H(173) in compound (1), H(71), H(72) and H(73) in (2)] were refined with slack constraints [C—H = 1.09 (5) Å]. Data collection: CAD-4F software. Programs used to solve structures: SHELXS86 (Sheldrick, 1986) and SIR88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). Program used to refine structures: CRYSTALS (Watkin, Carruthers & Betteridge, 1985). Drawings prepared using ORTEPII (Johnson, 1976).

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Structure of an Overcrowded Molecule, Benzylideneanthrone, at 193 K

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Abstract

The central six-membered ring of the anthrone in 10-benzylidene-9(10H)-anthracenone assumes a boat conformation because of close interactions with the benzylidene moiety. Other manifestations of the overcrowding are the 6.1° twist around the double bond, the −49.5° rotation of the phenyl ring, and the increase of the C10a—C10—C11 angle to 124.1°.

Comment

In continuation of the investigation (Roberts, Anderson, Khalaf & Low, 1971; Roberts, Bantel & Low, 1973; Khalaf & Roberts, 1972; Low & Roberts, 1973; Roberts & Abdel-Baset, 1976; Prasad & Roberts, 1991) of Freidel-Crafts intramolecular cyclialkylations, the title compound (I) was prepared in order to study its reaction with acid catalysts. Synthesis was accomplished in a condensation

(I)
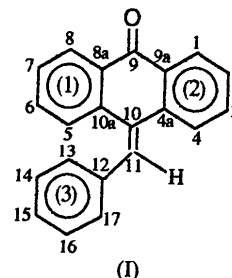
reaction by passing a stream of dry HCl into a stirred mixture of anthrone and benzaldehyde in a Claisen flask heated on a water bath. The product was crystallized from ethanol; the crystals were filtered, washed with a small volume of ethanol and dried. The molecule consists of an anthrone unit linked with a benzylidene moiety. All the rings are planar except the central ring (C4a, C9a, C9, C8a, C10a, C10) which has a boat conformation. The rings (1) (C5, C6, C7, C8, C8a, C10a) and (2) (C1, C2, C3, C4, C4a, C9a) are folded by 14.1 and 9.8° from the plane C4a-C9a-C8a-C10a, respectively. Ring (1) is involved in many short intramolecular contacts with ring (3) (C12, C13, C14, C15, C16, C17) (see below), and is bent downwards to a greater extent than ring (2). The dihedral angle between rings (1) and (2) is 156.2°, which is very similar to the angles found in 10-dicyanomethyleneanthrone (152°) and dianthronylideneethane (159.8 and 162.4°) (Silverman & Yannoni, 1967). Compounds exhibiting more severe overcrowding have smaller dihedral angles: α-bromo-9-(p-methoxybenzylidene)anthrone (139.6°) and α-tosyloxy-9-(p-methoxybenzylidene)anthrone (148.6°) (Kaftory, Apeloig & Rappaport, 1985); and dianthronylidene (131.9°) (Harnik & Schmidt, 1954). The double bond is twisted by 6.1°, as given by the cis-torsion angle, C12—C11—C10—C10a. Phenyl ring (3) is rotated around the C12—C11 bond as evidenced by the C10—C11—C12—C13 torsion angle of −49.5°. Many close interactions are observed as a result of overcrowding with atoms of the anthrone group interacting with the benzylidene group. These distances are: O··· H1 = 2.475; O···H8 = 2.508; C4···H11 = 2.555; C5···C12 = 3.098; C5···C13 = 3.152; C5···H13 = 3.066; C10···H13 = 3.073; C11···H4 = 2.687; C11···H5 = 2.778; C12···H5 = 2.544; C13···C10a = 3.336; C13···H5 = 2.804; C10a···H13 = 3.024; H4···H11 = 2.069; H11···H17 = 2.597 Å. As part of the mechanism to relieve over-

crowding, angles C10—C4a—C4 [122.0 (3)°] and C10—C10a—C5 [122.5 (3)°] have opened somewhat, resulting in narrowing of the angle C10a—C10—C4a to 115.9 (2)°. The angle C10a—C10—C11 *cis* to ring (3) is 124.1 (2)° compared to the *trans* angle, C4a—C10—C11, of 119.8 (2)°, indicating a bending of ring (3) away from ring (1). These interactions are alleviated by folding of the central ring, by a twist around the C=C bond, and rotation of the phenyl ring (3) around the C11—C12 bond.
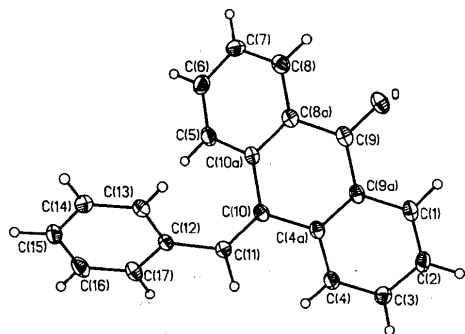

Fig. 1. View of $C_{21}H_{14}O$ showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 30% probability levels; H atoms are drawn as small circles of arbitrary radii.
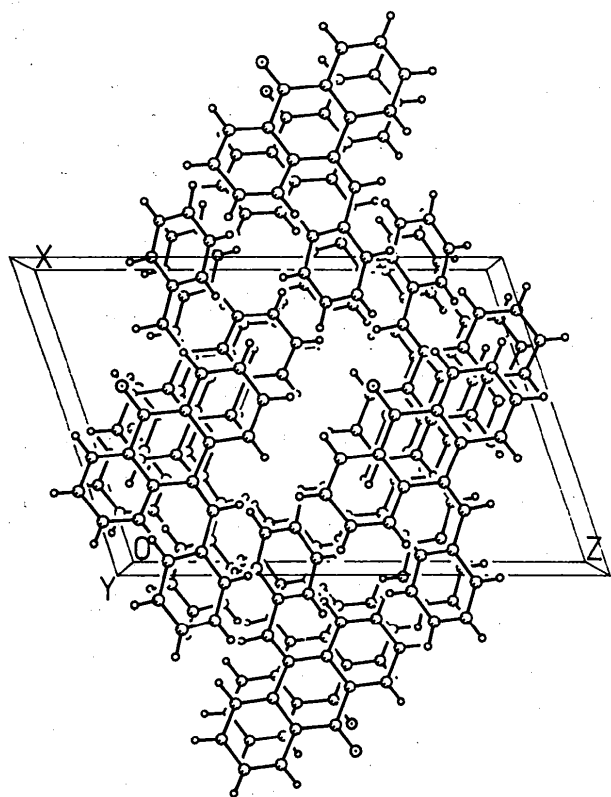

Fig. 2. Packing diagram of $C_{21}H_{14}O$. The view is approximately down the *b* axis.

Experimental

Crystal data

$C_{21}H_{14}O$	$D_x = 1.323$ Mg m^{-3}
$M_r = 282.34$	Mo $K\alpha$ radiation
Monoclinic	$\lambda = 0.71073$ Å
$P2_1/c$	Cell parameters from 32 reflections
$a = 11.953$ (3) Å	$\theta = 7.93–11.92°$
$b = 7.116$ (1) Å	$\mu = 0.74$ mm^{-1}
$c = 17.626$ (4) Å	$T = 193$ K
$\beta = 108.95$ (2)°	Pentagonal plate
$V = 1417.9$ (5) Å^3	$0.31 \times 0.31 \times 0.11$ mm
$Z = 4$	Yellow

Data collection

Nicolet $R3$ diffractometer	$h = -16 \rightarrow 16$
ω-scans	$k = 0 \rightarrow 10$
7079 measured reflections	$l = -23 \rightarrow 23$
3280 independent reflections	4 standard reflections
1866 observed reflections	monitored every 96
$[F > 4.0\sigma(I)]$	reflections
$R_{int} = 0.0216$	intensity variation: 1.56%
$\theta_{max} = 27.5°$	

Refinement

Refinement on F	Extinction correction:
Final $R = 0.0541$	$F^* = F[1 + 0.002\chi F^2$
$wR = 0.0592$	$/\sin(2\theta)]^{-1/4}$
$S = 1.18$	Extinction coefficient:
256 parameters	0.0010 (4)
All H-atom parameters refined	Atomic scattering factors from *International Tables*
$w = 1/[\sigma^2(F) + 0.00089F^2]$	for X-ray Crystallography (1974, Vol. IV, Table 2.2B)
$(\Delta/\sigma)_{max} = 0.0742$	
$\Delta\rho_{max} = 0.33$ e Å^{-3}	
$\Delta\rho_{min} = -0.20$ e Å^{-3}	

Data collection: *SHELXTL-Plus* (Sheldrick, 1991). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PLATON* (Spek, 1990).

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

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

	x	y	z	U_{eq}
O	0.5857 (2)	0.2046 (3)	0.14317 (12)	0.0480 (8)
C1	0.6279 (2)	0.1680 (4)	0.3088 (2)	0.0342 (9)
C2	0.6445 (3)	0.1534 (4)	0.3893 (2)	0.0379 (10)
C3	0.5476 (3)	0.1504 (4)	0.4154 (2)	0.0372 (10)
C4	0.4341 (2)	0.1615 (4)	0.3614 (2)	0.0353 (10)
C4a	0.4150 (2)	0.1769 (3)	0.2790 (2)	0.0282 (8)
C5	0.1752 (2)	0.0710 (4)	0.0833 (2)	0.0379 (10)
C6	0.1665 (3)	0.0221 (5)	0.0062 (2)	0.0438 (11)
C7	0.2615 (3)	0.0426 (5)	-0.0218 (2)	0.0435 (12)
C8	0.3679 (3)	0.1035 (4)	0.0305 (2)	0.0376 (10)
C8a	0.3802 (2)	0.1473 (3)	0.1095 (2)	0.0293 (9)
C9	0.5003 (2)	0.1840 (3)	0.1664 (2)	0.0317 (9)
C9a	0.5137 (2)	0.1774 (3)	0.2529 (2)	0.0293 (8)
C10	0.2944 (2)	0.1954 (3)	0.2197 (2)	0.0281 (8)
C10a	0.2815 (2)	0.1393 (3)	0.1365 (2)	0.0286 (8)
C11	0.2063 (2)	0.2674 (4)	0.2426 (2)	0.0316 (9)

C12	0.0845 (2)	0.3235 (4)	0.1942 (2)	0.0290 (9)
C13	0.0626 (2)	0.4384 (4)	0.1275 (2)	0.0351 (10)
C14	−0.0512 (3)	0.4974 (5)	0.0852 (2)	0.0439 (12)
C15	−0.1447 (3)	0.4378 (5)	0.1085 (2)	0.0456 (11)
C16	−0.1248 (3)	0.3249 (5)	0.1750 (2)	0.0440 (11)
C17	−0.0108 (2)	0.2696 (4)	0.2182 (2)	0.0386 (10)

Structures of Pyrazole Derivatives. II. A Potential Bioisoster of Acetazolamide

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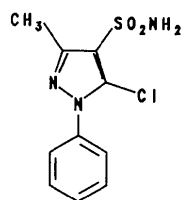
(*Received* 11 *August* 1992; *accepted* 15 *Ocotber* 1992)

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

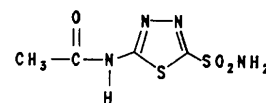|			
O—C9	1.226 (4)	C8a—C9	1.483 (3)
C1—C2	1.372 (4)	C8a—C10a	1.408 (4)
C1—C9a	1.401 (3)	C9—C9a	1.482 (4)
C2—C3	1.379 (5)	C10—C10a	1.479 (4)
C3—C4	1.383 (4)	C10—C11	1.346 (4)
C4—C4a	1.400 (4)	C11—C12	1.483 (3)
C4a—C9a	1.398 (4)	C12—C13	1.385 (4)
C4a—C10	1.486 (3)	C12—C17	1.392 (4)
C5—C6	1.373 (5)	C13—C14	1.387 (4)
C5—C10a	1.400 (3)	C14—C15	1.377 (5)
C6—C7	1.385 (5)	C15—C16	1.376 (5)
C7—C8	1.376 (4)	C16—C17	1.385 (4)
C8—C8a	1.388 (4)		
C2—C1—C9a	120.8 (3)	C1—C9a—C9	118.7 (3)
C1—C2—C3	119.4 (2)	C4a—C9a—C9	121.1 (2)
C2—C3—C4	120.8 (3)	C10a—C10—C11	124.1 (2)
C3—C4—C4a	120.8 (3)	C10a—C10—C4a	115.9 (2)
C4—C4a—C9a	118.0 (2)	C4a—C10—C11	119.8 (2)
C4—C4a—C10	122.0 (3)	C5—C10a—C8a	117.7 (3)
C9a—C4a—C10	119.9 (2)	C5—C10a—C10	122.5 (3)
C6—C5—C10a	120.7 (3)	C8a—C10a—C10	119.7 (2)
C5—C6—C7	121.3 (3)	C12—C11—C10	130.3 (3)
C6—C7—C8	118.8 (3)	C13—C12—C17	118.2 (2)
C7—C8—C8a	121.1 (3)	C13—C12—C11	121.8 (3)
C8—C8a—C9	118.7 (3)	C17—C12—C11	119.8 (2)
C8—C8a—C10a	120.2 (2)	C14—C13—C12	121.1 (3)
C9—C8a—C10a	120.8 (2)	C15—C14—C13	119.7 (3)
C9a—C9—O	121.6 (2)	C16—C15—C14	120.1 (3)
C9a—C9—C8a	116.6 (2)	C17—C16—C15	120.1 (3)
O—C9—C8a	121.6 (3)	C12—C17—C16	120.7 (3)
C1—C9a—C4a	120.2 (3)		

Abstract

In 5-Chloro-3-methyl-1-phenyl-4-pyrazolesulphonamide, the phenyl and pyrazole rings are planar making a dihedral angle of 54.4 (2)°. The molecular packing involves an intermolecular hydrogen bond: $N(3)\cdots N(2^i) = 2.951\,(8)$, $N(2^i)\cdots H'(N3) = 1.987\,(6)$ Å, $N(3)—H'(N3)\cdots N(2^i) = 154.8\,(4)°$ [symmetry operation: (i) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$].

Comments

Among the sulfonamide derivatives commonly used as diuretics, one of the most important is acetazolamide (2) (de Stevens, 1963) which is commercially available in Brazil as DIAMOX (DEF, 1991). Because of the close bioisosteric relationship between the pyrazole and the 1,3,4-thiodiazole groups, and following a research program aimed at synthesizing potentially bioactive functionalized pyrazoles (Caracelli, Zukerman-Schpector, Barreiro & Freitas, 1992), compound (1) was prepared (Freitas, 1991). In order to determine its overall conformation a three-dimensional crystal structure determination was undertaken.

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(1)   (2)

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