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Di-*p*-bromophenyl ether, a redetermined crystal structure derived from low-quality diffraction data

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We show that the lack of good quality data, normally essential to successful crystal structure analysis, can in part be compensated for by measuring data from several crystals and merging the resulting data sets. The crystal structure of the flame retardant di-*p*-bromophenyl ether, $C_{12}H_8Br_2O$, a twofold axially symmetric molecule, has been redetermined and refined from such a merged multi-crystal diffraction data set to an acceptable conventional R factor (R_1 = 0.06), a result which could not have been obtained from any one of our single-crystal diffraction data sets used alone in the normal manner.

1. Introduction

The compound bis(*p*-bromophenyl) ether, $C_{12}H_8Br_2O$ (I), belongs to a class of compounds known as flame-retardants. It was the subject of an earlier study (Toussaint, 1946), but the need for a better structural model initiated this reinvestigation. There are no coordinates available in the CSD (Allen, 2002) for the earlier study by Toussaint (1946). The different substitution patterns of various brominated diphenyl ethers (Örn *et al.*, 1996; Eriksson *et al.*, 1999; Mrse *et al.*, 2000; Eriksson & Hu, 2001, 2002*a*,*b*,*c*; Eriksson *et al.*, 2002*a*,*b*) result in quite different morphologies and mechanical properties in the corresponding crystals. Some of these ethers and similar flame-retardant compounds give very well formed prismatic single crystals, while others provide only notoriously ill-behaved crystal shapes, *e.g.* very thin plates, as is the case for (I) where the crystals are such that their plate dimension can barely be measured with an optical microscope. However, they do diffract to some degree but produce only rather broad diffraction 'spots'. The widths of the diffraction peaks can be as large as 3–5° in some directions and sometimes even wider.

This effect is illustrated in Fig. 1, which shows typical *hk*0, *h*0*l* and 0*kl* diffraction patterns obtained from one of our sample crystals of (I). The broadening of the diffraction spots in the *hk*0 and *h*0*l* zones is a strong indication that the thicker crystals are composed of a number of stacked plates, imperfectly aligned to each other. Diffraction patterns such as those shown in Fig. 1 are usually termed 'low quality' and would normally prompt a search for better crystals in the hope of obtaining both sharper diffraction spots and more significant scattering at high diffraction angles. In our case better crystals of (I) could not be obtained and we were unable to collect individual data sets of adequate quality. Thus, we resorted to using data from six different crystals and averaging the data sets by merging them. In this way it was hoped that the deleterious effects of aberrant intensities in any one data set would be minimized.

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2. Experimental

Compound (I) was synthesized by coupling the bromodiphenyl iodonium salt with bromophenylate (Beringer *et al.*, 1959; Ziegler & Marr, 1962; Hu, 1996, 1999) and thereafter recrystallized from methanol.

While the plate-like crystals could be handled and examined quite easily under the microscope, some of them were so thin that we could only estimate their thickness as being less than 1 µm. Many crystals were found, both very thin as well as some thicker, of seemingly good optical quality, showing good extinction in polarized light *etc.* The thicker crystals tended to show easy cleavage parallel to the surface of the plate. Several crystals were examined with a Stoe Image-Plate Diffraction System (IPDS: Stoe, 1997). The very thin crystals did not show more than a few faint spots that could be interpreted as diffraction maxima. The thicker crystals, however, diffracted with a clear indication of stacking faults, as mentioned above in connection with Fig. 1.

More than 20 different crystals were mounted and their diffraction patterns measured on the Stoe IPDS system (Stoe, 1997). Six of these data sets were selected for further analysis. The unit-cell parameters from least-squares fits to the peak positions from each of these data sets are given in supplementary Table S1[1] and vary considerably throughout the series in the ranges 26.14 (6)–26.98 (5), 7.577 (2)–7.759 (6) and 5.669 (5)–5.807 (15) Å for cell edges *a*, *b* and *c*, respectively. As a consequence, the cell used in the solution and refinement of the structure (Table 1) was obtained by least-squares fit (PUDER; Eriksson, 2000) to indexed *d* spacings (supplementary Table S2) from a powder diffraction pattern of (I) calibrated with Si (NIST SRM640a) as internal standard. The powder diffraction measurements were performed in transmission mode from a flat plate sample with a Stoe Stadi/P powder diffractometer system equipped with a focusing Ge monochromator set to diffract Cu $K\alpha_1$ radiation ($\lambda \simeq 1.5405981$ Å) and a linear position-sensitive detector covering approximately 5° in 2θ. The positions of the Si peaks were determined and used to calculate a correction curve for the 2θ scale, which was applied to the peak positions determined for sample (I). The unit-cell parameters from this powder diffraction experiment were considered to be less affected by features present in the individual single-crystal diffraction patterns and thus used as the most reliable set of unit-cell parameters. Reflection conditions indicated the space groups *Ccc*2 (number 37) or *Cccm* (number 66). The space group *Ccc*2 was favoured because the assumption of a non-H atom volume of 20 Å^3 provides $Z = 4$. This choice of space group gave a structure model without disorder and fitted the diffraction data better than the alternative *Cccm* and was also the choice in the previous structural study (Toussaint, 1946) based on photographic film data. Data sets from six different crystals were combined to provide 18 000 reflections in total, with 1166 unique and 495 with $I \geq 2\sigma(I)$. The individual data sets were corrected for absorption using *X-RED* (Stoe, 1997) before aggregation and merging. The structure was solved initially by direct methods using *SHELXS*97 (Sheldrick, 1990). The model, which included all atoms, was used first of all to compute batch scale factors for the different data sets using *SHELXL*97 (Sheldrick, 1997) by refining the structural model against unmerged reflection data using BASF and a different batch number for each data set. Having determined the different scale factors, they were applied to the individual data sets using the local program *REFLEX* (Eriksson, 2004).[2] A more detailed description of the procedure can be found in the supplementary data under *Appendix* 2. The combined individual scaled data sets were thereafter merged using

Table 1
Experimental table.

Crystal data	
Chemical formula	$C_{12}H_8Br_2O$
M_r	328.00
Cell setting, space group	Orthorhombic, *Ccc*2
a, b, c (Å)	26.645 (6), 7.6902 (14), 5.7223 (8)
V (Å^3)	1172.5 (4)
Z	4
D_x (Mg m^{-3})	1.858
Radiation type	Cu $K\alpha$
No. of reflections for cell parameters	19
θ range (°)	3.1–16.4
μ (mm^{-1})	6.88
Temperature (K)	293 (2)
Crystal form, colour	Plate, colourless
Crystal size (mm)	0.25 × 0.20 × 0.10
Data collection	
Diffractometer	Stoe IPDS
Radiation type	Mo $K\alpha$
Data collection method	Area-detector φ scans
Absorption correction	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.15
$T_{\max}$	0.45
No. of measured, independent and observed reflections	18 000, 1166, 495
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.397
$\theta_{\max}$ (°)	26.4
Range of h, k, l	$-32 \Rightarrow h \Rightarrow 32$ $-9 \Rightarrow k \Rightarrow 9$ $-7 \Rightarrow l \Rightarrow 7$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.148, 1.00
No. of reflections	1166
No. of parameters	70
H-atom treatment	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.020P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.34, −0.55
Absolute structure	(Flack, 1983)
Flack parameter	0.00 (5)

Computer programs used: *Expose*, *Cell*, *Integrate* (Stoe, 1997), *SHELXS*97 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997), *ORTEP*3 (Farrugia, 1997).

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM5012). Services for accessing these data are described at the back of the journal.

[2] The computer program *REFLEX* used to scale the individual data sets in this article is available as a WIN/NT executable upon request, from the corresponding author.

Table 2
Selected geometrical parameters (Å, °) for (I).

C1—O	1.415 (15)	C3—C4	1.379 (12)
C1—C2	1.395 (12)	C4—C5	1.357 (13)
C1—C6	1.380 (12)	C5—C6	1.403 (12)
C2—C3	1.392 (12)	C4—Br	1.892 (11)
C6—C1—C2	119.9 (10)	C5—C4—Br	118.3 (11)
C6—C1—O	126.7 (11)	C3—C4—Br	119.5 (9)
C2—C1—O	113.2 (11)	C4—C5—C6	119.4 (15)
C3—C2—C1	118.9 (12)	C1—C6—C5	120.2 (11)
C4—C3—C2	119.4 (10)	C1—O—C1^{i}	115.2 (18)
C5—C4—C3	122.2 (12)		
C6—C1—O—C1^{i}	−34.6 (10)	C2—C1—O—C1^{i}	150.4 (11)

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, z$.

*SHELXL*97 to produce a better structural model than could be obtained from any one of the individual data sets. Refinement of the structure from individual data sets mostly converged to almost the original structure, but with very unrealistic C—C distances in the benzene ring (*e.g.* 0.9–1.7 Å). Although it was possible to solve and refine the structure with heavy restraints on the ring geometry from the individual data sets, the averaged data set produced much more realistic bond distances using only the less rigorous restraint that the C—C bonds in the aromatic ring should be equal to within 0.02 Å. This restraint had only a small effect in that bond distances were altered by less than 0.02 Å between the restrained and unrestrained models when refining the structural model from the averaged data set. The use of the restraint is justified as being appropriate in the case of refinement based on limited intensity data of dubious quality. The final structural model was defined in terms of 70 parameters in total. All non-H atoms were refined with anisotropic displacement parameters. The H atoms were placed in calculated positions with C—H 0.93 Å and refined using a riding model with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Further details summarizing the data collection and structure refinement are given in Table 1. Notable in this table is the high $R_{\rm int}$ value of almost 0.40 associated with the merging of the aggregated scaled data sets. It is suggested that this is because the aberrations in the individual data sets are already large and accumulate additively when the data sets are aggregated. The final merging of the aggregated and scaled intensity data produced F^2 (see the deposited structure factors), with higher relative uncertainties than the same reflections in the input files and the files where the reflections are not merged. Thus, the final merging of the intensity data can be seen to reduce the influence of particularly aberrant reflections on the refinement process. Evidence for this is the successful outcome of the refinement and the well defined molecule shown in the electron density map (supplementary Fig. S1) computed from the merged final data using *PLATON* (Spek, 2003).

3. Results and discussion

Fig. 2 represents a molecule of (I), which has a twofold crystallographic axis passing through the O atom. Selected bond lengths and angles, which are entirely as expected for a molecule of this kind, are given in Table 2. The aromatic ring is planar to within 0.01 Å, with the Br atom not deviating from the ring plane and the O atom only displaced by 0.15 (2) Å


hk0

h0l

0kl

Figure 1
Reconstructed view of the three principal zones of reciprocal space for a crystal of (I).

from the ring plane. Similar displacements of the O atom are commonly found in related structures (Örn *et al.*, 1996; Eriksson *et al.*, 1999; Mrse *et al.*, 2000; Eriksson *et al.*, 2001; Eriksson & Hu, 2001, 2002*a*,*b*,*c*; Eriksson *et al.*, 2002*a*,*b*). The angle between the least-square planes of the two rings in the molecule is 57.8 (3)°.

The molecules are found in layers (Fig. 3) parallel to (100) and centred on $x = 1/4$ and 3/4. Only the Br atoms on the surfaces of the layers interact at the interfaces between them at $x = 0$ and 1/2, which is entirely compatible with the ready cleavage of the crystals along the (100) plane. The well ordered layers of molecules and the weakness of the interactions between them is conducive to slippage of the layers relative to one another, resulting in a slight misalignment between the layers and providing an explanation for the streaky *hk*0 and *h*0*l* but sharp 0*kl* reflections noted earlier.

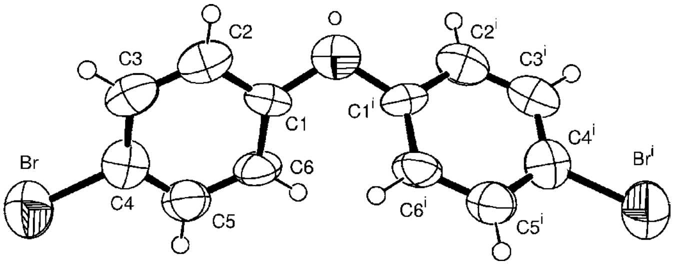

Figure 2
The molecule of (I) showing the labelling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms as spheres of arbitrary radius. Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, z$. Figure drawn using *ORTEP*3 for Windows (Farrugia, 1997)

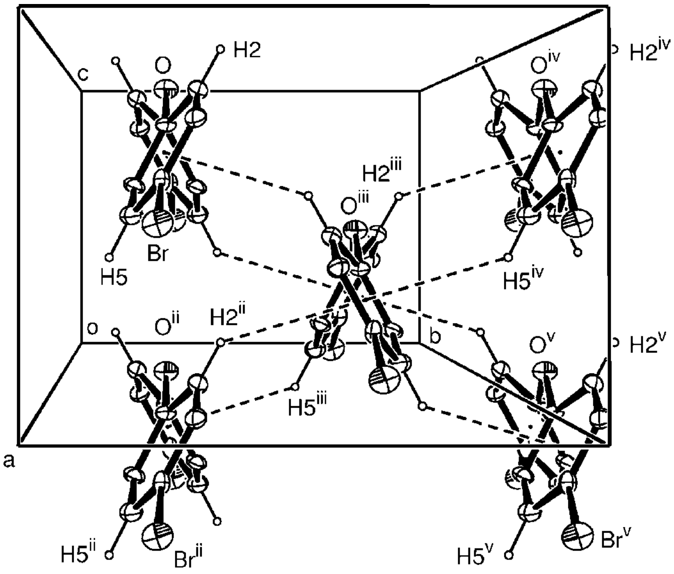

Figure 3
Intermolecular C—H$\cdots\pi$ contacts (dashed lines) within a layer of molecules of (I). Non-H atoms are shown as 10% probability displacement ellipsoids and those H atoms involved in such contacts as small circles of arbitrary radius. Only selected atoms are labelled. The geometric parameters of these contacts are given in supplementary Table S3. Symmetry codes: (ii) $x, y, z-1$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (iv) $x, 1+y, z$; (v) $x, 1+y, z-1$. Figure drawn by *ORTEP*3 for Windows (Farrugia, 1997).

The conformation of the molecule observed in this crystal structure agrees with energy minima in a conformational map calculated with the AM1-Hamiltonian using *MOPAC*6 (Stewart, 1990), while varying the two torsion angles describing the molecular conformation (supplementary Fig. S2). Low-energy valleys along one of the diagonals of the map are indicative of significant flexibility in the molecule. The lowest barrier between neighbouring lowest-energy valleys is of the order 8.4 kJ mol^{-1}. While semi-empirical calculations are known to be prone to large errors when reporting absolute energies, the relative error between energies of different conformations should be quite small. Details of the calculation of the contour map, which was drawn with *Easyplot* (Karon, 1999), are given in *Appendix* 1 of the supplementary information.

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