Table 2. *Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.357 (2) | C5—C6 | 1.381 (4) |
| O1—C8 | 1.382 (2) | C6—C7 | 1.380 (3) |
| O2—C1 | 1.216 (2) | C7—C8 | 1.384 (3) |
| C1—C2 | 1.452 (3) | C8—C9 | 1.390 (3) |
| C2—C3 | 1.344 (3) | C2—C10 | 1.501 (3) |
| C3—C9 | 1.425 (3) | C10—O3 | 1.328 (3) |
| C4—C5 | 1.372 (3) | C10—O4 | 1.199 (3) |
| C4—C9 | 1.404 (3) | | |
| C1—O1—C8 | 121.8 (2) | C6—C7—C8 | 117.8 (2) |
| O1—C1—O2 | 116.5 (2) | O1—C8—C7 | 117.2 (2) |
| O1—C1—C2 | 118.2 (2) | O1—C8—C9 | 120.6 (2) |
| O2—C1—C2 | 125.3 (2) | C7—C8—C9 | 122.2 (2) |
| C1—C2—C3 | 120.2 (2) | C3—C9—C4 | 123.5 (2) |
| C1—C2—C10 | 119.7 (2) | C3—C9—C8 | 118.3 (2) |
| C3—C2—C10 | 120.1 (2) | C4—C9—C8 | 118.2 (2) |
| C2—C3—C9 | 120.9 (2) | C2—C10—O3 | 116.7 (2) |
| C5—C4—C9 | 120.0 (2) | C2—C10—O4 | 122.6 (2) |
| C4—C5—C6 | 120.2 (2) | O3—C10—O4 | 120.7 (2) |
| C5—C6—C7 | 121.5 (2) | | |

Table 3. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H···O2 | 0.93 (3) | 1.72 (3) | 2.589 (2) | 153 (3) |

Scan widths were $(1.60 + 0.35\tan\theta)^\circ$ in $\omega$, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetry indicated by the intensity statistics led to unique assignment of the space group as $P2_1/n$ (No. 14); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions. The final refined C—H distances ranged from 0.94 (2) to 1.02 (2) Å, with a mean value of 0.97 (2) Å.

The maximum effect of extinction was 8.4% of $F_o$ for 202. The maximum peak in the final difference map occurred ~0.8 Å from C2 and ~0.9 Å from C1; the maximum negative peak occurred near the center of the C4—C9 ring.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FR1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Delettré, J., Delaitre, M.-E., Vigny, P. & Bisagni, E. (1986). *Acta Cryst.* C**42**, 1849–1851.
Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* **C52**. 3088-3091.
Gavuzzo, E., Mazza, F. & Giglio, E. (1974). *Acta Cryst.* B**30**, 1351–1357.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
Stuart, C. M. (1886). *J. Chem. Soc.* **49**, 365–367.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
Vasudevan, K. T., Puttaraja & Kulkarni, M. V. (1991). *Acta Cryst.* C**47**, 775–777.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

---

*Acta Cryst.* (1996). **C52**, 3083–3086

# 4-(2-Naphthyl)butanoic Acid

Allison J. Dobson and Roger E. Gerkin

*Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu*

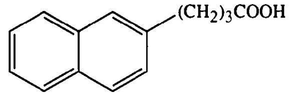
(*Received 9 May 1996; accepted 15 July 1996*)

## Abstract

4-(2-Naphthyl)butanoic acid, $C_{14}H_{14}O_2$, crystallizes in the centrosymmetric space group $P2_1/a$. The single type of hydrogen bond forms cyclic dimers about inversion centers. The carboxylic-O atoms are ordered as is the acid-H atom. The structure comprises double layers of aromatic rings in a herringbone array separated by double layers of hydrogen-bonded aliphatic strings, a pattern seen previously in related substances.

## Comment

This investigation of 4-(2-naphthyl)butanoic acid, (I), is part of a continuing series on hydrogen bonding in carboxylic acids. Also of interest was the packing of the ring (naphthalene), the string (the butyl chain) and the terminal carboxyl group of the molecule for comparison with the structural results from the (2-naphthyl)ethanoic acid analog.



(I)

In 4-(2-naphthyl)butanoic acid, Fig. 1, there is a single type of hydrogen bond which forms cyclic dimers about an inversion center. Geometric details are given in Table 3. The donor–acceptor distance, 2.668 (2) Å, is somewhat below average for organic O···O hydrogen bonds (2.77 Å; Ceccarelli, Jeffrey & Taylor, 1981). Data presented in Tables 1 and 2 for distances and angles involving the carboxylic group atoms show that the O atoms are ordered and that the carboxylic-H atom is also ordered.

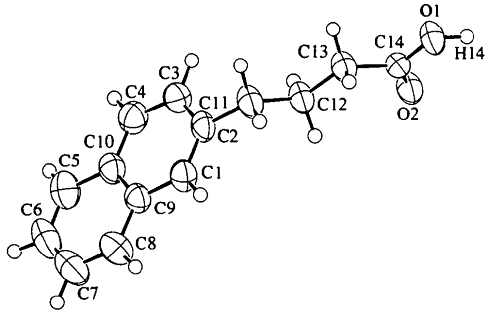


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of 4-(2-naphthyl)butanoic acid showing our numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H for which they have been set artificially small.

The leading aspect of the molecular geometry is perhaps the relations among the best least-squares planes describing the ring, the string and the carboxyl group. The average deviation of the ring C atoms from the best-fit plane through the naphthalene core is 0.007 (2) Å, while the maximum deviation is 0.012 (2) Å. As expected, the individual six-membered rings of the core are even closer to planarity: for the C1–4, C9, C10 ring the average deviation is 0.003 (2) Å, and for the C5–C10 ring, 0.002 (2) Å. Moreover, the core exhibits the expected pseudo-twofold symmetry: the e.s.d. of the ten bond distances which would be identical pairwise under twofold symmetry about the C9—C10 axis from the five respective means is 0.006 Å, while with respect to the pseudo-twofold axis at right angles to this, the corresponding e.s.d. is 0.005 Å. The best plane through the C11–C14 aliphatic string is such that the average deviation of these atoms from it is 0.041 (3) Å; the dihedral angle between the ring plane and the string plane is 75.9 (2)°. The dihedral angle between the carboxyl group plane and the string plane is 4.5 (3)°, and between the carboxyl plane and the ring plane, 80.5 (2)°.

The overall structure (Fig. 2) can be viewed as composed of double layers of naphthyl rings separated by a double layer of aliphatic chains connected to each other by cyclic dimer hydrogen bonds at the chain termini. Adjacent naphthyl groups adopt a herringbone pattern with an interplanar angle of 51.6 (4)°, virtually the same as that of naphthalene itself, 52.5° (calculated from Cruickshank, 1957). Qualitatively, this structure is quite similar to that of (2-naphthyl)ethanoic acid at 113 K (Barrett & Gellman, 1993) which also manifests hydrogen bonding of the cyclic dimer type about an inversion center and the same type of arrangement of the aromatic and aliphatic portions of the structure. The naphthyl rings in that instance adopt a herringbone pattern with a 48° angle which, as noted by those authors, is also very similar to that in naphthalene.

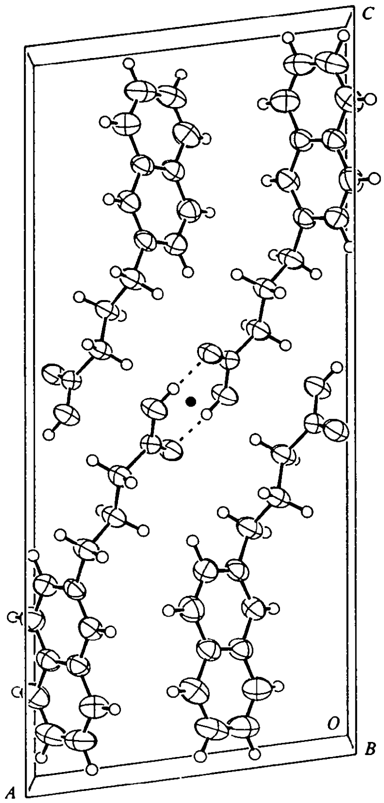


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of a portion of the 4-(2-naphthyl)butanoic acid structure including a unit cell. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H for which they have been set artificially small. Hydrogen bonds are drawn as dashed lines and the center of symmetry as a filled circle.

Furthermore, the alternating double layers of aromatic and aliphatic portions seen in the structures discussed above are seen also in an anthracene analog, 4-(2-anthryl)butanoic acid (Durfee, Gruszecka, Olszak, Storck, Bradaczek & Willig, 1989), though in this latter case there are also significant differences of detail in the aliphatic chain packing as well as disordered O atoms in the carboxyl group.

Excluding pairs of atoms involved in the hydrogen bonding, all intermolecular approach distances are at least slightly greater than the corresponding van der Waals radius sums (Bondi, 1964). This is atypical of the acid structures we have determined, and suggests a very satisfactory accommodation of the three types of components of the molecule in this spatial arrangement.

## Experimental

4-(2-Naphthyl)butanoic acid from Dr M. S. Newman's chemical collection was dissolved in ether and the solution was allowed to evaporate at room temperature to produce platy crystals, one of which was cut to provide the experimental sample.

### *Crystal data*

$C_{14}H_{14}O_2$
$M_r = 214.26$
Monoclinic
$P2_1/a$
$a = 10.058\,(1)$ Å
$b = 4.971\,(2)$ Å
$c = 22.924\,(2)$ Å
$\beta = 97.897\,(9)°$
$V = 1135.2\,(4)$ Å$^3$
$Z = 4$
$D_x = 1.254$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.5–17.3°$
$\mu = 0.077$ mm$^{-1}$
$T = 296$ K
Cut plate
0.34 × 0.31 × 0.31 mm
Colorless

### *Data collection*

AFC-5*S* diffractometer
$\omega$ scans
Absorption correction: none
3100 measured reflections
2938 independent reflections
1447 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.016$

$\theta_{\rm max} = 27.50°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 6$
$l = -29 \rightarrow 29$
6 standard reflections monitored every 150 reflections intensity decay: 3.0%

### *Refinement*

Refinement on $F$
$R = 0.040$
$wR = 0.048$
$S = 1.63$
1447 reflections
202 parameters
All H-atom parameters refined
$w = 1/\sigma_F^2$
$(\Delta/\sigma)_{\rm max} = <0.01$

$\Delta\rho_{\rm max} = 0.16$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.14$ e Å$^{-3}$
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $6\,(3) \times 10^{-7}$
Atomic scattering factors from Stewart, Davidson & Simpson (1965) (H), Cromer & Waber (1974) (C, O)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| O1 | 0.6098 (2) | 0.7827 (3) | 0.49675 (6) | 0.0587 (5) |
| O2 | 0.5621 (1) | 0.4316 (3) | 0.43746 (5) | 0.0558 (4) |
| C1 | 0.8077 (2) | 0.7084 (5) | 0.21067 (9) | 0.0558 (7) |
| C2 | 0.8586 (2) | 0.6361 (4) | 0.26637 (8) | 0.0501 (6) |
| C3 | 0.9542 (2) | 0.4287 (5) | 0.27431 (10) | 0.0590 (7) |
| C4 | 0.9974 (3) | 0.3033 (5) | 0.22764 (10) | 0.0643 (7) |
| C5 | 0.9904 (3) | 0.2552 (6) | 0.11942 (12) | 0.0739 (9) |
| C6 | 0.9386 (3) | 0.3325 (6) | 0.06419 (11) | 0.0819 (10) |
| C7 | 0.8433 (3) | 0.5346 (7) | 0.05592 (11) | 0.0808 (10) |
| C8 | 0.7989 (3) | 0.6572 (6) | 0.10219 (10) | 0.0721 (9) |
| C9 | 0.8492 (2) | 0.5830 (4) | 0.16043 (8) | 0.0532 (6) |
| C10 | 0.9464 (2) | 0.3779 (4) | 0.16947 (9) | 0.0543 (6) |
| C11 | 0.8188 (3) | 0.7799 (5) | 0.31928 (10) | 0.0593 (7) |
| C12 | 0.7361 (3) | 0.6152 (5) | 0.35706 (9) | 0.0529 (7) |
| C13 | 0.7152 (3) | 0.7678 (5) | 0.41210 (9) | 0.0533 (7) |
| C14 | 0.6223 (2) | 0.6420 (4) | 0.44954 (8) | 0.0437 (5) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C14 | 1.309 (2) | C5—C10 | 1.423 (3) |
| O2—C14 | 1.222 (2) | C6—C7 | 1.383 (4) |
| C1—C2 | 1.357 (3) | C7—C8 | 1.352 (4) |
| C1—C9 | 1.421 (3) | C8—C9 | 1.410 (3) |
| C2—C3 | 1.404 (3) | C9—C10 | 1.408 (3) |
| C2—C11 | 1.508 (3) | C11—C12 | 1.520 (3) |
| C3—C4 | 1.360 (3) | C12—C13 | 1.511 (3) |
| C4—C10 | 1.411 (3) | C13—C14 | 1.490 (3) |
| C5—C6 | 1.357 (4) | | |
| C2—C1—C9 | 122.1 (2) | C1—C9—C10 | 118.3 (2) |
| C1—C2—C3 | 118.6 (2) | C8—C9—C10 | 118.7 (2) |
| C1—C2—C11 | 121.6 (2) | C4—C10—C5 | 122.5 (2) |
| C3—C2—C11 | 119.7 (2) | C4—C10—C9 | 119.0 (2) |
| C2—C3—C4 | 121.4 (2) | C5—C10—C9 | 118.6 (2) |
| C3—C4—C10 | 120.6 (2) | C2—C11—C12 | 115.4 (2) |
| C6—C5—C10 | 120.6 (3) | C11—C12—C13 | 110.8 (2) |
| C5—C6—C7 | 120.2 (3) | C12—C13—C14 | 116.1 (2) |
| C6—C7—C8 | 121.2 (3) | C13—C14—O1 | 113.0 (2) |
| C7—C8—C9 | 120.7 (3) | C13—C14—O2 | 124.0 (2) |
| C1—C9—C8 | 123.0 (2) | O1—C14—O2 | 123.0 (2) |

Table 3. *Hydrogen-bonding geometry (Å, °)*

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1—H14$\cdots$O2$^{\rm i}$ | 0.93 (3) | 1.74 (3) | 2.668 (2) | 178 (2) |

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Scan widths were $(1.30 + 0.35\tan\theta)°$ in $\omega$, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and the centrosymmetry indicated by the intensity statistics led to assignment of the space group as $P2_1/a$ (No. 14); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions. The final refined values of C—H distances ranged from 0.89 (2)–1.02 (2) Å with a mean value of 0.97 Å. The final refined value of the O1—H14 distance was 0.93 (3) Å.

The maximum effect of extinction was 2.1% of $F_o$ for 211. The maximum peak in the final difference map occurred ~0.8 Å from O2 and ~1.0 Å from C14; the maximum negative peak occurred ~1.2 Å from C1 and C9.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

It is a pleasure to acknowledge partial support provided to AJD by a National Needs Fellowship. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: BK1262). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Barrett, D. G. & Gellman, S. H. (1993). *J. Am. Chem. Soc.* **115**, 9343–9344.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Ceccarelli, C., Jeffrey, G. A. & Taylor, R. J. (1981). *J. Mol. Struct.* **70**, 255–271.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cruickshank, D. W. J. (1957). *Acta Cryst.* **10**, 504–508.

Durfee, W. S., Gruszecka, M., Olszak, T. A., Storck, W., Bradaczek, H. & Willig, H. (1989). *J. Am. Chem. Soc.* **111**, 3699–3702.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

---

*Acta Cryst.* (1996). C**52**, 3086-3088

# *sym*-Hexahydropyrene

Allison J. Dobson and Roger E. Gerkin

*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu*

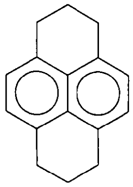
(*Received 10 July 1996; accepted 26 July 1996*)

## Abstract

In 1,2,3,6,7,8-hexahydropyrene, $C_{16}H_{16}$, the unsaturated rings lie essentially in a plane, the r.m.s. deviation of the atoms defining this plane from the best-fit plane being 0.006 (2) Å. The saturated rings are substantially non-planar, but the character of the non-planarity of the saturated rings is quite different from that observed in octahydrochrysene. The C—C bond distances in the saturated rings are quite uniform, ranging from 1.505 (2) to 1.520 (2) Å. No intermolecular distance is less than the sum of the corresponding van der Waals radii; closest approaches involve both C···H and H···H interactions.

## Comment

Hydroaromatic hydrocarbons are of interest as potential host crystal materials for magnetic or optical studies of dilutely substituted guest molecules such as aromatic hydrocarbons. This study of *sym*-hexahydropyrene, (I), follows a study of octahydrochrysene (Burd, Dobson & Gerkin, 1996).



(I)

In this $P2_1/c$ structure, the asymmetric unit is half of the *sym*-hexahydropyrene molecule, the other half being generated by an inversion center. These features duplicate those of octahydrochrysene.

The atoms constituting the naphthalenoid core of this molecule (C4–C8 and their inversion partners) are described by a best-fit plane from which their r.m.s. deviation is 0.006 Å, the e.s.d. of the individual deviations being 0.001 Å. The corresponding value for the naphthalenoid core of octahydrochrysene is 0.013 (2) Å. Atoms C1, C3, $C1^i$ and $C3^i$ [symmetry code: (i) $1-x$, $1-y$, $1-z$] lie close to this plane (Fig. 1). Indeed, the r.m.s. deviation of all the non-H atoms, except for the 'terminal' C2 and $C2^i$ atoms, from the best-fit plane describing them is only 0.018 Å, the e.s.d. of the individual deviations being 0.001 Å. The deviations of atoms C2 and $C2^i$ from this plane are of magnitude 0.665 Å. The saturated rings are thus substantially non-planar, as expected, but due to only one of the three outer C atoms; in octahydrochrysene, the non-planarity involves all (four) outer C atoms. In contrast, in pyrene itself, the r.m.s. deviation for the entire set of C atoms from the best-fit plane through them is variously 0.007 Å [as calculated from the neutron diffraction data of Hazell, Larsen & Lehmann (1972)], 0.008 Å [as calculated from the X-ray data of Allmann (1970)] or 0.010 Å [as calculated from the 113 K X-ray data of Kai, Hama, Yasuoka & Kasai (1978)]. The dihedral angle between the sets of non-