The Crystal and Molecular Structure of
9-Methylphenanthro[4,3-a]dibenzothiophene

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The crystal structure of 9-methylphenanthro[4,3-a]dibenzothiophene, $C_{25}H_{16}S$, $M_r = 348.47$, has been determined. Monoclinic, $P2_1/c$, a = 11.364(3), b, = 14.257(3), c = 11.575(2)Å, β = 116.26(2)°, V = 1681.9(7)Å^3, Z = 4, D_x = 1.38 g/cc, MoKα radiation λ = .71069 Å, F(000) = 728, T = 163K, R = .0458 for 2330 reflections. The structure compares favorably with that of hexahelicene and methylated derivatives. The thiophene moiety increases the helical core radius and decreases the pitch with respect to hexahelicene and its derivatives.

Introduction.

Recently, as a part of our ongoing study of non-planar sulfur containing polynuclear aromatic systems, we have reported the total assignment of the proton and carbon nmr spectra of phenanthro[3,4-b]thiophene (**1a**) [1], 1-methylphenanthro[3,4-b]thiophene (**1b**) [2], phenanthro[4,3-a]dibenzothiophene (**2a**) [3] and 9-methylphenanthro[4,3-a]dibenzothiophene (**2b**) [4]. In the case of **1a** and **1b**, one-dimensional nuclear Overhauser difference spectra (nOeds) were used to determine the separation between the bay region substituents. In the case of the latter two compounds, **2a** and **2b**, the highly congested proton spectra precluded the use of nOeds to determine the separation between the bay region protons H1 and H15, although it was evident that the molecules were non-planar since there were numerous proton resonances shifted upfield in each case. Upfield proton shifts observed in the spectra of **2a** and **2b** infer that the protons from one ring are in the π-electron cloud at the other terminus of the helix. (This is illustrated in Figure 1.) Thus, we now wish to report the X-ray crystal structure of 9-methylphenanthro[4,3-a]dibenzothiophene (**2b**) and a comparison to other hexahelicene crystal structures.

Results and Discussion.

The crystal structure of 9-methylphenanthro[4,3-a]dibenzothiophene (**2b**) shares some features in common with the hexahelicenes to which it is related, but also has some striking differences. Common to **2b**, hexahelicene [5] and 2-methylhexahelicene [6], the carbon-carbon bonds around


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 1                    2
a  R = H           a  R = H
b  R = CH3         b  R = CH3

         3
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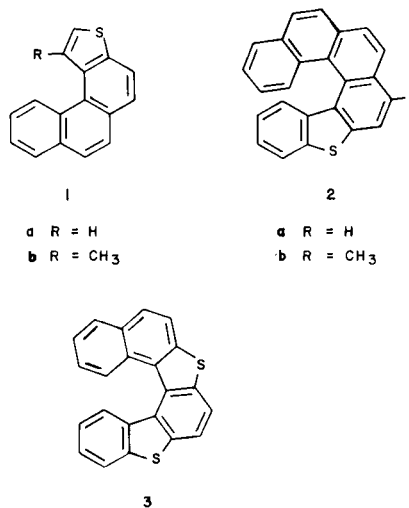
the inside of the helix are elongated and there is a pattern of alternating shortened and lengthened carbon-carbon bonds around the outside of the helix. The average bond length inside of the helical structure of **2b** is 1.450(10)Å whereas the overall average of the shortened bonds around the perimeter of the helix is 1.364(12)Å in comparison with an average of 1.412(15)Å for the lengthened perimeter bonds. These bond lengths compare favorably with hexahelicene [5] and methylated analogs [6,7]. It is also interesting to note that the thiophene ring appears to have a local effect on the perimeter bonds. Thus, relative to the perimeter lengthened bond average of 1.412Å, the C10-C10a and C11a-C12 bonds are shortened somewhat

with an average length of 1.402 Å (Figure 2). In contrast, the C9-C10 and C12-C13 bonds have an average length of 1.367 Å which is slightly longer than the average length of 1.354 Å for bonds C3-C4, C5-C6 and C7-C8. Perimeter average bond lengths of hexahelicene [5] in comparison were 1.346(23) and 1.414(17) Å for the short and long bonds, respectively, with none of the regional variance observed in the title compound.
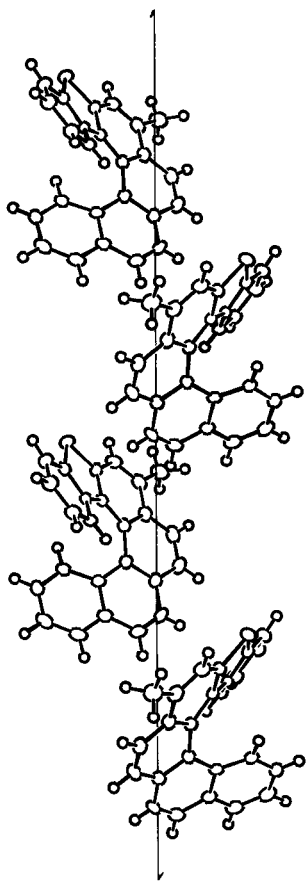
the molecule. Torsional angles along the interior of the helical turn on the purely benzenoid half of the molecule are quite comparable to those observed in the hexahelicenes [5,6]. In contrast, the torsional angles are slightly smaller on the thiophene containing side of the molecule (Table II) relative to those of the hexahelicenes.
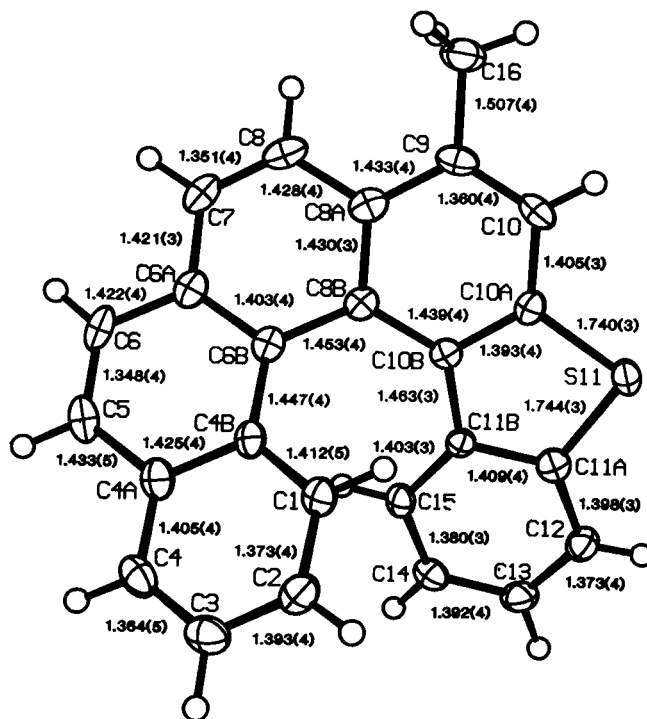

Figure 1. Molecules of like chirality oriented along a 2_1 screw axis.

Figure 2. Bond distances for non-hydrogen atoms.

The two closest atoms, C1 and C15, in the terminal rings of 2b are separated by 2.968 Å, as compared to 3.22 and 3.16 Å for the corresponding atoms of hexahelicene and 2-methylhexahelicene, respectively [5,6]. In contrast, the distance between the corresponding atoms of benzo[d]-naphtho[1,2-d']benzo[1,2-b:4,3-b']bithiophene (3) [8], is 2.91 Å. From this observed trend, it appears that the thiophene ring influences the pitch of the helix, thus, as the number of thiophene rings in the helicene increases, the helical pitch of the molecule appears to correspondingly decrease. Further support for the influence of the thiophene rings on the pitch of the helix is afforded by a comparison of the torsional angles between the two halves of

Table I

Close Intramolecular Contacts Observed for
9-Methylphenanthro[4,3-a]dibenzothiophene (2b)

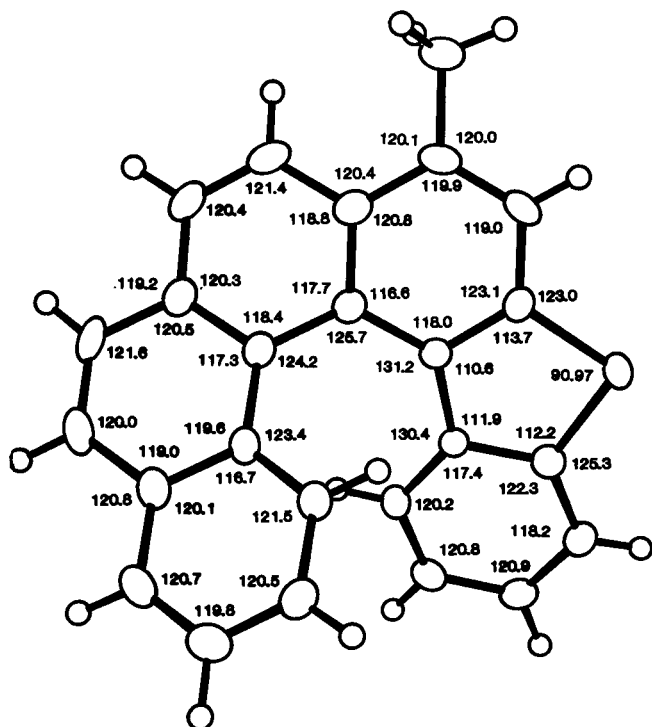| Atoms	Interatomic Distance (Å)
C15····C1	2.968(4)
C15····C2	3.602(4)
C15····H1	2.99(3)
C15····H2	3.93(3)
C14····C1	3.910(4)
C14····C2	>4.0
C14····H1	3.97(3)
C14····H2	3.75(3)
H1····H15	3.08(4)
H1····H14	>4.0
H2····H15	>4.0
H2····H14	>4.0
C1····H15	2.82(3)
C1····H14	>4.0
C2····H15	3.50(3)
C2····H14	>4.0

Figure 3. Bond angles for non-hydrogen atoms. ESD's range from 0.13 -0.30°.

Dihedral angles between the least squares planes of adjacent rings range from 7.90(12)° to 12.45(10)° (Table III). More interesting is the dihedral angle between the planes of the terminal rings which is 47.50(10)° in the title compound (see Figure 1), as compared to 58.5° for hexahelicene [5] and 54.8° for 2-methylhexahelicene [6]. In all probability, the shallower angle between the terminal rings of **2b** may be attributed to a combination of factors. First, wider bond angles in the helix at the thiophene-benzene junctions (C8b-C10b-C11b and C10b-C11b-C15) of 131.2° and 130.4°, respectively, create less overlap of terminal rings and, thus, less need for helical twisting than in the hexahelicenes. Analogous angles on the benzenoid half (C1-C4b-C6b and C4b-C6b-C8b) are 123.4° and 124.2°, respectively. In addition, the thiophene is more resistant to out-of plane twisting than the more flexible 6-membered benzene rings. Comparison of the torsional angle defined by C11a-C11b-C10b-C10a of 8.2° with the corresponding torsional angle of 15.9° proscribed by C4a-C4b-C6b-C6a on the opposite side of the molecule supports this contention.

In conclusion, the molecular structure of 9-methylphenanthro[4,3-a]dibenzothiophene (**2b**) is helical in character, the thiophene ring causing pronounced local differences in torsional angles, bond lengths and in the pitch of the helix. Both H14 and H15 project into the π-cloud of ring I, accounting for the pronounced upfield shift of these resonances in the 300 MHz ¹H-nmr spectrum

Table II

Inner Core Torsional Angles

Atom Sequence	**2b**	Hexahelicene
C1-C4b-C6b-C8b	17.3(4)°	15.2(5)°
C4b-C6b-C8b-C10b	24.6(5)°	30.3(5)°
C6b-C8b-C10b-C11b	23.9(6)°	30.0(5)°
C8b-C10b-C11b-C15	8.6(6)°	11.3(4)°

Table III

Dihedral Angles Between Ring Planes

Planes (see Figure 1)	**2b**	Hexahelicene
I-II	11.75(11)°	10.06(13)°
II-III	10.42(10)°	15.47(12)°
III-IV	12.45(10)°	14.83(12)°
IV-V	12.32(11)°	14.43(12)°
V-VI	7.90(12)°	11.39(14)°
I-VI	47.50(10)°	58.56(12)°

of **2b** [4]. In contrast, the pitch of the helix projects H1 into the π-cloud of ring VI, but at a greater distance, resulting in a correspondingly lesser degree of shielding relative to H14 and H15 [9] (7.97 vs. 6.72 and 6.83 respectively [4]).

EXPERIMENTAL

A pale yellow crystal of approximate dimensions .30mm × .21mm × .11mm was obtained by slow evaporation from a chloroform solution. Data were collected on a Syntex P2₁ diffractometer with a graphite monochromator and LT-1 low temperature delivery system(163K). Lattice parameters were obtained from least-squares refinement of the setting angles of 45 reflections with 2θ between 20.1° and 27.2°. Data were collected using the omega scan technique, 2θ range from 4 to 52°, 1° scan range in ω at a scan rate of 2 to 5° per minute. A total of 3387 reflections were measured (range of h,k,l:0 to 14 in h, 0 to 17 in k, −14 to 12 in l). Four reflections (2,−3,−2;1,1,−3;−1,−3,1;0,2,2) were remeasured every 96 reflections to monitor instrument and crystal stability. Data were corrected for Lp effects and absorption (μ = 1.88 cm⁻¹; transmission factor range: 0.958 - 0.982). Data reduction is described in Riley and Davis [10]. Reflections with $F_o < 4(\sigma(F_o))$ were considered unobserved (1057 reflections). The S atom position was located via the heavy-atom method; all other non-H atoms were located in subsequent electron density maps. After several cycles of full-matrix least-squares refinement with anisotropic thermal parameters, positions for the H atoms were obtained from a ΔF map and refined isotropically. Functioned minimized: $\Sigma(w(|F_o| - |F_c|)^2)$, where $w = 1/(\sigma(F_o)^2)$. Final R = .0458 using 2330 reflections, with a wR = .0461 (R using all data = .0815, wR using all data = .0517) and a goodness of fit, S = 1.223; where R = $\Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$ and wR = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ and S = $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. The maximum |shift/esd| in the final refinement cycle was < .01, while the minimum and maximum peaks in the final ΔF map were −.26 and .33 e⁻/Å³, respectively. Scattering factors for the non-H atoms were taken from Cromer and Mann [11] with anomalous-dispersion corrections from Cromer and Liberman [12]; while scattering factors for the H atoms were taken from Stewart, Davidson

and Simpson [13]. The linear absorption coefficient was calculated using values in the International Tables for X-ray Crystallography [14]. The least-squares plane program was supplied by Cordes [15]; other computer programs are listed in reference 11 of Gadol and Davis [16].

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