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Hydrogen bonding in nitroaniline analogues: 4-nitrobenzaldehyde hydrazone forms hydrogen-bonded sheets of $R_4^4(26)$ rings

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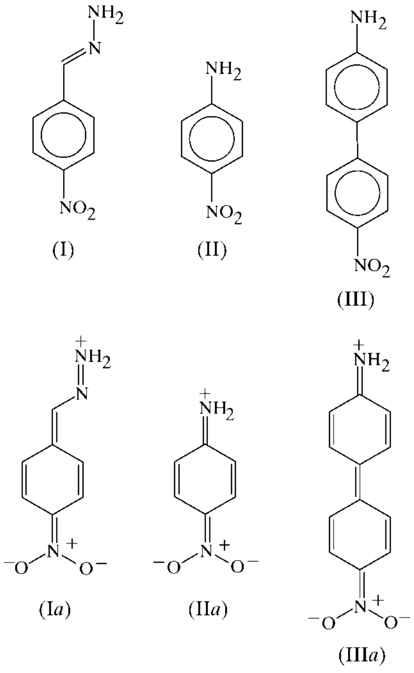
Molecules of the title compound, $C_7H_7N_3O_2$, are linked by two N—H···O hydrogen bonds [H···O = 2.42 and 2.47 Å, N···O = 3.191 (4) and 3.245 (4) Å, and N—H···O = 150 and 151°] into sheets built from a single type of $R_4^4(26)$ ring.

Comment

The title compound, (I) (Fig. 1), may be regarded as a chain-extended analogue of 4-nitroaniline, (II), just as 4-amino-4′-nitrobiphenyl, (III), can be regarded as a phenyl-extended analogue of (II).



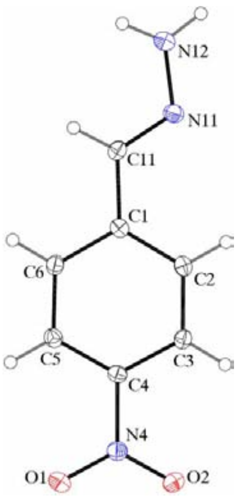


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

In the molecules of (I), the only significant deviation from overall planarity is the 7.9 (2)° twist of the nitro group out of the plane of the phenyl ring. The C—NO_2 distance (Table 1) is less than the lower-quartile value (1.460 Å; Allen *et al.*, 1987) for bonds of this type, while both of the N—O bonds in the nitro group are much longer than the upper-quartile value for such bonds. In addition, the C1—C11 bond is at the lower-quartile value for conjugated C(aryl)—C═N bonds, while there are indications of quinonoid bond fixation in the aryl ring. These observations taken together point to a modest contribution of the polarized form (I*a*) to the overall molecular–electronic structure, just as the dimensions of (II) (Tonogaki *et al.*, 1993) and (III) (Graham *et al.*, 1989) point to the participation of forms (II*a*) and (III*a*), respectively.

The molecules of (I) are linked into sheets by two N—H···O hydrogen bonds (Table 2). Amino atom N12 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atoms

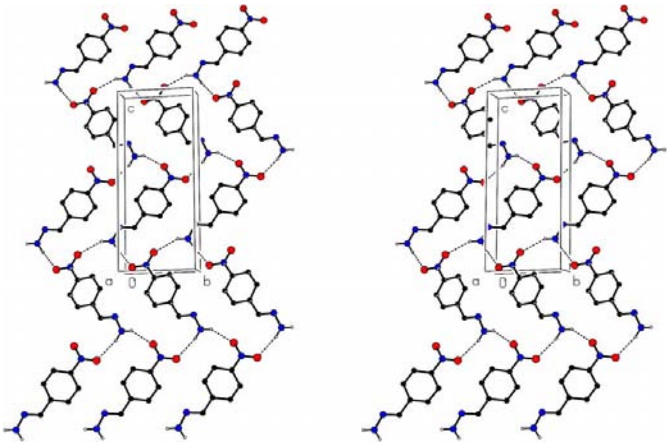


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a (102) sheet of $R_4^4(26)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted.

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H12*A* and H12*B*, respectively, to nitro atoms O1 and O2 in the molecules at $(1+x,\ 1-y,\ -\frac{1}{2}+z)$ and $(1+x,\ -y,\ -\frac{1}{2}+z)$, respectively. These two hydrogen bonds produce two independent *C*(10) (Bernstein *et al.*, 1995) chains, both running parallel to the $[20\overline{1}]$ direction and generated by the *c*-glide planes at $y=\frac{1}{2}$ and 0, respectively (Fig. 2). The combination of these two motifs generates a (102) sheet in the form of a (4,4)-net (Batten & Robson, 1998) built from a single type of $R_4^4(16)$ ring (Fig. 2). We may compare this sheet with that formed in (II), where the rings are of the $R_4^4(22)$ type (Tonogaki *et al.*, 1993); however, whereas the sheets in (II) are linked by weak aromatic π–π stacking interactions, there are no direction-specific interactions between adjacent sheets in the structure of (I).

Experimental

Compound (I) was prepared by heating under reflux for 1 h a solution of 4-nitrobenzaldehyde (5 g) and hydrazine hydrate (10 g) in ethanol (50 ml). After cooling to ambient temperature, the mixture was diluted with water (50 ml) and then extracted with $CHCl_3$; this extract was dried and evaporated, and the resulting solid was recrystallized from ethanol, yielding (I) (m.p. 407–408 K). Crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared sample.

Crystal data

$C_7H_7N_3O_2$
$M_r = 165.16$
Monoclinic, *Pc*
$a = 3.7070$ (2) Å
$b = 6.3963$ (3) Å
$c = 15.4047$ (10) Å
$\beta = 95.064$ (2)°
$V = 363.84$ (4) Å^3
$Z = 2$

$D_x = 1.508$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 829 reflections
$\theta = 3.2$–27.4°
$\mu = 0.12$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
0.20 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.967$, $T_{\max} = 0.994$
4784 measured reflections
829 independent reflections

765 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.071$
$\theta_{\max} = 27.4$°
$h = -4 \rightarrow 4$
$k = -8 \rightarrow 8$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.102$
$S = 1.17$
829 reflections
109 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.1524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

C1—C2	1.397 (4)	C1—C11	1.466 (4)
C2—C3	1.381 (4)	C11—N11	1.271 (4)
C3—C4	1.399 (4)	N11—N12	1.380 (4)
C4—C5	1.383 (4)	C4—N4	1.456 (4)
C5—C6	1.380 (4)	N4—O1	1.239 (3)
C6—C1	1.401 (4)	N4—O2	1.226 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12*A*···O1$^{\rm i}$	0.86	2.47	3.245 (4)	151
N12—H12*B*···O2$^{\rm ii}$	0.86	2.42	3.191 (4)	150

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

Crystals of (I) are monoclinic, and the systematic absences permitted *Pc* and *P*2/*c* as possible space groups; *Pc* was selected and confirmed by the subsequent structure analysis. All H atoms were located from difference maps and treated as riding atoms, with C—H distances of 0.93 Å and N—H distances of 0.86 Å. In the absence of significant anomalous scattering it was not possible to establish the correct orientation of the structure with respect to the polar-axis directions; accordingly, the Friedel equivalents were merged prior to the final refinements. Although the data are essentially 100% complete, the ratio of data to parameters is rather low.

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 *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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1201). 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.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Graham, E. M., Miskowski, V. M., Perry, J. W., Coulter, D. R., Stiegman, A. E., Schaefer, W. P. & Marsh, R. E. (1989). *J. Am. Chem. Soc.* **111**, 8771–8779.
McArdle, P. (2003). *OSCAIL*. Version 10 for Windows. 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). *SHELXS*97 and *SHELXL*97. 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.

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