

1-Methylphenanthro[3,4-*b*]thiophene: Determination of the Tertiary Structure in Solution and in the Crystalline State by NMR Spectroscopy and X-Ray Diffraction

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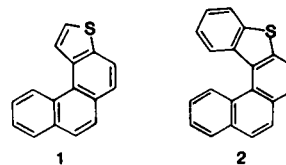
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1-Methylphenanthro[3,4-*b*]thiophene was prepared by the photocyclization of 1-(4'-methyl-2'-thienyl)-2-(2''-naphthyl)ethene. The ^1H and ^{13}C -nmr spectra were assigned using two-dimensional $^1\text{H}/^{13}\text{C}$ heteronuclear chemical shift correlation and relayed coherence transfer (RELAY) experiments. From nuclear Overhauser difference spectra, the H11-C1 methyl-H intramolecular distance was determined to be 2.10 Å. The molecule crystallized from chloroform in the monoclinic system, space group $P2_1/c$. A total of 3536 unique reflections were measured and the structure was solved by direct methods and refined to a final $R = 0.049$. The molecule is helical with both chiral forms observed in the crystal. The H11-C1 methyl-H distance in the crystal was 2.12(3) Å in excellent agreement with the distance measured in solution by NOE techniques.

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Recent work reported from these laboratories has dealt with the assignment of the ^1H and/or ^{13}C -nmr spectra of a number of polynuclear aromatic thiophenes which have included: phenanthro[1,2-*b*]thiophene [2]; phenanthro[3,4-*b*]thiophene (**1**) [3]; benzo[2,3]phenanthro[4,5-*bcd*]thiophene [4]; phenanthro[4,3-*a*]dibenzothiophene [5]; and most recently benzo[*b*]phenanthro[4,3-*d*]thiophene (**2**) [1]. Interestingly, this work has demonstrated that phenanthro[3,4-*b*]thiophene (**1**) [3] and benzo[*b*]phenanthro[4,3-*d*]thiophene [1] have pronounced tertiary helical structures in solution, the separation between the bay region protons is 1.99 Å in the former and 1.91 Å in the latter. Likewise, although its tertiary structure remains to be elucidated, phenanthro[4,3-*a*]dibenzothiophene is also predicted to have a helical structure since there are very large upfield shifts of the bay region protons from their normal downfield positions as a result of the overlap of rings A and F. Thus, we were interested in the increased deviations from planarity which might plausibly be caused by substituents such as a methyl group when substituted for a bay region proton. On this basis, we undertook the synthesis of 1-methylphenanthro[3,4-*b*]thiophene (**6**). We would now

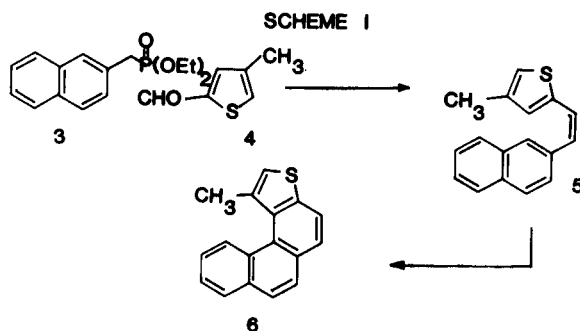
like to report the assignment of the ^1H - and ^{13}C -nmr spectra of the molecule by two-dimensional nmr techniques, the determination of the solution tertiary structure from NOE difference measurements and the crystal structure of the molecule.



Synthetic Preparation.

Introduction of a methyl substituent into the bay region of phenanthro[3,4-*b*]thiophene (**1**) affords two possible alternatives; the synthesis of 1-methylphenanthro[3,4-*b*]thiophene (**6**) or 11-methylphenanthro[3,4-*b*]thiophene, both of which were unknown at the outset of this work. Predominantly for reasons of starting material availability, the former was chosen as the target molecule. Thus, diethyl-2-naphthylmethylphosphonate (**3**) when allowed to react with sodium hydride produced the phosphonate carbanion

which reacted readily with 4-methyl-2-thiophenecarboxaldehyde (**4**) (Wadsworth-Emmons conditions) to give 1-(4'-methyl-2'-thienyl)-2-(2''-naphthyl)ethene (**5**) in 65% yield (Scheme I). Subsequent photocyclization of **5** afforded the desired 1-methylphenanthro[3,4-*b*]thiophene (**6**) in a 38% yield.



NMR Spectral Assignment.

Determination of the solution tertiary structure of 1-methylphenanthro[3,4-*b*]thiophene (**6**) required the prior assignment of the proton nmr spectrum of the molecule. Unequivocal spectral assignment, as in the cases of the previously reported members of this series [1-5] required the utilization of two-dimensional nmr techniques. Thus, a

proton-carbon chemical shift correlation spectrum [6-8] and relayed coherence transfer spectrum [5,9-14] were obtained and are presented as contour plots in Figures 1A and 1B, respectively.

Assignment of the proton nmr spectrum of **6** is a somewhat simpler task than the assignment of the corresponding spectra of the higher homologs of the series [1-5]. The H11 resonance is readily identified as the multiplet furthest downfield, resonating at $\delta = 8.28$, which is a significant upfield shift from the position of this resonance in the parent system at $\delta = 9.16$. Identification and assignment of the balance of the members of the four spin system, which is probably best classified as an ABKL spin system, is readily achieved from the relayed coherence spectrum (Figure 1B). One of the two spin systems contained in the

molecule appeared as an AB system which could be assigned as H4/H5 on the basis of the carbon chemical shift of C4 at $\delta = 121.63$, the identity of the H4 resonance provided by the proton-carbon chemical shift correlation spectrum as the resonance at $\delta = 8.04$. Additional support for this assignment was also provided by the existence of a long range coupling between H2-H5. The remaining two spin system appeared as a single, very intense resonance at $\delta = 7.87$, the vicinal coupling disappearing as a func-

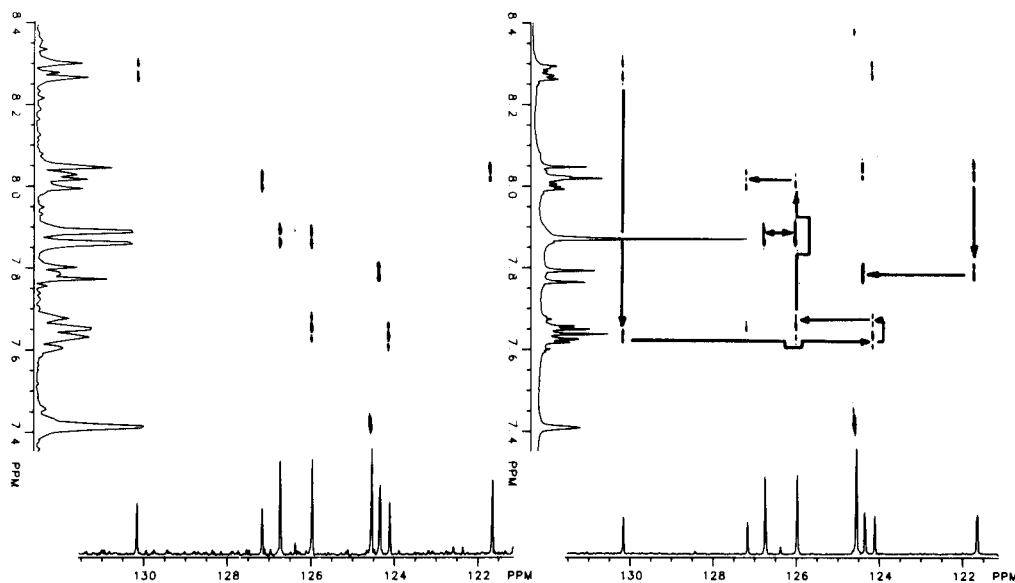


Figure 1. Contour plots of the two-dimensional nmr spectra of 1-methylphenanthro[3,4-*b*]thiophene (**6**) in deuteriochloroform at observation frequencies of 300.068 and 75.457 MHz for ^1H and ^{13}C , respectively: (A) $^1\text{H}/^{13}\text{C}$ heteronuclear chemical shift correlation; (B) (right hand spectrum) $^1\text{H}/^{13}\text{C}$ heteronuclear relayed coherence transfer (RELAY). The ^{13}C spectrum (F_2 axis) is the projection. The conventional ^1H -nmr spectrum is shown along the left side of (F_1 axis) the RELAY spectrum shown in B to illustrate the degeneracy of H6/H7. The projected ^1H spectrum is plotted along the F_1 axis (left) of the $^1\text{H}/^{13}\text{C}$ chemical shift correlation spectrum in A showing the doublet structure of H6 and H7 in this experiment.

tion of the identical chemical shifts of the two protons. In the proton-carbon chemical shift correlation and relayed coherence transfer experiments, however, both of the carbons showed proton doublet responses with $J = 8.5$ Hz. Here the degeneracy is broken since the proton detected is exclusively attached to ^{13}C , this resulting in a small but significant difference in chemical shift because of the isotopic effects shown for the two different isotopomers in Figure 2 which is sufficient to break the degeneracy of the chemical shifts [15]. Finally, the H2 resonance appeared as a single response with fine structure due to coupling to the methyl protons, H2 resonating at $\delta = 7.41$. A complete summary of the proton and carbon chemical shift assignments of **6** and the parent phenanthro[3,4-*b*]thiophene (**1**) system is presented in Table I.

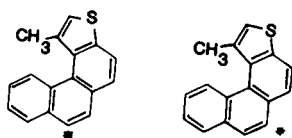


Figure 2. ^{13}C - ^{12}C Isotopomers of **6** which would account for the appearance of H6 and H7 as doublets in the $^1\text{H}/^{13}\text{C}$ heteronuclear chemical shift correlation and RELAY spectra.

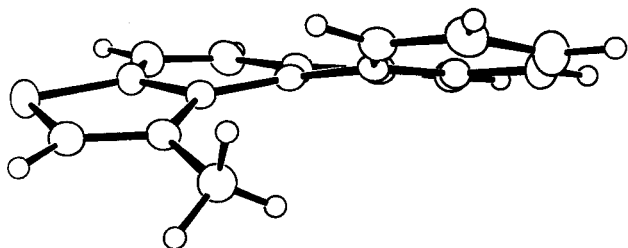


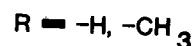
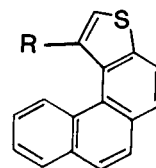
Figure 3. Edge view of 1-methylphenanthro[3,4-*b*]thiophene (**6**) showing the helical character of the molecule. The distance between H11 and the nearest methyl proton was $2.12(3)\text{\AA}$.

Determination of the Tertiary Structure from NOE Difference Measurements.

Having completed the assignments of the proton and carbon nmr spectra of **6**, it was possible to undertake the determination of the tertiary structure of the molecule using NOE difference techniques. Thus, a four second irradiation of the H11 resonance gave an observed NOE of 4.6% at H10 and 9.7% at the C1-methyl resonance. Using the H10-H11 bond distance determined crystallographically which was 2.37\AA (measuring a Dreiding model gave 2.38\AA) allowed the computation of an H11-methyl separa-

Table I

Comparison of the ^1H and ^{13}C -NMR Chemical Shifts of Phenanthro[3,4-*b*]thiophene (**1**, $\text{R} = -\text{H}$) and 1-Methylphenanthro[3,4-*b*]thiophene (**6**, $\text{R} = -\text{CH}_3$) in Deuteriochloroform



Position	1 , $\text{R} = -\text{H}$ [3]		6 , $\text{R} = -\text{CH}_3$	
	δ ^1H [a]	δ ^{13}C [b]	δ ^1H [b]	δ ^{13}C [b]
1	8.65	125.42	—	124.53
2	7.75	126.11	7.41	134.90 [c]
3a	—	140.56	—	140.83
4	8.09	121.29	8.04	121.63
5	7.85	125.56	7.78	124.33
5a	—	130.86	—	128.72 [d]
6	7.88	127.30	7.87	126.73 [e]
7	7.83	126.31	7.87	125.95 [e]
7a	—	133.38	—	132.57
8	8.01	128.68	8.00	127.16
9	7.66	125.92	7.65	125.94
10	7.74	126.20	7.63	124.09
11	9.16	126.24	8.28	130.16
11a	—	130.78	—	130.45 [d]
11b	—	126.94	—	127.26
11c	—	135.31	—	134.71 [c]
CH_3	—	—	2.56	19.91

[a] Chemical shifts measured at 500.052 MHz. [b] Chemical shifts measured at 300.068 MHz for ^1H or 75.457 MHz for ^{13}C . [c] [d] [e] Pairs of assignments which may be permuted.

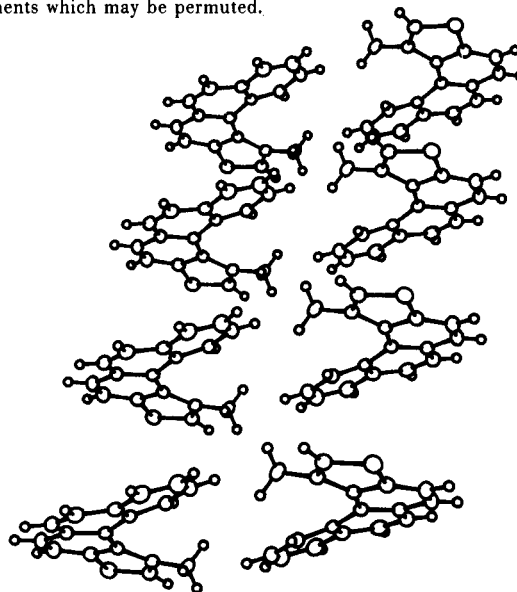


Figure 4. Molecular packing showing both chiral helical forms of **6** and the orientation of molecules in the centrosymmetric $P2_1/c$ space group.

tion of 2.10 Å. Ultimately, this value for the solution separation of H11 and the methyl group was found to be in excellent agreement with that in the crystal which was 2.12(3) Å.

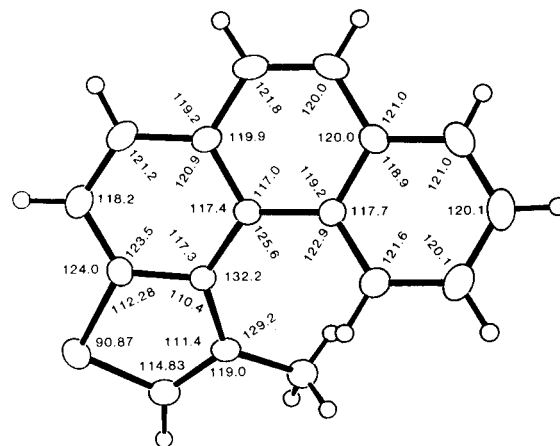
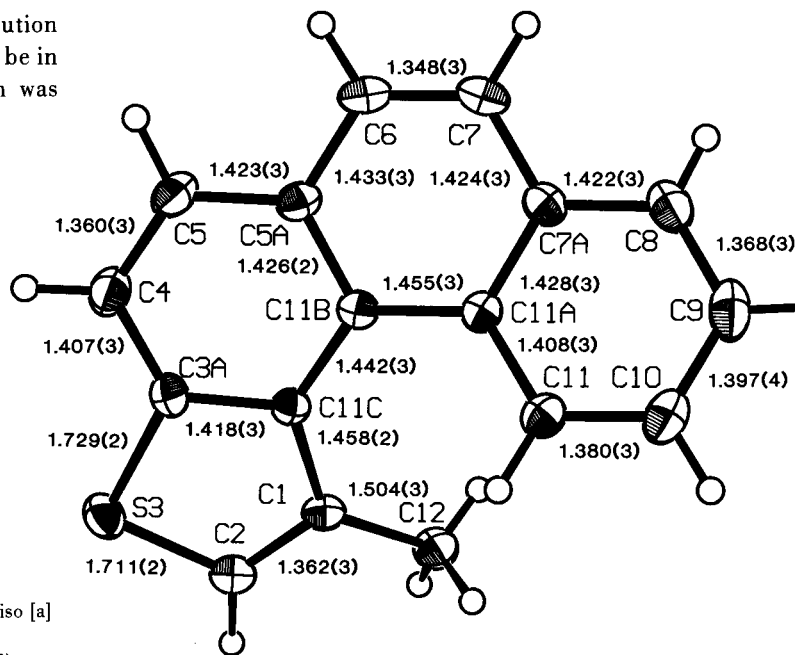


Figure 5. (A) Bond distances between the non-hydrogen atoms of **6**; (B) bond angles between the non-hydrogen atoms of **6**.

in the crystal is non-planar and is twisted helically as shown by the edge on view in Figure 3. Each individual ring is also non-planar with the phenyl rings approaching a twist-boat conformation. Furthermore, since the molecule crystallizes in the centrosymmetric $P2_1/c$ space group, **6** is also chiral with both forms observed in the crystal (Figure 4).

Distortions from planarity observed for **6** were greatest in the central rings with the terminal rings less distorted.

Table II

Positional and Thermal Parameters for
1-Methylphenanthro[3,4-*b*]thiophene

Atom	X	Y	Z	Ueq/Uiso [a]
S	-.05008(6)	.43664(8)	.90114(3)	.0270(2)
C(5)	.3667(2)	.5959(3)	.90756(12)	.0272(7)
C(4)	.2492(2)	.5314(3)	.93315(13)	.0277(7)
C(3a)	.1166(2)	.4916(3)	.87812(11)	.0220(6)
C(11c)	.1014(2)	.5064(3)	.79728(11)	.0179(5)
C(11b)	.2344(2)	.5467(3)	.77103(11)	.0182(5)
C(11a)	.2513(2)	.5273(3)	.69224(11)	.0183(6)
C(11)	.1598(2)	.4163(3)	.63776(12)	.0230(6)
C(10)	.1758(3)	.4042(3)	.56282(13)	.0298(7)
C(9)	.2869(3)	.5007(4)	.53974(13)	.0350(8)
C(8)	.3857(3)	.5994(3)	.59246(13)	.0298(7)
C(7a)	.3745(2)	.6106(3)	.67057(12)	.0218(6)
C(7)	.4885(2)	.6930(3)	.72771(13)	.0252(7)
C(6)	.4860(2)	.6818(3)	.80295(13)	.0253(6)
C(5a)	.3615(2)	.6075(3)	.82724(12)	.0212(6)
C(1)	-.0550(2)	.4881(3)	.75646(12)	.0203(6)
C(2)	-.1428(2)	.4492(3)	.80601(12)	.0239(6)
C(12)	-.1278(2)	.5254(3)	.67320(13)	.0266(7)
H(C5)	.456(3)	.635(3)	.9446(14)	.035(7)
H(C4)	.256(3)	.515(3)	.9878(14)	.031(6)
H(C11)	.088(2)	.339(3)	.6549(12)	.018(5)
H(C10)	.110(3)	.332(3)	.5251(14)	.036(7)
H(C9)	.302(3)	.494(4)	.490(2)	.054(9)
H(C8)	.461(2)	.657(3)	.5813(13)	.022(6)
H(C7)	.569(2)	.749(3)	.7125(12)	.025(6)
H(C6)	.563(3)	.729(3)	.8424(14)	.035(7)
H(C2)	-.252(3)	.437(3)	.7943(14)	.036(7)
H121	-.223(3)	.573(3)	.6744(15)	.040(7)
H122	-.074(3)	.606(3)	.6535(13)	.027(6)
H123	-.138(3)	.411(4)	.6434(15)	.038(7)

[a] For anisotropic atoms, the U value is Ueq, 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 i^{th} and j^{th} direct space unit cell vectors.

Crystal Structure Determination.

Interestingly, 1-methylphenanthro[3,4-*b*]thiophene (**6**)

Table III

Bond Distances and Angles for the Hydrogen Atoms of 1-Methylphenanthro[3,4- <i>b</i>]thiophene				
1	2	3	1-2	1-2-3
H(C5)	C(5)	C(4)	.97(2)	120.(2)
H(C5)	C(5)	C(5a)		119.(2)
H(C4)	C(4)	C(3a)	.97(3)	121.0(14)
H(C4)	C(4)	C(5)		120.8(14)
H(C11)	C(11)	C(10)	.98(2)	119.4(12)
H(C11)	C(11)	C(11a)		118.8(12)
H(C10)	C(10)	C(9)	.96(2)	118.(2)
H(C10)	C(10)	C(11)		121.2(2)
H(C9)	C(9)	C(8)	.93(3)	117.(2)
H(C9)	C(9)	C(10)		122.(2)
H(C8)	C(8)	C(7a)	.88(2)	115.7(14)
H(C8)	C(8)	C(9)		123.3(14)
H(C7)	C(7)	C(6)	.95(2)	120.6(13)
H(C7)	C(7)	C(7a)		119.2(13)
H(C6)	C(6)	C(5a)	.94(2)	116.(2)
H(C6)	C(6)	C(7)		122.(2)
H(C2)	C(2)	S	.99(2)	116.9(15)
H(C2)	C(2)	C(1)		128.1(15)
H121	C(1)	H122	.95(3)	110.(2)
H121	C(1)	H123		111.(2)
H121	C(1)	C(11)		104.(2)
H122	C(1)	H123	.91(3)	112.(2)
H122	C(1)	C(11)		110.6(13)
H123	C(1)	C(11)	1.01(3)	108.7(14)

Table IV

Torsion Angles for 1-Methylphenanthro[3,4- <i>b</i>]thiophene				
1	2	3	4	1-2-3-4
C(3a)	S	C(2)	C(1)	1.7(2)
C(3a)	S	C(2)	H(C2)	-174.(2)
C(2)	S	C(3a)	C(4)	170.8(2)
C(2)	S	C(3a)	C(11c)	-4.3(2)
C(4)	C(5)	C(5a)	C(11b)	-2.0(3)
C(4)	C(5)	C(5a)	C(6)	177.9(2)
C(5a)	C(5)	C(4)	C(3a)	-5.9(3)
C(5a)	C(5)	C(4)	H(C4)	175.(2)
H(C5)	C(5)	C(4)	C(3a)	174.(2)
H(C5)	C(5)	C(4)	H(C4)	-5.(2)
H(C5)	C(5)	C(5a)	C(11b)	178.(2)
H(C5)	C(5)	C(5a)	C(6)	-2.(2)
H(C4)	C(4)	C(3a)	S	8.(2)
H(C4)	C(4)	C(3a)	C(11c)	-177.(2)
H(C5)	C(4)	C(3a)	S	-171.1(2)
H(C5)	C(4)	C(3a)	C(11c)	3.4(3)
S	C(3a)	C(11c)	C(11b)	-178.20(15)
S	C(3a)	C(11c)	C(1)	5.7(2)
C(4)	C(3a)	C(11c)	C(11b)	6.7(3)
C(4)	C(3a)	C(11c)	C(1)	-169.4(2)
C(11b)	C(11c)	C(1)	C(2)	-179.7(2)
C(11b)	C(11c)	C(1)	C(12)	-7.2(4)
C(1)	C(11c)	C(11b)	C(11a)	-20.3(3)
C(1)	C(11c)	C(11b)	C(5a)	161.1(2)
C(3a)	C(11c)	C(11b)	C(11a)	164.7(2)
C(3a)	C(11c)	C(11b)	C(5a)	-14.0(3)
C(3a)	C(11c)	C(1)	C(2)	-4.4(3)
C(3a)	C(11c)	C(1)	C(12)	168.1(2)
C(11a)	C(11b)	C(5a)	C(5)	-166.7(2)

Table IV (continued)

1	2	3	4	1-2-3-4
C(11a)	C(11b)	C(5a)	C(6)	13.4(3)
C(5a)	C(11b)	C(11a)	C(11)	157.6(2)
C(5a)	C(11b)	C(11a)	C(7a)	-16.3(3)
C(11c)	C(11b)	C(11a)	C(11)	-21.1(3)
C(11c)	C(11b)	C(11a)	C(7a)	165.1(2)
C(11c)	C(11b)	C(5a)	C(5)	12.0(3)
C(11c)	C(11b)	C(5a)	C(6)	-167.8(2)
C(11)	C(11a)	C(7a)	C(8)	9.4(3)
C(11)	C(11a)	C(7a)	C(7)	-166.6(2)
C(7a)	C(11a)	C(11)	C(10)	-7.9(3)
C(7a)	C(11a)	C(11)	H(C11)	167.3(14)
C(11b)	C(11a)	C(11)	C(10)	178.2(2)
C(11b)	C(11a)	C(11)	H(C11)	-6.7(15)
C(11b)	C(11a)	C(7a)	C(8)	-176.5(2)
C(11b)	C(11a)	C(7a)	C(7)	7.6(3)
H(C11)	C(11)	C(10)	C(9)	-173.8(14)
H(C11)	C(11)	C(10)	H(C10)	8.(2)
C(11b)	C(11)	C(10)	C(9)	1.3(3)
C(11b)	C(11)	C(10)	H(C10)	-177.(2)
H(C10)	C(10)	C(9)	C(8)	-177.(2)
H(C10)	C(10)	C(9)	H(C9)	-2.(3)
C(11)	C(10)	C(9)	C(8)	3.9(4)
C(11)	C(10)	C(9)	H(C9)	179.(2)
H(C9)	C(9)	C(8)	C(7a)	-177.(2)
H(C9)	C(9)	C(8)	H(C8)	1.(3)
C(10)	C(9)	C(8)	C(7a)	-2.2(4)
C(10)	C(9)	C(8)	H(C8)	-176.(2)
H(C8)	C(8)	C(7a)	C(11a)	177.(2)
H(C8)	C(8)	C(7a)	C(7)	-7.(2)
C(9)	C(8)	C(7a)	C(11a)	-4.5(3)
C(9)	C(8)	C(7a)	C(7)	171.3(2)
C(11a)	C(7a)	C(7)	C(6)	4.7(3)
C(11a)	C(7a)	C(7)	H(C7)	-179.(2)
C(8)	C(7a)	C(7)	C(6)	-171.1(2)
C(8)	C(7a)	C(7)	H(C7)	5.(2)
H(C7)	C(7)	C(6)	C(5a)	176.(2)
H(C7)	C(7)	C(6)	H(C6)	1.(2)
C(7a)	C(7)	C(6)	C(5a)	-7.9(3)
C(7a)	C(7)	C(6)	H(C6)	176.(2)
H(C6)	C(6)	C(5a)	C(5)	-5.(2)
H(C6)	C(6)	C(5a)	C(11b)	174.(2)
C(7)	C(6)	C(5a)	C(5)	178.7(2)
C(7)	C(6)	C(5a)	C(11b)	-1.4(3)
C(2)	C(1)	C(12)	H121	29.(2)
C(2)	C(1)	C(12)	H122	147.(2)
C(2)	C(1)	C(12)	H123	-90.(2)
C(12)	C(1)	C(2)	S	-172.1(2)
C(12)	C(1)	C(2)	H(C2)	3.(2)
C(11a)	C(1)	C(2)	S	1.3(2)
C(11c)	C(1)	C(2)	H(C2)	176.(2)
C(11c)	C(1)	C(12)	H121	-143.(2)
C(11c)	C(1)	C(12)	H122	-25.(2)
C(11c)	C(1)	C(12)	H123	98.(2)

Dihedral angles between individual rings ranged from 10.38(9)° to 11.39(8)° which is smaller than the range observed for helicenes by Kuroda [16]. Additionally, the greatest deviation of the torsion angles from ideality involves the inner atoms of the helix. There are no unusually close intermolecular interactions which would influence the geometry of the molecule. There are, however, some

Table V

Least-Squares Planes and Dihedral Angles for 1-Methylphenanthro[3,4-*b*]thiophene

Plane 1

Equation of plane

$$-1.82576x + 7.42180y + 2.60838z - 5.68478 = 0$$

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

S	-.0022(6)	C(3a)	.042(2)	C(11c)	-.032(2)	C(1)	.012(2)
C(2)	.012(2)	C(12)*	.204(3)				

 χ^2 for plane 704.27

Plane 2

Equation of plane

$$2.99299x - 7.19907y - 1.07648z + 4.13997 = 0$$

Distances of atoms from plane

C(5)	.029(2)	C(4)	-.056(2)	C(3a)	-.004(2)	C(11c)	.060(2)
C(11b)	.076(2)	C(5a)	.042(2)				

 χ^2 for plane 3561.50

Plane 3

Equation of plane

$$4.07352x - 6.74775y + .51019z + 2.25093 = 0$$

Distance of atoms from plane

C(11b)	-.090(2)	C(11a)	.070(2)	C(7a)	-.001(2)	C(7)	-.064(2)
C(6)	.040(2)	C(5a)	.046(2)				

 χ^2 for plane 5247.17

Plane 4

Equation of plane

$$5.14410x - 5.98809y + 2.20488z + .29221 = 0$$

Distances of atoms from plane

C(11a)	-.046(2)	C(11)	.028(2)	C(10)	.017(2)	C(9)	-.040(3)
C(8)	-.007(2)	C(7a)	.041(2)				

 χ^2 for plane 1498.70

Plane 5

Equation of plane

$$4.07465x - 6.67145y + 1.43951z + 1.45593 = 0$$

Distances of atoms from plane

C(5)	-.281(2)	C(4)	-.269(2)	C(3a)	.085(2)	C(11c)	.361(2)
C(11b)	.126(2)	C(11a)	.041(2)	C(11)	-.248(2)	C(10)	-.286(2)
C(9)	-.061(2)	C(8)	.118(2)	C(7a)	.126(2)	C(7)	.129(2)
C(6)	-.043(2)	C(5a)	-.067(2)				

 χ^2 for plane 109598.16

Plane 6

Equation of plane

$$-2.85986x + 7.17975y - .76681z - 2.64406 = 0$$

Distances of atoms from plane

S	-.0569(6)	C(5)	-.110(2)	C(4)	-.257(2)	C(3a)	-.121(2)
C(11c)	.090(2)	C(11b)	.020(2)	C(11a)	-.108(2)	C(11)	-.601(2)
C(10)	-.676(2)	C(9)	-.283(3)	C(8)	.102(2)	C(7a)	.154(2)
C(7)	.377(2)	C(6)	.246(2)	C(5a)	.049(2)	C(1)	.438(2)
C(2)	.372(2)	C(12)	.977(2)				

χ^2 for plane 475100.82

Dihedral Angles for Selected Planes

Planes	Angle
1 2	10.13(9)
1 3	20.34(8)
1 4	31.73(8)
2 3	10.22(7)
2 4	21.61(7)
3 4	11.39(8)

close intramolecular contacts which force the molecule to twist. The methyl carbon, C(12) is 2.980(3) Å from atom C(11) while H123 is 2.12(3) Å from H(C11) (the atom labeling scheme is shown in Figure 5A accompanied by the bond distances while the bond angles are shown in Figure 5B). H(C11) is moved away from the methyl group and is 0.16(2) Å out of the plane of the terminal phenyl ring. The

H123...H(C11) contact distance is slightly longer than the closest H...H contacts observed in benzo[*c*]phenanthrene [17], 1,12-dimethylbenzo[*c*]phenanthrene [17] and phenanthrene itself [18]. The H123...H(C11) distance also agrees very favorably with the 2.10 Å distance determined for the molecule in solution from the NOE difference measurements.

Carbon-carbon bond distances (Figure 5A) in **6** also exhibit some interesting behavior. The C-C bond distances for the bridgehead carbon atoms are generally longer than those involving the remaining carbon atoms in the ring system which is consistent with that for phenanthrene [18], benzo[*c*]phenanthrene and 1,12-dimethylbenzo[*c*]phenanthrene [17] and the higher helicenes [16]. There are also alternating long and short C-C distances around the molecule which may be due to an increase in the localization of electron density throughout the π -system as a result of the non-planarity.

The geometry of the thiophene ring shows some distortion upon fusion of the phenanthrene system. The C-S bond distances are nonequivalent although the C-S-C angle is normal. The C(3a)-C(11c) and C(1)-C(2) distances are substantially different with the latter bond distance being close to that observed for an unconjugated C-C double bond [19]. In addition, the distance between C(11c) and C(1) is indicative of an sp²C-sp²C single bond [19]. The exocyclic bond angles at C(11b), C(11a), C(1) and C(3a) (Figure 5B) deviate significantly from values that would be

expected in the absence of steric effects. The angles at C(11b) and C(11a) are comparable to those observed in benzo[*c*]phenanthrene and 1,12-dimethylbenzo[*c*]phenanthrene [17]. The angle at C(11c) is greater than the angle at C(3a) less than the comparable angles in dibenzothiophene [20], which can be accounted for by the steric crowding of **6**.

Conclusions.

The solution and crystal tertiary helical structures of 1-methylphenanthro[3,4-*b*]thiophene (**6**) have been shown to be very favorably comparable with measured intramolecular distances of 2.10 and 2.12(3) Å respectively. Based upon this observation, it is reasonable to infer that a similar correspondence should exist between the solution and as yet unreported crystal tertiary helical structures of the parent phenanthro[3,4-*b*]thiophene (**1**) and benzo[*b*]phenanthro[4,3-*d*]thiophene (**2**). From the observed chirality of **6** which is illustrated in Figure 4, oxidative enzymatic metabolism of this or similar helical systems could lead to pairs of diastereomeric metabolites. Interestingly, the shortest C-C bond distance in the molecule, that between C6-C7 corresponds to what would normally be considered to be the "K-region" of the molecule [21]. Based upon the observed mutagenicity of the closely related parent system, **1** [22], whose metabolites are as yet unknown, it is quite probable that both **1** and **6** will undergo 6,7-epoxidation and subsequent ring opening to give a 6,7-*trans*-diol. Further work on the various aspects of the chemistry of related systems possessing tertiary helical structures is at present underway in these laboratories and will serve as the basis for forthcoming reports.

EXPERIMENTAL

Synthesis.

1-(4'-Methyl-2'-thienyl)-2-(2''-naphthyl)ethene (5).

Sodium hydride (50% dispersion in mineral oil, 4 g, 0.165 mole) was washed twice with petroleum ether and suspended in 200 ml of dimethoxyethane. The slurry was cooled to 20° and 11.5 g (0.0412 mole) of diethyl 2-naphthylmethylphosphonate (3) was added slowly with stirring. After the addition, the reaction mixture was stirred at room temperature for 30 minutes. To this solution maintained below 25° and under a dry nitrogen atmosphere, 5.2 g (0.0412 mole) of 4-methylthiophene-2-carboxaldehyde (4) was added dropwise with stirring. After the addition, the reaction mixture was stirred at room temperature for 2.5 hours and then

heated to 50° for 30 minutes. A large excess of water was added and the resulting precipitate was collected by filtration. The product, 5, was recrystallized from benzene to give 6.7 g (65% yield) of colorless crystals, mp 137-138°; ms: m/e 250 (M⁺, 100), 251 (M⁺+1, 21).

Anal. Calcd. for C₁₇H₁₄S: C, 81.6; H, 5.6; S, 12.8. Found: C, 81.3; H, 5.2; S, 12.9.

1-Methylphenanthro[3,4-b]thiophene (6).

One g (0.004 mole) of 1-(4'-methyl-2'-thienyl)-2-(2''-naphthyl)ethene (5) was dissolved in 250 ml of benzene and 0.1 g of iodine was added. The solution was irradiated for 4 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 evaporated *in vacuo* and the residue chromatographed on a silica gel column using hexane as the eluent and 0.37 g (38% yield) of colorless prisms was obtained, mp 141-142°.

Anal. Calcd. for C₁₇H₁₂S: C, 82.2; H, 4.9; S, 12.9. Found: C, 82.4; H, 5.1; S, 13.0.

NMR Spectroscopy.

All of the nmr spectra were obtained on a sample of 6 prepared by dissolving 65 mg of analytically pure material in 0.4 ml of deuteriochloroform, after which the sample was degassed by entrainment with zero grade Argon for 20 minutes. The spectra were recorded using an NT-300 spectrometer controlled by a 293-C pulse programmer at observation frequencies of 300.068 and 75.457 MHz for ¹H/¹³C in a 5 mm dual turned probe. The ¹H/¹³C heteronuclear chemical shift correlation spectrum shown in Figure 1A was acquired using the pulse sequence of Bodenhausen and Freeman [7] with phase cycling as described by Bax and Morris [8]. The spectrum was acquired overnight as a 256 × 1K data matrix which was processed to give the 256 × 512 data point, six level contour plot shown in Figure 1A. The projected ¹H spectrum is shown along the F₁ axis to the left of Figure 1A. The conventional spectrum is shown between Figures 1A and 1B, the "singlet" at δ = 7.87 in the conventional spectrum appearing as a doublet in the projected proton spectrum of the two-dimensional spectra [15]. The heteronuclear relayed coherence transfer spectrum shown in Figure 1B was acquired overnight using the pulse sequence and parameters reported previously [5] as a 256 × 1K point data matrix which was processed to give the 256 × 512 data point spectrum shown as a four level contour plot in Figure 1B.

The intramolecular distances were measured using nuclear Overhauser difference spectra which were obtained with 4 sec irradiation and a 6 sec interpulse delay. A reference spectrum was obtained by irradiating ~400 Hz downfield of the H11 resonance. All spectra were processed with a 1 Hz exponential multiplication prior to subtraction.

X-Ray Crystallography.

Crystals of 6 (approximate dimensions 0.25 mm × 0.21 mm × 0.29 mm) obtained by slow evaporation from a chloroform solution are monoclinic, space group P₂/c (D_x = 1.36 g/cc). Cell dimensions were obtained by least-squares refinement of the setting angles of 45 reflections with 20.2° < 2θ < 30.2°. These refined values are: a = 9.201(2) Å, b =

7.6143(8) Å, c = 17.812(4) Å, β = 103.602(14)°, V = 1212.9(4) Å³. Data were collected at 163°K on a Syntex P2₁ diffractometer with a graphite monochromator using MoKα radiation (λ = .71069 Å). Data were collected to 60° in 2θ (range of h,k,l: 0-12, 0-10, -24-24). A total of 3536 unique reflections were measured using the omega scan technique at a variable scan rate of 3-6°/min over a scan range of 1° θ. Background was measured at ±1° offset from the Kα position with the total background counting time equal to the scan time. Instrument and crystal stability were monitored by remeasurement of 4 reflections (121, 113, 211, 004) every 96 reflections and the data analyzed and detailed in Henslee and Davis [23]; data were corrected for absorption (μ = 2.31 cm⁻¹) and decay (maximum correction on I < .02). The structure was solved by direct methods using MULTAN 78 [25] which afforded the positions of all non-H atoms. After several cycles of full-matrix least-squares refinement (function minimized Σw(|F_o| - |F_c|)² where w = σ⁻²F_o) with anisotropic thermal parameters for all non-H atoms, positions for the H atoms were located from a difference electron density map. The H atoms were refined with isotropic thermal parameters. The final R was 0.049 for 2522 reflections (criterion for unobserved reflections, F_o < 4 σF_o) with a weighted R of 0.053 and a goodness of fit of 1.40. The minimum and maximum peaks in the final difference map were -.27 and .40 e/Å³, respectively. The maximum shift/esd in the final refinement cycle was -0.008. The least-squares planes program was provided by Cordes [26]; all other programs are listed in reference 11 of Gadol and Davis [27].

Positional and thermal parameters for 6 are contained in Table II. Bond distances and angles for the non-hydrogen atoms of 6 are shown in Figures 5A and 5B, respectively, while the corresponding information for the hydrogen atoms of 6 are contained in Table III. Torsional angles for 6 are contained in Table IV while finally, the least-squares planes and dihedral angles of 6 are presented in Table V.

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