organic compounds

2,4,5,7-Tetramethylphenanthrene at 150 K

Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA
Correspondence e-mail: gerkin@chemistry.ohio-state.edu

The title compound, $C_{18}H_{18}$, crystallized in the centrosymmetric space group $P2_1/c$ with one molecule as the asymmetric unit. The methyl-group H atoms at the 4 and 5 positions are ordered, while those at the 2 and 7 positions are disordered. The torsion of the bay region of the core is notably similar to that of other 4,5-dimethylphenanthrenes. No substantial C—H$\cdots\pi$ interaction occurs in this structure.

Comment

2,4,5,7-Tetramethylphenanthrene, (I), was of interest because of its potential for C—H$\cdots\pi$ interactions as well as for structural comparisons with 4,5-dimethylphenanthrene [(IIa): Armstrong *et al.*, 1987; (IIb): Cosmo *et al.*, 1987; (IIc): Imashiro *et al.*, 1987]; and with 3,4,5,6-tetramethylphenanthrene [(III): Armstrong *et al.*, 1987], which are identically substituted in the (crowded) bay region. Compound (I) crystallized in the centrosymmetric space group $P2_1/c$ with one molecule as the asymmetric unit. The refined molecule and the labeling scheme are given in Fig. 1. The fully refined methyl groups at the 4 and 5 positions are ordered, while those at the 2 and 7 positions, refined with only their U_{iso}'s fixed, have their H atoms disordered over two sets of sites with refined populations 0.54 (3) and 0.46, and 0.66 (2) and 0.34, respectively. The most striking molecular feature is, as expected, the departure of the core from the near planarity of phenanthrene itself (*e.g.* Kay *et al.*, 1971), due to crowding in the bay region. A satisfactory measure of this departure is the magnitude of the bay torsion angle C4—C12—C13—C5, which is 32.4 (2)° in (I). This result is in very good accord with the values reported for 4,5-dimethylphenanthrene at room temperature: 31.5 (3), 33.0 and 32.2° for (IIa,b and c), respectively. It is also in very good accord with the corresponding value for 3,4,5,6-tetramethylphenanthrene, (III), 32.9 (2)°, further confirming the evidence from Armstrong *et al.* (1987) that the placement of additional methyl groups in a 4,5-dimethylphenanthrene is of little importance in determining this torsion angle. In 4,5-diiodophenanthrene at 150 K (hereafter, DIP) (present labeling; Bock *et al.*, 1998), the bay torsion angle is enlarged to 63°. However, other aspects of the ring geometries are very similar to those found in (I). Thus, C9—C10 and C12—C13

measure 1.348 (2) and 1.466 (2) Å in (I), and 1.348 (7) and 1.461 (5) Å (mean values) in DIP. Also, the mean values of C16—C4—C12 and C17—C5—C13 and of C4—C12—C13 and C5—C13—C12 are 123.39 (9) and 124.88 (9)° in (I), while the corresponding mean values (I—C—C and C—C—C) are given for DIP as 123.0 (3) and 126.2 (3)°. Thus, the geometric distortion of the individual rings is not significantly correlated with the torsion angle of the bay region. No substantial C—H$\cdots\pi$ interaction occurs in this structure.

(I)
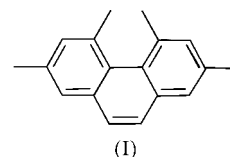
Selected bond distances and angles are given in Table 1. In (I), the molecular core displays very nearly twofold symmetry with respect to an axis through the midpoints of the C9—C10 and C12—C13 bonds. Thus, for example, the r.m.s. difference within the seven corresponding pairs of distances, which range
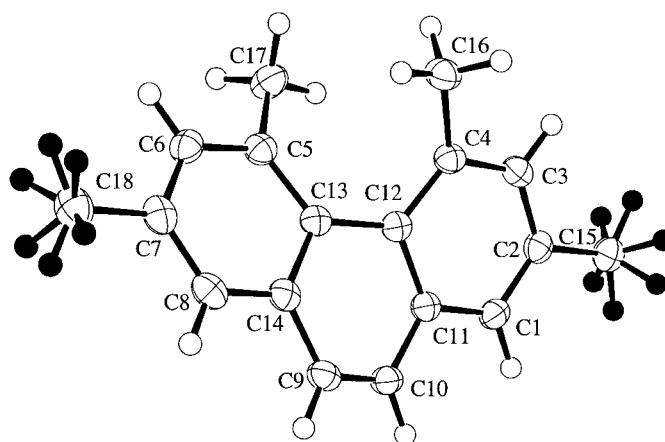

Figure 1
The molecular structure of (I) showing the labeling scheme, with displacement ellipsoids at the 50% probability level. Shaded spheres depict partial-occupancy H atoms.
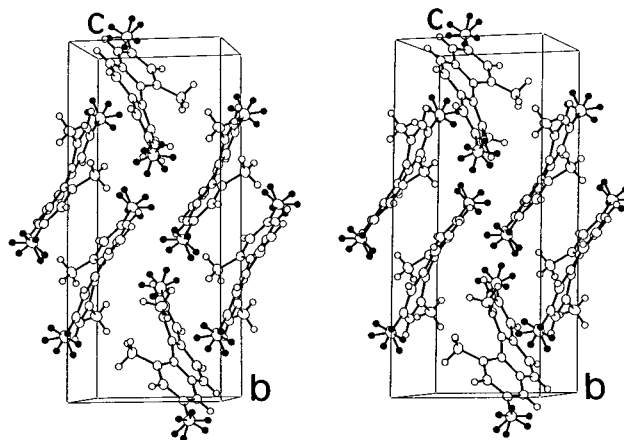

Figure 2
Packing diagram of (I) viewed nearly down the a axis, with displacement ellipsoids at the 50% probability level. Shaded spheres depict partial-occupancy H atoms.

from 1.378 (2) to 1.439 (2) Å, is 0.002 Å, while the r.m.s. difference within the 11 corresponding pairs of core carbon angles, which range from 116.81 (9) to 124.90 (9)°, is 0.2°. The packing diagram, Fig. 2, makes clear the molecular orientations, which place the terminal methyl-group H atoms no farther than 1.76 Å from the *bc* faces of the unit cell. The closest intermolecular approaches are between H15*A* and H17*C*(x, $\frac{3}{2} - y$, $-\frac{1}{2} + z$) and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.20 Å. This suggests some preference for pairing of H15*A*,*B*,*C* occupancy with H18*D*,*E*,*F* occupancy, and *vice versa*.

Experimental

Compound (I) was obtained as coarse colorless crystals from a sample in Dr M. S. Newman's chemical collection. Evaporation of a solution of these in ethanol/acetone produced satisfactory crystals. A synthesis is described by Karnes *et al.* (1965).

Crystal data

$C_{18}H_{18}$	$D_x = 1.198$ Mg m^{-3}
$M_r = 234.34$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 832
$a = 8.3604$ (2) Å	reflections
$b = 8.15670$ (10) Å	$\theta = 2.14$–$27.49°$
$c = 19.1388$ (4) Å	$\mu = 0.067$ mm^{-1}
$\beta = 95.4670$ (10)°	$T = 150$ K
$V = 1299.20$ (4) Å^3	Irregular hexagonal slab, colorless
$Z = 4$	$0.38 \times 0.27 \times 0.15$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.036$
ω scans with κ offsets	$\theta_{max} = 27.49°$
25 832 measured reflections	$h = -10 \rightarrow 10$
2981 independent reflections	$k = -10 \rightarrow 10$
2381 reflections with $I > 2\sigma_I$	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma_{cs}^2 + (0.027I)^2]$
$R(F) = 0.043$	$(\Delta/\sigma)_{max} = 0.002$
$wR(F^2) = 0.096$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
$S = 1.92$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
2981 reflections	Extinction correction: Zachariasen
226 parameters	(1963, 1968)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 13 (3) × 10^{-7}

Fourier difference methods were used to locate the initial H-atom positions, and these H atoms were refined. It was then apparent that the methyl-H atoms on C15 and C18 were disordered, and two sets of H-atom sites, and occupancies, were refined on each. Absence of any further disorder was obvious since none of the subsequent top 25 difference peaks was suitable as a potential H atom. Refined C—H distances for the 12 full-occupancy H atoms ranged from 0.98 (1) to 1.02 (1) Å, with a mean value of 1.00 (2) Å; their U_{iso} values ranged

Table 1
Selected geometric parameters (Å, °).

C2—C3	1.3969 (14)	C4—C12	1.4229 (13)
C3—C4	1.3857 (13)	C11—C12	1.4220 (13)
C1—C2—C3	117.09 (9)	C6—C7—C8	117.03 (9)
C3—C4—C12	118.89 (9)	C9—C10—C11	120.97 (9)
C6—C5—C13	119.10 (9)	C9—C14—C13	118.81 (9)
C4—C12—C13—C5	32.43 (15)	C11—C12—C13—C14	22.21 (13)

from 1.0 to 1.6 times the U_{eq} values of the attached C atoms. The ring H atoms were then made canonical, with C—H = 0.98 Å and U_{iso} = $1.2U_{eq}$ of the attached C atom, and U_{iso} of the partial-occupancy H atoms was fixed at $1.2U_{eq}$ of the attached C atom. Final refined C—H distances for the 12 partial-occupancy H atoms ranged from 0.94 (4) to 1.07 (4) Å, with a mean value of 1.03 (4) Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992–1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

References

Armstrong, R. N., Ammon, H. L. & Darnow, J. N. (1987). *J. Am. Chem. Soc.* **109**, 2077–2082.
Bock, H., Sievert, M. & Havlas, Z. (1998). *Chem. Eur. J.* **4**, 677–685.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Cosmo, R., Hambley, T. W. & Sternhell, S. (1987). *J. Org. Chem.* **52**, 3119–3123.
Imashiro, F., Saika, A. & Taira, Z. (1987). *J. Org. Chem.* **52**, 5727–5729.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Karnes, H. A., Kybett, B. D., Wilson, M. H., Margrave, J. L. & Newman, M. S. (1965). *J. Am. Chem. Soc.* **87**, 5554–5558.
Kay, M. I., Okaya, Y. & Cox, D. E. (1971). *Acta Cryst.* B**27**, 26–33.
Molecular Structure Corporation (1992–1997). *TEXSAN*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.