Acta Cryst. (1997). C**53**, 769–771

1,8-Bis(hydroxymethyl)anthracene

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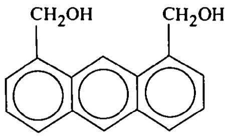
(Received 10 October 1996; accepted 22 January 1997)

Abstract

Anthracene-1,8-dimethanol, $C_{16}H_{14}O_2$, crystallized in the centrosymmetric space group $P2_1/n$. The anthracene core is nearly planar and shows good agreement with the anthracene core of anthracene-1,8-dicarboxylic acid. The geometric disposition of the hydroxymethyl groups and the values of the hydrogen-bond parameters are strikingly similar to those in the naphthalene analog. As in that structure, each hydroxyl group participates both as a donor and acceptor in an infinite zigzag chain of hydrogen bonds which propagates along the [010] direction. Moreover, the disposition of the entire molecule in the cell of the present compound is also strikingly similar to that of the naphthalene analog in its cell.

Comment

1,8-Bis(hydroxymethyl)anthracene (BHMA) was of interest as a potential hydrogen-bonding species, particularly since hydrogen bonding in the naphthalene analog, 1,8-bis(hydroxymethyl)naphthalene (BHMN), has been described previously (Bennett, Fitzgerald & Gerkin, 1993). Furthermore, the structures of naphthalene-1,8-dicarboxylic acid and anthracene-1,8-dicarboxylic acid, which have also been reported (Fitzgerald, Gallucci & Gerkin, 1991; Fitzgerald & Gerkin, 1996), are dissimilar in their hydrogen-bonding patterns for no apparently compelling reason, making the comparison of hydrogen bonding in the 1,8-bis(hydroxymethyl) analogs of special interest.



BHMA

A view of BHMA, which gives the atom labeling and shows the geometric disposition of the hydroxymethyl groups with respect to the anthracene core, is presented in Fig. 1. A packing diagram of the structure showing the hydrogen bonds is given in Fig. 2. Each hydroxyl group in BHMA is involved in substantial hydrogen bonds, once as a donor and once as an acceptor. Parameters for the two inequivalent hydrogen bonds are given in Table 2. As can be inferred from Fig. 2, each BHMA molecule participates in two infinite zigzag chains of hydrogen bonds which propagate along the [010] direction.

The C atoms of the two hydroxymethyl groups in BHMA lie on opposite sides of the anthracene core

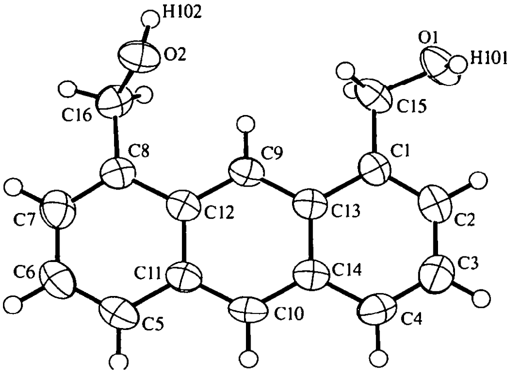


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the 1,8-bis(hydroxymethyl)anthracene molecule showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small.

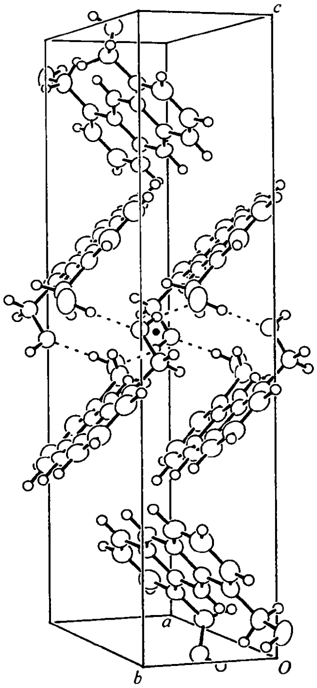


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of 1,8-bis(hydroxymethyl)anthracene. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small. Hydrogen bonds are depicted with dashed lines. The center of symmetry is depicted by a filled circle.

plane at distances of −0.075 (3) and 0.086 (3) Å. This placement is very similar to that observed in BHMN, for which the corresponding values are −0.068 and 0.104 Å. Furthermore, the entire dispositions of the hydroxymethyl groups and the values of the hydrogen-bond parameters are strikingly similar to those found in BHMN (Fig. 1 and Table 2 of Bennett, Fitzgerald & Gerkin, 1993).

Indeed, the disposition of the entire BHMA molecule in its cell is also strikingly similar to that of BHMN in its cell as is demonstrated by the similarity of the angles between the cell edges and the long and short in-plane molecular axes for the two structures. (In each molecule, the long in-plane axis is taken in the C1—C8 direction, while the short in-plane axis is taken in the C9—C10 direction.) For the long in-plane axis, the angles with the *a*, *b* and *c* axes are, respectively, ~10, ~73 and ~81° for BHMA, and ~15, ~86 and ~80° for BHMN; for the short in-plane axis, the angles with the *a*, *b* and *c* axes are, respectively, ~85, ~47 and ~43° for BHMA, and ~89, ~46 and ~44° for BHMN. Since, so far as packing is concerned, the principal difference in the molecular geometries is in the length of the long in-plane axes and since these lie nearly along cell edge **a**, the similarities cited above are consistent with the fact that only the **a** cell edges differ appreciably; for BHMA, the cell edges are 11.049 (1), 4.7982 (9) and 22.682 (1) Å, while for BHMN, they are 8.549 (4), 4.856 (3) and 22.604 (4) Å. Moreover, the difference in the **a** cell edges (~2.5 Å) is very nearly equal to the width of the additional benzenoid ring (~2.4 Å), which is consistent with very similar end-to-end molecular packing in the two cases.

The anthracene core of BHMA exhibits moderate conformity to mirror symmetry with respect to a mirror through the C9 and C10 atoms; for the eight pairs of distances which would be identical under this symmetry, the r.m.s. deviation within pairs is 0.006 Å, while the e.s.d. of individual distances is 0.004–0.005 Å. For the pseudo-mirror at right angles to this, the r.m.s. deviation within the analogous six pairs of distances is 0.011 Å. The average difference between corresponding distances in the cores of the 1,8-diacid and BHMA is 0.007 Å, while the individual e.s.d.'s are 0.007–0.009 and 0.004–0.005 Å, respectively.

All distances and angles in the molecular core fall within normal ranges. The refined C—H distances in the hydroxymethyl groups range from 0.97 (3) to 1.05 (3) Å, with a mean value of 1.01 Å; the refined O—H distances appear in Table 2.

The molecular core of BHMA is almost planar. The maximum distance of a core atom from the best-fit core plane is 0.030 (4) Å; the average distance is 0.012 Å, which may be compared with a value of 0.018 Å for the 1,8-diacid. The dihedral angle between the two orientations of the best-fit anthracene core planes in BHMA (the modified herring-bone motif angle) is 86.43 (7)°; the corresponding value for BHMN is 88.64 (6)°.

Excepting pairs of atoms involved in hydrogen bonds, the closest intermolecular approaches are between atoms O2 and $H7^{iii}$ [symmetry code: (iii) $2-x$, $-y$, $1-z$]. These closest approaches are 0.16 Å less than the corresponding sum of the Bondi (1964) radii.

Akiyama, Misumi & Nakagawa (1962*b*) reported that their crystallization of BHMA from ethanol produced light-yellow cubes. It appears likely, however, that their phase and the one reported here are identical (though the crystal morphologies are different), since a small macroscopic object with angles 90, 90.108 and 90°, consistent with the present unit cell, would be indistinguishable by eye from one with angles 90, 90 and 90°.

Experimental

1,8-Bis(hydroxymethyl)anthracene was synthesized and purified starting from 1,8-dichloroanthraquinone following the procedures of Vance (1993) which were adapted from those of Akiyama, Misumi & Nakagawa (1960, 1962*a*,*b*) and Akiyama & Nakagawa (1971). Crystals were obtained from a slowly cooled hot ethanol solution of BHMA. Recrystallization a second time from ethanol produced flat columns, one of which was cut to provide the experimental sample.

Crystal data

$C_{16}H_{14}O_2$
$M_r = 238.29$
Monoclinic
$P2_1/n$
$a = 11.049 (1)$ Å
$b = 4.7982 (9)$ Å
$c = 22.682 (1)$ Å
$\beta = 90.108 (6)°$
$V = 1202.5 (3)$ Å^3
$Z = 4$
$D_x = 1.316$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.1–17.5°$
$\mu = 0.080$ mm^{-1}
$T = 296$ K
Cut prismatic column
0.46 × 0.27 × 0.19 mm
Gold

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
3271 measured reflections
3116 independent reflections
1368 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.018$

$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 6$
$l = -29 \rightarrow 29$
6 standard reflections every 150 reflections intensity variation: ±1.4% (average maximum relative intensity)

Refinement

Refinement on F
$R = 0.060$
$wR = 0.060$
$S = 1.67$

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $2 (3) \times 10^{-7}$

1368 reflections
188 parameters
H atoms: see below
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{\max} = <0.01$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Scattering factors from Stewart, Davidson & Simpson (1965) (H atoms) and Cromer & Waber (1974) (C and O atoms)

Table 1. *Selected geometric parameters (Å, °)*

C1—C15	1.505 (4)	C8—C16	1.498 (4)
O1—C15	1.425 (4)	O2—C16	1.438 (4)
C2—C1—C15	121.8 (3)	C7—C8—C16	119.4 (3)
C13—C1—C15	119.5 (3)	C12—C8—C16	120.9 (3)
O1—C15—C1	113.3 (3)	O2—C16—C8	110.3 (3)
C15—O1—H1O1	106 (2)	C16—O2—H1O2	106 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O1···O2^{i}	0.92 (5)	1.80 (5)	2.710 (3)	168 (4)
O2—H1O2···O1^{ii}	0.88 (4)	1.85 (4)	2.715 (3)	168 (3)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.

The scan widths used were $(1.50 + 0.35\tan\theta)^\circ$ in ω, with a background to scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry-indicated space group $P2_1/n$ (No. 14) and since refinement proceeded well it was adopted. Fourier difference methods were used to locate the H-atom positions. In later stages of refinement, the ring H atoms H2–H7, H9 and H10 were made canonical, with a C—H distance of 0.98 Å and $U_{\rm iso}$ values $1.2U_{\rm eq}$ of the associated C atom. All the H atoms of the two hydroxymethyl groups were refined isotropically. The maximum effect of extinction was 1.2% of F_o for 014. The maximum positive residual peak was located near the midpoint of the C9—C12 bond and the maximum negative peak was located near the center of the C1–C4/C13–C14 ring. A second crystal was oriented on the diffractometer to demonstrate that the *b* axis is oriented along the long column axis of these crystals. It is noted that the proportion of observed reflections is rather low (~44%), the reason for this not being known.

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*.

The authors 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 atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1309). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Akiyama, S., Misumi, S. & Nakagawa, M. (1960). *Bull. Chem. Soc. Jpn*, **33**, 1293–1298.

Akiyama, S., Misumi, S. & Nakagawa, M. (1962*a*). *Bull. Chem. Soc. Jpn*, **35**, 1826–1829.

Akiyama, S., Misumi, S. & Nakagawa, M. (1962*b*). *Bull. Chem. Soc. Jpn*, **35**, 1829–1836.

Akiyama, S. & Nakagawa, M. (1971). *Bull. Chem. Soc. Jpn*, **44**, 3158–3160.

Bennett, G. D., Fitzgerald, L. J. & Gerkin, R. E. (1993). *Acta Cryst.* C**49**, 64–68.

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.)

Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1991). *Acta Cryst.* B**47**, 776–782.

Fitzgerald, L. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**, 1838–1841.

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

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

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

Sheldrick, G. M. (1985). *SHELX*86. In *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.

Vance, D. H. (1993). PhD dissertation, The Ohio State University, Columbus, Ohio, USA.

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

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

Acta Cryst. (1997). C**53**, 771–773

4-Hydroxy-6-methoxy-9-phenylsulfonylcarbazol-3-yl Methyl Ketone

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(*Received 10 July 1996; accepted 17 December 1996*)

Abstract

The asymmetric unit of the crystals of the title compound, $C_{21}H_{17}NO_5S$, contains two crystallographically independent molecules, each consisting of a carbazole