phenanthro[2,1-*b*]thiophene (**33**) was obtained by photocyclization of 1.5 g (0.005 mole) of **32** in 360 ml of benzene in the presence of 0.2 g (0.00078 mole) of iodine. A slow stream of air was passed through the vessel during the reaction. The reaction, as confirmed by thin layer chromatography, was complete after ten hours. Evaporation of the solvent and purification of the crude product by chromatography over neutral alumina (benzene:hexane (1:1)) gave 1.20 g (81% yield) of **33** mp 199-200°; ¹H-nmr (deuteriochloroform): 300 MHz, Table I; ¹³C-nmr (deuteriochloroform): 75 MHz, Table I; ms: m/e 298 (M⁺, 100), 299 (24.7), 300 (7.2), 282 (26.7), 295 (29.4).

Anal. Calcd. for C₂₁H₁₄S: C, 84.53; H, 4.73; S, 10.74. Found: C, 84.30; H, 4.84; S, 10.66.

Two-Dimensional NMR Experiments.

Autocorrelated Proton (COSY) Two-Dimensional NMR Spectroscopy.

The pulse sequence employed for the acquisition of the COSY spectra in this study was that originally reported by Aue, Bartholdi and Ernst [31] modified with the phase cycling to provide quadrature in both frequency domains as described by Freeman and co-workers [32,33]. Data was typically acquired using an initial data matrix consisting of 256 x 512 complex points. Zero filling was employed prior to both Fourier transformations. The data was subjected to sinusoidal multiplication prior to Fourier transformation to suppress tailing and, following processing, was symmetrized [82].

Heteronuclear Chemical Shift Correlation.

Several variants of the heteronuclear chemical shift correlation experiment were employed in the course of this study. The routine heteronuclear proton-carbon chemical shift correlation experiment [34-37], the modification described by Bax [58] which provides homonuclear broadband proton decoupling and long range optimized heteronuclear chemical shift correlation [57,59-68] were all employed. The 90° pulse from the decoupler coils in these experiments was set by taking 90° = 1/4(γ H₂/2π) = 25.4 μseconds. Details concerning the optimization and parameters employed in the individual variants of these experiments follow.

Heteronuclear Proton-Carbon Chemical Shift Correlation.

The conventional heteronuclear chemical shift correlation experiments performed in this work utilized the pulse sequence of Freeman and Morris [35] modified with the sixteen step phase cycling scheme of Bax and Morris to provide quadrature detection in both frequency domains [36]. Additionally, the antiecho rather than the echo was recorded

to provide better artifact suppression [37]. The duration of the delays, Δ₁ and Δ₂, was optimized on the basis of an assumed one bond heteronuclear coupling constant of 165 Hz which gave durations of 3.0 and 2.0 mseconds, respectively. The data was typically acquired as 256 x 1K complex points and was zero filled as necessary during processing.

Heteronuclear Chemical Shift Correlation With Broadband Homonuclear Proton Decoupling.

Because of the inherently high congestion in the proton spectra of some of the systems studied, it was advantageous to determine proton chemical shifts using the heteronuclear chemical shift correlation experiment with broadband homonuclear proton decoupling as described by Bax [58] in some cases. The pulse sequence differs from the conventional homonuclear chemical shift correlation sequence in that the 180° ¹³C refocusing pulse midway through the evolution period (t₁) is replaced by a 90° ¹H-1/2J_{CH}-180° ¹H/180° ¹³C-1/2J_{CH}-90° ¹H sequence, in which the interval 1/2J_{CH} = 3.0 mseconds, based on an assumed 165 Hz heteronuclear coupling constant. Again, as in the conventional heteronuclear chemical shift correlation experiment, the coherence transfer echo was detected [37]. The data was collected as 256 x 1K points and was processed using double exponential apodization in both dimensions with zero filling to give a 512 x 1K matrix. Proton chemical shift locations were determined by zero filling individual interferograms corresponding to the individual carbon resonances to 4K points prior to the second Fourier transform followed by double exponential apodization. Chemical shifts of the individual protons determined in this fashion were calculated to be accurate to 0.01 ppm.

Long Range Optimized Heteronuclear 1H/13C Chemical Shift Correlation.

The pulse sequence employed for the long range optimized chemical shift correlation experiment was identical to that employed for the conventional heteronuclear chemical shift correlation experiment, the sole difference being the durations selected for the Δ₁ and Δ₂ intervals. Based upon the previous work of Reynolds and co-workers [59] a 10 Hz long range coupling was assumed to be an optimal setting which gave values for the delays of 50.0 and 33.3 mseconds, respectively. Data, once again, were collected using an initial 256 x 1K points. The data were processed using a 2.5 Hz exponential broadening and zero filling to 2K points prior to the first Fourier transform and double exponential apodization and zero filling to give 1K points after the second Fourier transform, thus affording a final data matrix consisting of 1K x 1K points.

Heteronuclear Relayed Coherence Transfer (RCT2D).

The heteronuclear relayed coherence transfer (RCT2D) experiment was performed using the pulse sequence and phase cycling reported previously [53]. The Δ₁ and Δ₂ parameters were set as in the heteronuclear chemical shift correlation experiment with the exception that the Δ₁ delay was set to Δ₁/2 because of the 180° ¹³C refocusing pulse applied midway through the Δ₁ interval in this experiment. The mixing time was set to 2/10³J_{HH} = 28.56 mseconds. A 1 second interpulse delay was employed. As in the heteronuclear chemical shift correlation experiment described above, the data were collected as an initial 256 x 1K matrix. The data were also processed as above to give a final 512 x 512 matrix.

¹³C-¹³C Double Quantum Coherence (INADEQUATE).

The ¹³C-¹³C double quantum (INADEQUATE) spectrum was recorded using a General Electric GN-500 spectrometer operating at an observation frequency of 125.762 MHz for ¹³C. The pulse sequence was essentially that of Freeman and co-workers [38-41] modified with a 135° read pulse as in the work of Mareci and Freeman [42] and employing a 128 step phase cycle. The data were acquired as 30 x 8K complex points and were processed to give the 64 x 4K real point matrix shown. Total acquisition time for the experiment was 19 hours. The 90° pulse length on the GN-500 spectrometer was 17.5 μseconds. The ¹³C-¹³C double quantum INADEQUATE experiment was optimized based on an assumed ¹³C-¹³C coupling of 50 Hz, giving 1/4J_{CC} = 5.0 mseconds. Finally, an interpulse

delay of 2.7 seconds was employed for this experiment.

X-Ray Crystallography.

Crystals of benzo[3,4]phenanthro[1,2-*b*]thiophene (7) and 1-methyl benzo[3,4]phenanthro[2,1-*b*]thiophene (33) were obtained by slow evaporation of chloroform solutions. The x-ray data for both were collected on a Syntex P2 diffractometer at 163°K. Details pertaining to the crystal data, data collection and structure refinement are collected in Table IV. Both structures were solved using the S atom position as determined from a sharpened Patterson map. Positions for all other non-hydrogen atoms were obtained from subsequent electron density maps. After several cycles of full-matrix least-squares refinement with anisotropic thermal parameters, the hydrogen atoms were located in a difference map and refined with isotropic thermal parameters. Scattering factors anomalous dispersion corrections for all atoms were used as input in SHELX76 [83]; the linear absorption coefficient was calculated using values from the International Tables for X-ray Crystallography [84]. The least-squares planes program was supplied by Cordes [85]; other computer programs used in solution of the structures are listed in reference [11] of Gadol and Davis [86].

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