(1RS,2RS)-N,N′-Bis(4-nitrophenylmethylene)cyclohexane-1,2-diamine: complex sheets built from C—H···O and C—H···π(arene) hydrogen bonds

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The racemic title compound, $C_{20}H_{20}N_4O_4$, crystallizes with $Z' = 2$ in the space group $P2_1/c$. Each independent molecule exhibits approximate twofold rotation symmetry, but conformational differences between the molecules preclude any higher symmetry. The molecules are linked into complex sheets by a combination of four C—H···O hydrogen bonds and two C—H···π(arene) hydrogen bonds.

Comment

We have recently reported the structure of enantiopure (1R,2R)-N,N′-bis(4-nitrophenylmethylene)cyclohexane-1,2-diamine, (I) (Glidewell *et al.*, 2005). This compound crystallizes with $Z' = 2$ in space group $C2$, and the independent molecules both exhibit approximate but not crystallographic twofold rotational symmetry. There is a single C—H···O hydrogen bond linking the two independent molecules, but there are no other direction-specific interactions in the structure. In this paper, we report the structure of another isomeric form, the racemic 1RS,2RS compound, (II).

Compound (II) crystallizes in the centrosymmetric space group $P2_1/c$ with $Z' = 2$ (Fig. 1). In the selected asymmetric unit each of the molecules has the 1R,2R configuration, but the space group accommodates equal numbers of 1R,2R and 1S,2S enantiomers, as required by the racemic nature of (II). In each of the molecules, the cyclohexane ring adopts a chain conformation, with the pendent substituent units in equatorial positions. Each molecule adopts approximate, but not exact, twofold rotational symmetry, as shown by the leading torsion angles (Table 1), and the differences between corresponding values for the two molecules are sufficient to preclude any additional symmetry. The dihedral angles between the nitro

groups containing N14X and N24X ($X = A$ or B) and their adjacent aryl rings are 9.7 (2) and 3.3 (2)° in molecule A, and 16.0 (2) and 12.0 (2)° in molecule B.
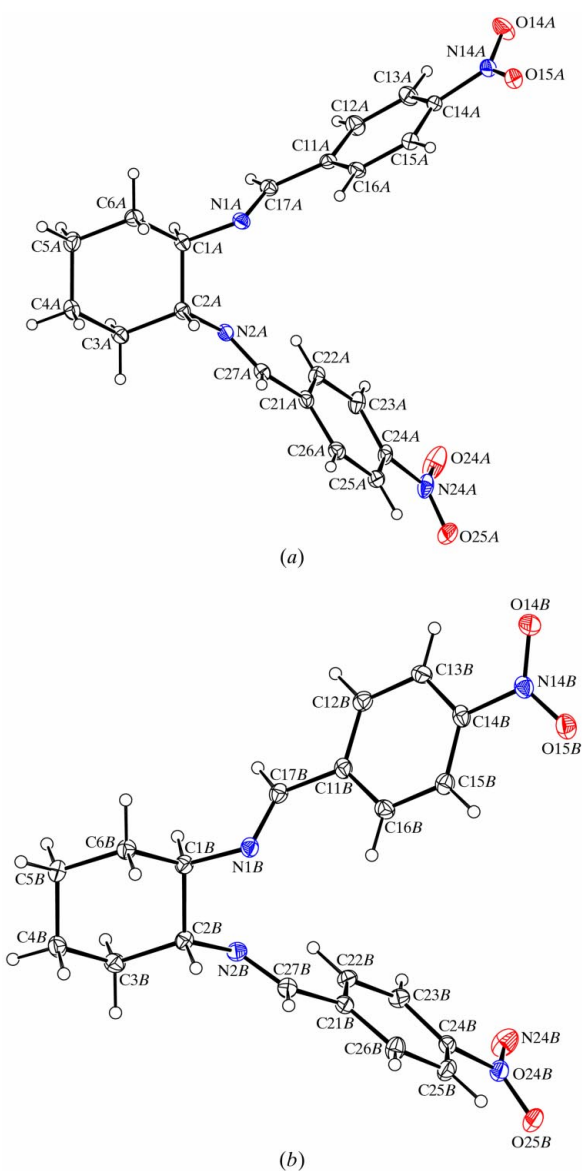

(I)

(II)
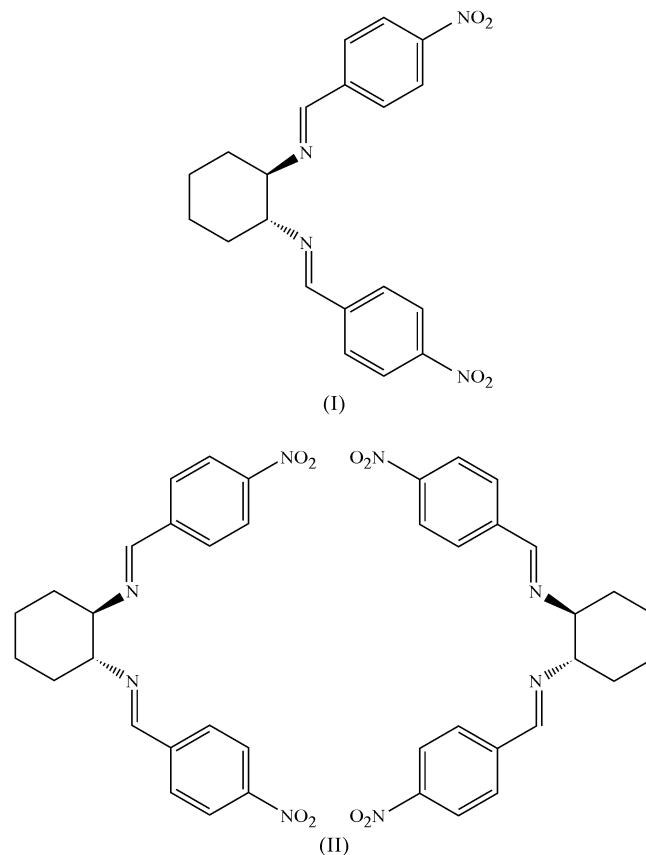
The molecules of (II) are linked into complex sheets by a combination of four C—H···O hydrogen bonds and two C—H···π(arene) hydrogen bonds (Table 2), and the formation of the sheet is best approached in terms of the component substructures, each of which depends on a small subset of the hydrogen bonds.

The basic building blocks within the structure of (II) are two centrosymmetric $R_2^2(32)$ dimers, formed by molecules of types A and B, respectively; for the selected asymmetric unit, the type A dimer is centred at $(0, 0, \frac{1}{2})$ and the type B dimer is centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The overall structure can then be envisaged in terms of series of chains which result from the linking of these dimers. There are four such chains, two of which incorporate just one type of dimer, A or B, and the other two of which incorporate both types of dimer, A and B.

Within the asymmetric unit, aryl atom C22A acts as hydrogen-bond donor to nitro atom O15B, and propagation by inversion of this hydrogen bond links the two types of $R_2^2(32)$ dimer into a chain of rings running parallel to the [110] direction (Fig. 2). In addition, aryl atom C27B, which lies in the type B dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as hydrogen-bond donor to atom O24A at $(x, 1 + y, z)$, which lies in the type A dimer centred at $(0, 1, \frac{1}{2})$, and propagation of this interaction, again by inversion, links the $R_2^2(32)$ dimers into another chain of rings, this time running parallel to the [1$\bar{1}$0] direction (Fig. 3).
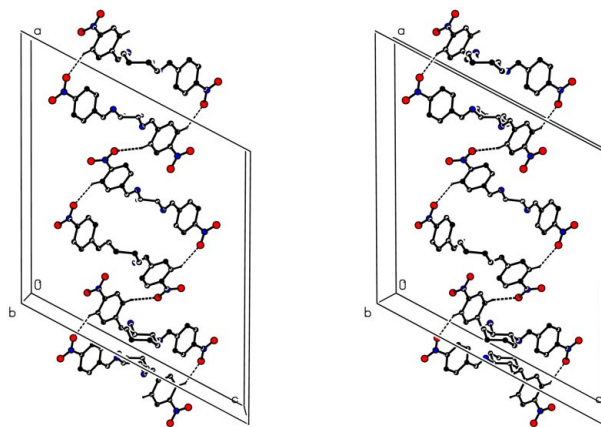
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Two further chains are generated by the linking of $R_2^2(32)$ dimers by means of C—H⋯π(arene) hydrogen bonds. These chains differ from those generated by C—H⋯O hydrogen bonds (Figs. 2 and 3) only in that each type of chain involving C—H⋯π(arene) hydrogen bonds is built from just one type of molecule. In the first of these, atom C4A in the type A molecule at (x, y, z), part of the type A dimer centred at $(0, 0, \frac{1}{2})$, acts as hydrogen-bond donor, via atom H41A, to the C21A–C26A ring of the type A molecule at $(x, 1 + y, z)$, itself part of the type A dimer centred at $(0, 1, \frac{1}{2})$. Hence, a chain of dimers is formed along $(0, y, \frac{1}{2})$ (Fig. 4). In the second chain of this type, atom C5B in the molecule at (x, y, z), which is part of the type B dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as hydrogen-bond donor, via atom H51B, to the C11B–C16B ring in the type B molecule at $(x, 1 + y, z)$, which forms part of the type B dimer centred at $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$, so forming a chain of dimers along $(\frac{1}{2}, y, \frac{1}{2})$ (Fig. 5).

The combination of the [010], [110] and [1$\bar{1}$0] chains (Figs. 2–5) is sufficient to produce an (001) sheet lying in the domain $0.14 < z < 0.86$ and generated by inversion centres at $z = \frac{1}{2}$. A second such sheet, related to the first by the translational symmetry, is generated by the centres of inversion at $z = 1.0$. There is one rather weak interaction between molecules in adjacent sheets, an approximately perpendicular nitro–nitro interaction involving type B molecules only. Atom O15B in the type B molecule at (x, y, z), part of the sheet centred at $z = \frac{1}{2}$, makes a short contact with atom O25B in the type B molecule at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, part of the sheet centred at $z = 1.0$, with O15B⋯O25B^i = 2.873 (2) Å, N14B—O15B⋯O25B^i = 86.4 (2)° and O15B⋯O25B^i—N24B^i = 135.9 (3)° [symmetry
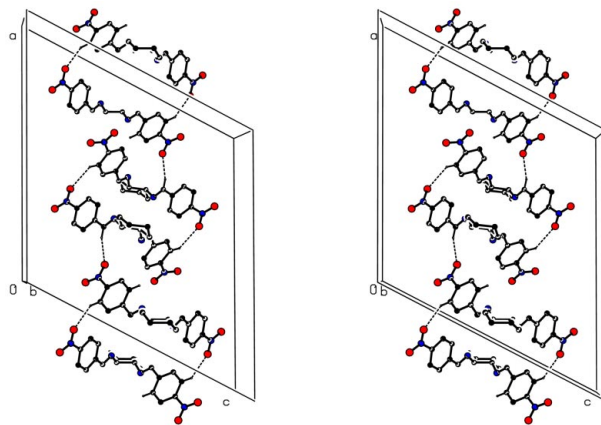

Figure 1
The 1R,2R enantiomers of the two independent molecules in compound (II), showing the atom-labelling schemes for (a) the type A molecule and (b) the type B molecule. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Figure 2
A stereoview of part of the crystal structure of compound (II), showing the linking of the $R_2^2(32)$ dimers of types A and B into a chain along [110]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

Figure 3
A stereoview of part of the crystal structure of compound (II), showing the linking of the $R_2^2(32)$ dimers of types A and B into a chain along [1$\bar{1}$0]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.
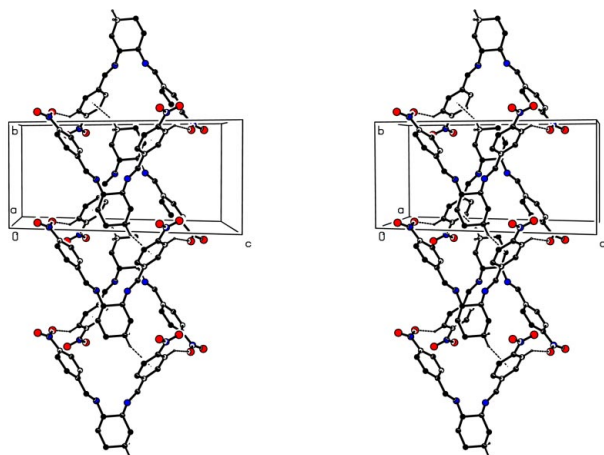
Figure 4
A stereoview of part of the crystal structure of compound (II), showing the linking of $R_2^2(32)$ dimers of type A only into an [010] chain along $(0, y, \frac{1}{2})$. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.
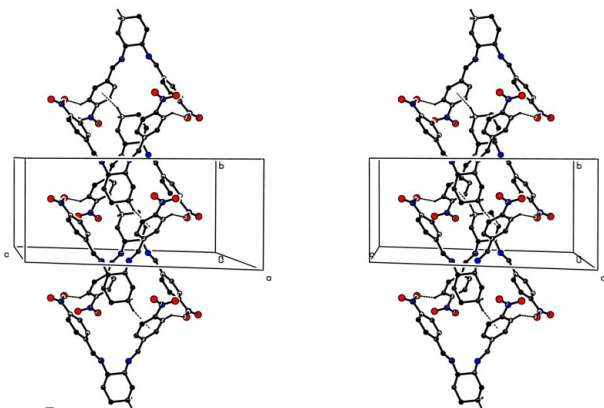

Figure 5
A stereoview of part of the crystal structure of compound (II), showing the linking of $R_2^2(32)$ dimers of type B only into an [010] chain along $(\frac{1}{2}, y, \frac{1}{2})$. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$]. However, there are no significant π–π stacking interactions.

Experimental

A mixture of racemic *trans*-cyclohexane-1,2-diamine (0.228 g, 2 mmol) and 4-nitrobenzaldehyde (0.604 g, 4 mmol) in MeOH (30 ml) was heated under reflux for 30 min. The solution was then cooled to ambient temperature and the solvent was removed. The resulting solid was recrystallized from aqueous ethanol (1:1 v/v).

Table 1
Selected torsion angles (°).

C2A—C1A—N1A—C17A	122.19 (14)	C2B—C1B—N1B—C17B	134.10 (14)
C1A—N1A—C17A—C11A	178.52 (13)	C1B—N1B—C17B—C11B	177.12 (12)
N1A—C17A—C11A—C12A	179.48 (15)	N1B—C17B—C11B—C12B	−164.89 (14)
C13A—C14A—N14A—O14A	8.0 (2)	C13B—C14B—N14B—O14B	15.7 (2)
C1A—C2A—N2A—C27A	131.08 (14)	C1B—C2B—N2B—C27B	113.68 (15)
C2A—N2A—C27A—C21A	177.00 (13)	C2B—N2B—C27B—C21B	179.59 (13)
N2A—C27A—C21A—C26A	−167.26 (14)	N2B—C27B—C21B—C26B	−175.66 (15)
C23A—C24A—N24A—O24A	3.5 (2)	C23B—C24B—N24B—O24B	11.1 (2)

Crystal data

$C_{20}H_{20}N_4O_4$	$D_x = 1.339$ Mg m^{-3}
$M_r = 380.40$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8633
$a = 22.4197$ (5) Å	reflections
$b = 8.9687$ (2) Å	$\theta = 3.1$–27.5°
$c = 21.2076$ (4) Å	$\mu = 0.10$ mm^{-1}
$\beta = 117.7179$ (11)°	$T = 120$ (2) K
$V = 3774.99$ (14) Å^3	Block, yellow
$Z = 8$	$0.40 \times 0.40 \times 0.20$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	8633 independent reflections
	6275 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.043$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SADABS*; Sheldrick, 2003)	$h = -29 \rightarrow 29$
$T_{min} = 0.968$, $T_{max} = 0.981$	$k = -10 \rightarrow 11$
43594 measured reflections	$l = -27 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 1.1744P]$
$wR(F^2) = 0.129$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
8633 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
505 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H-atom parameters constrained	

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

$Cg1$ and $Cg2$ are the centroids of rings C21A–C26A and C11B–C16B, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C22A—H22A$\cdots$O15B	0.95	2.39	3.280 (2)	157
C25A—H25A$\cdots$O15A^i	0.95	2.43	3.144 (2)	132
C13B—H13B$\cdots$O24B^{ii}	0.95	2.52	3.225 (2)	131
C27B—H27B$\cdots$O24A^{iii}	0.95	2.35	3.167 (2)	143
C4A—H41A$\cdots$Cg1^{iii}	0.99	2.65	3.596 (2)	159
C5B—H51B$\cdots$Cg2^{iii}	0.99	2.56	3.515 (2)	161

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

The space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and were then treated as riding atoms, with C—H distances of 0.95 (aromatic and –CH=), 0.99 (CH$_2$) or 1.00 Å (aliphatic CH), and with U_{iso}(H) = $1.2U_{eq}$(C).

Data collection: *COLLECT* (Hooft, 1999; Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *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: SK1864). Services for accessing these data are described at the back of the journal.

References

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

Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* E**61**, o1699–o1701.

Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.

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

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.