Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen-bonded dimers in 2-nitrobenzaldehyde hydrazone and a three-dimensional hydrogen-bonded framework in 3-nitrobenzaldehyde hydrazone

Christopher Glidewell,[a]* John N. Low,[b] Janet M. S. Skakle[b] and James L. Wardell[c]

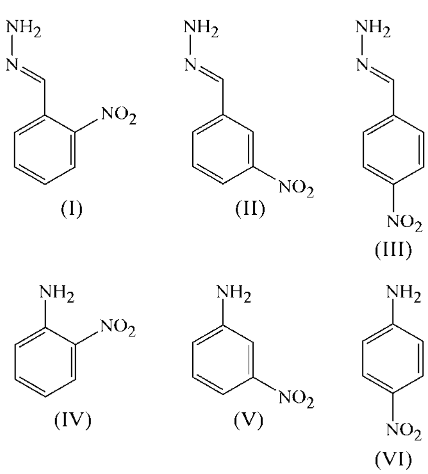
[a]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: cg@st-andrews.ac.uk

Received 13 July 2004
Accepted 26 July 2004
Online 21 August 2004

Molecules of 2-nitrobenzaldehyde hydrazone, $C_7H_7N_3O_2$, where $Z' = 2$, are linked by two N—H···N hydrogen bonds into isolated dimers, whereas in the isomeric 3-nitrobenzaldehyde hydrazone, where $Z' = 1$, the molecules are linked by one N—H···O hydrogen bond and one N—H···N hydrogen bond into a three-dimensional framework structure.

Comment

We report here the structures of the isomeric title compounds, 2-nitrobenzaldehyde hydrazone, (I) (Fig. 1), and 3-nitrobenzaldehyde hydrazone, (II) (Fig. 2), and compare their supramolecular structures with that of the further isomer 4-nitrobenzaldehyde hydrazone, (III), which was reported recently (Glidewell *et al.*, 2004).



All three isomers crystallize in non-centrosymmetric space groups with unit cells having short *a* dimensions [in (III), *a* = 3.7070 (2) Å in space group *Pc*], and in all three isomers the molecules are essentially planar, with the *E* configuration at the C═N double bond. The bond lengths and angles are all normal for their types (Allen *et al.*, 1987). However, the patterns of the intermolecular hydrogen bonds are all different, with N—H···N hydrogen bonds in (I), N—H···O hydrogen bonds in (III), and both N—H···N and N—H···O hydrogen bonds in (II). Moreover, the dimensionality of the resulting supramolecular structures is different for all three isomers, being finite (zero-dimensional) in (I), three-dimensional in (II) and two-dimensional in (III).

In compound (I), the molecules are linked by two independent N—H···N hydrogen bonds (Table 1) to form an $R_2^2(6)$ (Bernstein *et al.*, 1995) dimer (Fig. 1). The marked differences in the dimensions of the two hydrogen bonds are

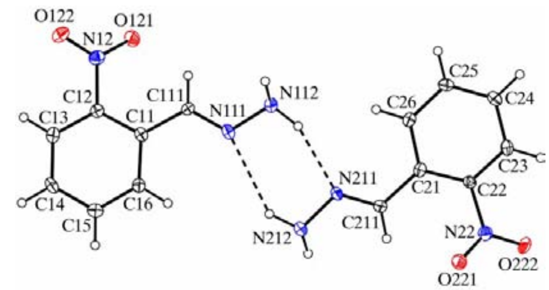


Figure 1
The two independent molecules of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

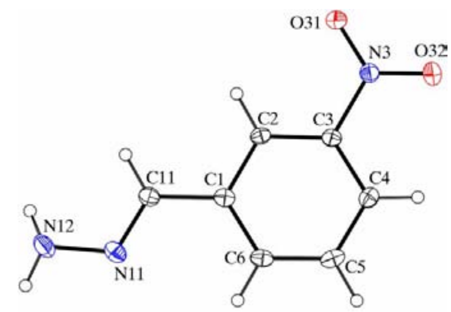


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

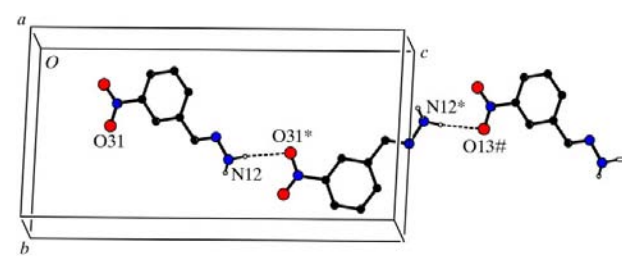


Figure 3
Part of the crystal structure of (II), showing the formation of a *C*(9) chain along [001]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$) and ($x, y, 1 + z$), respectively.

 DOI: 10.1107/S0108270104018323 *Acta Cryst.* (2004). C**60**, o686–o689

sufficient to preclude the possibility of any additional symmetry. There are four of these dimeric units in each unit cell, but there are no direction-specific interactions between these units. In view of the excess of potential hydrogen-bond acceptors in this system, in the form of the nitro-group O atoms, the non-participation in the hydrogen bonding of half of the N—H bonds is unexpected.

The molecules of compound (II) (Fig. 2) are linked by two hydrogen bonds, one each of the N—H···O and N—H···N types (Table 2), into a three-dimensional framework structure, the formation of which is most readily analysed in terms of three distinct one-dimensional substructures. Two of these substructures each utilize just one of the hydrogen bonds, whereas the third utilizes both hydrogen bonds. In the first of the substructures utilizing only one hydrogen bond, atom N12 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H12A, to nitro atom O31 in the molecule at ($\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$), so forming a $C(9)$ chain running parallel to the [001] direction and generated by the 2_1 screw axis along ($\frac{1}{4}$, $\frac{1}{2}$, z) (Fig. 3). In the second substructure of this type, atom N12 at (x, y, z) acts as hydrogen-bond donor, *via* atom H12B, to atom N12 in the molecule at ($x - \frac{1}{2}$, $\frac{3}{2} - y$, $1 - z$), so forming a $C(2)$ chain parallel to the [100] direction and generated by the 2_1 screw axis along (x, $\frac{3}{4}$, $\frac{1}{2}$) (Fig. 4).

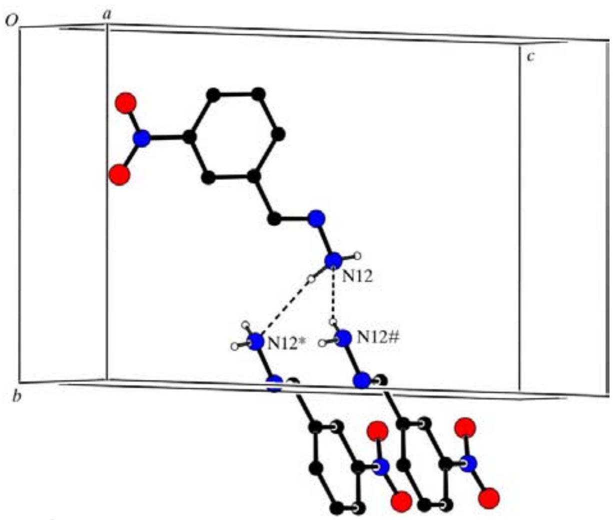


Figure 4
Part of the crystal structure of (II), showing the formation of a $C(2)$ chain along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($x - \frac{1}{2}$, $\frac{3}{2} - y$, $1 - z$) and ($\frac{1}{2} + x$, $\frac{3}{2} - y$, $1 - z$), respectively.

The third one-dimensional substructure in (II) contains alternating N—H···O and N—H···N hydrogen bonds. Atom N12 in the molecule at ($\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$) acts as donor, *via* atom H12B, to atom N12 in the molecule at ($1 - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$), and atom N12 in this molecule acts as donor, *via* atom H12A, to nitro atom O31 in the molecule at ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$). Finally, atom N12 at ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$) acts as donor, *via* atom H12B, to atom N12 in the molecule at (x, $y - 1$, z). This combination of the two hydrogen bonds thus generates a $C_2^2(11)$ chain running parallel to the [010] direction (Fig. 5).

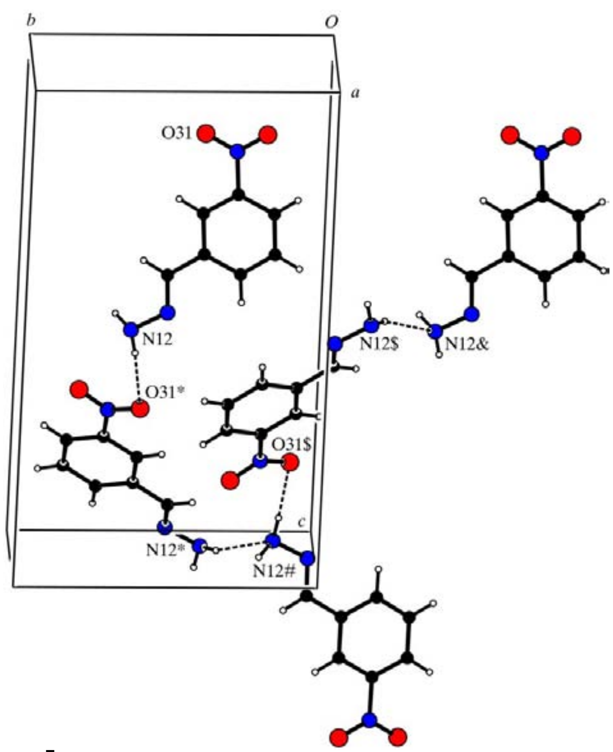


Figure 5
Part of the crystal structure of (II), showing the formation of a $C_2^2(11)$ chain along [010]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($) or an ampersand (&) are at the symmetry positions ($\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$), ($1 - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$), ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$) and (x, $y - 1$, z), respectively.

The pairwise combination of these one-dimensional substructures generates two-dimensional substructures. For example, the combination of the [010] and [001] chains generates a (100) sheet (Fig. 6) in the form of a (6,3)-net (Batten & Robson, 1998) built from a single type of $R_6^6(40)$ ring, and the formation of this net in (II) may be contrasted

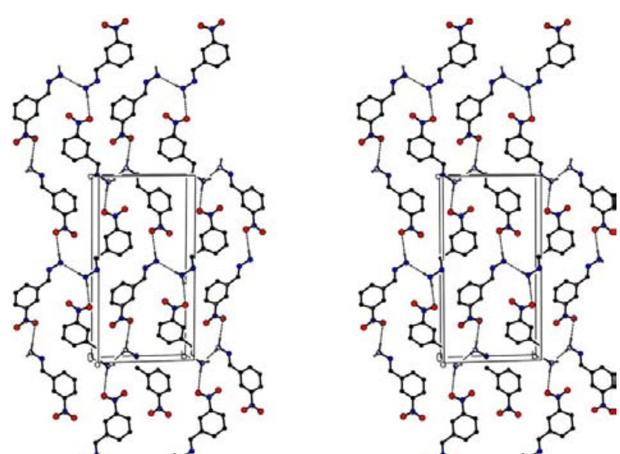


Figure 6
Stereoview of part of the crystal structure of (II), showing the formation of a (100) sheet of $R_6^6(40)$ rings by combination of the [010] and [001] chains. For the sake of clarity, H atoms bonded to C atoms have been omitted.

with the formation of a (4,4)-net parallel to (102) in compound (III). The combination of all three of the one-dimensional motifs in (II) suffices to generate a single three-dimensional framework.

Isomers (I)–(III) can all be regarded as chain-extended analogues of the simple isomeric nitroanilines (IV)–(VI), and it is of interest to compare the supramolecular structures of (I)–(III) with their aniline analogues. In (IV), where $Z' = 2$ in space group $P2_1/n$ (Dhaneshwar *et al.*, 1978), the molecules are linked by N—H···O hydrogen bonds into simple $C_2^2(12)$ chains. In (V) (Ploug-Sørensen & Andersen, 1986), a combination of N—H···O and N—H···N hydrogen bonds generates a (4,4)-net of $R_4^4(18)$ rings, while in (VI) (Tonogaki *et al.*, 1993), the molecules are linked by two N—H···O hydrogen bonds into (4,4)-nets of $R_4^4(22)$ rings. Hence, the patterns of the hydrogen bonds employed, as well as the resulting supramolecular structures, are different in each of (IV)–(VI).

Much effort continues to be expended in attempts to predict the crystal structures of simple organic compounds (Lommerse *et al.*, 2000; Motherwell *et al.*, 2002). Variations in supramolecular aggregation behaviour within a series of isomeric compounds, such as those of (I)–(III) described here or of (IV)–(VI), provide a keen test of computational methods for crystal structure prediction. The accurate prediction of behaviour, especially the correct prediction of space groups and the particular hydrogen bonds involved within such series of isomeric species, would generate real confidence in the efficacy of the predictive methods employed.

Experimental

Compounds (I) and (II) were prepared by heating under reflux for 1 h a solution of the appropriate nitrobenzaldehyde (5 g) and hydrazine hydrate (10 g) in ethanol (50 ml). After cooling to ambient temperature, the mixtures were diluted with water (50 ml) and then extracted with $CHCl_3$. These extracts were dried and evaporated, and the resulting solids were recrystallized from ethanol to yield (I) (m.p. 348–349 K) and (II) (m.p. 381–383 K). Crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared samples.

Compound (I)

Crystal data

$C_7H_7N_3O_2$
$M_r = 165.16$
Orthorhombic, $P2_12_12_1$
$a = 3.6675$ (2) Å
$b = 13.938$ (1) Å
$c = 28.796$ (2) Å
$V = 1471.98$ (17) Å^3
$Z = 8$
$D_x = 1.490$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 1913 reflections
$\theta = 3.0$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 120$ (2) K
Needle, yellow
0.25 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.957$, $T_{max} = 0.997$
11 485 measured reflections
1966 independent reflections
1247 reflections with $I > 2\sigma(I)$
$R_{int} = 0.089$
$\theta_{max} = 27.5°$
$h = -4 \rightarrow 4$
$k = -18 \rightarrow 17$
$l = -29 \rightarrow 37$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.113$
$S = 1.02$
1966 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N212—H21*B*···N111	0.95	2.51	3.307 (4)	141
N112—H11*B*···N211	0.95	2.17	3.027 (4)	150

Compound (II)

Crystal data

$C_7H_7N_3O_2$
$M_r = 165.16$
Orthorhombic, $P2_12_12_1$
$a = 3.7231$ (2) Å
$b = 10.2200$ (7) Å
$c = 19.4119$ (12) Å
$V = 738.62$ (8) Å^3
$Z = 4$
$D_x = 1.485$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1029 reflections
$\theta = 3.7$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 120$ (2) K
Block, yellow
0.42 × 0.32 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.965$, $T_{max} = 0.989$
5442 measured reflections
1029 independent reflections
897 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 27.5°$
$h = -4 \rightarrow 3$
$k = -12 \rightarrow 13$
$l = -24 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.092$
$S = 1.06$
1029 reflections
112 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.0869P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.041 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
N12—H12*A*···O31^{i}	0.88	2.34	3.210 (2)	170
N12—H12*B*···N12^{ii}	0.88	2.41	3.245 (3)	158

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

For each of compounds (I) and (II), the space group $P2_12_12_1$ was uniquely assigned from the systematic absences. All H atoms were located from difference Fourier maps and subsequently treated as riding. H atoms bonded to N atoms were allowed to ride at the N—H distances identified from the difference maps, namely 0.95 Å in (I) and 0.88 Å in (II), with U_{iso}(H) = $1.2U_{eq}$(N). H atoms bonded to C atoms were constrained to C—H distances of 0.95 Å and U_{iso}(H) = $1.2U_{eq}$(C). In the absence of significant anomalous dispersion, the values of the Flack (1983) parameters were both indeterminate (Flack & Bernardinelli, 2000), and hence the correct absolute configuration for the crystals under study could not be established (Jones, 1986), although this has no chemical significance. Accordingly, Friedel-equivalent reflections were merged prior to the final refinements for both (I) and (II).

For compound (I), data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*. For compound (II), data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*. For both compounds, program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data 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: SK1751). 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.

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.

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**, 2507–2509.

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

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.

Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2004). *Acta Cryst.* C**60**, o33–o34.

Jones, P. G. (1986). *Acta Cryst.* A**42**, 57.

Lommerse, J. P. M., Motherwell, W. D. S., Ammon, H. L., Dunitz, J. D., Gavezzotti, A., Hofmann, D. W. M., Leusen, F. J. J., Mooij, W. T. M., Price, S. L., Schweizer, B., Schmidt, M. U., van Eijck, B. P., Verwer, P. & Williams, D. E. (2000). *Acta Cryst.* B**56**, 697–714.

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

Motherwell, W. D. S., Ammon, H. L., Dunitz, J. D., Dzyabchenko, A., Erk, P., Gavezzotti, A., Hofmann, D. W. M., Leusen, F. J. J., Lommerse, J. P. M., Mooij, W. T. M., Price, S. L., Schweizer, B., Schmidt, M. U., van Eijck, B. P., Verwer, P. & Williams, D. E. (2002). *Acta Cryst.* B**58**, 647–761.

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

Nonius (1998). *COLLECT*. 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.

Ploug-Sørensen, G. & Andersen, E. K. (1986). *Acta Cryst.* C**42**, 1813–1815.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. 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.

Tonogaki, M., Kawata, T., Ohba, S., Iwata, Y. & Shibuya, I. (1993). *Acta Cryst.* B**49**, 1031–1039.