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Bis(4-aminophenoxy)methane

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Key indicators

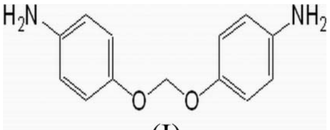
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.050
wR factor = 0.129
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the asymmetric unit of the title compound, $C_{13}H_{14}N_2O_2$, there are one complete molecule and two half-molecules; in each of the latter a twofold rotation axis passes through the central C atom. In the crystal structure, a three-dimensional network is formed though intermolecular N—H···N and N—H···O hydrogen bonds.

Comment

Ether-containing aromatic diamines are useful monomers for preparing soluble polyimides (Yang *et al.*, 2002). Polyimides are a very interesting group of incredibly strong and astoundingly heat- and chemical-resistant polymers (Butt *et al.*, 2005). However, in many cases, they are insoluble and do not react below their decomposition temperature, which restricts their application as engineering materials (Im & Jung, 2000). Many efforts have been made to improve their processability while maintaining their excellent thermal and mechanical properties (Chol *et al.*, 2001). Incorporation of a flexible segment such as –O– was found to be successful in altering crystallinity and intermolecular interactions and to increase solubility (Eastmond *et al.*, 1996). To extend the scope of the application of polyimides, it is desirable that they contain the appropriate ether-containing functional groups (Maya *et al.*, 2005). Different structural modifications of the polymer backbone have been studied to reduce the chain interaction (Yan *et al.*, 2005); for example, the introduction of a flexible link such as –O– or –CH_2– into the main chain disrupts the conjugation and increases the chain flexibility. This hinders the chain packing but does not affect the glass transition temperature (Martin & Timothy, 2003).



(I)

A view of the molecular structure of (I) is shown in Fig. 1. The asymmetric unit contains one complete molecule and two half-molecules, the complete molecules being generated by twofold symmetry. Bond lengths and angles in (I) are normal (Cambridge Structural Database, Version 5.27, updated January 2006; *MOGUL* Version 1.1; Allen, 2002). Although the torsion angles about the O—CH_2 bonds are essentially the same in all three molecules (Table 1), the torsion angles about the C_{ar}—O bonds differ for each molecule. For the molecule in a general position, the torsion angles are 37.5 (5)° for C1—O1—C11—C12 and −15.6 (5)° for C1—O2—C21—C26. In each of the two other molecules, because of symmetry, there is only one unique related torsion angle. The torsion angles are

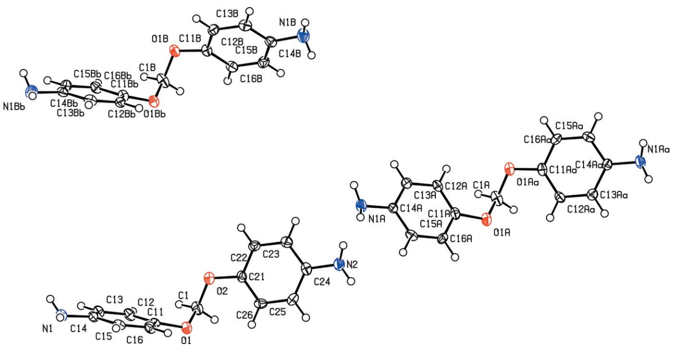


Figure 1
The molecular structure of (I), showing symmetry-complete molecules. Displacement ellipsoids are drawn at the 50% probability level. Atoms labelled with the lower case suffixes 'a' and 'b' are related by the symmetry operations ($-x, y, \frac{3}{2} - z$) and ($1 - x, y, \frac{3}{2} - z$), respectively.

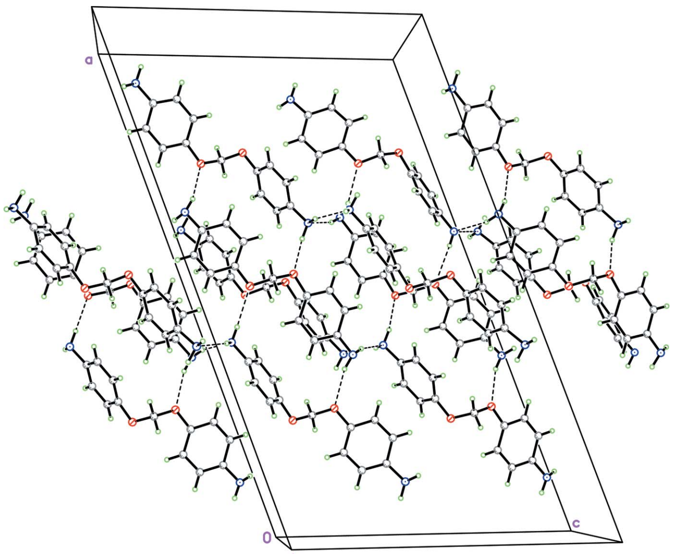


Figure 2
The crystal packing, viewed approximately along [010], with hydrogen bonds indicated by dashed lines.

−13.4 (5)° for C1*A*—O1*A*—C11*A*—C12*A* and 39.9 (5)° for C1*B*—O1*B*—C11*B*—C16*B*. Hence, it appears that the conformation of each benzene ring, with respect to the central –O—C—O– unit, in the molecule in a general position is a combination of those found in the molecules which lie on symmetry sites. In the crystal structure, a three-dimensional network is formed *via* N—H···N and N—H···O hydrogen bonds (Table 2 and Fig. 2).

Experimental

Bis(4-nitrophenoxy)methane was prepared by Williamson's reaction of 4-nitrophenol and dichloromethane. A mixture of 4-nitrophenol (13.9 g, 0.10 mol), dichloromethane (3.2 ml, 0.05 mol) and potassium carbonate (16.6 g, 0.12 mol) in DMF (100 ml) was heated with stirring at 428 K for 20 h. After the solvent had been removed, water was added to the reaction mixture, which was then extracted with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed. The product was purified by recrystallization from methanol to afford bis(4-nitrophenoxy)methane. Bis(4-aminophenoxy)methane was prepared by catalytic hydrogenation of bis(4-nitrophenoxy)methane. A two-necked 250 ml round-bottomed flask was charged with bis(4-nitrophenoxy)methane (2.0 g, 6.9 mmol), hydrazine monohydrate (20 ml), ethanol (100 ml) and 5% palladium (0.12 g) on charcoal (Pd–C). The reaction mixture was refluxed for 16 h and then filtered to remove Pd–C and the crude solid was recrystallized from ethanol to yield 92.2% bis(4-aminophenoxy)methane. The recrystallized product was stored in dry air-tight glass bottles for further studies (m.p. 372 K). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.46 (*s*, 4H, NH_2); 5.51(*s*, 2 H, methylene), 6.58–6.63 (*dt*, 4H, and Ar H). Elemental analysis calculated for $C_{13}H_{14}N_2O_2$ (wt%): C 67.82, H 6.08, N 12.17; found: C 67.74, H 6.23, N 11.98. IR (KBr pellet, cm^{-1}): 3406 and 3329 (NH_2), 1620 (N—H bending), 1211(C—O—C), 1463 (N—H deformation).

Crystal data

$C_{13}H_{14}N_2O_2$
$M_r = 230.26$
Monoclinic, $C2/c$
$a = 29.375$ (4) Å
$b = 9.6601$ (10) Å
$c = 17.090$ (2) Å
$\beta = 109.867$ (9)°
$V = 4560.9$ (10) Å^3
$Z = 16$
$D_x = 1.341$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 173$ (2) K
Needle, colourless
0.18 × 0.09 × 0.07 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: none
13252 measured reflections
4243 independent reflections
1628 reflections with $I > 2\sigma(I)$
$R_{int} = 0.097$
$\theta_{max} = 25.6°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.129$
$S = 0.85$
4243 reflections
333 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00159 (14)

Table 1
Selected torsion angles (°).

O2—C1—O1—C11	83.0 (3)	O1*A*^{i}—C1*A*—O1*A*—C11*A*	82.6 (3)
O1—C1—O2—C21	85.5 (3)	O1*B*^{ii}—C1*B*—O1*B*—C11*B*	80.0 (3)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N1*B*^{iii}	0.92 (3)	2.31 (2)	3.158 (5)	154 (3)
N1—H1*B*···O1*A*^{iv}	0.91 (3)	2.52 (2)	3.223 (4)	134 (3)
N2—H2*A*···O1*B*^{v}	0.91 (2)	2.38 (2)	3.261 (4)	163 (3)
N2—H2*B*···N1*A*	0.91 (3)	2.23 (3)	3.129 (5)	167 (3)
N1*A*—H1*A*1···N1^{vi}	0.92 (3)	2.31 (3)	3.208 (5)	165 (3)
N1*A*—H1*A*2···O2^{vii}	0.92 (3)	2.30 (1)	3.196 (4)	165 (3)
N1*B*—H1*B*1···N2^{viii}	0.91 (3)	2.26 (2)	3.097 (5)	152 (3)
N1*B*—H1*B*2···O1^{vii}	0.90 (3)	2.48 (2)	3.285 (4)	149 (3)

Symmetry codes: (iii) $x, y, z - 1$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (viii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

H atoms were located in a difference Fourier map. Those bonded to C atoms were positioned geometrically and refined using a riding

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model, with C—H = 0.95 and 0.99 Å for aromatic and methylene H atoms, respectively. The coordinates of the NH atoms were refined using a distance restraint of 0.91 (1) Å. All $U_{\rm iso}$(H) values were set at $1.2U_{\rm eq}$ of the parent atom. The compound crystallized as very fine needles and therefore the intensity data were weak overall and the small proportion of observed data (38%) used in the refinement may lower the precision of the structure.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

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