

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C1	1.328 (2)	N1—C3	1.351 (2)
O2—C1	1.196 (2)	N1—C10	1.462 (2)
O3—C3	1.236 (2)	C1—C2	1.523 (3)
O4—C15	1.378 (2)	C2—C21	1.533 (3)
N1—C2	1.448 (2)	C3—C4	1.471 (3)
C2—N1—C3	121.71 (16)	N1—C2—C21	113.20 (16)
C2—N1—C10	124.49 (16)	C1—C2—C21	109.97 (17)
C3—N1—C10	112.88 (16)	O3—C3—N1	124.18 (19)
O1—C1—O2	124.3 (2)	O3—C3—C4	128.72 (19)
O1—C1—C2	110.17 (18)	N1—C3—C4	107.07 (18)
O2—C1—C2	125.55 (19)	O4—C15—C14	117.2 (2)
N1—C2—C1	110.12 (16)	O4—C15—C16	122.2 (2)
C3—N1—C2—C1	-86.6 (2)	C2—N1—C3—O3	-5.7 (3)
O2—C1—C2—N1	-19.9 (3)	C1—C2—C21—C11	170.0 (2)
O2—C1—C2—C21	105.5 (2)	C2—C21—C11—C16	122.7 (2)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O4 ⁱ	0.82	1.88	2.668 (2)	160
O4—H4...O3 ⁱⁱ	0.82	1.86	2.653 (2)	164
C6—H6...Cg1 ⁱⁱⁱ	0.93	2.64	3.542 (3)	165
C10—H10A...O2 ^{iv}	0.97	2.43	3.225 (3)	139
C21—H21A...Cg2 ^{iv}	0.97	2.86	3.553 (3)	129

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x, 1 + y, z$; (iii) $2 - x, 1 - y, 2 - z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

Molecule (I) as synthesized is a DL racemic mixture and crystallized in the monoclinic system with space group $P2_1/n$ determined from the systematic absences. H atoms were allowed for as riding atoms with C—H in the range 0.93 to 0.98 \AA and O—H 0.82 \AA . Fig. 3, a view of the $\text{C}_{\text{arene}}\text{—H}\cdots\pi_{\text{arene}}$ hydrogen bonding interactions, has been deposited as a supplementary diagram.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *NRCVAX96* and *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *NRCVAX96*, *ORTEPIII* (Burnett & Johnson, 1996), *ORTEX* (McArdle, 1995) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PREP8* (Ferguson, 1998).

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Decabromodiphenyl ether

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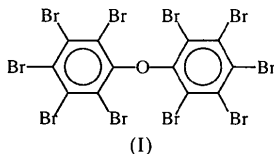
Abstract

Bis(pentabromophenyl) ether, $\text{C}_{12}\text{Br}_{10}\text{O}$, shows strange differences in the endocyclic angles between the two different rings, although they are both substituted in the same manner. Several short van der Waals contact

distances give clues to the anomalous endocyclic angles and some hints to the formation of decomposition products. We suggest that the intermolecular Br···Br contacts contribute to the distortions of the ring systems. Usually distortions of this kind would be explained from highly anisotropic TLS behaviour, but the data from the title compound do not show any conclusive TLS effects.

Comment

One of the most important groups of flame retardants are the brominated diphenyl ethers. There are 209 possible congeners, but most of the commercially available mixtures consist of highly brominated congeners such as decabromodiphenyl ether (Örm *et al.*, 1996). Brominated diphenyl ethers are additive flame retardants, which means that they are only mixed together with the material and therefore migrate more easily to the environment than if they had been covalently bonded with the polymer material (Kuryla & Papa, 1979). One interesting circumstance with this kind of chemical is that they are not often found in the environment to the same extent as they are used. One possible reason is that they are decomposed by sunlight, radicals or biotically (Örm *et al.*, 1996). Knowledge of the three-dimensional structure is necessary in order to understand the decomposition phenomena and to find reaction pathways for the photochemical degradation. We describe here the structure of decabromodiphenyl ether, (I).



The packing of the molecules shows unusually short intermolecular Br···Br contact distances [Br10···Br7(1+x, -1+y, z) = 3.480(1) Å and Br5···Br9(-x, 1-y, 1-z) = 3.543(1) Å] compared with hexabromobenzene (Baharie & Pawley, 1979), a fact which we believe contributes to the rapid decomposition of decabromodiphenyl ether in the environment. Packing effects are plausible explanations for the distorted shape of the molecule around the central O atom. The Br···O distances are Br1···O = 2.933(4), Br5···O = 3.105(3), Br6···O = 2.901(4) and Br10···O = 3.205(4) Å. This distortion is connected to the unusually acute angles (O—C7—C8 and C1—C6—O). The angle between the two ring planes is 78.7(2)°. Three Br atoms deviate significantly [Br5 0.125(8), Br3 -0.113(8) and Br10 0.210(7) Å] from the least-square planes defined by the corresponding C atoms of each benzene ring. The r.m.s. deviations of the fitted C atoms are 0.01(1) Å for each ring. The analyses of the endocyclic C—C—C bond angles show that two angles in the same ring (C1—C6) are much smaller than the rest of the C—C—C endo-

cyclic angles and all angles in the other ring (C7—C12) are close to 120°, even though both rings are substituted in the same manner. This behaviour makes it meaningless to discuss the endocyclic angles in relation to the substitution pattern (Domenicano & Murray-Rust, 1979). We suggest that the short intermolecular Br···Br contact distances contribute to the ring distortions. A comparison with data from the Cambridge Structural Database (Allen & Kennard, 1993) gives, unfortunately, no conclusive answer to the reason for the distortions in the rings. The average Br—C distance in the title compound is 1.893(10) Å and the average Br—C distances of three similar compounds in the Cambridge Structural Database (Allen & Kennard, 1993) are: 1.914(7) (BAJ-VOX; Capon *et al.*, 1981), 1.867(14) (TEDDIP; Il'in *et al.*, 1996) and 1.892(11) Å (TOQBAC; Örm *et al.*, 1996).

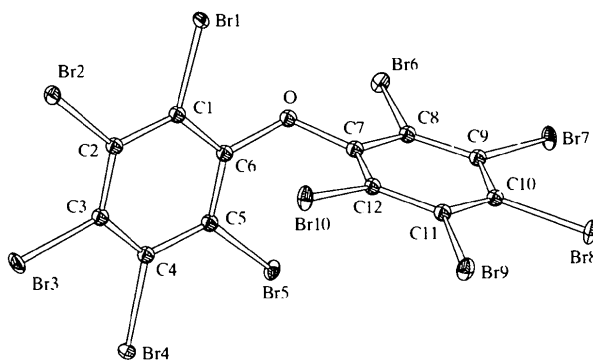


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

Experimental

The title compound was recrystallized from toluene at ambient temperature.

Crystal data

C₁₂Br₁₀O
M_r = 959.22
 Triclinic
P $\bar{1}$
a = 8.338(1) Å
b = 8.973(1) Å
c = 14.393(2) Å
 α = 80.337(14)°
 β = 84.339(14)°
 γ = 63.179(13)°
V = 947.0(2) Å³
Z = 2
D_x = 3.364 Mg m⁻³
D_m not measured

Mo *K* α radiation
 λ = 0.7107 Å
 Cell parameters from 126 reflections
 θ = 2.5–28.0°
 μ = 21.154 mm⁻¹
T = 100(2) K
 Prism
 0.17 × 0.10 × 0.07 mm
 Colourless

Data collection

Stoe IPDS diffractometer
 Area-detector scans

3347 reflections with
I > 2 σ (*I*)

Absorption correction:
numerical (XRED; Stoe
& Cie, 1997a)
 $T_{\min} = 0.031$, $T_{\max} = 0.233$
9080 measured reflections
4196 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.044$
 $S = 1.844$
4196 reflections
144 parameters
 $w = 1/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.273 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.865 \text{ e } \text{\AA}^{-3}$

$R_{\text{int}} = 0.048$
 $\theta_{\max} = 28.06^\circ$
 $h = -11 \rightarrow 10$
 $k = -11 \rightarrow 11$
 $l = -18 \rightarrow 18$

Extinction correction:
SHELXL93 (Sheldrick,
1993)
Extinction coefficient:
0.00139 (11)
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Br1—C1	1.894 (5)	C1—C6	1.374 (7)
Br2—C2	1.871 (5)	C1—C2	1.407 (7)
Br3—C3	1.908 (5)	C2—C3	1.408 (7)
Br4—C4	1.902 (5)	C3—C4	1.380 (7)
Br5—C5	1.885 (6)	C4—C5	1.404 (7)
Br6—C8	1.899 (6)	C5—C6	1.394 (6)
Br7—C9	1.891 (5)	C7—C12	1.374 (8)
Br8—C10	1.895 (5)	C7—C8	1.405 (7)
Br9—C11	1.886 (6)	C8—C9	1.390 (7)
Br10—C12	1.898 (5)	C9—C10	1.404 (8)
O—C7	1.389 (6)	C10—C11	1.390 (7)
O—C6	1.406 (5)	C11—C12	1.408 (8)
C1—C6—C5	122.0 (4)	C12—C7—O	125.8 (5)
C1—C6—O	116.1 (4)	C12—C7—C8	119.8 (5)
C5—C6—O	121.9 (5)	O—C7—C8	114.1 (5)
C7—O—C6—C1	125.2 (5)	C6—O—C7—C12	-39.0 (6)
C7—O—C6—C5	-56.0 (7)	C6—O—C7—C8	146.4 (4)

All Br atoms were refined with anisotropic displacement parameters. The large positive and negative differences are located near the Br atoms. Refining the C atoms with anisotropic displacement parameters yielded some of them as slightly non-positive definite, but with no significant improvement in the residual factors. Since the thermal vibrations were rather small due to the low-temperature experiment, it was decided to use isotropic C atoms in the structure model in order to avoid non-physical displacement parameters.

Data collection: EXPOSE (Stoe & Cie, 1997b). Cell refinement: CELL (Stoe & Cie, 1997c). Data reduction: INTEGRATE (Stoe & Cie, 1997d). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: DIAMOND (Bergerhoff, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1314). Services for accessing these data are described at the back of the journal.

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L-Alanyl-L-phenylalanine-2-propanol (1/2) (α -form), L-valyl-L-phenylalanine-2-propanol (1/1) and L-leucyl-L-phenylalanine-2-propanol (1/1) (β -form)

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Abstract

Small crystals of L-Ala-L-Phe-2-propanol (1/2), $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_3 \cdot 2\text{C}_3\text{H}_8\text{O}$, L-Val-L-Phe-2-propanol (1/1), $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_3 \cdot \text{C}_3\text{H}_8\text{O}$, and L-Leu-L-Phe-2-propanol (1/1), $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_3 \cdot \text{C}_3\text{H}_8\text{O}$, were obtained after considerable effort. The three structures have intricate packing interactions with up to four peptide molecules in the asymmetric unit and variable hydrogen-bond connectivities for the carboxylate groups. For each peptide, two or more different crystal forms were obtained in the crystallization experiments.

Comment

For dipeptides with two hydrophobic residues our previous (Görbitz, 1997, and references therein) and ongoing work has identified two different modes of