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Two 9-alkylthiophenanthrenes at 193 K (alkyl = dodecyl and tetradecyl)

Jarno Kansikas[a]* and Kaija Sipilä[b]

[a]Department of Chemistry, Laboratory of Inorganic Chemistry, PO Box 55, 00014 University of Helsinki, Finland, and [b]Department of Chemistry, Laboratory of Organic Chemistry, PO Box 55, 00014 University of Helsinki, Finland
Correspondence e-mail: jarno.kansikas@helsinki.fi

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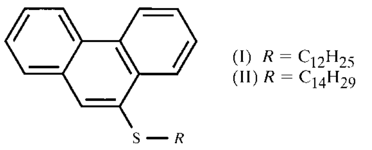
Two isostructural 9-thiophenanthrene derivatives, 9-dodecylthiophenanthrene, $C_{26}H_{34}S$, (I), and 9-tetradecylthiophenanthrene, $C_{28}H_{38}S$, (II), are reported. They crystallize in the monoclinic space group $P2_1/c$ with four molecules in a unit cell. The $S-C_{phenanthrene}$ bonds are 1.767 (2) and 1.772 (4) Å and $S-C_{alkyl}$ bonds are 1.809 (2) and 1.804 (4) Å for (I) and (II), respectively. The bond angles at S are 104.04 (11) and 104.0 (2)° for (I) and (II), respectively.

Comment

In connection with our studies concerning 9-thioderivatives of phenanthrene (Kansikas & Sipilä, 1997; Sipilä *et al.*, 1999) two new compounds with a long straight alkyl chain were synthesized and characterized by X-ray analysis. The long, colourless needles of 9-dodecylthiophenanthrene, (I), and 9-tetradecylthiophenanthrene, (II), have melting points of 347 (1) and 350 (1) K, respectively. They were measured in open capillary tubes with an electrothermal apparatus and are uncorrected.



The present compounds (Figs. 1 and 2) are isostructural with the earlier reported 9-alkylthiophenanthrenes [alkyl = ethyl (III), propyl (IV) and butyl (V); Kansikas & Sipilä, 1997]. Among these structures the *b*-axis lengthening, from 20.644 (9) to 38.696 (2) Å, is nearly linear; a 1.5 Å increase per one added C atom in the alkyl chain. The molecular packing which is presented in Figs. 3 and 4, shows tubular channels through the phenanthrene rings in the *c*-axis direction and a herring-bone pattern when viewed along the *a* axis. However, the phenanthrene planes are tilted so that there is no perpendicular stacking overlap between the successive molecules as seen in Fig. 4. The angles between the phenanthrene group and the *ab, ac* and *bc* planes are 119.3 (1), 78.0 (1) and 34.7 (1)° for (I) and 119.1 (1), 78.1 (1) and 34.7 (1)° for (II).

The phenanthrene groups in the adjacent sheets form an interplanar angle of 69.0 (1)° for (I) and 69.3 (1)° for (II). Both molecules are nearly planar. The phenanthrene group comprises three planes formed by rings 1 (C1, C2, C3, C4, C4a, C10a), 2 (C4a, C4b, C8a, C9, C10, C10a) and 3 (C4b, C5, C6, C7, C8, C8a). The planar alkyl chains C12–C23 for (I) and C12–C25 for (II) form a fourth plane. Within the phenanthrene groups the interplanar angles are: 1.36 (12) and 1.53 (22)° for 1^2, 0.76 (12) and 0.91 (23)° for 1^3 and 1.00 (12) and 0.95 (22)° for 2^3. The fourth plane through the alkyl chains forms angles of 3.67 (11) and 3.94 (20)° with ring 2 for compounds (I) and (II), respectively.

We have studied the structures of 9-phenylthiophenanthrene (VI) and 9-*tert*-butylthiophenanthrene (VII; Sipilä *et al.*, 1999). In these compounds the substituents deviate from the phenanthrene planes. Various bonding parameters, involving the S atom, of compounds (III)–(VII) are compared here to those obtained for (I) and (II). The C9—S—C12 bond angle is between 104.0 (1) and 104.5 (1)° for the aliphatic substituents and 102.1 (1)° for the phenyl group. The molecular geometry can be described by the values of the C10—C9—S—C12 torsion angle, which ranges from −0.1 (2) to 5.9 (2)° in the straight-chain molecules, but is 92.1 (1) and 91.7 (1)° for (VI) and (VII), respectively. The S—C9 bond length is 1.767 (2), 1.772 (4), 1.765 (7), 1.764 (2), 1.766 (3), 1.779 (2)

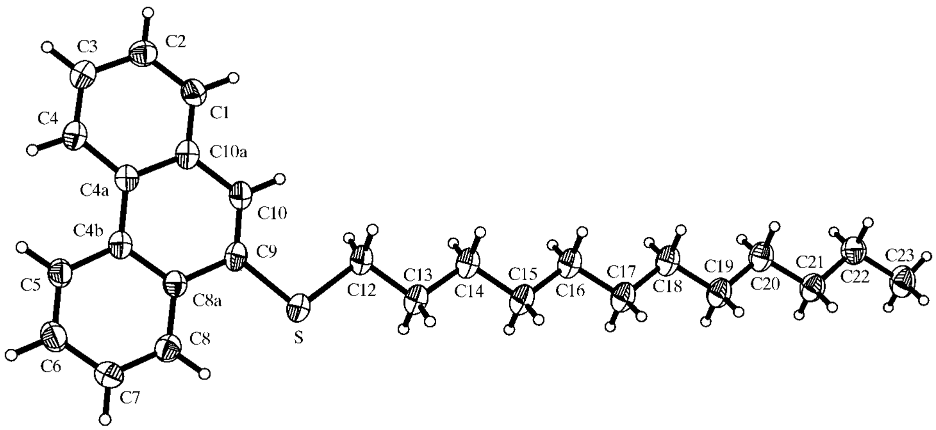


Figure 1
View of $C_{26}H_{34}S$, (I), showing atom labels. Displacement ellipsoids are drawn at the 50% probability level.

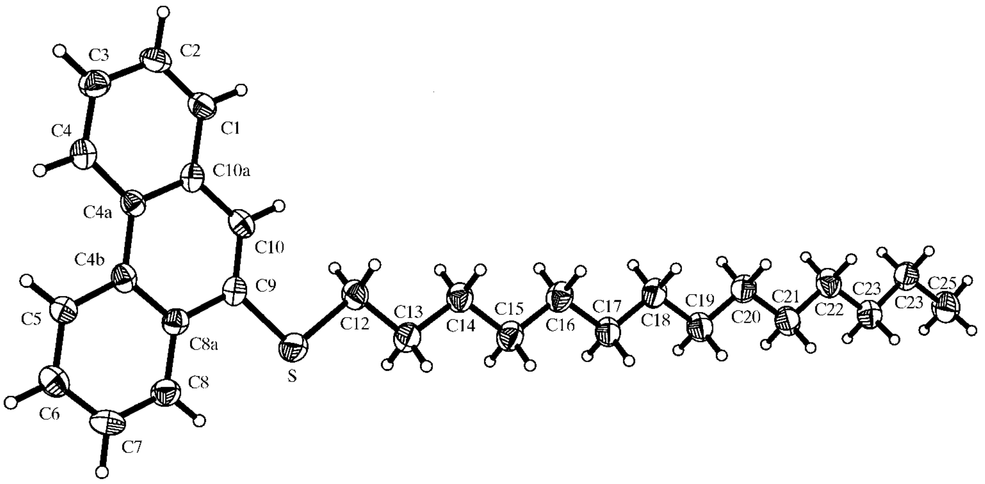


Figure 2
View of $C_{28}H_{38}S$, (II), showing atom labels. Displacement ellipsoids are drawn at the 50% probability level.

and 1.777 (2) Å for compounds (I)–(VII), respectively. These are normal $S-C_{aromatic}$ bond distances, as is also the $S-C_{phenyl}$ value of 1.769 (2) Å in (VI). For the straight-chain alkyl groups, the S—C12 bond distances are longer ranging from 1.794 (4) to 1.806 (2) Å for compounds (I)–(V), while in (VII) it is 1.861 (2) Å.

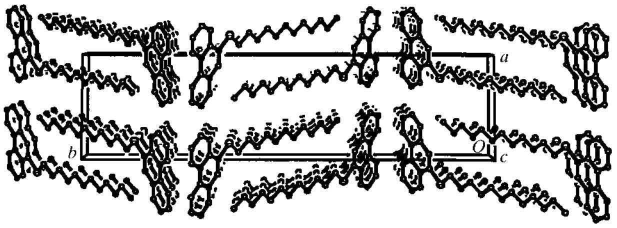


Figure 3
View of the molecular packing of compound (I) down the *c* axis.

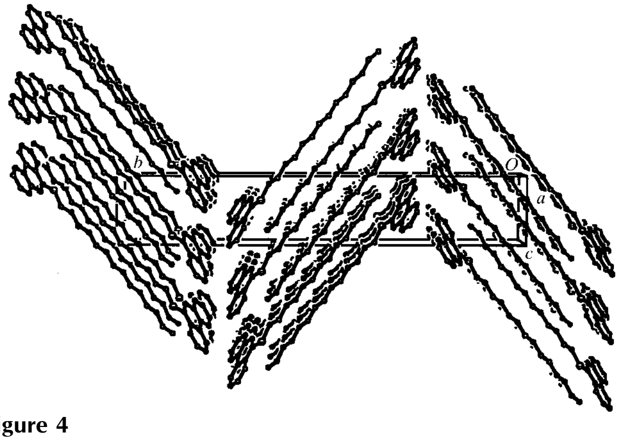


Figure 4
View of the molecular packing of compound (II) along the *a* axis.

Experimental

The 9-alkylthiophenanthrenes were prepared from 9-bromophenanthrene, KOH and alkylthiol in dimethylformamide according to a previously reported procedure (Sipilä & Hase, 1997). The side product dialkyl disulfide was removed by flash chromatography and the crystals suitable for X-ray analysis were obtained by recrystallization from ethanol.

Compound (I)

Crystal data

$C_{26}H_{34}S$
$M_r = 378.59$
Monoclinic, $P2_1/c$
$a = 9.105$ (2) Å
$b = 35.679$ (7) Å
$c = 6.7840$ (14) Å
$\beta = 99.28$ (3)°
$V = 2175.0$ (8) Å^3
$Z = 4$
$D_x = 1.156$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4$–10°
$\mu = 1.348$ mm^{-1}
$T = 193$ (2) K
Needle, colourless
0.31 × 0.12 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3928 measured reflections
3688 independent reflections
3198 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 64.95°$
$h = -10 \rightarrow 1$
$k = -29 \rightarrow 41$
$l = -7 \rightarrow 7$
3 standard reflections every 200 reflections intensity decay: 0.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.118$
$S = 1.136$
3664 reflections
244 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 1.4963P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

S—C9	1.767 (2)	C4b—C8a	1.420 (3)
S—C12	1.809 (2)	C8a—C9	1.455 (3)
C4—C4a	1.413 (3)	C9—C10	1.350 (3)
C4a—C4b	1.453 (3)	C10—C10a	1.439 (3)
C4a—C10a	1.418 (3)	C12—C13	1.527 (3)
C4b—C5	1.407 (3)	C13—C14	1.524 (3)
C9—S—C12	104.01 (10)	C8a—C9—S	116.0 (2)
C4—C4a—C4b	123.5 (2)	C10—C9—S	123.9 (2)
C4b—C4a—C10a	119.0 (2)	C9—C10—C10a	122.1 (2)
C4a—C4b—C5	122.1 (2)	C4a—C10a—C10	119.5 (2)
C4a—C4b—C8a	119.9 (2)	C13—C12—S	108.2 (2)
C4b—C8a—C9	119.4 (2)	C12—C13—C14	111.2 (2)
C8a—C9—C10	120.1 (2)	C13—C14—C15	113.7 (2)
C8a—C4b—C4a—C10a	0.0 (3)	C4b—C8a—C9—S	−178.44 (15)
C4a—C4b—C8a—C9	−0.2 (3)	C12—S—C9—C10	−0.1 (2)
C8—C8a—C9—C10	−178.7 (2)	C12—S—C9—C8a	179.4 (2)
C4b—C8a—C9—C10	1.1 (3)	C8a—C9—C10—C10a	−1.7 (3)
C8—C8a—C9—S	1.8 (3)	S—C9—C10—C10a	177.8 (2)

Table 2
Selected geometric parameters (Å, °) for (II).

S—C9	1.772 (4)	C4b—C8a	1.427 (5)
S—C12	1.804 (4)	C8a—C9	1.451 (6)
C4—C4a	1.415 (5)	C9—C10	1.344 (5)
C4a—C4b	1.443 (5)	C10—C10a	1.440 (5)
C4a—C10a	1.408 (6)	C12—C13	1.530 (5)
C4b—C5	1.400 (6)	C13—C14	1.527 (6)
C9—S—C12	104.0 (2)	C8a—C9—S	115.7 (3)
C4—C4a—C4b	123.1 (4)	C10—C9—S	123.4 (3)
C4b—C4a—C10a	119.0 (4)	C9—C10—C10a	121.1 (4)
C4a—C4b—C5	122.7 (4)	C4a—C10a—C10	120.3 (3)
C4a—C4b—C8a	119.7 (4)	C13—C12—S	108.4 (3)
C4b—C8a—C9	119.0 (3)	C12—C13—C14	111.8 (3)
C8a—C9—C10	120.9 (4)	C13—C14—C15	114.3 (3)
C10a—C4a—C4b—C8a	−0.1 (5)	C4b—C8a—C9—S	178.6 (3)
C4a—C4b—C8a—C9	0.3 (5)	C12—S—C9—C10	0.2 (4)
C8—C8a—C9—C10	178.3 (4)	C12—S—C9—C8a	−179.7 (3)
C4b—C8a—C9—C10	−1.2 (6)	C8a—C9—C10—C10a	2.0 (6)
C8—C8a—C9—S	−1.8 (5)	S—C9—C10—C10a	−177.9 (3)

Compound (II)

Crystal data

$C_{28}H_{38}S$
$M_r = 406.64$
Monoclinic, $P2_1/c$
$a = 9.1000$ (14) Å
$b = 38.696$ (2) Å
$c = 6.804$ (8) Å
$\beta = 99.67$ (3)°
$V = 2361.9$ (27) Å^3
$Z = 4$
$D_x = 1.144$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4$–10°
$\mu = 1.272$ mm^{-1}
$T = 193$ (2) K
Needle, colourless
0.30 × 0.09 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8468 measured reflections
4007 independent reflections
2146 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.092$
$\theta_{\rm max} = 64.95°$
$h = -10 \rightarrow 10$
$k = -45 \rightarrow 18$
$l = -6 \rightarrow 7$
3 standard reflections every 200 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.142$
$S = 1.177$
3997 reflections
262 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 2.3038P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\rm max} = 0.47$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

For compound (II), the Laue class and extinction rules indicated clearly the $P2_1/c$ space group and it was possible to solve the structure. In this solution, however, the alkyl chains were exactly overlapping, but in opposite directions. Thus the phenanthrene groups, including the S atoms, had an occupancy factor of 0.5. When the structure was solved in the $P\bar{1}$ space group with two molecules in an asymmetric unit, molecular packing was similar to that in compound (I). One of the two molecules was then removed, the monoclinic symmetry operations were added again and the remaining molecule was seen to possess a correct location. However, the torsion angles revealed it to be in the inverted position compared to (I).

For both compounds, data collection: *CAD*-4 *Express Software* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *Express Software*; data reduction: *WinGX* (Farrugia, 1998); program(s) used to solve structures: *SHELXTL*/*PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1072). Services for accessing these data are described at the back of the journal.

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