

Hydrogen-bonded sheets in (*E*)-2-nitrobenzaldehyde 4-nitro- phenylhydrazone and a hydrogen- bonded framework structure in (*E*)-4-nitrobenzaldehyde 4-nitro- phenylhydrazone

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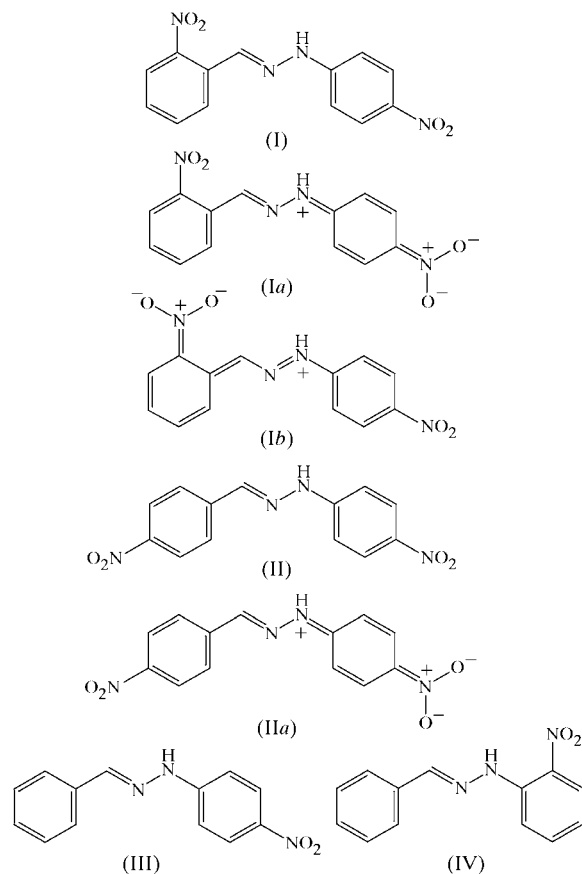
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Molecules of (*E*)-2-nitrobenzaldehyde 4-nitrophenylhydrazone, C₁₃H₁₀N₄O₄, exhibit a strongly polarized molecular-electronic structure. The molecules are linked into sheets of some complexity, where pairs of hydrogen bonds act co-operatively to generate two independent substructures, each in the form of a chain of rings. In the isomeric compound (*E*)-4-nitrobenzaldehyde 4-nitrophenylhydrazone, the molecules exhibit orientational disorder; an extensive series of hydrogen bonds links the molecules into a continuous three-dimensional framework, whose formation is independent of the disorder.

Comment

We have recently reported the molecular and supramolecular structures of the three isomeric nitrobenzaldehyde hydrazones, all of which crystallized with the *E* configuration (Glidewell *et al.*, 2004*a,b*). In 2-nitrobenzaldehyde hydrazone, the molecules are linked by paired N—H···N hydrogen bonds into isolated R₂²(6) dimers; in 3-nitrobenzaldehyde hydrazone, a combination of one N—H···N hydrogen bond and one N—H···O hydrogen bond links the molecules into a three-dimensional framework structure; and in 4-nitrobenzaldehyde hydrazone, the molecules are linked into sheets of R₄⁴(26) rings by two independent N—H···O hydrogen bonds. Intrigued by the different combinations of hydrogen bonds utilized in these simple isomers and by the different supramolecular structures that result, no two of which are even of the same dimensionality, we have now investigated an analogous and closely related series of isomers, namely the 4-nitrophenylhydrazones of the isomeric nitrobenzaldehydes. We report here on two of these, *viz.* 2-nitrobenzaldehyde 4-nitrophenylhydrazone, (I),

and 4-nitrobenzaldehyde 4-nitrophenylhydrazone, (II). Despite considerable effort, we have so far been unable to obtain any crystalline samples of 3-nitrobenzaldehyde 4-nitrophenylhydrazone that are suitable for single-crystal X-ray diffraction.



The molecules of (I) (Fig. 1) are effectively planar, as shown by the leading torsion angles (Table 1). Associated with this planarity, the bond distances point to significant electronic polarization in the 4-nitrophenyl ring. The C4—N4 bond is significantly shorter than its counterpart in the 2-nitrophenyl ring, C12—N12, and the C4—N4 bond is, in fact, short for its type, the mean value being 1.468 Å (Allen *et al.*, 1987). Similarly, the N—O bonds at atom N4 are significantly longer than those at atom N12. In addition, there is marked bond fixation in the C1—C6 ring, where the C2—C3 and C5—C6

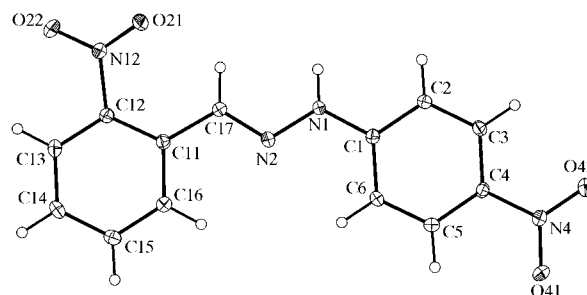


Figure 1
 The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

bonds are significantly shorter than the remaining C—C bonds. These observations taken together point to the polarized form (Ia) as a significant contributor to the overall molecular–electronic structure. However, the C12—N12 and C17—N2 distances, together with the strong bond fixation in the central spacer unit, effectively rule out any significant contribution from form (Ib). This deduction is also supported by the C—C distances in the C11—C16 ring, where C13—C14 is the shortest bond, although in representation (Ib) this would be a single bond.

The molecules of (II) (Fig. 2), including the nitro groups, are effectively planar (Table 3). Possibly because of this, each

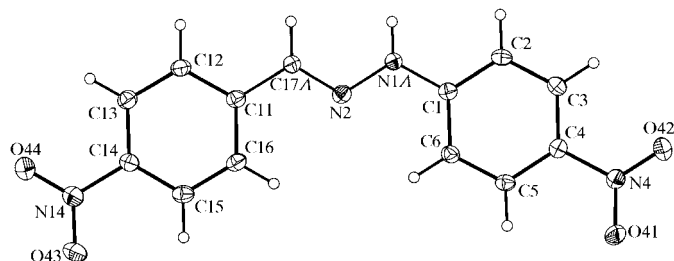


Figure 2

The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. In the alternative molecular orientation, atoms N1B and C17B take the place of atoms C17A and N1A, respectively (see *Comment*).

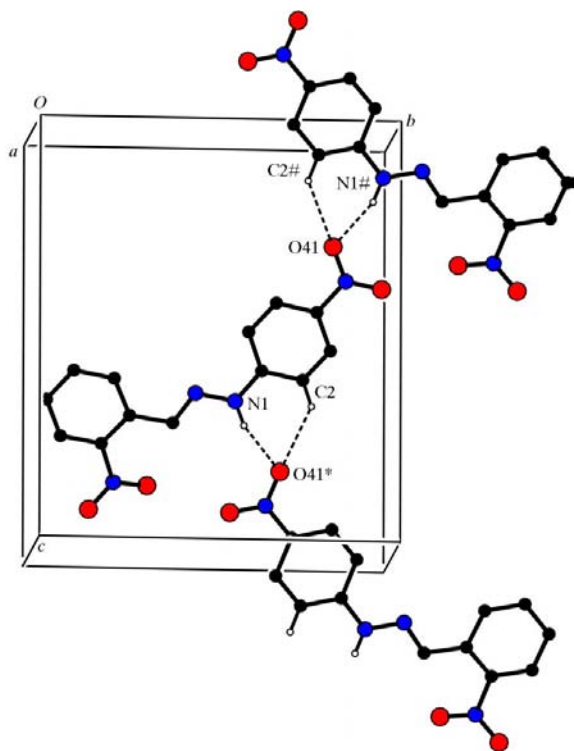


Figure 3

Part of the crystal structure of (I), showing the formation of a [101] chain of rings generated by the *n*-glide plane at $y = \frac{3}{4}$. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, respectively.

molecule can adopt two distinct orientations within the same physical space, which corresponds to a disorder in the occupancy of the two outer sites in the central three-atom spacer unit. The refinement showed that each of these sites was occupied by $(0.5C + 0.5N)$ atoms; in one orientation, the atoms concerned are denoted C17A and N1A (*cf.* Fig. 2), and in the other, they are denoted N1B and C17B. Hence atoms N1A and C17B are alternative occupants of one of these sites, while atoms N1B and C17A are the alternative occupants of the

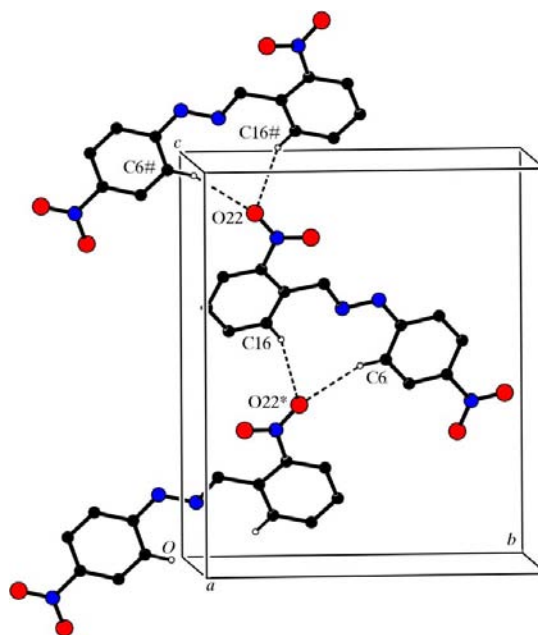


Figure 4

Part of the crystal structure of (I), showing the formation of a [101] chain of rings generated by the *n*-glide plane at $y = \frac{1}{4}$. For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively.

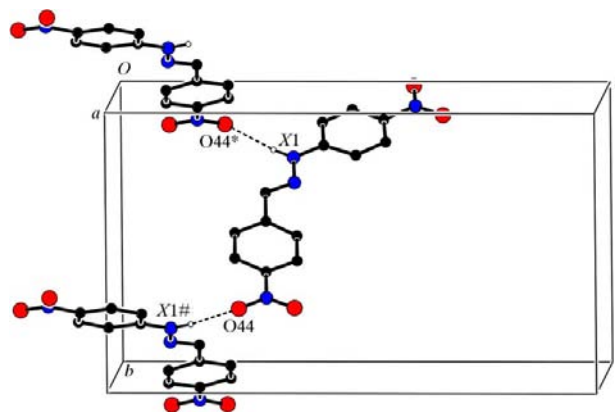


Figure 5

Part of the crystal structure of (II), showing the formation of a hydrogen-bonded chain along [010]. The atom site denoted X1 is occupied by $(0.5C + 0.5N)$ atoms (see *Comment*). For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

other site. Detailed analysis of the molecular geometry in (II) is, of course, complicated by the orientational disorder. Nonetheless, the pattern of the C—C bond distances in the aryl rings coupled with the dimensions of the nitro groups provides evidence for some contribution from the polarized form (IIa).

Molecules of (I) are linked into sheets by a combination of N—H···O and C—H···O hydrogen bonds (Table 2), which act in pairs to form two distinct one-dimensional substructures. Atoms N1 and C2 in the molecule at (x, y, z) both act as donors to atom O41 in the molecule at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, so forming a $C(6)C(6)[R_2^1(6)]$ (Bernstein *et al.*, 1995) chain of rings running parallel to the $[101]$ direction and generated by the n -glide plane at $y = \frac{3}{4}$ (Fig. 3). Similarly, atoms C6 and C16 at (x, y, z) both act as donors, albeit rather weakly, to atom O22 in the molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, so forming a second $[101]$ chain, this time of $C(9)C(10)[R_2^1(10)]$ type, generated by the n -glide plane at $y = \frac{1}{4}$ (Fig. 4). The combined action of the two types of $[101]$ chain generates a $(10\bar{1})$ sheet. Two sheets of this type, related to one another by inversion, pass through each unit cell, but there are no significant direction-specific interactions between adjacent sheets.

The molecules of (II) are linked by an extensive series of hydrogen bonds (Table 4), and the pattern of intermolecular aggregation is independent of the molecular orientation at any particular site. Atoms N1A and C17B in the molecule at (x, y, z) , which are alternative occupants of the same site, both act as hydrogen-bond donors to atom O44 in the molecule at $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, and propagation of these interactions produces a chain running parallel to the $[010]$ direction and generated

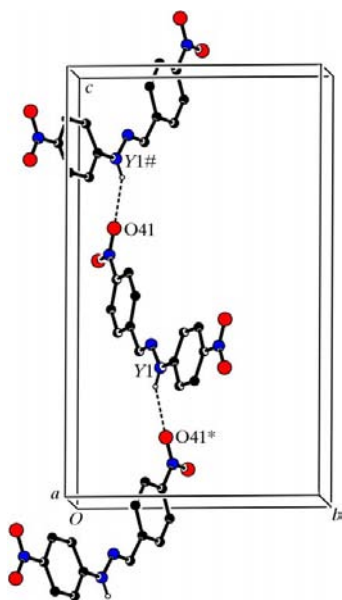


Figure 6

Part of the crystal structure of (II), showing the formation of a hydrogen-bonded chain along $[101]$. The atom site denoted Y1 is occupied by $(0.5C + 0.5N)$ atoms (see *Comment*). For clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively.

by the 2_1 screw axis along $(\frac{3}{4}, y, \frac{1}{4})$ (Fig. 5). If all the donor sites within this chain were of the same atomic type, the chain would be of $C(10)$ type; on the other hand, if the site-occupancies occur at random within each chain, as seems probable, no periodically repeating motif can be defined.

In a similar manner, atoms N1B and C17A in the molecule at (x, y, z) both act as hydrogen-bond donors to atom O41 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, so producing a chain running parallel to the $[10\bar{1}]$ direction and generated by the n -glide plane at $y = \frac{1}{4}$ (Fig. 6). Again, this chain would be of $C(10)$ type if all donor sites were of the same type. The combination of the $[010]$ and $[10\bar{1}]$ chains then generates a (101) sheet, and adjacent sheets are linked by a third hydrogen-bond motif in which a chain of centrosymmetric rings is formed by two further C—H···O hydrogen bonds.

Atoms C3 and C6 in the molecule at (x, y, z) act as donors, respectively, to atoms O42 and O43 in the molecules at $(-1 - x, -y, 1 - z)$ and $(2 - x, 1 - y, 1 - z)$, so generating a chain of alternating $R_2^2(10)$ and $R_2^2(24)$ rings running parallel to the $[310]$ direction, in which both types of ring are centrosymmetric (Fig. 7). The combination of (101) sheets and $[310]$ chains generates a continuous three-dimensional framework. Despite the effective planarity of the molecules, intermolecular π – π stacking interactions are absent.

It is of interest to compare the structures reported here with those of the analogous compounds benzaldehyde 4-nitrophenylhydrazone, (III) (Vickery *et al.*, 1985), and benzaldehyde 2-nitrophenylhydrazone, (IV) (Drew *et al.*, 1984). In (III), the molecules are linked by one N—H···O hydrogen bond and one C—H···O hydrogen bond into $C(6)C(8)[R_2^2(8)]$ chains of rings, while in (IV), pairs of N—H···O hydrogen bonds generate isolated $R_2^2(4)$ dimers. Thus, no two of the compounds discussed here, whether nitrobenzaldehyde hydrazones, nitrobenzaldehyde nitrophenylhydrazones or benzaldehyde nitrophenylhydrazones, show similar patterns of supramolecular aggregation.

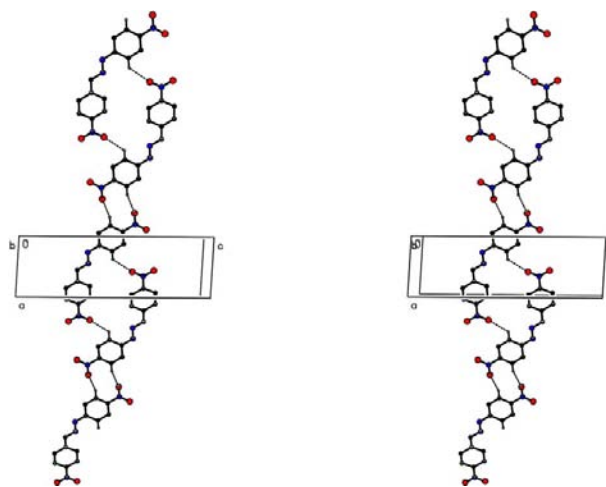


Figure 7

A stereoview of part of the crystal structure of (II), showing the formation of a $[310]$ chain of alternating $R_2^2(10)$ and $R_2^2(24)$ rings. For clarity, H atoms not involved in the motifs shown have been omitted.

Experimental

Equimolar quantities of 4-nitrophenylhydrazine and the appropriate nitrobenzaldehyde were ground finely, and then the mixtures were heated on an electric hotplate, in the absence of solvent, until the evolution of water had ceased. After cooling, the solid residues were dissolved in ethanol. The resulting solutions were filtered and then evaporated slowly to yield crystals of (I) and (II) suitable for single-crystal X-ray diffraction.

Compound (I)

Crystal data

$C_{13}H_{10}N_4O_4$
 $M_r = 286.25$
 Monoclinic, $P2_1/n$
 $a = 7.1134$ (2) Å
 $b = 12.0842$ (5) Å
 $c = 14.3190$ (6) Å
 $\beta = 92.624$ (2)°
 $V = 1229.57$ (8) Å³
 $Z = 4$

$D_x = 1.546$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2798 reflections
 $\theta = 3.1$ – 27.5 °
 $\mu = 0.12$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 $0.36 \times 0.12 \times 0.11$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.951$, $T_{\max} = 0.987$
 16 111 measured reflections
 2798 independent reflections

2244 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\max} = 27.5$ °
 $h = -9 \rightarrow 9$
 $k = -15 \rightarrow 15$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.112$
 $S = 1.02$
 2798 reflections
 190 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 0.2415P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.18$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

C1–C2	1.4062 (18)	C12–C13	1.3877 (18)
C2–C3	1.3737 (18)	C13–C14	1.3775 (19)
C3–C4	1.3929 (18)	C14–C15	1.393 (2)
C4–C5	1.3895 (18)	C15–C16	1.3787 (19)
C5–C6	1.3716 (19)	C16–C11	1.4027 (18)
C4–N4	1.4334 (16)	C12–N12	1.4716 (16)
N4–O41	1.2453 (14)	N12–O21	1.2248 (15)
N4–O42	1.2290 (14)	N12–O22	1.2268 (15)
C1–N1	1.3694 (16)	C11–C17	1.4669 (18)
N1–N2	1.3550 (15)	C17–N2	1.2834 (17)
C11–C12	1.4051 (18)		
C1–N1–N2–C17	177.91 (12)	N1–N2–C17–C11	179.60 (11)
N2–N1–C1–C2	–176.85 (11)	N2–C17–C11–C12	174.12 (12)
C3–C4–N4–O41	177.11 (11)	C13–C12–N12–O21	154.42 (12)

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 ⁱ ···O41 ⁱ	0.88	2.05	2.8871 (14)	160
C2–H2 ⁱ ···O41 ⁱ	0.95	2.56	3.3201 (16)	137
C6–H6 ⁱ ···O22 ⁱⁱ	0.95	2.55	3.4644 (17)	160
C16–H16 ⁱ ···O22 ⁱⁱ	0.95	2.60	3.4746 (17)	154

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

Compound (II)

Crystal data

$C_{13}H_{10}N_4O_4$
 $M_r = 286.25$
 Monoclinic, $P2_1/n$
 $a = 5.9635$ (2) Å
 $b = 11.0881$ (6) Å
 $c = 18.9959$ (10) Å
 $\beta = 93.048$ (3)°
 $V = 1254.31$ (10) Å³
 $Z = 4$

$D_x = 1.516$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2870 reflections
 $\theta = 3.5$ – 27.5 °
 $\mu = 0.12$ mm⁻¹
 $T = 120$ (2) K
 Plate, orange
 $0.30 \times 0.16 \times 0.08$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.956$, $T_{\max} = 0.991$
 17 468 measured reflections
 2870 independent reflections

1643 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.078$
 $\theta_{\max} = 27.5$ °
 $h = -7 \rightarrow 7$
 $k = -14 \rightarrow 14$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.137$
 $S = 0.96$
 2870 reflections
 190 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0735P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³
 Extinction correction: SHELXL
 Extinction coefficient: 0.013 (2)

Table 3

Selected geometric parameters (Å, °) for (II).

C1–C2	1.399 (3)	C11–C12	1.400 (3)
C2–C3	1.376 (3)	C12–C13	1.377 (3)
C3–C4	1.385 (3)	C13–C14	1.386 (3)
C4–C5	1.386 (3)	C14–C15	1.383 (3)
C5–C6	1.375 (3)	C15–C16	1.374 (3)
C6–C1	1.399 (3)	C16–C11	1.398 (3)
C4–N4	1.451 (3)	C14–N14	1.450 (3)
N4–O41	1.236 (2)	N14–O43	1.230 (2)
N4–O42	1.224 (2)	N14–O44	1.233 (2)
C1–N1A	1.3690 (10)	C1–C17B	1.4670 (10)
N1A–N2	1.3561 (10)	C17B–N2	1.2831 (10)
N2–C17A	1.2835 (10)	N2–N1B	1.3557 (10)
C17A–C11	1.4678 (10)	N1B–C11	1.3690 (10)
C1–N1A–N2–C17A	178.8 (6)	C1–C17B–N2–N1B	–178.2 (5)
N1A–N2–C17A–C11	176.4 (5)	C17B–N2–N1B–C11	178.8 (6)
N2–N1A–C1–C2	172.2 (4)	N2–C17B–C1–C2	178.2 (5)
N2–C17A–C11–C12	–179.6 (4)	N2–N1B–C11–C12	171.6 (3)
C3–C4–N4–O41	179.33 (17)	C13–C14–N14–O43	–174.94 (18)

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1A–H1A ⁱ ···O44 ⁱ	0.88	2.28	3.151 (2)	173
C17B–H17B ⁱ ···O44 ⁱ	0.95	2.23	3.145 (3)	162
N1B–H1B ⁱⁱ ···O41 ⁱⁱ	0.88	2.30	3.108 (3)	154
C17A–H17A ⁱⁱⁱ ···O41 ⁱⁱⁱ	0.95	2.38	3.157 (4)	139
C3–H3 ^{iv} ···O42 ⁱⁱⁱ	0.95	2.47	3.378 (3)	160
C6–H6 ^{iv} ···O43 ^{iv}	0.95	2.49	3.200 (2)	132

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

For both (I) and (II), space group $P2_1/n$ was uniquely assigned from the systematic absences. It was apparent from an early stage in

the refinement of (II) that the acyclic spacer unit showed disorder. This disorder was modelled by assigning the central atom as N, with the two outer atom sites in this unit occupied overall by one C atom and one N atom, but with each atom type distributed between the two sites. Under these conditions, the site occupancies for each atom type refined to 0.50 (3) and hence they were fixed at 0.50, equivalent to equal occupancies of two alternative orientations of the entire molecule. Thereafter, with independent isotropic displacement parameters for the partial C and N atoms, the refinement proceeded smoothly and satisfactorily. For both (I) and (II), the H atoms were all located from difference maps, and then treated as riding atoms, with C—H distances of 0.95 Å, N—H distances of 0.88 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C,N})$.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; 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).

X-ray data for (I) and (II) were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants

which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1791). Services for accessing these data are described at the back of the journal.

References

- 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.* **A51**, 33–37.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Drew, M. G. B., Vickery, B. & Willey, G. R. (1984). *Acta Cryst.* **C40**, 304–306.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2004a). *Acta Cryst.* **C60**, o33–o34.
- Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2004b). *Acta Cryst.* **C60**, o686–o689.
- 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.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Vickery, B., Willey, G. R. & Drew, M. G. B. (1985). *Acta Cryst.* **C41**, 1072–1075.