Hydrogen-bonded molecular ladders in *trans*-1,2-bis(2-nitroanilino)cyclohexane

Solange M. S. V. Wardell,[a] James L. Wardell,[a] Mark F. Ward,[a] John N. Low[b]* and Christopher Glidewell[c]

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [b]Department of Applied Physics and Electronic and Mechanical Engineering, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland, and [c]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland Correspondence e-mail: j.n.low@dundee.ac.uk

Crystals of the title compound, $C_{18}H_{20}N_4O_4$, contain equal numbers of (*R,R*) and (*S,S*) molecules, but these are not precise enantiomorphs, neither are they related by crystallographic symmetry; in addition, each molecule exhibits approximate, but not exact, twofold rotational symmetry. There are intramolecular N—H⋯O hydrogen bonds [N⋯O 2.609 (4)–2.638 (5) Å; N—H⋯O 125–132°] and the molecules are linked into molecular ladders by C—H⋯O hydrogen bonds [C⋯O 3.306 (6)–3.386 (6) Å; C—H⋯O 146–160°].

Comment

As part of a continuing study of the interplay between molecular conformation and supramolecular aggregation in compounds containing 2-nitrophenyl groups (Low, Storey *et al.*, 2000; Low, Glidewell & Wardell, 2000), we now report the structure of *trans*-1,2-bis(2-nitroanilino)cyclohexane, (O_2N-$C_6H_4NH)_2C_6H_{10}$, (I), which exhibits pseudosymmetry as well as a supramolecular arrangement in the form of hydrogen-bonded molecular ladders.

(I)

(I*a*)   (I*b*)   (I*c*)
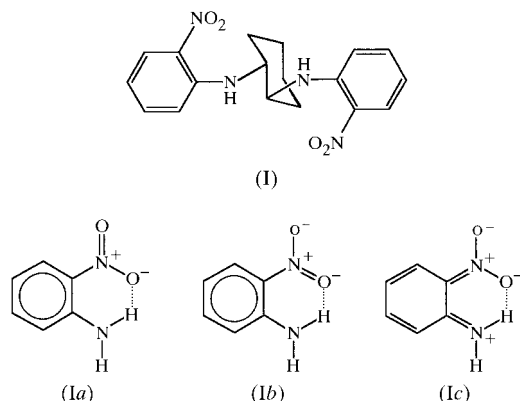
Compound (I) crystallizes in space group $P2_1/n$ with two independent molecules in the asymmetric unit (Fig. 1). In both

molecules, the cyclohexane rings adopt the chair conformation with the two amino substituents in mutually *trans* equatorial sites. There are two enantiomeric forms present and the asymmetric unit was selected to contain one (*R,R*) molecule and one (*S,S*) molecule. In molecule 1 (defined by N1–N4), the stereogenic atoms C1 and C2 both have the *R* configuration, while in molecule 2 (defined by N5–N8), the corresponding C19 and C20 atoms both have the *S* configuration. Each molecule, in addition, has approximate C_2 rotational symmetry. However, despite these observations, a search for possible additional crystallographic symmetry showed that none was present.

When the H atoms in the amino groups were all refined isotropically, the configurations about all the amino N atoms were found to be planar within experimental uncertainty; subsequently, the configurations of these N atoms were
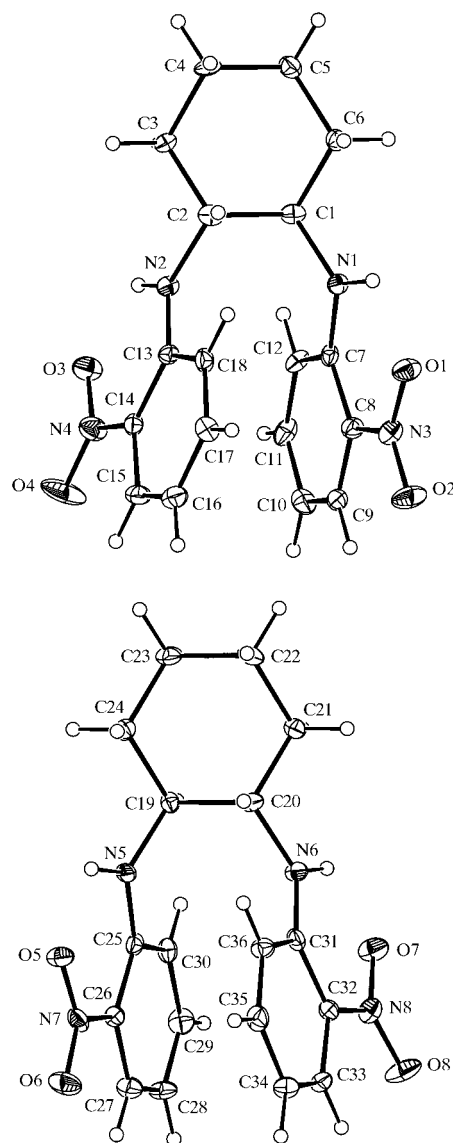

Figure 1
A view of the two independent molecules of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

organic compounds

constrained to be planar. Associated with this planarity are the very wide C—N—C angles (Table 1), all around 125°, and the short N—C(aryl) distances [1.334 (5)–1.379 (5) Å, mean 1.356 Å], which are typical of such distances involving planar nitrogen (mean value 1.355 Å; Allen *et al.*, 1987). The corresponding mean distance for bonds involving pyramidal nitrogen is 1.394 Å (Allen *et al.*, 1987). The N—H bonds are all essentially coplanar with the adjacent aryl rings, as are the nitro groups, and there is thus an intramolecular N—H···O hydrogen bond formed by each amino group (Table 2), forming an $S(6)$ motif (Bernstein *et al.*, 1995). The C(aryl)—NO_2 bonds are all significantly shorter than the mean value, 1.468 Å, for bonds of this type (Allen *et al.*, 1987).

Within the aryl rings, there is evidence of some bond fixation; together with the short C(aryl)—N bonds, this is consistent with a significant admixture of the canonical form (I*c*) into the more conventional forms (I*a*) and (I*b*). Form (I*c*), where both the hydrogen-bond donor and the acceptor are charged, strongly favours the formation of a strong intermolecular hydrogen bond (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994). Also worthy of note are the consistently small C—C—C angles in the aryl rings *ipso* to the amino substituents (*i.e.* at C7, C13, C25 and C31) associated with the electron-donating properties of the amino group (Domenicano & Murray-Rust, 1979). There is a consistent difference between the two exocyclic C—C—NO_2 angles (Table 2) and, in every case, the angle nearer the ami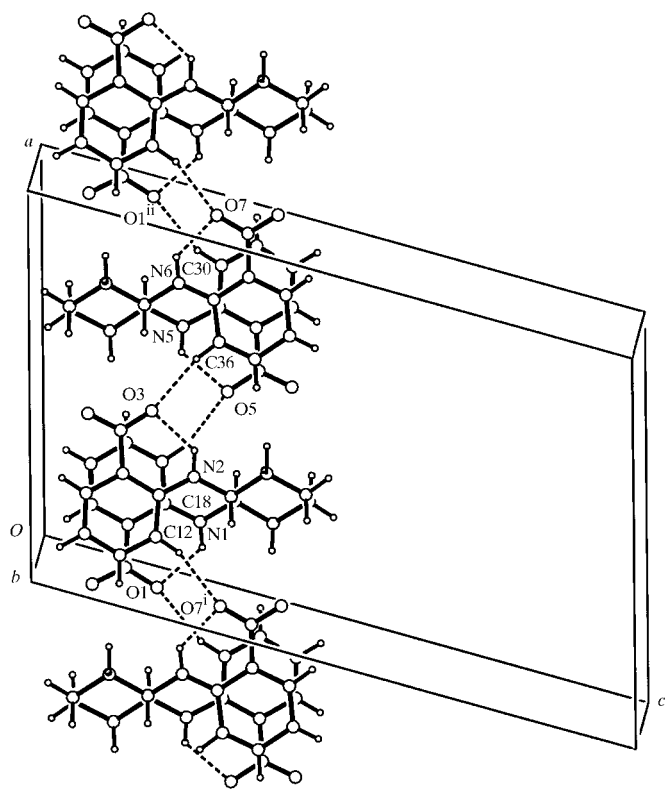no group is the larger. This arises from the need to accommodate the long H···O distances within the planar $S(6)$ ring.

In the structure of 2-nitroaniline itself (Dhaneshwar *et al.*, 1978), the geometries reported for the two independent molecules are so different that no firm conclusions can be drawn. However, in 4-methyl-2-nitroaniline (Ellena *et al.*, 1996), there is evidence for bond fixation of exactly the type observed here in compound (I); of particular note in 4-methyl-2-nitroaniline are the C—NO_2 bond length, 1.434 (3) Å, and the range of C—C bond lengths in the aryl ring, 1.343 (5)–1.406 (4) Å.

In each of the two independent molecules in (I), the two aryl rings are nearly parallel; in molecule 1, the dihedral angle between the two ring planes is 16.1 (2)°, while in molecule 2, the corresponding angle is 11.5 (2)°. The distance between the rings is *ca* 3.39 Å in molecule 1 and *ca* 3.31 Å in molecule 2, and the centroid offsets are 1.46 and 1.29 Å, respectively; these values are appropriate for intramolecular aromatic π···π stacking interactions. On the other hand, there are no intermolecular interactions of this type.

The molecules are linked into ladders by C—H···O hydrogen bonds (Table 2 and Fig. 2). The ladders are generated by translation along the [100] direction and alternate molecules within any ladder are of opposite chirality. Each molecule acts as a double donor and a double acceptor of hydrogen bonds (Table 2) and in the ladder, the uprights are formed by antiparallel $C_2^2(12)$ chains, one containing O1 and O5 as acceptors, the other containing O3 and O7. Only half of the O atoms participate in the hydrogen bonding (Table 2). The rungs of the ladder are formed by the diaminocyclohexane units, and each neighbouring pair of rungs encloses an $R_2^2(22)$ ring. These rings are approximately, but not exactly centrosymmetric, and they are centred close to ($n/2 + 0.47$, 0.17, 0.25) (n = zero or integer). Hence, each individual molecule exhibits pseudosymmetry, having near C_2 rotational symmetry, and the two independent molecules also exhibit a pseudosymmetric relationship in that neighbouring pairs lie across pseudo-centres of inversion. The precise values of corresponding geometric parameters, both intra- and intermolecular are, however, significantly different in many cases (Tables 1 and 2).

The pseudosymmetry can perhaps best be understood by reference to Fig. 2, which shows both the approximate twofold axes running through each molecule and lying approximately normal to the [100] direction, and the pseudo-inversions between adjacent molecules. While only a minor adjustment in the angle β, from 105.594 (7) to 108.23°, is required to generate a metrically orthorhombic cell, the cell contents do not exhibit orthorhombic symmetry.

Experimental

A mixture of 2-fluoronitrobenzene (5.64 g, 40 mmol), *trans*-cyclohexane-1,2-diamine (2.28 g, 20 mmol) and sodium hydrogen carbonate (3.70 g, 44 mmol) was heated in refluxing ethanol (50 ml) for 2 h. The hot reaction mixture was poured into ice water (100 ml) and extracted with CH_2Cl_2 (3 × 150 ml). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo* to

Figure 2
Part of the crystal structure of (I), showing the formation of a molecular ladder [symmetry codes: (i) −1 + *x, y, z*; (ii) 1 + *x, y, z*].

yield an oily orange solid, which was crystallized from ethanol to yield bright orange needle-like crystals (5.17 g, 73%, m.p. 493–494 K).

Crystal data

$C_{18}H_{20}N_4O_4$	$D_x = 1.407$ Mg m^{-3}
$M_r = 356.38$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6356
$a = 13.1140$ (10) Å	reflections
$b = 12.7121$ (19) Å	$\theta = 1.66-25.87°$
$c = 20.959$ (3) Å	$\mu = 0.102$ mm^{-1}
$\beta = 105.594$ (7)°	$T = 150$ (2) K
$V = 3365.3$ (8) Å^3	Needle, orange
$Z = 8$	$0.30 \times 0.03 \times 0.02$ mm

Data collection

KappaCCD diffractometer	1853 reflections with $I > 2\sigma(I)$
φ and ω scans with κ offsets	$R_{int} = 0.107$
Absorption correction: multi-scan	$\theta_{max} = 25.87°$
(*SORTAV*; Blessing, 1995, 1997)	$h = -16 \rightarrow 15$
$T_{min} = 0.970$, $T_{max} = 0.998$	$k = -14 \rightarrow 15$
19 380 measured reflections	$l = -23 \rightarrow 25$
6356 independent reflections	Intensity decay: negligible

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2]$
$wR(F^2) = 0.140$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.862$	$(\Delta/\sigma)_{max} = 0.003$
6356 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
472 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—N3	1.253 (5)	O5—N7	1.261 (4)
O2—N3	1.240 (5)	O6—N7	1.227 (5)
O3—N4	1.247 (5)	O7—N8	1.244 (5)
O4—N4	1.242 (5)	O8—N8	1.231 (5)
N1—C1	1.465 (5)	N5—C19	1.459 (5)
N1—C7	1.357 (5)	N5—C25	1.379 (5)
N2—C2	1.459 (5)	N6—C20	1.458 (5)
N2—C13	1.351 (5)	N6—C31	1.334 (5)
N3—C8	1.444 (5)	N7—C26	1.437 (5)
N4—C14	1.435 (5)	N8—C32	1.445 (5)
C1—N1—C7	124.3 (4)	C19—N5—C25	125.0 (4)
C2—N2—C13	126.5 (4)	C20—N6—C31	126.3 (4)
O1—N3—O2	121.8 (4)	O5—N7—O6	121.0 (4)
O3—N4—O4	121.7 (4)	O7—N8—O8	120.8 (4)
C8—C7—C12	115.0 (5)	C26—C25—C30	115.4 (5)
C7—C8—N3	122.3 (5)	C25—C26—N7	122.3 (5)
C9—C8—N3	116.0 (5)	C27—C26—N7	115.9 (5)
C14—C13—C18	115.4 (5)	C32—C31—C36	113.9 (5)
C13—C14—N4	122.9 (5)	C31—C32—N8	121.0 (5)
C15—C14—N4	115.6 (5)	C33—C32—N8	116.3 (4)
N1—C1—C2—N2	−54.2 (5)	N5—C19—C20—N6	56.9 (5)
O1—N3—C8—C7	−2.5 (7)	O5—N7—C26—C25	3.2 (7)
O2—N3—C8—C7	−179.8 (5)	O6—N7—C26—C25	−176.3 (5)
O3—N4—C14—C13	−0.7 (7)	O7—N8—C32—C31	−4.0 (7)
O4—N4—C14—C13	−179.5 (5)	O8—N8—C32—C31	174.7 (5)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H11N$\cdots$O1	0.88	2.03	2.638 (5)	126
N2—H12N$\cdots$O3	0.88	1.95	2.617 (4)	132
N5—H15N$\cdots$O5	0.88	2.03	2.632 (5)	125
N6—H16N$\cdots$O7	0.88	1.95	2.609 (4)	131
C12—H12$\cdots$O5	0.95	2.53	3.385 (6)	149
C18—H18$\cdots$O7^i	0.95	2.41	3.306 (6)	156
C30—H30$\cdots$O1^{ii}	0.95	2.56	3.386 (6)	146
C36—H36$\cdots$O3	0.95	2.46	3.368 (5)	160

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

Compound (I) crystallized in the monoclinic system; space group $P2_1/n$ from the systematic absences. H atoms were treated as riding atoms with C—H = 0.95–1.00 Å and N—H = 0.88 Å. Examination of the structure with *PLATON* (Spek, 1999) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

References

Aakeröy, C. B. & Seddon, K. R. (1993). *Chem. Soc. Rev.* **22**, 397–407.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.

Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.

Dhaneshwar, N. N., Tavale, S. S. & Pant, L. M. (1978). *Acta Cryst.* B**34**, 2507–2508.

Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.

Ellena, J., Punte, G. & Rivero, B. E. (1996). *Acta Cryst.* C**52**, 2074–2076.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Gilli, P., Bertolasi, V., Ferretti, V. & Gilli, G. (1994). *J. Am. Chem. Soc.* **116**, 909–915.

Low, J. N., Glidewell, C. & Wardell, J. L. (2000). *Acta Cryst.* C**56**, 689–691.

Low, J. N., Storey, E. J., McCarron, M., Wardell, J. L., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* B**56**, 58–67.

Nonius (1997). *KappaCCD Server Software*. Windows 3.11 version. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1999). *PLATON*. January 1999 version. University of Utrecht, The Netherlands.