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1,4-Bis(4-aminophenoxy)benzene

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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.040; wR factor = 0.110; data-to-parameter ratio = 13.7.

The title compound, $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$, is a precursor for the synthesis of polyimides. The molecule is located on a crystallographic inversion center and the terminal amino-phenoxy rings are almost perpendicular to the central benzene ring with a dihedral angle of 85.40 (4)°. The molecular conformation is stabilized by $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ intermolecular hydrogen-bonding interactions.

Related literature

For related literature on polyimides and their solubility, see: Yang *et al.* (2002). For examples of chemical- and heat-resistant polyimides, see: Butt *et al.* (2005). Choi *et al.* (2001) discuss polyimides with various length (n -alkoxy)phenoxy side branches. For polyimides with improved properties such as processing from the melt or from solution, see: Eastmond & Paprotny (1996). For different structural modifications of the polymer backbone to reduce the chain interaction and their effect on chain packing and glass transition temperature, see: Yan *et al.* (2005) and references therein.



Experimental

Crystal data

$\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$
 $M_r = 292.33$
Monoclinic, $P2_1/c$
 $a = 6.9579$ (9) Å
 $b = 22.664$ (3) Å

$c = 5.1202$ (7) Å
 $\beta = 111.287$ (2)°
 $V = 752.34$ (17) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 0.09$ mm⁻¹
 $T = 296$ (2) K

$0.42 \times 0.40 \times 0.20$ mm

Data collection

Bruker SMART APEX area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.912$, $T_{\max} = 0.983$

6563 measured reflections
1805 independent reflections
1324 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.110$
 $S = 1.03$
1805 reflections
132 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.11$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H2A}\cdots\text{N1}^i$	0.930 (17)	2.321 (18)	3.2303 (17)	165.6 (14)
$\text{N1}-\text{H1A}\cdots\text{O1}^{\text{ii}}$	0.884 (17)	2.412 (17)	3.1968 (17)	148.1 (14)

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, WinGX (Farrugia, 1999) and Mercury (Macrae *et al.*, 2006).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2055).

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supporting information

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1,4-Bis(4-aminophenoxy)benzene

Ahsan M. Shemsi, Saeed M. Butt, Mohammed Fettouhi, Humaira M. Siddiqi and Zareen Akhter

S1. Comment

Ether containing aromatic diamines are useful monomers for the preparation of soluble polyimides (Yang *et al.*, 2002) which form a group of incredibly strong and astoundingly heat and chemical resistant polymers (Butt *et al.*, 2005). Many efforts have been made to improve their processability while maintaining their excellent thermal and mechanical properties (Choi *et al.*, 2001). Incorporation of flexible groups such as ether linkages were found successful in altering the crystallinity and the intermolecular interactions and to increase the solubility (Eastmond *et al.*, 1996). Different structural modifications of the polymer backbone have been studied to reduce the chain interaction, such as the introduction of flexible links, such as –O– and CH₂, to the main chain. This alteration disrupts the conjugation and increases the chain flexibility, which affects the chain packing but not the glass transition temperature (Yan *et al.*, 2005 and references therein).

The title compound crystallizes in the monoclinic space group $P2_1/c$ and the molecule is located on a crystallographic inversion center. The bond lengths and bond angles are in normal ranges. The terminal aminophenoxy rings are almost perpendicular to the central benzene ring with a dihedral angle of 85.40 (4) °.

The compound exhibits a zigzag like packing pattern (figure 2). The hydrogen atoms of the amino groups are engaged in two types of intermolecular hydrogen bonding interactions. The first one with the nitrogen atoms of other amino groups and the second with the oxygen atoms of the phenoxy groups (Table 1). Intermolecular C—H \cdots π contacts between adjacent phenoxy groups are also present (Fig. 3). The C—C distance of C6—H6 \cdots C6ⁱⁱⁱ (iii = $x, 0.5 - y, 1/2 + z$) is 2.74 (2) Å and C—H \cdots C angle is 175 (1) °, while the dihedral angle between the two phenoxy mean planes is 88.82 (3) °. Additional contacts take place between the central phenyl group and the adjacent terminal phenoxy group with a C—C distance for C9—H9 \cdots C2^{iv} (iv = $1 + x, y, z$) of 2.180 (1) %Å.

S2. Experimental

The title compound was synthesized in two steps. In the first step a mixture of 2.00 g (0.0180 mol) of hydroquinone, 5.00 g (0.0360 mol) of anhydrous K₂CO₃ and 3.81 ml (0.036 mol) of 4-fluoronitrobenzene in a two neck round bottom flask having 70 ml of dimethyl acetamide was heated at 373 K for 20 h under a nitrogen atmosphere. The colour of the solution changes from yellow to dark brown as the reaction proceeds. After cooling to room temperature, the reaction mixture was poured in 800 ml of water to precipitate a yellow solid which was washed thoroughly with water and then separated by filtration. In the second step a 250 ml two neck flask was charged with 1.00 g (2.84 mmol) of the yellow solid, 10 ml of hydrazine monohydrate, 80 ml of ethanol and 0.06 g of 5% palladium on carbon (Pd/C). The mixture was refluxed for 16 h and then filtered to remove Pd/C. The solvent was evaporated and the resulting crude solid was recrystallized from ethanol to afford crystals suitable for X-ray analysis (yield:85%, m.p.: 455 K).

S3. Refinement

All hydrogen atoms were located from the difference Fourier map and refined isotropically.

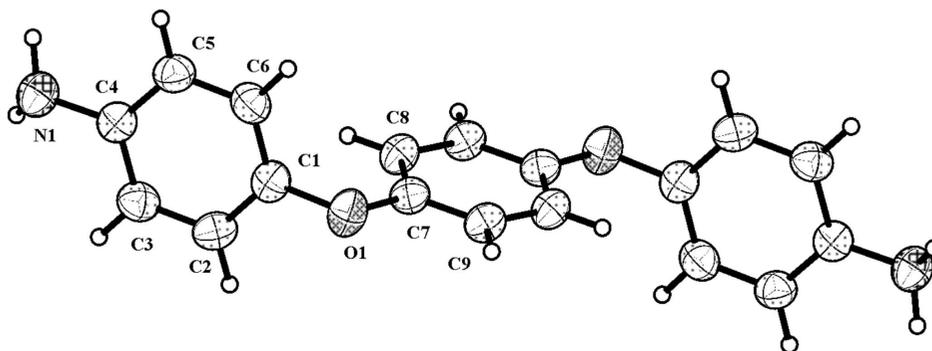


Figure 1

The molecular structure of the compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms. The non-labeled atoms have the symmetry operator $(-x, -y + 1, -z + 1)$.

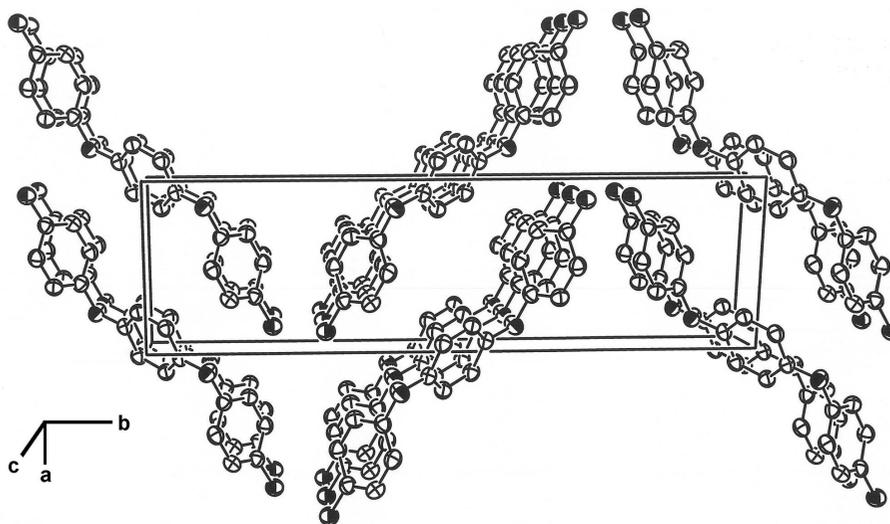


Figure 2

The packing of the compound, viewed down the *c* axis, showing the zig zag packing pattern.

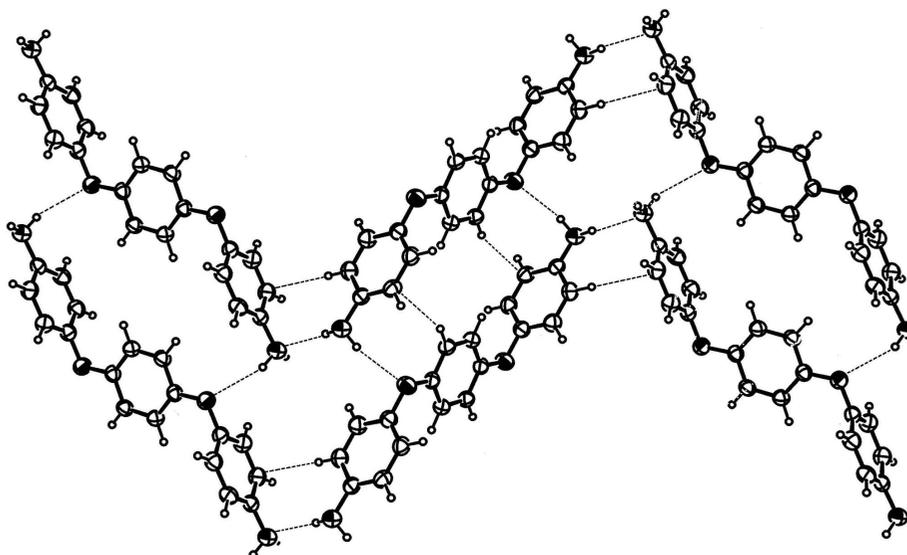


Figure 3

Hydrogen bonding and part of the C—H... π interactions in the title compound.

1,4-Bis(4-aminophenoxy)benzene

Crystal data

$C_{18}H_{16}N_2O_2$

$M_r = 292.33$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 6.9579$ (9) Å

$b = 22.664$ (3) Å

$c = 5.1202$ (7) Å

$\beta = 111.287$ (2)°

$V = 752.34$ (17) Å³

$Z = 2$

$F(000) = 308$

$D_x = 1.290$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6563 reflections

$\theta = 1.8$ – 28.3 °

$\mu = 0.09$ mm⁻¹

$T = 296$ K

Parallelepiped, colorless

$0.42 \times 0.40 \times 0.20$ mm

Data collection

Bruker SMART APEX area-detector
diffractometer

Radiation source: normal-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.912$, $T_{\max} = 0.983$

6563 measured reflections

1805 independent reflections

1324 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 1.8$ °

$h = -9 \rightarrow 9$

$k = -29 \rightarrow 29$

$l = -6 \rightarrow 6$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.110$

$S = 1.03$

1805 reflections

132 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.0611P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.11 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.70301 (18)	0.32300 (5)	0.8436 (3)	0.0594 (3)
C2	0.7083 (2)	0.36502 (6)	1.0429 (3)	0.0682 (4)
C3	0.5311 (2)	0.39239 (6)	1.0395 (3)	0.0689 (4)
C4	0.3455 (2)	0.37764 (5)	0.8382 (3)	0.0624 (3)
C5	0.3356 (2)	0.33551 (6)	0.6415 (3)	0.0701 (4)
C6	0.5135 (2)	0.30869 (6)	0.6426 (3)	0.0679 (4)
C7	0.08726 (18)	0.45198 (5)	0.6667 (2)	0.0575 (3)
C8	0.1848 (2)	0.47745 (6)	0.5030 (3)	0.0627 (3)
C9	-0.0966 (2)	0.47461 (6)	0.6631 (3)	0.0623 (3)
N1	0.8832 (2)	0.29346 (6)	0.8572 (3)	0.0754 (4)
O1	0.16450 (15)	0.40403 (4)	0.8428 (2)	0.0768 (3)
H1A	0.992 (2)	0.3169 (8)	0.917 (3)	0.087 (5)*
H2A	0.871 (2)	0.2739 (8)	0.692 (4)	0.090 (5)*
H2	0.837 (2)	0.3742 (7)	1.188 (3)	0.083 (4)*
H3	0.536 (2)	0.4215 (7)	1.172 (3)	0.081 (4)*
H5	0.210 (2)	0.3248 (7)	0.503 (3)	0.091 (5)*
H6	0.506 (2)	0.2798 (7)	0.504 (3)	0.081 (4)*
H8	0.311 (2)	0.4623 (6)	0.505 (3)	0.076 (4)*
H9	-0.1617 (18)	0.4570 (6)	0.778 (3)	0.072 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0652 (7)	0.0540 (6)	0.0638 (7)	-0.0033 (5)	0.0290 (6)	0.0066 (5)
C2	0.0649 (8)	0.0724 (8)	0.0656 (8)	-0.0120 (6)	0.0218 (7)	-0.0073 (6)
C3	0.0792 (9)	0.0634 (7)	0.0692 (8)	-0.0088 (6)	0.0329 (7)	-0.0109 (6)
C4	0.0691 (8)	0.0560 (7)	0.0680 (7)	0.0028 (5)	0.0318 (6)	0.0093 (5)
C5	0.0670 (8)	0.0707 (8)	0.0645 (8)	-0.0007 (6)	0.0142 (6)	-0.0013 (6)
C6	0.0771 (9)	0.0615 (7)	0.0640 (8)	-0.0012 (6)	0.0244 (6)	-0.0075 (6)
C7	0.0640 (7)	0.0510 (6)	0.0590 (7)	-0.0040 (5)	0.0242 (5)	-0.0042 (5)
C8	0.0612 (7)	0.0617 (7)	0.0716 (8)	-0.0002 (6)	0.0317 (6)	-0.0022 (6)
C9	0.0661 (7)	0.0610 (7)	0.0680 (7)	-0.0056 (6)	0.0342 (6)	-0.0008 (6)

N1	0.0687 (8)	0.0761 (8)	0.0871 (9)	-0.0012 (6)	0.0351 (7)	-0.0007 (6)
O1	0.0797 (6)	0.0731 (6)	0.0908 (7)	0.0131 (5)	0.0469 (5)	0.0202 (5)

Geometric parameters (Å, °)

C1—C6	1.3847 (19)	C6—H6	0.953 (16)
C1—C2	1.3865 (18)	C7—C9	1.3722 (17)
C1—N1	1.4009 (17)	C7—C8	1.3819 (17)
C2—C3	1.3746 (19)	C7—O1	1.3897 (15)
C2—H2	0.956 (15)	C8—C9 ⁱ	1.3789 (18)
C3—C4	1.3695 (19)	C8—H8	0.941 (14)
C3—H3	0.939 (15)	C9—C8 ⁱ	1.3789 (18)
C4—C5	1.3717 (19)	C9—H9	0.950 (13)
C4—O1	1.4017 (15)	N1—H1A	0.884 (17)
C5—C6	1.3772 (19)	N1—H2A	0.930 (17)
C5—H5	0.935 (15)		
C6—C1—C2	118.16 (12)	C5—C6—H6	119.7 (9)
C6—C1—N1	121.22 (13)	C1—C6—H6	119.6 (9)
C2—C1—N1	120.50 (13)	C9—C7—C8	119.77 (12)
C3—C2—C1	121.09 (13)	C9—C7—O1	116.11 (11)
C3—C2—H2	119.6 (9)	C8—C7—O1	124.12 (11)
C1—C2—H2	119.3 (9)	C9 ⁱ —C8—C7	119.76 (12)
C4—C3—C2	119.75 (13)	C9 ⁱ —C8—H8	120.0 (9)
C4—C3—H3	119.4 (9)	C7—C8—H8	120.2 (9)
C2—C3—H3	120.8 (9)	C7—C9—C8 ⁱ	120.46 (12)
C3—C4—C5	120.29 (13)	C7—C9—H9	119.1 (8)
C3—C4—O1	119.40 (12)	C8 ⁱ —C9—H9	120.4 (8)
C5—C4—O1	120.25 (12)	C1—N1—H1A	111.7 (10)
C4—C5—C6	119.95 (13)	C1—N1—H2A	113.4 (10)
C4—C5—H5	121.5 (10)	H1A—N1—H2A	112.7 (14)
C6—C5—H5	118.6 (9)	C7—O1—C4	117.44 (9)
C5—C6—C1	120.75 (13)		
C7—O1—C4—C3	98.03 (15)	C7—O1—C4—C5	-84.85 (15)

Symmetry code: (i) $-x, -y+1, -z+1$.*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H2A \cdots N1 ⁱⁱ	0.930 (17)	2.321 (18)	3.2303 (17)	165.6 (14)
N1—H1A \cdots O1 ⁱⁱⁱ	0.884 (17)	2.412 (17)	3.1968 (17)	148.1 (14)

Symmetry codes: (ii) $x, -y+1/2, z-1/2$; (iii) $x+1, y, z$.