Structure of Dibenzo[b,b']furo[3,2-e;4,5-e']bis(benzofuran)*

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Abstract. $C_{24}H_{12}O_3$, monoclinic, $P2_1/c$, $a = 3.912$ (1), $b = 20.406$ (3), $c = 20.271$ (2) Å, $\beta = 101.4$ (3)°, $Z = 4$, $V = 1588.3$ Å³, $D_x = 1.46$ Mg m⁻³, μ(Cu $K\alpha$) = 80 mm⁻¹. The final R value is 0.055 for 1648 data for which $I_{net} \geq 4\sigma(I_{net})$. The intramolecular overcrowding caused by electronic interactions between overlapping aromatic rings is responsible for a helicoidal configuration. The interplanar angle between terminal rings is 37°.

Introduction. This X-ray analysis has been undertaken as a part of a program concerning crystal structure studies of condensation products of quinones, which has included the structure of the dimer 2,8-dimethoxydibenzofuran, and the trimer, 2,11-dimethoxybenzo-[1,2-b;3,4-b']bis(benzofuran) (Berg, Karlsson, Pilotti & Söderholm, 1978, 1980). We describe here the structure of the open tetramer, dibenzo[b,b']furo[3,2-e;4,5-e']bis(benzofuran).

Cell dimensions and reflexion intensities were measured from a crystal with approximate dimensions 0.10 × 0.16 × 0.19 mm on a Philips PW 1100 computer-controlled diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The lattice constants were obtained from a least-squares fit of the θ values for 25 accurately centered reflexions. The θ–2θ scan technique was employed to measure 3576 reflexions out to $\theta = 70°$. Of these, 1648 unique reflexions fulfilled the condition $\sigma(I_{net})/I_{net} \leq 0.25$ and were selected for the subsequent refinements. Lorentz and polarization factors were applied, but no correction for absorption was made. 23 non-hydrogen atoms were positioned from an E map using phases assigned by *MULTAN* (Germain, Main & Woolfson, 1971). The remaining atoms, including H, were obtained from repeated Fourier maps. The structure was refined by standard full-matrix least-squares methods to an R value of 0.055. The H atoms were assigned the final isotropic thermal parameters of the atoms to which they are attached, and only their positional parameters were included in the refinements. Scattering factors for C and O were taken from *International Tables for*

X-ray Crystallography (1962), and those for H from Stewart, Davidson & Simpson (1965). Hughes's (1941) weighting scheme was used with an $F_{o,min} = 4.0$. The final positional parameters together with their e.s.d.'s are listed in Table 1.†

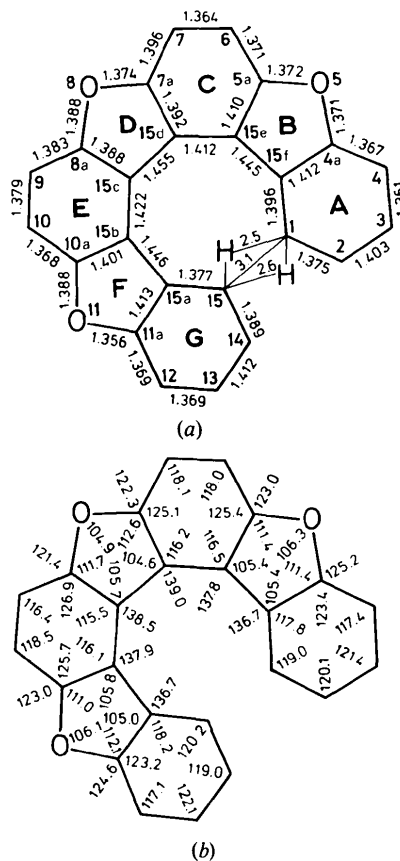Fig. 1. (*a*) Bond distances (Å) and numbering scheme. (*b*) Bond angles (°).

Table 1. *Positional parameters for the atoms with e.s.d.'s in parentheses*

Values are ×10⁴ for the non-hydrogen atoms and ×10³ for the hydrogens.

	x	y	z
C(1)	−291 (10)	1820 (2)	6438 (2)
C(2)	−125 (13)	1504 (2)	7042 (2)
C(3)	1135 (14)	860 (2)	7134 (2)
C(4)	2132 (13)	520 (2)	6624 (2)
C(4a)	2023 (10)	842 (1)	6029 (2)
O(5)	2802 (7)	568 (1)	5458 (1)
C(5a)	2131 (10)	1041 (1)	4969 (2)
C(6)	2177 (11)	920 (2)	4305 (2)
C(7)	1045 (11)	1402 (2)	3850 (2)
C(7a)	62 (9)	2000 (1)	4091 (1)
O(8)	−1338 (7)	2499 (1)	3669 (1)
C(8a)	−1856 (10)	3008 (1)	4093 (1)
C(9)	−3351 (12)	3593 (2)	3843 (2)
C(10)	−3560 (12)	4077 (2)	4308 (2)
C(10a)	−2187 (11)	3956 (1)	4969 (2)
O(11)	−1865 (8)	4434 (1)	5464 (1)
C(11a)	29 (11)	4160 (1)	6027 (2)
C(12)	1095 (16)	4484 (2)	6622 (2)
C(13)	3145 (15)	4144 (2)	7132 (2)
C(14)	4213 (13)	3493 (2)	7049 (2)
C(15)	3136 (10)	3186 (2)	6433 (2)
C(15a)	944 (9)	3504 (1)	5921 (1)
C(15b)	−633 (9)	3367 (1)	5229 (1)
C(15c)	−746 (8)	2842 (1)	4764 (1)
C(15d)	271 (8)	2156 (1)	4766 (1)
C(15e)	1093 (8)	1634 (1)	5227 (1)
C(15f)	896 (8)	1497 (1)	5918 (1)
H(C1)	855 (9)	274 (1)	132 (1)
H(C2)	−66 (11)	329 (2)	240 (2)
H(C3)	160 (11)	429 (2)	261 (2)
H(C4)	684 (9)	−5 (2)	324 (1)
H(C6)	299 (10)	48 (2)	418 (1)
H(C7)	80 (10)	136 (1)	335 (2)
H(C9)	574 (10)	364 (1)	336 (2)
H(C10)	552 (11)	445 (2)	416 (2)
H(C12)	−3 (10)	6 (2)	158 (2)
H(C13)	389 (11)	66 (2)	257 (2)
H(C14)	589 (11)	175 (2)	239 (2)
H(C15)	393 (10)	224 (1)	141 (1)

Discussion. Fig. 1 shows the bond lengths and angles involving the non-hydrogen atoms. Standard deviations are of the order 0·005–0·008 Å for the bond lengths and 0·3–0·6° for the angles.

To allow sufficient clearance between the non-bonded carbon atoms C(1) and C(15), with their attached H atoms, either there must be a very severe distortion of the angles and bond lengths in the aromatic rings, or else the molecule must assume a non-planar shape. The separation of 3·1 Å between C(1) and C(15) is achieved by a helical configuration. The H(C1)···H(C15) distance is 2·11 Å. Fig. 1(a) indicates the shortest C···H intramolecular distances in the inner core of the molecule. They are of the order of 2·5 Å – considerably shorter than expected for van der Waals contacts, in spite of the adopted helical configuration. The average C–H length is 0·98 Å.

The distortion from planarity in the molecule leads one to expect a decrease in double-bond character and, thus, longer bonds. An examination of individual bond lengths reveals that the six bonds bordering the inner core of the helix are all longer than the average. This is the region most subjected to distortion.

Calculations of least-squares planes for the individual rings (Fig. 2) show that they deviate from planarity. The deviations for the terminal rings are not, however, as significant as for the inner ones. Isotropic e.s.d.'s are of the order of 0·003–0·006 Å for the atoms. The interplanar angle between the terminal rings A and G is 37·3°. Torsion angles for the perimeter of the molecule are also included in Fig. 2.

The molecule has point symmetry 2. The twofold axis is not, however, a crystallographic axis. Fig. 3 shows the molecule viewed along this axis. If the bonds in corresponding positions on the left and right branches of the molecule are compared, the r.m.s. average difference between such pairs of bonds is 0·010 Å, with a maximum discrepancy of 0·016 Å between the O(5)–C(5a) and C(10a)–O(11) bonds. The r.m.s. average difference between corresponding angles is 0·8°; the largest discrepancy of 1·8° is that between the C(7)–C(7a)–C(15d) and C(9)–C(8a)–C(15c) angles.
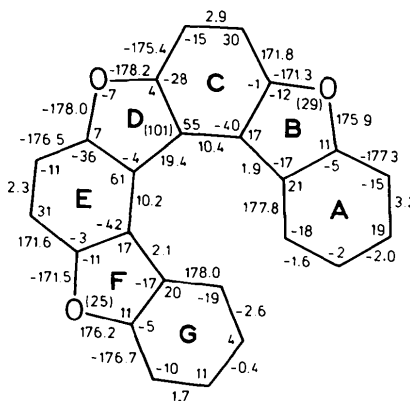

Fig. 2. Deviations from least-squares planes (Å, ×10³) for the individual rings are given as inner ring values. (Values within parentheses are not included in the least-squares calculations.) The outer ring values represent torsion angles (°) for the perimeter of the molecule.

Fig. 3. An *ORTEP* (Johnson, 1965) stereoscopic view of the molecule along the twofold axis. The O atoms are shown as shaded ellipsoids.

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