Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Three isomeric (*E*)-nitrobenzaldehyde nitrophenylhydrazones: chains of rings in isomorphous (*E*)-2-nitrobenzaldehyde 3-nitrophenylhydrazone and (*E*)-3-nitrobenzaldehyde 2-nitrophenylhydrazone, and centrosymmetric dimers in (*E*)-4-nitrobenzaldehyde 2-nitrophenylhydrazone

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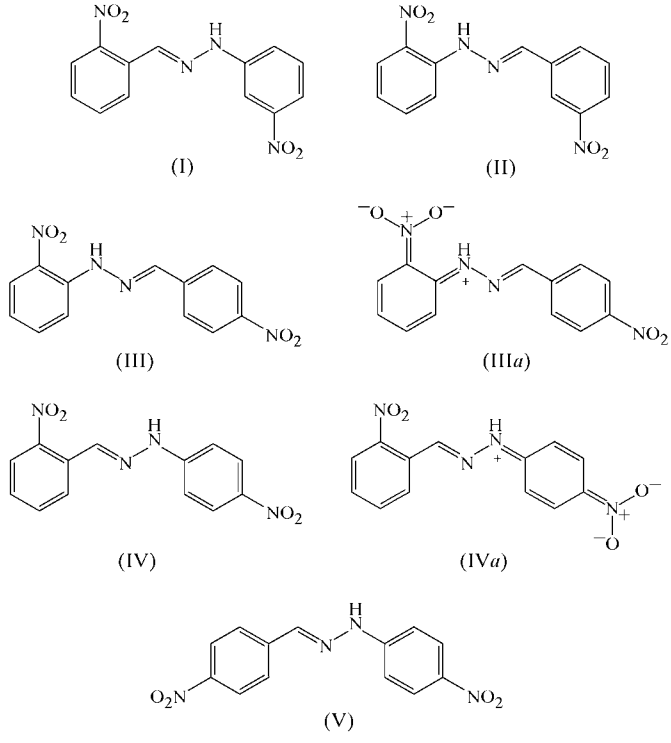
Received 8 September 2005
Accepted 12 September 2005
Online 30 September 2005

The isomeric compounds (*E*)-2-nitrobenzaldehyde 3-nitrophenylhydrazone and (*E*)-3-nitrobenzaldehyde 2-nitrophenylhydrazone, both $C_{13}H_{10}N_4O_4$, are isomorphous and effectively isostructural, and in both, the molecules are disordered across centres of inversion in the space group $P2_1/c$. The molecules are linked into complex chains of rings by N—H···O and C—H···O hydrogen bonds. In the isomeric compound (*E*)-4-nitrobenzaldehyde 2-nitrophenylhydrazone, the fully ordered molecules are linked by N—H···O hydrogen bonds into centrosymmetric dimers.

Comment

As part of our continuing studies of the supramolecular arrangements in imines and hydrazones, we report here the structures of three isomeric nitrobenzaldehyde nitrophenyl hydrazones, (I)–(III), which we compare briefly with two further isomers, (IV) and (V) (see scheme) (Shan *et al.*, 2004; Wardell *et al.*, 2005).

In isomers (I) and (II) (Figs. 1 and 2), the molecules are disordered over two sets of sites related by a centre of inversion, selected for the sake of convenience as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The asymmetric units for (I) and (II) were selected so that the coordinates of the atoms in the nitro groups were approximately the same. This then led to close correspondence between the coordinates for atoms C11–C16 in (I) with those for atoms C16/C11–C15, respectively, in (II). Likewise, the coordinates for atoms N1, N2 and C27 in the reference asymmetric unit at (x, y, z) in (I) closely correspond to those in (II) for atoms C27, N2 and N1, respectively, at $(1 - x, 1 - y, 1 - z)$. The unit-cell dimensions indicate that (I) and (II) are isomorphous, and the atom coordinates indicate that these compounds are effectively isostructural, but with atoms N1 and C27 interchanged between (I) and (II) (Figs. 1 and 2). By contrast, all atoms in isomer (III) (Fig. 3) are fully ordered in general positions. While all of the atoms in isomer (IV) are fully ordered, in isomer (V) the NH and CH sites in the central bridge are randomly scrambled, with the two heavy-atom sites each occupied by (0.5C + 0.5N) (Wardell *et al.*, 2005).



In each of isomers (I)–(III), the molecules are essentially planar, and all have the *E* configuration at the C═N double bond. In (III), the bond distances (Table 3) show strong evidence for the development of the polarized quinonoid form, (III*a*). In particular, with the C11–C16 aryl ring, the C13—C14 and C15—C16 distances are significantly shorter than the remaining distances, the C11—C12 distance is the longest and the C12—N12 distance is short for its type, while the N12—O21 and N12—O22 distances are both long (Allen *et al.*, 1987). By contrast, the C21–C26 aryl ring shows no evidence for the development of a quinonoid form. The structure of the isomer (IV), which differs from (III) by the notional reversal of the spacer fragment, has been determined both at 295 K (Shan *et al.*, 2004) and at 120 K (Wardell *et al.*, 2005). The same phase is present at both temperatures and both structures show evidence for the development of the polarized form, (IV*a*), although this was not remarked upon by Shan *et al.* (2004).

In each of (I) and (II), there is a short intramolecular *X*—H···O contact (Tables 1 and 2), where *X* is atom C27 in (I)

 DOI: 10.1107/S0108270105028799

and atom N1 in (II). We first discuss the intermolecular hydrogen bonds on the assumption of local ordering and then consider the consequences of the disorder across inversion centres. In (I), the molecules are linked by the concerted action of three hydrogen bonds (Table 1): atoms N1 and C27 in the molecule at (x, y, z) both act as hydrogen-bond donors to atom O31 in the molecule at $(1 + x, -1 + y, z)$, while atom C16 at (x, y, z) similarly acts as donor to atom O32, also at $(1 + x, -1 + y, z)$. Hence, this multi-point interaction generates by translation a complex chain of rings running parallel to the $[1\bar{1}0]$ direction (Fig. 1). An entirely similar chain of rings is formed in compound (II), where atoms N1 and C27 at (x, y, z) act as donors to atom O21 at $(-x, 2 - y, 1 - z)$, while atom C15 acts as donor to atom O22 at $(1 + x, -1 + y, z)$ (Fig. 2). In each isomer, therefore, a given molecule will form four hydrogen bonds with each of its neighbours within the $[1\bar{1}0]$ chain, provided only that there is local ordering within the chain in question. The multi-point recognition makes it appear probable that, within a given chain, the molecules are, in fact, ordered in this manner. Two chains of this type pass through each unit cell in (I) and (II), but there are no direction-specific interactions between adjacent chains. Accordingly, there is no necessity for the orientation of molecules in adjacent chains to show any correlation.

The supramolecular structure of (III), by contrast, is extremely simple. In addition to forming an intramolecular hydrogen bond (Table 4) which gives rise to an $S(6)$ ring, amino atom N1 in the molecule at (x, y, z) acts as hydrogen-bond donor to nitro atom O21 in the molecule at $(1 - x, 1 - y, 1 - z)$, so forming a centrosymmetric dimer containing an $S(6)R_2^2(4)S(6)$ motif (Fig. 4). There are no direction-specific interactions between adjacent dimers. In particular, C—

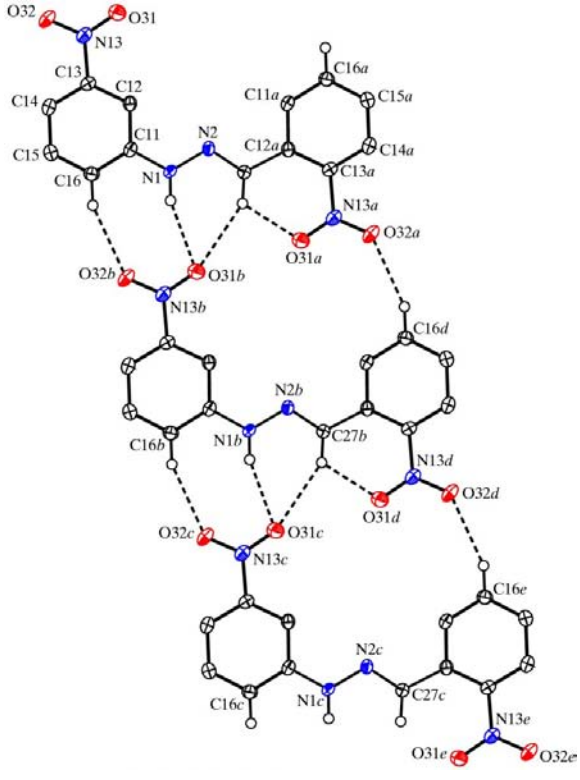


Figure 1
Part of the crystal structure of isomer (I), showing the atom-labelling scheme and the formation of an ordered chain of rings along $[1\bar{1}0]$. Displacement ellipsoids are drawn at the 30% probability level. Atoms N1, N2 and C27 and their pendent H atoms have 0.5 occupancy, as do the H atoms bonded to atoms C11 and C16. Atoms marked with the suffixes *a*–*e* are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(1 + x, -1 + y, z)$, $(2 + x, -2 + y, z)$, $(2 - x, -y, 1 - z)$ and $(3 - x, -1 - y, 1 - z)$, respectively. For the sake of clarity, H atoms not involved in the motifs shown have been omitted, as has the unit-cell outline.

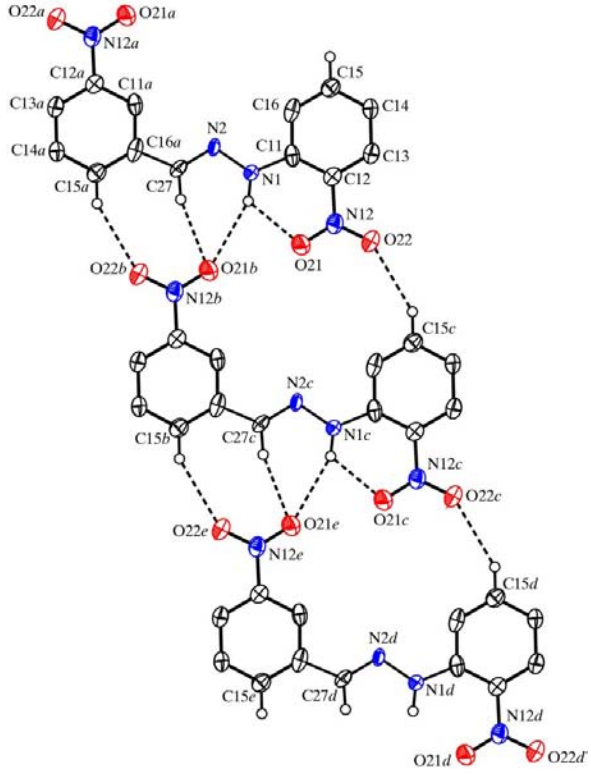


Figure 2
Part of the crystal structure of isomer (II), showing the atom-labelling scheme and the formation of an ordered chain of rings along $[1\bar{1}0]$. Displacement ellipsoids are drawn at the 30% probability level. Atoms N1, N2 and C27 and their pendent H atoms have 0.5 occupancy, as do the H atoms bonded to atoms C11 and C12. Atoms marked with the suffixes *a*–*e* are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(-x, 2 - y, 1 - z)$, $(-1 + x, 1 + y, z)$, $(-1 - x, 3 - y, 1 - z)$ and $(-2 + x, 2 + y, z)$, respectively. For the sake of clarity, H atoms not involved in the motifs shown have been omitted, as has the unit-cell outline.

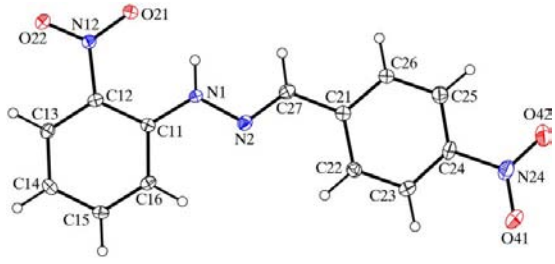


Figure 3
The molecule of isomer (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

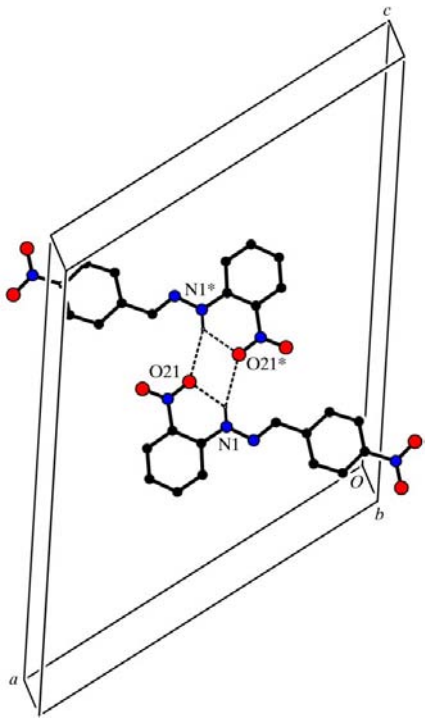


Figure 4
Part of the crystal structure of isomer (III), showing the formation of a centrosymmetric dimer. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

H···π(arene) hydrogen bonds and aromatic π–π stacking interactions are both absent. The supramolecular structure of (III) thus consists of isolated dimers.

In isomer (IV), the close analogue of (III), the molecules are linked into complex sheets by a combination of one N—H···O hydrogen bond and three independent C—H···O hydrogen bonds (Wardell *et al.*, 2005). In the earlier report on this compound (Shan *et al.*, 2004), the C—H···O hydrogen bonds were all overlooked; instead, those authors suggested the occurrence of π–π stacking interactions, but such interactions are, in fact, absent (Wardell *et al.*, 2005). In the disordered isomer, (V), an extensive series of N—H···O and C—H···O hydrogen bonds generates a three-dimensional framework structure, the formation of which is independent of the disorder (Wardell *et al.*, 2005).

Experimental

Isomer (I) was obtained by the reaction of equimolar quantities (2 mmol) of 2-nitrobenzaldehyde and 3-nitrophenylhydrazine hydrochloride in MeOH (20 ml). The reaction mixture was heated under reflux for 30 min and, after cooling, the solvent was removed under reduced pressure. The solid residue was recrystallized from methanol–1,2-dichloroethane (1:1 *v*/*v*). IR: 3295, 1616, 1573, 1566 cm^{-1}. Isomers (II) and (III) were obtained from the reactions of equimolar quantities (2 mmol) of 2-nitrophenylhydrazine and the appropriate nitrobenzaldehyde in MeOH (20 ml). The reaction mixtures were heated under reflux for 30 min and, after cooling, the solvents were removed under reduced pressure. Compounds (II) and (III) were obtained on recrystallization of the appropriate reaction residue from ethyl acetate. IR: for (II), 3299, 1615, 1573, 1545 cm^{-1}; for (III), 3286, 1619, 1595, 1569 cm^{-1}. Crystals of (II) were very fragile, and attempts to cut small fragments from larger crystals consistently resulted in shattering.

Isomer (I)

Crystal data

$C_{13}H_{10}N_4O_4$
M_r = 286.25
Monoclinic, $P2_1/c$
a = 5.9845 (2) Å
b = 5.5962 (2) Å
c = 19.1168 (6) Å
β = 104.558 (2)°
V = 619.67 (4) Å^3
Z = 2
D_x = 1.534 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1415 reflections
θ = 4.3–27.5°
μ = 0.12 mm^{-1}
T = 120 (2) K
Block, orange
0.60 × 0.25 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.942, T_{max} = 0.988
8294 measured reflections
1415 independent reflections
1286 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 27.5°
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -23 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.149
S = 1.07
1415 reflections
111 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 1.7995P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.089 (12)

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O31^{i}	0.88	2.29	3.133 (5)	161
C16—H16···O32^{i}	0.95	2.42	3.318 (3)	158
C27—H27···O31^{i}	0.95	2.49	3.335 (5)	149
C27—H27···O31^{ii}	0.95	2.13	2.698 (5)	117

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

Isomer (II)

Crystal data

$C_{13}H_{10}N_4O_4$
M_r = 286.25
Monoclinic, $P2_1/c$
a = 6.2280 (7) Å
b = 5.3947 (10) Å
c = 19.249 (4) Å
β = 106.847 (11)°
V = 618.98 (19) Å^3
Z = 2
D_x = 1.536 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1415 reflections
θ = 3.5–27.6°
μ = 0.12 mm^{-1}
T = 120 (2) K
Plate, red
0.62 × 0.12 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.947, T_{max} = 0.997
5521 measured reflections
1415 independent reflections
744 reflections with $I > 2\sigma(I)$
R_{int} = 0.077
θ_{max} = 27.6°
$h = -8 \rightarrow 7$
$k = -7 \rightarrow 6$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0905P)^2 + 0.3625P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.068$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.208$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.30$ e Å^{-3}
1415 reflections	
109 parameters	
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O21	0.88	2.11	2.696 (6)	123
N1—H1···O21^{i}	0.88	2.46	3.282 (6)	156
C15—H15···O22^{ii}	0.95	2.52	3.379 (4)	151
C27—H27···O21^{i}	0.95	2.35	3.268 (7)	163

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

Isomer (III)

Crystal data

$C_{13}H_{10}N_4O_4$	$D_x = 1.565$ Mg m^{-3}
$M_r = 286.25$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2795 reflections
$a = 17.9563$ (16) Å	$\theta = 3.9$–$27.7°$
$b = 3.7160$ (2) Å	$\mu = 0.12$ mm^{-1}
$c = 22.0624$ (17) Å	$T = 120$ (2) K
$\beta = 124.406$ (5)°	Plate, orange
$V = 1214.58$ (16) Å^3	0.36 × 0.34 × 0.02 mm
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	2795 independent reflections
	1794 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.077$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 27.7°$
	$h = -22 \rightarrow 23$
$T_{min} = 0.964$, $T_{max} = 0.998$	$k = -4 \rightarrow 4$
20354 measured reflections	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 1.5262P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.069$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.170$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -0.31$ e Å^{-3}
2795 reflections	
190 parameters	
H-atom parameters constrained	

Table 3
Selected bond lengths (Å) for (III).

C11—C12	1.421 (4)	C21—C22	1.405 (4)
C12—C13	1.395 (4)	C22—C23	1.380 (4)
C13—C14	1.368 (4)	C23—C24	1.386 (4)
C14—C15	1.392 (4)	C24—C25	1.375 (4)
C15—C16	1.370 (4)	C25—C26	1.388 (4)
C16—C11	1.410 (4)	C26—C21	1.397 (4)
C12—N12	1.437 (3)	C24—N24	1.470 (4)
N12—O21	1.250 (3)	N24—O41	1.219 (3)
N12—O22	1.231 (3)	N24—O42	1.232 (3)

Table 4
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O21	0.88	1.97	2.609 (3)	128
N1—H1···O21^{i}	0.88	2.54	3.364 (3)	157

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

For each compound, the space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and subsequently treated as riding atoms, with distances C—H = 0.95 Å and N—H = 0.88 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N). It became apparent at an early stage that in each of (I) and (II) the molecules were disordered over two sets of sites related by a centre of inversion, selected in each case as that at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). Each isomer was then modelled using a single aryl ring with a single nitro substituent, all having unit occupancy, and an acyclic fragment –CH═N—NH– having 0.5 occupancy. The atom-labelling schemes (Figs. 1 and 2) were such that atom N1 was bonded to atom C11, and the aryl ring was numbered to provide the lowest locant for the nitro group. The H-atom sites bonded to atoms C11 and C12 also have 0.5 occupancy.

For the three title isomers, data collection: *COLLECT* (Nonius, 1999); 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).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton; the authors thank the staff for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1867). Services for accessing these data are described at the back of the journal.

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