

## 4,4'-Bis(4-iodophenylaminomethyl)- azoxybenzene: hydrogen-bonded sheets built from C—H···O and C—H··· $\pi$ (arene) hydrogen bonds

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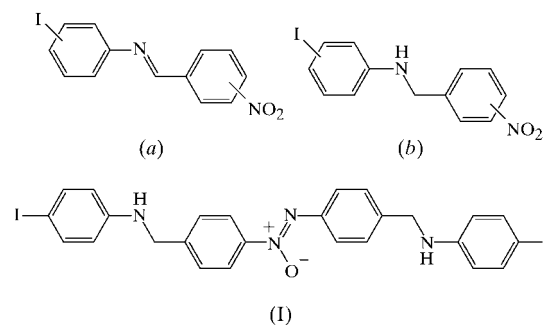
Borohydride reduction of *N*-(4-nitrobenzylidene)-4-iodoaniline has yielded the title compound, 1,2-bis[4-(4-iodophenylaminomethyl)phenyl]diazene 1-oxide, C<sub>26</sub>H<sub>22</sub>I<sub>2</sub>N<sub>4</sub>O. The molecules lie across centres of inversion in *P*2<sub>1</sub>/*c*, with the azoxy O atom disordered over two sites, each having an occupancy of 0.5. The molecules are linked into sheets by a combination of C—H···O and C—H··· $\pi$ (arene) hydrogen bonds.

### Comment

Reduction of *N*-(nitrobenzylidene)iidoanilines, (*a*), using sodium borohydride, generally yields the corresponding *N*-(nitrobenzyl)iidoanilines (*b*), and six of the isomeric compounds (*b*) have so far been structurally characterized (Glidewell *et al.*, 2002, 2003). However, the analogous reduction of *N*-(4-nitrobenzylidene)-4-iodoaniline yielded not the expected 4-iodo-*N*-(4-nitrobenzyl)aniline but instead the title compound, (I), a further reduction of the nitrobenzylidene presumed to have been the initial product of reduction.

Molecules of (I) lie across centres of inversion in space group *P*2<sub>1</sub>/*c*, with the reference molecule selected to lie across the inversion centre at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . The azoxy O atom is thus disordered over two sites, each with an occupancy of 0.5. The molecular conformation can be defined in terms of four independent dihedral angles (Fig. 1 and Table 1). The C11–C16 inner ring is nearly coplanar with the central azoxy unit, as is typically found in azoxybenzenes (Ejmsont, Domański *et*

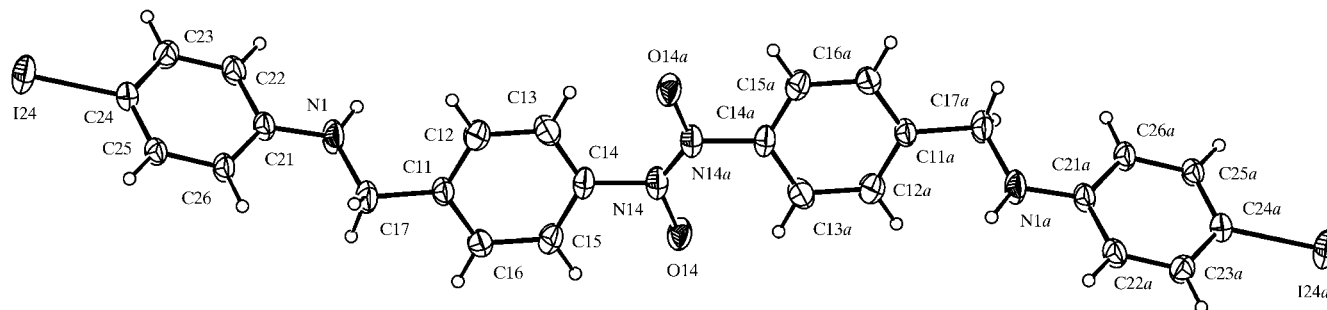
*al.*, 2000; Ejmsont, Broda *et al.*, 2002), and the terminal part of the molecule, comprising the C11–C17–N1–C21– unit and the iodinated outer ring, is also nearly planar. However, the C11–C16 ring and terminal fragment are far from being coplanar, as shown by the C12–C11–C17–N1 torsion angle.



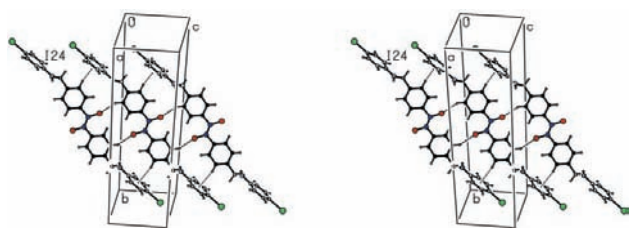
The molecules are linked by C—H···O and C—H··· $\pi$ (arene) hydrogen bonds (Table 2). Because of the partial occupancy of the O-atom sites, we first discuss the effect of the C—H··· $\pi$ (arene) hydrogen bonds. Atom C16 at  $(x, y, z)$ , which lies in the molecule centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , acts as hydrogen-bond donor to the C21–C26 ring at  $(x, y, 1+z)$ , which lies in the molecule centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ , and propagation of this interaction by inversion and translation generates a molecular ladder running parallel to the [001] direction (Fig. 2). This ladder is reinforced by C—H···O hydrogen bonds. Atom C12 at  $(x, y, z)$ , which is part of the molecule centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , acts as hydrogen-bond donor to O14 at  $(x, y, -1+z)$ , which is part of the molecule centred at  $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ . Since each molecule contains only one O atom, each molecule can accept only one C—H···O hydrogen bond of this type, and a given pair of molecules, related by translation along the [001] direction, may in fact be linked by zero, one or two C—H···O hydrogen bonds, although on average there will be one such bond between each adjacent pair. The occurrence of exactly one C—H···O hydrogen bond between each pair of adjacent molecules would require perfect correlation of the O-atom site occupancies within a given ladder, although there need be no correlation between neighbouring ladders.

A similar, although more weakly bonded, ladder is generated along the [101] direction. Atom C25 at  $(x, y, z)$ , in the molecule centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , acts as hydrogen-bond donor to the inner ring at  $(-1+x, y, -1+z)$ , which forms part of the molecule centred at  $(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ , while C17 at  $(x, y, z)$  acts as donor, *via* H17B, to O14, also at  $(-1+x, y, -1+z)$ . Propagation of these interactions by inversion and translation generates the [101] ladder (Fig. 3), and the combination of ladders along [001] and [101] generates a sheet parallel to (010). Two such sheets run through each unit cell, in the domains  $0.28 < y < 0.72$  and  $-0.22 < y < 0.22$ , but there are no direction-specific interactions between adjacent sheets. In particular, there are no aromatic  $\pi$ – $\pi$ -stacking interactions, despite the number of aryl rings present. Note that the amino N atom plays no role in the supramolecular aggregation.

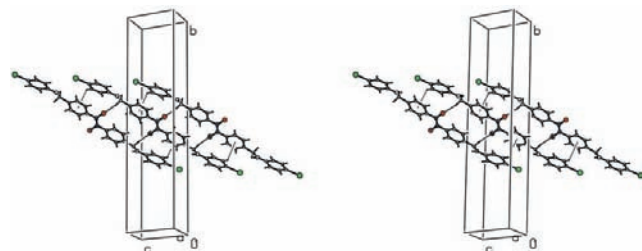
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**Figure 1**

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level. Atom O14 has an occupancy of 0.5 and atoms marked with the suffix 'a' are at the symmetry position  $(1-x, 1-y, 1-z)$ .


**Figure 2**

A stereoview of part of the crystal structure of (I), showing the formation of a molecular ladder along  $[001]$ .


**Figure 3**

A stereoview of part of the crystal structure of (I), showing the formation of a molecular ladder along  $[101]$ .

## Experimental

A sample of (I) was obtained by reduction of the corresponding *N*-(benzylidene)aniline using a fivefold molar excess of  $\text{NaBH}_4$  in refluxing methanol for 1 h. After work-up, crystals of (I) suitable for single-crystal X-ray diffraction were grown by the slow evaporation of a solution in ethanol.

### Crystal data

$\text{C}_{26}\text{H}_{22}\text{I}_2\text{N}_4\text{O}$   
 $M_r = 660.28$   
 Monoclinic,  $P2_1/c$   
 $a = 5.6959$  (7) Å  
 $b = 30.061$  (3) Å  
 $c = 7.2017$  (8) Å  
 $\beta = 99.526$  (2)°  
 $V = 1216.1$  (2) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.803$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 4439 reflections  
 $\theta = 2.7\text{--}33.0^\circ$   
 $\mu = 2.61$  mm<sup>-1</sup>  
 $T = 291$  (2) K  
 Plate, colourless  
 $0.40 \times 0.30 \times 0.02$  mm

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\min} = 0.403$ ,  $T_{\max} = 0.946$   
 12 146 measured reflections

4439 independent reflections  
 3092 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$   
 $\theta_{\text{max}} = 33.0^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -39 \rightarrow 46$   
 $l = -11 \rightarrow 10$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.065$   
 $wR(F^2) = 0.156$   
 $S = 1.13$   
 4439 reflections  
 154 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 3.3092P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.07$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.19$  e Å<sup>-3</sup>

**Table 1**

Selected torsion angles (°).

C13—C14—N14—N14 <sup>i</sup>	17.4 (9)	C11—C17—N1—C21	−170.8 (5)
C12—C11—C17—N1	51.7 (8)	C17—N1—C21—C22	−173.5 (6)

Symmetry code: (i)  $1-x, 1-y, 1-z$ .

**Table 2**

Hydrogen-bonding geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of rings C11—C16 and C21—C26, respectively.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C12—H12...O14 <sup>ii</sup>	0.93	2.24	3.078 (9)	150
C17—H17B...O14 <sup>iii</sup>	0.97	2.45	3.380 (10)	162
C16—H16... <i>Cg</i> 2 <sup>iv</sup>	0.93	2.78	3.536 (5)	139
C25—H25... <i>Cg</i> 1 <sup>iii</sup>	0.93	2.97	3.631 (5)	130

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

Compound (I) is monoclinic and the space group  $P2_1/c$  was uniquely assigned from the systematic absences. H atoms were treated as riding atoms, with C—H distances of 0.93 (aromatic) and 0.97 Å (CH<sub>2</sub>), and N—H distances of 0.86 Å. Refinement of the site-occupancy factor for atom O14 gave a value of 0.52 (3); this factor was thereafter fixed at 0.50.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1624). Services for accessing these data are described at the back of the journal.

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