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Acenaphtho[1,2-*a*]acenaphthylene at 178 K

BY PETER G. JONES AND PETER BUBENITSCHKEK

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany

GEORGE M. SHELDRIK

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, W-3400 Göttingen, Germany

AND GERALD DYKER

Institut für Organische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany

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Abstract. C₂₂H₁₂, $M_r = 276.3$, monoclinic, $P2_1/c$, $a = 10.946$ (4), $b = 5.817$ (2), $c = 10.551$ (4) Å, $\beta = 94.15$ (3)°, $V = 670.0$ Å³, $Z = 2$, $D_x = 1.370$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.08$ mm⁻¹, $F(000) = 288$, $T = 178$ K, $R = 0.049$ for 711 reflections. The molecule possesses crystallographic inversion symmetry and is planar to within 0.004 Å. The molecular strain is apparent, for example, in C—C—C bond angles as high as 141°. The quantitative agreement of bond lengths with those calculated by Dasgupta & Dasgupta [*J. Mol. Struct.* (1975), **27**, 113–116] is only moderate; in particular, the central C—C bond at 1.390 (5) Å is 0.02 Å longer than predicted.

Introduction. Acenaphtho[1,2-*a*]acenaphthylene is an interesting target for calculations (Bose, 1966; Dasgupta & Dasgupta, 1975) and synthetic studies (Mitchell, Fyles & Ralph, 1977) because of its ring strain and its spectroscopic properties. The semi-benzenoid hydrocarbon is rationally and efficiently prepared from 1,8-diiodonaphthalene and acenaphthylene by a new palladium-catalyzed annelation reaction (Dyker, 1991). We have determined the crystal structure in order to characterize the molecular geometry of the hexacyclic $(4n + 2)\pi$ system and to compare the experimental parameters with calculated values (*op. cit.*).

Experimental. Single crystals in the form of red prisms and plates were obtained from chloroform. Intensity data were collected from two crystals, (1) $0.38 \times 0.24 \times 0.22$ mm, (2) $0.42 \times 0.40 \times 0.18$ mm, mounted on glass fibres with inert oil and transferred

to the cold gas stream of a Siemens R3 diffractometer with LT-2 low-temperature attachment. Intensities were measured to $2\theta_{\text{max}} = 50^\circ$ using monochromated Mo $K\alpha$ radiation. Of 1398 reflections (1), 2356 reflections (2), 1184 were unique ($R_{\text{int}} = 0.038$ after application of a refined scale factor, index ranges $h - 12$ to 13, $k 0$ to 6, $l 0$ to 12) and 711 $> 3\sigma(F)$ were considered observed. The cell constants were refined from setting angles of 50 reflections in the 2θ range 20–23°. Three check reflections showed no significant intensity variation. No absorption correction was applied.

The structure was solved by direct methods; the solution with the second best combined figure-of-merit proved to be correct, the apparently best solution consisting of 'chicken wire'. Full-matrix anisotropic least-squares refinement on F was then performed. H atoms were included using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00025F^2$; final $R = 0.049$, with $wR = 0.048$; 100 parameters; $S = 1.5$; maximum $\Delta/\sigma = 0.001$, maximum, minimum $\Delta\rho = 0.16, -0.17$ e Å⁻³. The program system used was *SHELXTL-Plus* (Sheldrick, 1989), which contained the atomic scattering factors and f' , f'' values. Final atom coordinates are given in Table 1, with derived bond lengths and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55118 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0107]

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^4$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	3632 (2)	3350 (5)	5250 (2)	301 (9)
C(2)	2926 (2)	1665 (5)	5736 (2)	347 (10)
C(3)	1660 (3)	1627 (5)	5364 (3)	367 (10)
C(4)	1111 (3)	3194 (5)	4540 (3)	362 (10)
C(4a)	1818 (2)	4968 (5)	4018 (2)	323 (9)
C(5)	1396 (3)	6727 (5)	3168 (2)	360 (10)
C(6)	2201 (3)	8305 (5)	2747 (2)	363 (10)
C(7)	3467 (3)	8285 (5)	3149 (3)	345 (9)
C(8)	3899 (2)	6614 (5)	3979 (2)	292 (9)
C(8a)	3058 (2)	4964 (5)	4394 (2)	311 (9)
C(9)	5079 (3)	5965 (4)	4627 (2)	330 (9)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

C(1)—C(2)	1.370 (4)	C(1)—C(8a)	1.418 (4)
C(1)—C(9 ⁱ)	1.463 (4)	C(2)—C(3)	1.413 (4)
C(3)—C(4)	1.368 (4)	C(4)—C(4a)	1.424 (4)
C(4a)—C(5)	1.416 (4)	C(4a)—C(8a)	1.386 (4)
C(5)—C(6)	1.368 (4)	C(6)—C(7)	1.419 (4)
C(7)—C(8)	1.370 (4)	C(8)—C(8a)	1.421 (4)
C(8)—C(9)	1.466 (4)	C(9)—C(9 ⁱ)	1.390 (5)
C(2)—C(1)—C(8a)	118.4 (2)	C(2)—C(1)—C(9 ⁱ)	136.7 (2)
C(8a)—C(1)—C(9 ⁱ)	104.9 (2)	C(1)—C(2)—C(3)	118.4 (3)
C(2)—C(3)—C(4)	122.9 (3)	C(3)—C(4)—C(4a)	120.1 (3)
C(4)—C(4a)—C(5)	127.4 (2)	C(4)—C(4a)—C(8a)	115.9 (2)
C(5)—C(4a)—C(8a)	116.7 (3)	C(4a)—C(5)—C(6)	120.1 (2)
C(5)—C(6)—C(7)	122.4 (3)	C(6)—C(7)—C(8)	118.8 (3)
C(7)—C(8)—C(8a)	118.3 (2)	C(7)—C(8)—C(9)	137.1 (3)
C(8a)—C(8)—C(9)	104.6 (2)	C(1)—C(8a)—C(4a)	124.3 (3)
C(1)—C(8a)—C(8)	112.1 (2)	C(4a)—C(8a)—C(8)	123.6 (2)
C(8)—C(9)—C(1 ⁱ)	141.5 (2)	C(8)—C(9)—C(9 ⁱ)	109.3 (3)
C(1 ⁱ)—C(9)—C(9 ⁱ)	109.2 (3)		

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

Discussion. The molecule of the title compound (Fig. 1) is exactly centrosymmetric, a crystallographic inversion centre bisecting the bond C(9)—C(9ⁱ), and is planar (mean deviation of all C atoms from the least-squares plane 0.004 \AA , maximum torsion angle 1.1 $^\circ$). The actual molecular symmetry is, however, close to the ideal $mm2$; the maximum differences between chemically equivalent bond lengths and angles are 0.008 \AA and 0.8 $^\circ$ (corresponding to 2σ , 3–4 σ , respectively). The strain in the system is apparent, e.g., from the bond angles C(8)—C(9)—C(1ⁱ) of 141.5 and C(7)—C(8)—C(9) of 137.1 $^\circ$.

A comparison of the observed bond lengths [e.s.d.'s 0.005 \AA for the central bond C(9)—C(9ⁱ), otherwise 0.004 \AA] with the predicted values (Bose, 1966; Dasgupta & Dasgupta, 1975) reveals some interesting features:

(i) The observed values are mostly shorter than predicted. This could be a result of libration effects; however, these should not be too pronounced at 178 K. Since the overall thermal motion does not correspond to rigid-body libration, in contrast to acenaphthylene itself (Wood, Welberry & Rae, 1985), no libration correction is possible.

(ii) The general prediction of short or long bonds proves reasonably valid except for the internal bonds C(4a)—C(8a), observed at 1.386 \AA , calculated (Dasgupta & Dasgupta, 1975) at 1.410 or 1.406 \AA (two theoretical models), and C(9)—C(9ⁱ), observed at 1.390, calculated at 1.375 or 1.367 \AA . The central double bond is the most reactive site of the molecule (e.g. towards bromination) and the short calculated bond would rationalize this; however, the observed bond is not remarkably short compared to conventional aromatic systems.

(iii) The quantitative agreement is only moderate, the mean absolute deviations (calculated where appropriate from averages of chemically equivalent observed bonds) being 0.012 and 0.016 \AA for the two theoretical models. Apart from the values noted above, large deviations occur for C(1)—C(9ⁱ) and C(8)—C(9), the longest bonds in the molecule at 1.463 and 1.466 \AA (calculated at 1.447 and 1.461 \AA), and for C(1)—C(2) and C(7)—C(8), observed at 1.370 \AA ($\times 2$), calculated at 1.387 and 1.382 \AA .

A comparison of molecular dimensions with those of acenaphthylene is not valid because the extent of

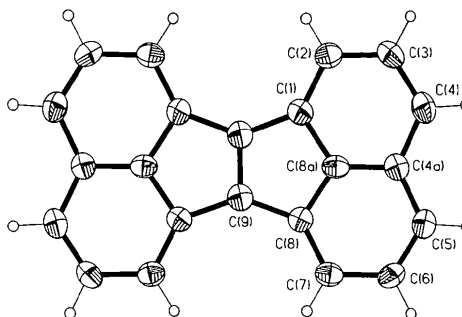


Fig. 1. The molecule of the title compound in the crystal, showing the numbering scheme of the asymmetric unit. Ellipsoids correspond to 50% probability. H-atom radii are arbitrary.

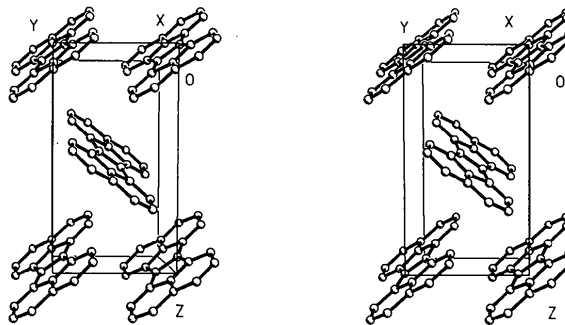


Fig. 2. Stereographic packing diagram of the title compound (H atoms omitted).

disorder was such that the molecular dimensions cannot be very reliable (Wood, Welberry & Rae, 1985).

The molecular packing is shown in Fig. 2. The shortest non-bonded contact between C atoms is C(4)⋯C(4) ($-x, 1-y, 1-z$) at 3.408 (6) Å.

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Structure of Racemic (\pm)-6,8-Dimethyl-6,12-methano-6*H*,12*H*,13*H*-[1]benzopyran[4,3-*d*][1,3]benzodioxocin-13-one

BY EDWARD J. VALENTE AND GERARD RUGGIERO

Department of Chemistry, Mississippi College, Clinton, MS 39058, USA

AND DRAKE S. EGGLESTON

Department of Physical Structural Chemistry, SmithKline Beecham Laboratories, King of Prussia, PA 19406, USA

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Abstract. C₂₀H₁₆O₄, $M_r = 320.35$, monoclinic, $P2_1/n$, $a = 10.482$ (3), $b = 8.084$ (1), $c = 18.081$ (4) Å, $\beta = 92.59$ (2)°, $V = 1530.5$ (5) Å³, $Z = 4$, $D_x = 1.390$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70930$ Å, $\mu = 0.902$ cm⁻¹, $F(000) = 672$, $T = 225$ K, final $R = 0.051$ on 1776 observations. The title molecule, a derivative of warfarin formed by spontaneous dehydration of 2'-hydroxy-3'-methylwarfarin, is a cyclic ketal in which the side-chain phenyl is disposed pseudo-axially and is linked through a 2'-O atom to the ketal C atom in a fixed *cis* 1,3-diaxial configuration. Two dihydropyran rings are formed. One is fused with the benzopyran ring and adopts an *e,f*-diplanar shape; the other is a chroman and adopts a similar conformation.

Introduction. As part of a continuing study of the structures of dihydropyran derivatives containing various 2-oxygen substituents, the compound described here is one of a series of crystalline warfarin derivatives. Warfarins generally crystallize as hemiketals: 4-substituted 2-hydroxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one; the parent in the series has a 4-phenyl substituent. A number of 2-hydroxy and 2-methoxy-4-aryl and

4-alkyl analogs have been made and studied crystallographically, revealing an operative anomeric effect in the uniform axial disposition of the 2-oxygen substituents, local influences on C—O bond lengths, and conformational preferences associated with the exoanomeric effect (Valente, Eggleston & Schomaker, 1986; Ruggiero, Thaggard, Valente & Eggleston, 1990). This contribution describes the structure of a 2-aryloxy warfarin ketal.

Experimental. Michael-type addition of 4-hydroxycoumarin to α,β -unsaturated ketones leads to 3-substituted 4-hydroxycoumarins of the warfarin group (Ikawa, Stahmann & Link, 1944). Synthesis of 2'-hydroxy-3'-methylwarfarin (I), through 4-(2'-hydroxy-3'-methylphenyl)but-3-en-2-one with 4-hydroxycoumarin, leads instead to a higher melting compound not soluble in dilute alkali. This substance is the racemic cyclic 2-aryloxy ketal (II) formed through spontaneous intramolecular dehydration (Porter & Trager, 1977). The homo-chiral dehydrated product is obtained by resolution (West, Preis, Schroeder & Link, 1961) of the addition product of 4-(2'-methoxy-3'-methylphenyl)-3-buten-2-one with 4-hydroxycoumarin followed by treat-