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Structure of Dibenzofuran-d_8, $C_{12}D_8O$, at 173 K

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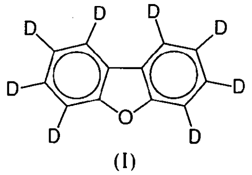
Abstract

Crystalline dibenzofuran-d_8 has been found to exhibit disorder of the type described previously for dibenzofuran. The disordered molecules are related to the ordered molecules by a 180° rotation about an axis passing through the molecular center of mass and perpendicular to the furan ring. In the present structure 11(2)% of the molecules were found to adopt this alternate orientation. The molecules are bisected by a mirror plane normal to the furan ring and containing the O atom. The average bond length in the benzenoid ring is 1.392 (10) Å. The furan ring and the benzenoid ring are separately planar, but form a dihedral angle of 1.45 (9)° with each other.

Comment

The crystal structure of dibenzofuran, $C_{12}H_8O$, as determined by Reppart, Gallucci, Lundstedt & Gerkin (1984), was found to manifest a type of disorder such that 9(2)% of the molecules are related to the ordered molecules by a 180° rotation about an axis passing through the molecular center of mass and perpendicular to the furan ring. The present study of the crystal structure of dibenzofuran-d_8, $C_{12}D_8O$ (I), was undertaken to determine to what extent such disorder might be present in this close analog of dibenzofuran.



(I)

Dibenzofuran-d_8 with a stated isotopic purity of 98.8 at. % was used as received from MSD Isotopes. The experimental sample was obtained by sublimation at low pressure. Analysis of the crystal structure showed that the type of disorder present in dibenzofuran is present also in dibenzofuran-d_8, and to a very similar extent: the refined population of the disordered molecule in the present study is 11(2)%.

Most bond lengths and angles for the ordered and disordered molecules of dibenzofuran-d_8 agree with the values for dibenzofuran within the combined e.s.d.'s; the three bond lengths which do not are found to agree within twice the combined e.s.d.'s. The average bond length for the benzenoid ring of dibenzofuran-d_8 is 1.392 (10) Å. The molecules are bisected by a mirror plane normal to the furan ring and containing O. The furan ring and benzene ring are separately planar, but form a dihedral angle of 1.45 (9)° with each other.

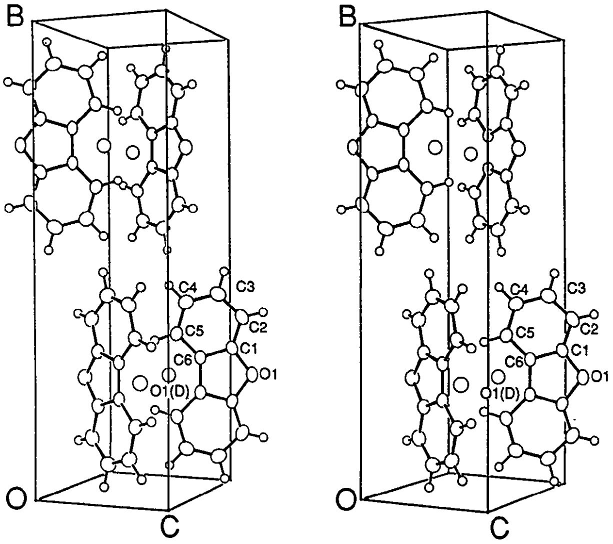


Fig. 1. A stereoview of the unit cell for dibenzofuran-d_8 drawn using *ORTEP*II (Johnson, 1976). One asymmetric unit is labeled using our numbering scheme. The position of the O atom of a disordered molecule is also shown.

Experimental

Crystal data

$C_{12}D_8O$
$M_r = 176.20$
Orthorhombic
Pnma
$a = 7.526$ (2) Å
$b = 19.107$ (2) Å
$c = 5.785$ (2) Å
$V = 831.9$ (4) Å^3
$Z = 4$
$D_x = 1.41$ Mg m^{-3}
Mo $K\overline{\alpha}$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 25 reflections
$\theta = 13.5$–$15.0°$
$\mu = 0.0786$ mm^{-1}
$T = 173$ (2) K
Plate
0.50 × 0.46 × 0.23 mm
Colorless
Crystal source: sublimation [temperature $\simeq$ 348(5) K; pressure $\simeq$ 13.33 Pa]

0108-2701/93/020398-03$06.00

Data collection

Rigaku AFC-5S diffractometer
ω–2θ scans
2539 measured reflections
2539 independent reflections
1122 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 37.5°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 32$
$l = 0 \rightarrow 9$
6 standard reflections monitored every 150 reflections intensity variation: ±2.4%

Refinement

Refinement on F
Final $R = 0.051$
$wR = 0.064$
$S = 2.11$
1122 reflections
105 parameters
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: $2.8(7)\times10^{-6}$
Atomic scattering factors from Cromer & Waber (1974) for C and O; Stewart, Davidson & Simpson (1965) for H

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

Atoms O(1D) and C(1D) to C(6D) were refined isotropically. For atoms O(1) and C(1) to C(6), $B_{\rm eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B/B_{\rm eq}$
O(1)	0.2518 (2)	0.2500	0.2294 (3)	2.69 (7)
C(1)	0.2026 (2)	0.3076 (1)	0.3594 (3)	2.23 (5)
C(2)	0.2331 (2)	0.3759 (1)	0.2960 (3)	2.76 (7)
C(3)	0.1766 (2)	0.4271 (1)	0.4522 (3)	2.96 (7)
C(4)	0.0939 (2)	0.4093 (1)	0.6604 (3)	2.83 (7)
C(5)	0.0661 (2)	0.3399 (1)	0.7204 (3)	2.39 (6)
C(6)	0.1224 (2)	0.2877 (1)	0.5669 (2)	1.98 (5)
O(1D)	0.040 (4)	0.250	0.770 (5)	2.7 (5)
C(1D)	0.091 (3)	0.308 (1)	0.645 (5)	2.2 (4)
C(2D)	0.071 (5)	0.377 (3)	0.701 (6)	3.2 (5)
C(3D)	0.123 (5)	0.423 (2)	0.563 (9)	3.2 (5)
C(4D)	0.209 (4)	0.408 (2)	0.356 (8)	3.4 (5)
C(5D)	0.232 (4)	0.334 (2)	0.294 (6)	2.9 (5)
C(6D)	0.171 (3)	0.289 (1)	0.429 (5)	1.9 (4)

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

O(1)—C(1)	1.384 (2)	O(1D)—C(1D)	1.38 (3)
C(1)—C(2)	1.375 (2)	C(1D)—C(2D)	1.37 (6)
C(2)—C(3)	1.397 (3)	C(2D)—C(3D)	1.26 (8)
C(3)—C(4)	1.397 (3)	C(3D)—C(4D)	1.39 (7)
C(4)—C(5)	1.386 (3)	C(4D)—C(5D)	1.47 (6)
C(5)—C(6)	1.400 (2)	C(5D)—C(6D)	1.25 (6)
C(6)—C(1)	1.397 (2)	C(6D)—C(1D)	1.43 (4)
C(6)—C(6$^{\rm i}$)	1.441 (3)	C(6D)—C(6$D^{\rm i}$)	1.49 (5)
C(1)—O(1)—C(1$^{\rm i}$)	105.5 (2)	C(1D)—O(1D)—C(1$D^{\rm i}$)	107 (3)
O(1)—C(1)—C(2)	124.5 (2)	O(1D)—C(1D)—C(2D)	128 (3)
O(1)—C(1)—C(6)	111.4 (1)	O(1D)—C(1D)—C(6D)	112 (3)
C(2)—C(1)—C(6)	124.0 (2)	C(2D)—C(1D)—C(6D)	120 (3)
C(1)—C(2)—C(3)	116.1 (2)	C(1D)—C(2D)—C(3D)	120 (3)
C(2)—C(3)—C(4)	121.5 (2)	C(2D)—C(3D)—C(4D)	123 (4)
C(3)—C(4)—C(5)	121.0 (2)	C(3D)—C(4D)—C(5D)	118 (3)
C(4)—C(5)—C(6)	118.4 (2)	C(4D)—C(5D)—C(6D)	118 (3)
C(1)—C(6)—C(5)	118.8 (2)	C(1D)—C(6D)—C(5D)	122 (2)
C(1)—C(6)—C(6$^{\rm i}$)	105.8 (1)	C(1D)—C(6D)—C(6$D^{\rm i}$)	105 (3)
C(5)—C(6)—C(6$^{\rm i}$)	135.4 (1)	C(5D)—C(6D)—C(6$D^{\rm i}$)	133 (3)

Symmetry code: (none) x, y, z; (i) $x, -y+0.5, z$.

The experimental sample was mounted on a quartz pin and cooled to 173 K on a Rigaku AFC-5S diffractometer utilizing a Molecular Structure Corporation low-temperature apparatus. The stated temperature was measured continuously during data collection in the cold gas flow just upstream of the crystal; the estimated uncertainty of the crystal temperature is ±2 K. Unit-cell parameters were obtained from a symmetry-constrained least-squares fit of 25 centered reflections. Systematic absences ($0kl$, $k + l$ = odd; $hk0$, h = odd) were consistent with two space groups: *Pnma* and *Pna*2$_1$. Since intensity statistics indicated a centrosymmetric space group, *Pnma* (No. 62) was given initial preference; refinement proceeded well and it was adopted. Scan widths were $(1.4 + 0.35\tan\theta)°$ in ω. No corrections were made for decay or absorption; the data were corrected for Lorentz and polarization effects. Extinction was treated (Zachariasen, 1967) and the extinction coefficient refined in the least-squares process. The largest effect of extinction was 7.1% of 210. The direct methods program *MITHRIL* (Gilmore, 1984) in the *TEXSAN* structure analysis package (Molecular Structure Corporation, 1989) produced an E map from which the initial positions of the ordered non-D atoms were identified. D atoms of the ordered molecule and C and O atoms of the disordered molecule were subsequently identified using difference Fourier methods. The C and O atoms of the ordered molecule were refined anisotropically; the D atoms of the ordered molecule and the C and O atoms of the disordered molecule were refined isotropically. D atoms of the disordered molecule were assigned positions consistent with canonical benzene geometry (C—D distance = 0.95 Å; $B = 1.2 \times B_{\rm eq}$ of the attached disordered C atom). Weighting scheme $w = \sigma_F^{-2}$, where $\sigma_F = \sigma_I/2F\text{Lp}$ and $\sigma_I^2 = \sigma_{\rm cs}^2(I) + (0.03I)^2$. In order to separate the electron density of the disordered molecule from the bonding electron density of the ordered molecule, a high-angle refinement was performed on the 649 reflections satisfying the conditions $2\theta \geq 45°$ and $I > 3\sigma(I)$ using *SHELX*76 (Sheldrick, 1976). The resultant positional and displacement parameters of the disordered molecule, as well as the occupancy factors for all the atoms, were then held constant in a refinement of the ordered molecule using all of the data.

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Lists of structure factors, anisotropic displacement parameters, D-atom coordinates and isotropic displacement parameters, and data pertaining to least-squares best-fit planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55508 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1020]

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Structure of 1,2,2,3,3,4,4,5-Octamethyl-6,7,8-trioxabicyclo[3.2.1]octane

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Abstract

Crystals of the unusually stable secondary symmetric ozonide of the title compound (m.p. 374–376 K) contain two crystallographically independent but very similar molecules. The five-membered trioxolane rings have envelope conformations and the pyran rings have chair conformations in both molecules, with ether O-atom apices. The seven-membered dioxepine rings have boat conformations with the peroxide O atoms and the opposite C atom out of the plane of the other ring atoms.

Comment

The structure determination of the title compound was undertaken in order to establish the mechanism of the 1,3-dipolar cycloadditions. Details of the synthetic work will be published elsewhere (Mayr, 1991). Fig. 1 illustrates one of the two crystallographically independent molecules *A* and *B*, with the non-H atoms of the two molecules fitted, and the atomic numbering system. Final atomic parameters are given in Table 1 and selected interatomic distances and bond angles in Table 2. The two molecules have the same geometry (within the limits of 3 e.s.d.). An important structural aspect of this study is the conformation of the ozonide rings; for their description, the method of Cremer & Pople (1975) was employed, in which the geometry of the puckered plane is represented in terms of amplitudes and phase coordinates. A list of puckering parameters has been deposited (see footnote). The trioxolane rings have envelope conformations with ether O atom O3 above the plane of C9, C13, O1 and O2. The pyran rings have chair conformations deformed towards envelope conformations with ether O atom O3 under the plane of C9, C10, C12 and C13. The conformation of the dioxepine ring may be described as a boat with peroxide O atoms O1 and O2, and the opposite C atom C11 above the plane of C9, C10, C12 and C13. As a consequence of the conformation, short intramolecular C4—H43···O1 and C4—H43···O2 contacts are observed (Table 2). Similar close contacts between C—H groups and O atoms have also been found in other organic compounds (Ilczyszyn, Lis, Baran & Ratajczak, 1992, and references therein). The C3 and C6 methyl groups are in axial positions. As a result, the C11—C12 and C10—C11 bonds are longer than the standard Csp^3—Csp^3 bond distance. The observed O—O and C—O bond lengths are in reasonable agreement with the values reported for the ozonides (Miura *et al.*, 1983; Miljković *et al.*, 1984; Karban *et al.*, 1978; Mullica *et al.*, 1979; Oliver *et al.*, 1979). The crystal packing scheme is shown in Fig. 2. The whole structure is held together by van der Waals interactions.

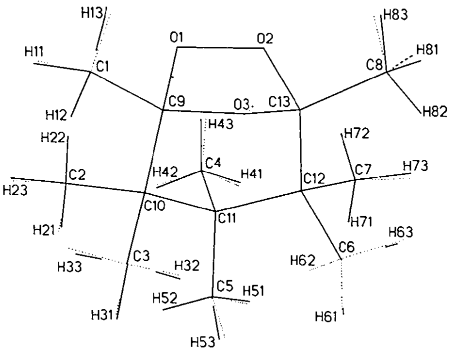

Fig. 1. A view of one of the two crystallographically independent molecules *A* and *B*, with the non-H atoms of the two molecules fitted.

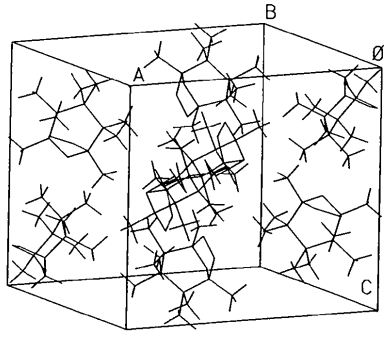

Fig. 2. Molecular packing in the crystal of 1,2,2,3,3,4,4,5-octamethyl-6,7,8-trioxabicyclo[3.2.1]octane.

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