organic papers

A hydrogen-bonded *C*(6) chain in glyoxal 3-nitrophenylhydrazone

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The molecules of the title compound, $C_8H_7N_3O_3$, which are nearly planar, are linked into simple *C*(6) chains by an N—H⋯O hydrogen bond.

Comment

The title compound, (I), was prepared as part of our continuing study of the supramolecular arrangements of *N*-(nitropheny)imide and hydrazone derivatives. We have recently reported the supramolecular structure of the isomeric compound glyoxal 4-nitrophenylhydrazone, (II), in which triple helices enclose two types of channel lying respectively along $\bar{4}$, and 4_1 or 4_3 axes in space group $I4_1/a$ (Glidewell *et al.*, 2005): the supramolecular structure of (I), by contrast, is very simple.
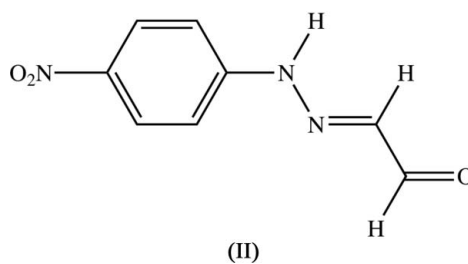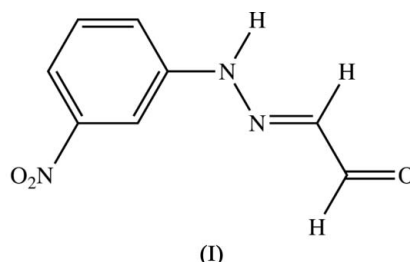
The molecules of compound (I) (Fig. 1) are almost planar, as shown by the leading torsion angles (Table 1); the side chain between atoms N1 and O1 adopts a planar all-*trans* conformation, and the nitro group is nearly coplanar with the aryl ring. There is strong bond fixation in the side chain with very short N2—C11 and C12—O1 bonds, with no evidence for bond polarization in this fragment.

A single hydrogen bond (Table 2) links the molecules into chains; atom N1 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O1 in the molecule at ($-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$), forming a *C*(6) chain running parallel to the [10$\bar{1}$] direction and generated by the *n*-glide plane at y = 0.25 (Fig. 2). Two such chains pass through each unit cell, but there are no direction-specific interactions between adjacent chains.
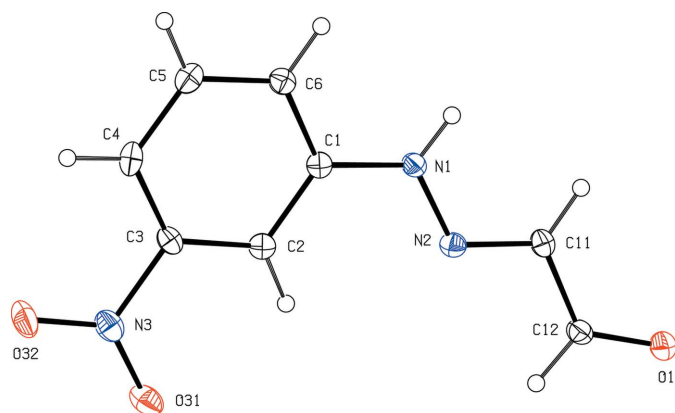
Figure 1
A molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
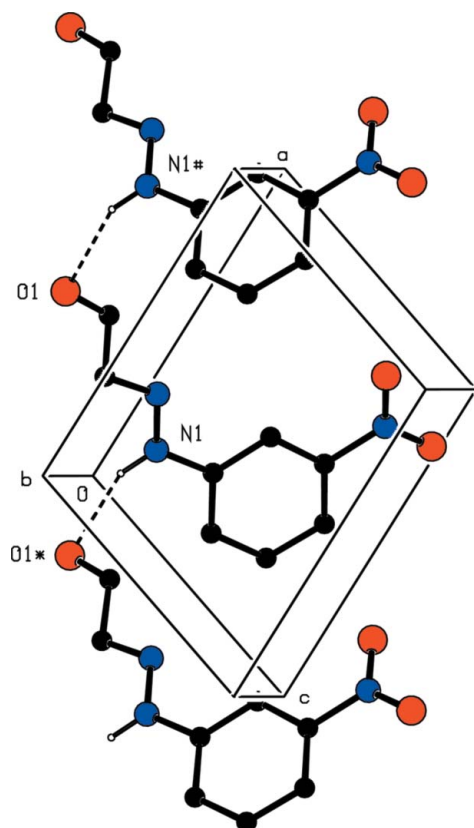
Figure 2
Part of the crystal structure of compound (I), showing the formation of a $C(6)$ hydrogen-bonded chain along $[10\bar{1}]$. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively.

Experimental

Compound (I) was prepared by heating under reflux for 1 h a solution of glyoxal (1 mmol as a 40% aqueous solution) and 3-nitrophenyl-hydrazine (1 mmol) in methanol (40 ml). The mixture was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was crystallized from ethanol to yield crystals suitable for single-crystal X-ray diffraction.

Crystal data

$C_8H_7N_3O_3$	$Z = 4$
$M_r = 193.17$	$D_x = 1.507$ Mg m^{-3}
Monoclinic, Cc	Mo $K\alpha$ radiation
$a = 7.4737$ (4) Å	$\mu = 0.12$ mm^{-1}
$b = 19.7711$ (13) Å	$T = 120$ (2) K
$c = 6.0262$ (4) Å	Lath, yellow
$\beta = 107.080$ (4)°	$0.16 \times 0.08 \times 0.02$ mm
$V = 851.18$ (9) Å^3	

Data collection

Bruker–Nonius KappaCCD diffractometer	7928 measured reflections
	987 independent reflections
φ and ω scans	871 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$R_{int} = 0.063$
	$\theta_{max} = 27.6°$
$T_{min} = 0.961$, $T_{max} = 0.998$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.1446P]$
$wR(F^2) = 0.098$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
987 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.395 (3)	C11—C12	1.445 (4)
N1—N2	1.331 (3)	C12—O1	1.224 (3)
N2—C11	1.294 (3)		
C2—C1—N1—N2	−3.6 (4)	N2—C11—C12—O1	−177.1 (3)
C1—N1—N2—C11	−175.8 (2)	C2—C3—N3—O31	6.7 (4)
N1—N2—C11—C12	−179.1 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^i	0.88	2.15	2.940 (3)	149

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

All H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.95 Å and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$. In the absence of significant anomalous dispersion the Flack (1983) parameter was indeterminate and it was not possible to determine the correct orientation of the structure with respect to the polar axis directions. Accordingly, the Friedel-equivalent reflections were merged prior to the final refinement.

Data collection: *COLLECT* (Hooft, 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).

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supporting information

A hydrogen-bonded *C*(6) chain in glyoxal 3-nitrophenylhydrazone

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Glyoxal 3-nitrophenylhydrazone

Crystal data

$C_8H_7N_3O_3$	$F(000) = 400$
$M_r = 193.17$	$D_x = 1.507$ Mg m^{-3}
Monoclinic, Cc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: C -2yc	Cell parameters from 987 reflections
$a = 7.4737$ (4) Å	$\theta = 3.0–27.6°$
$b = 19.7711$ (13) Å	$\mu = 0.12$ mm^{-1}
$c = 6.0262$ (4) Å	$T = 120$ K
$\beta = 107.080$ (4)°	Lath, yellow
$V = 851.18$ (9) Å^3	$0.16 \times 0.08 \times 0.02$ mm
$Z = 4$	

Data collection

Bruker–Nonius KappaCCD diffractometer	$T_{min} = 0.961$, $T_{max} = 0.998$
Radiation source: Bruker–Nonius FR591 rotating anode	7928 measured reflections
	987 independent reflections
Graphite monochromator	871 reflections with $I > 2\sigma(I)$
Detector resolution: 9.091 pixels mm^{-1}	$R_{int} = 0.063$
φ and ω scans	$\theta_{max} = 27.6°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -9 \rightarrow 9$
	$k = -25 \rightarrow 25$
	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.098$	
$S = 1.08$	H-atom parameters constrained
987 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.1446P]$ where $P = (F_o^2 + 2F_c^2)/3$
127 parameters	
2 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.17$ e Å^{-3}
	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.2050 (3)	0.15679 (11)	0.1679 (3)	0.0221 (5)
N2	0.3161 (3)	0.19066 (11)	0.0702 (4)	0.0221 (5)
C11	0.2384 (4)	0.22429 (13)	−0.1177 (5)	0.0237 (6)

C12	0.3675 (4)	0.25897 (14)	−0.2160 (5)	0.0249 (6)
O1	0.3218 (3)	0.29536 (11)	−0.3877 (3)	0.0327 (5)
C1	0.2813 (4)	0.12344 (13)	0.3786 (4)	0.0219 (5)
C2	0.4747 (4)	0.12149 (13)	0.4849 (4)	0.0228 (6)
C3	0.5377 (4)	0.08816 (14)	0.6942 (4)	0.0240 (6)
N3	0.7413 (4)	0.08596 (12)	0.8066 (4)	0.0295 (6)
O31	0.8425 (3)	0.11907 (12)	0.7197 (3)	0.0346 (5)
O32	0.8008 (3)	0.05119 (12)	0.9815 (4)	0.0415 (6)
C4	0.4212 (4)	0.05643 (14)	0.8030 (5)	0.0270 (6)
C5	0.2295 (4)	0.05803 (13)	0.6913 (5)	0.0276 (6)
C6	0.1600 (4)	0.09135 (13)	0.4822 (5)	0.0232 (5)
H1	0.0830	0.1607	0.1044	0.027*
H11	0.1066	0.2260	−0.1859	0.028*
H12	0.4975	0.2531	−0.1418	0.030*
H2	0.5594	0.1424	0.4154	0.027*
H4	0.4702	0.0344	0.9484	0.032*
H5	0.1458	0.0360	0.7596	0.033*
H6	0.0289	0.0924	0.4085	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0188 (10)	0.0265 (11)	0.0201 (11)	−0.0011 (9)	0.0042 (9)	0.0022 (9)
N2	0.0209 (11)	0.0241 (11)	0.0216 (11)	−0.0011 (9)	0.0067 (9)	−0.0015 (8)
C11	0.0233 (12)	0.0261 (13)	0.0194 (12)	0.0017 (10)	0.0029 (10)	0.0004 (11)
C12	0.0193 (12)	0.0315 (14)	0.0220 (14)	−0.0021 (11)	0.0030 (10)	0.0021 (12)
O1	0.0271 (10)	0.0389 (11)	0.0288 (11)	−0.0020 (9)	0.0031 (8)	0.0096 (9)
C1	0.0236 (13)	0.0211 (13)	0.0208 (12)	0.0004 (9)	0.0064 (11)	−0.0017 (10)
C2	0.0236 (14)	0.0227 (13)	0.0225 (13)	−0.0007 (10)	0.0073 (11)	−0.0024 (11)
C3	0.0215 (15)	0.0277 (14)	0.0203 (13)	0.0023 (10)	0.0022 (11)	−0.0019 (10)
N3	0.0276 (13)	0.0323 (13)	0.0257 (12)	0.0039 (10)	0.0035 (10)	−0.0043 (10)
O31	0.0230 (10)	0.0507 (14)	0.0297 (11)	0.0021 (9)	0.0072 (9)	−0.0021 (10)
O32	0.0348 (13)	0.0468 (14)	0.0330 (11)	0.0074 (10)	−0.0055 (10)	0.0090 (10)
C4	0.0368 (16)	0.0230 (14)	0.0223 (13)	0.0083 (11)	0.0103 (12)	0.0045 (11)
C5	0.0339 (16)	0.0228 (13)	0.0298 (15)	0.0014 (11)	0.0150 (13)	0.0016 (11)
C6	0.0220 (13)	0.0231 (13)	0.0249 (13)	0.0016 (10)	0.0076 (10)	−0.0021 (11)

Geometric parameters (Å, º)

C1—N1	1.395 (3)	C2—H2	0.95
N1—N2	1.331 (3)	C3—C4	1.384 (4)
N1—H1	0.88	C3—N3	1.473 (3)
N2—C11	1.294 (3)	N3—O32	1.227 (3)
C11—C12	1.445 (4)	N3—O31	1.228 (3)
C11—H11	0.95	C4—C5	1.393 (4)
C12—O1	1.224 (3)	C4—H4	0.95
C12—H12	0.95	C5—C6	1.381 (4)
C1—C6	1.395 (4)	C5—H5	0.95

C1—C2	1.399 (4)	C6—H6	0.95
C2—C3	1.378 (4)		
N2—N1—C1	119.9 (2)	C2—C3—C4	123.8 (2)
N2—N1—H1	117.6	C2—C3—N3	117.6 (2)
C1—N1—H1	122.0	C4—C3—N3	118.5 (2)
C11—N2—N1	117.9 (2)	O32—N3—O31	123.5 (3)
N2—C11—C12	114.9 (2)	O32—N3—C3	118.4 (2)
N2—C11—H11	122.6	O31—N3—C3	118.1 (2)
C12—C11—H11	122.6	C3—C4—C5	117.5 (2)
O1—C12—C11	124.8 (2)	C3—C4—H4	121.3
O1—C12—H12	117.6	C5—C4—H4	121.3
C11—C12—H12	117.6	C6—C5—C4	120.7 (3)
C6—C1—N1	118.4 (2)	C6—C5—H5	119.7
C6—C1—C2	120.2 (2)	C4—C5—H5	119.7
N1—C1—C2	121.4 (2)	C5—C6—C1	120.3 (2)
C3—C2—C1	117.5 (2)	C5—C6—H6	119.8
C3—C2—H2	121.3	C1—C6—H6	119.8
C1—C2—H2	121.3		
C2—C1—N1—N2	−3.6 (4)	C4—C3—N3—O32	6.3 (4)
C1—N1—N2—C11	−175.8 (2)	C2—C3—N3—O31	6.7 (4)
N1—N2—C11—C12	−179.1 (2)	C4—C3—N3—O31	−173.8 (2)
N2—C11—C12—O1	−177.1 (3)	C2—C3—C4—C5	0.7 (4)
N2—N1—C1—C6	176.8 (2)	N3—C3—C4—C5	−178.8 (2)
C6—C1—C2—C3	−1.2 (3)	C3—C4—C5—C6	−1.3 (4)
N1—C1—C2—C3	179.2 (2)	C4—C5—C6—C1	0.6 (4)
C1—C2—C3—C4	0.5 (4)	N1—C1—C6—C5	−179.7 (2)
C1—C2—C3—N3	180.0 (2)	C2—C1—C6—C5	0.7 (4)
C2—C3—N3—O32	−173.2 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1[i]	0.88	2.15	2.940 (3)	149

Symmetry code: (i) *x*−1/2, −*y*+1/2, *z*+1/2.