

Glyoxal 2-nitrophenylhydrazone: a hydrogen-bonded chain of $R_2^2(12)$ and $R_4^4(24)$ rings

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Key indicators

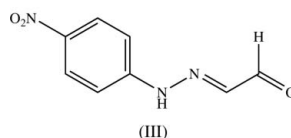
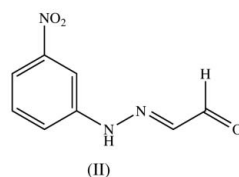
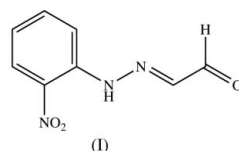
Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.090
 wR factor = 0.268
 Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Molecules of the title compound, $\text{C}_8\text{H}_7\text{N}_3\text{O}_3$, are effectively planar and are linked into chains of edge-fused $R_2^2(12)$ and $R_4^4(24)$ rings by a combination of $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Comment

We report here the molecular and supramolecular structure of the title compound, (I), which completes the series of isomeric glyoxal nitrophenylhydrazones (I)–(III). These three isomers prove to adopt wholly different supramolecular structures. In isomer (II), the molecules are linked into simple $C(6)$ (Bernstein *et al.*, 1995) chains by a single $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond (Low *et al.*, 2006), while in isomer (III), the molecules are linked by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to form triply intertwined helices, which are themselves linked by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds into a three-dimensional channel structure enclosing two types of channel (Glidewell *et al.*, 2005).



We have now taken the opportunity to determine the supramolecular structure of compound (I). This isomer forms crystals of rather poor quality, which are subject to non-merohedral twinning. Accordingly, the quality of the structure determination is not high, but the essential features of the supramolecular aggregation are beyond doubt.

The molecules of isomer (I) (Fig. 1) are almost planar, as shown by the key torsion angles (Table 1). There is clear bond fixation in the exocyclic portion of the molecule, and the exocyclic bond angles at C1 and C2 indicate that the short intramolecular $\text{H11}\cdots\text{O21}$ contact (Table 2) is repulsive in nature.

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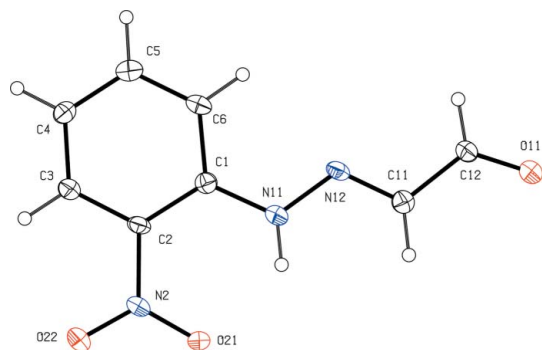


Figure 1

The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

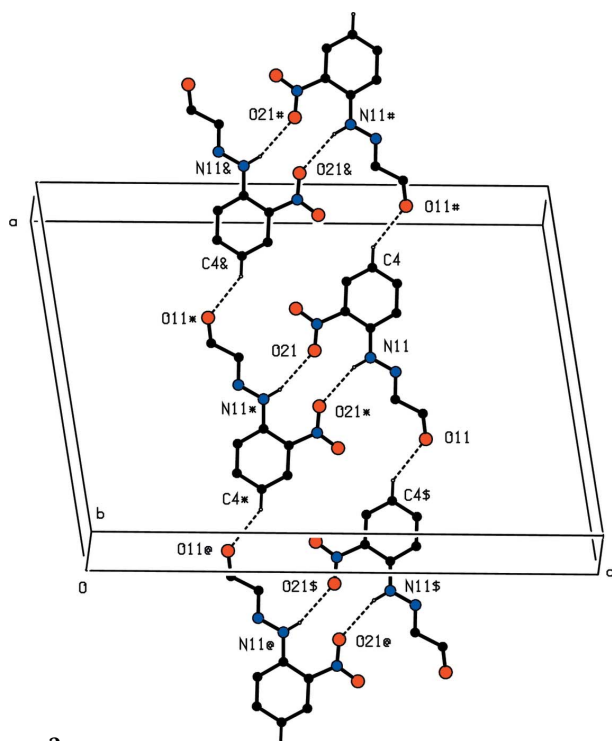


Figure 2

Part of the crystal structure of compound (I), showing the formation of a chain of edge-fused $R_2^2(12)$ and $R_4^4(24)$ rings along [130]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign (\$), an ampersand (&) or an 'at' sign (@) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(\frac{1}{2}+x, \frac{3}{2}+y, z)$, $(-\frac{1}{2}+x, -\frac{3}{2}+y, z)$, $(\frac{3}{2}-x, \frac{1}{2}-y, 1-z)$ and $(\frac{1}{2}-x, -\frac{1}{2}-y, 1-z)$, respectively.

Two hydrogen bonds (Table 2) link the molecules into a chain of edge-fused centrosymmetric rings running parallel to the [130] direction and generated by inversion. There are $R_2^2(12)$ rings centred at $(\frac{1}{2}n, -1 + \frac{3}{2}n, \frac{1}{2})$ ($n = \text{zero or integer}$) and $R_4^4(24)$ rings centred at $(\frac{1}{4} + \frac{1}{2}n, -\frac{1}{4} + \frac{3}{2}n, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 2). Two chains of this type, related to one another by the action of the twofold rotation axes, pass through each unit cell, but there are no direction-specific interactions between the chains.

We also note here that not only are the supramolecular structures of the isomers (I)–(III) wholly distinct, but they also crystallize in three different space groups ($C2/c$, Cc and $I4_1/a$,

respectively), with markedly different unit-cell dimensions, having $Z = 8, 4$, and 16 , 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 2-nitrophenylhydrazine (1 mmol) in methanol (40 ml). The mixture was then cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was recrystallized from ethanol to yield crystals of (I) suitable for single-crystal X-ray diffraction (m.p. 442–444 K).

Crystal data

$C_8H_7N_3O_3$
 $M_r = 193.17$
 Monoclinic, $C2/c$
 $a = 18.670(4) \text{ \AA}$
 $b = 3.7723(4) \text{ \AA}$
 $c = 23.896(5) \text{ \AA}$
 $\beta = 96.429(6)^\circ$
 $V = 1672.4(5) \text{ \AA}^3$

$Z = 8$
 $D_x = 1.534 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
 Needle, orange
 $0.34 \times 0.05 \times 0.02 \text{ mm}$

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.971$, $T_{\max} = 0.998$

6609 measured reflections
 1903 independent reflections
 975 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.101$
 $\theta_{\max} = 27.6^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.090$
 $wR(F^2) = 0.268$
 $S = 1.09$
 1903 reflections
 128 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1249P)^2 + 0.4829P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1–N11	1.382 (5)	C11–C12	1.447 (6)
N11–N12	1.347 (5)	C12–O11	1.215 (5)
N12–C11	1.285 (5)		
C2–C1–N11	123.3 (4)	C1–C2–N2	122.5 (4)
C6–C1–N11	119.9 (4)	C3–C2–N2	116.7 (4)
C2–C1–N11–N12	177.4 (4)	N12–C11–C12–O11	−172.8 (4)
C1–N11–N12–C11	−174.3 (4)	C1–C2–N2–O21	−7.7 (6)
N11–N12–C11–C12	177.7 (3)		

Table 2

Parameters (\AA , $^\circ$) for hydrogen bonds and short intramolecular contacts.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N11–H11 \cdots O21	0.88	2.01	2.629 (5)	126
N11–H11 \cdots O21 ⁱ	0.88	2.50	3.327 (5)	157
C4–H4 \cdots O11 ⁱⁱ	0.95	2.50	3.298 (5)	141

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

All H atoms were located in a difference map and then treated as riding atoms, with $C-H = 0.95 \text{ \AA}$ and $N-H = 0.88 \text{ \AA}$, and with

$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The TwinRotMat option in *PLATON* (Spek, 2003) indicated non-merohedral twinning, and the twin refinement gave twin fractions of 0.302 (5) and 0.698 (5).

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, UK; the authors thank the staff for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

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supporting information

Acta Cryst. (2006). E62, o2204–o2206 [https://doi.org/10.1107/S1600536806016047]

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$M_r = 193.17$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 18.670$ (4) Å

$b = 3.7723$ (4) Å

$c = 23.896$ (5) Å

$\beta = 96.429$ (6)°

$V = 1672.4$ (5) Å³

$Z = 8$

$F(000) = 800$

$D_x = 1.534$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1760 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 0.12$ mm⁻¹

$T = 120$ K

Needle, orange

$0.34 \times 0.05 \times 0.02$ mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer

Radiation source: Bruker-Nonius FR591 rotating anode

Graphite monochromator

Detector resolution: 9.091 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

$T_{\min} = 0.971$, $T_{\max} = 0.998$

6609 measured reflections

1903 independent reflections

975 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.101$

$\theta_{\max} = 27.6$ °, $\theta_{\min} = 3.4$ °

$h = -24 \rightarrow 24$

$k = -4 \rightarrow 4$

$l = -24 \rightarrow 30$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.090$

$wR(F^2) = 0.268$

$S = 1.09$

1903 reflections

128 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1249P)^2 + 0.4829P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.31$ e Å⁻³

$\Delta\rho_{\min} = -0.30$ e Å⁻³

Special details

Experimental. IR (KBr disk, ν , cm⁻¹): 3294, 2832, 1687, 1611, 1584, 1558, 1493, 1426, 1370, 1341, 1302, 1271, 1223, 1156, 1119, 1075, 1037, 997, 898, 860, 785, 744, 690, 651, 614, 491.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5988 (2)	0.9186 (11)	0.61085 (19)	0.0248 (10)
N11	0.53270 (19)	0.7496 (9)	0.60542 (16)	0.0305 (9)
N12	0.49995 (19)	0.6830 (9)	0.65175 (15)	0.0266 (9)
C11	0.4415 (2)	0.5000 (11)	0.6465 (2)	0.0301 (11)
C12	0.4100 (2)	0.4244 (11)	0.6978 (2)	0.0278 (11)
O11	0.35891 (17)	0.2276 (8)	0.70018 (14)	0.0366 (9)
C2	0.6383 (2)	0.9861 (11)	0.56497 (19)	0.0275 (11)
N2	0.6123 (2)	0.8881 (10)	0.50804 (17)	0.0343 (10)
O21	0.55688 (17)	0.7048 (9)	0.49938 (14)	0.0388 (9)
O22	0.6451 (2)	0.9858 (10)	0.46949 (16)	0.0572 (12)
C3	0.7059 (2)	1.1489 (12)	0.5732 (2)	0.0326 (12)
C4	0.7350 (2)	1.2471 (12)	0.6258 (2)	0.0322 (12)
C5	0.6964 (2)	1.1903 (11)	0.6707 (2)	0.0315 (11)
C6	0.6299 (2)	1.0281 (11)	0.6637 (2)	0.0289 (11)
H11	0.5122	0.6861	0.5720	0.037*
H11A	0.4202	0.4188	0.6109	0.036*
H12	0.4304	0.5350	0.7316	0.033*
H3	0.7318	1.1915	0.5419	0.039*
H4	0.7814	1.3534	0.6314	0.039*
H5	0.7159	1.2642	0.7073	0.038*
H6	0.6047	0.9902	0.6955	0.035*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.028 (2)	0.022 (2)	0.024 (3)	0.0001 (18)	0.001 (2)	0.003 (2)
N11	0.032 (2)	0.041 (2)	0.019 (2)	-0.0040 (18)	0.0035 (16)	0.0004 (18)
N12	0.031 (2)	0.033 (2)	0.016 (2)	0.0025 (17)	0.0025 (16)	0.0015 (17)
C11	0.032 (2)	0.031 (2)	0.028 (3)	-0.003 (2)	0.004 (2)	0.001 (2)
C12	0.029 (2)	0.033 (3)	0.022 (3)	-0.001 (2)	0.004 (2)	0.002 (2)
O11	0.0372 (19)	0.047 (2)	0.026 (2)	-0.0079 (17)	0.0051 (15)	0.0017 (15)
C2	0.036 (2)	0.031 (2)	0.015 (3)	-0.004 (2)	0.002 (2)	-0.0004 (19)
N2	0.038 (2)	0.047 (2)	0.018 (2)	-0.007 (2)	0.0057 (18)	-0.0010 (19)
O21	0.0367 (18)	0.059 (2)	0.0205 (19)	-0.0192 (17)	0.0019 (14)	-0.0055 (16)
O22	0.059 (2)	0.089 (3)	0.026 (2)	-0.035 (2)	0.0144 (19)	-0.004 (2)
C3	0.037 (3)	0.039 (2)	0.022 (3)	-0.010 (2)	0.004 (2)	0.001 (2)
C4	0.031 (2)	0.036 (3)	0.029 (3)	-0.009 (2)	-0.001 (2)	0.000 (2)
C5	0.036 (3)	0.029 (2)	0.027 (3)	0.002 (2)	-0.003 (2)	-0.003 (2)
C6	0.038 (3)	0.031 (2)	0.018 (3)	0.003 (2)	0.003 (2)	0.000 (2)

Geometric parameters (\AA , $^\circ$)

C1—N11	1.382 (5)	C2—N2	1.440 (6)
C1—C6	1.391 (6)	N2—O22	1.219 (5)
C1—C2	1.411 (6)	N2—O21	1.242 (5)

N11—N12	1.347 (5)	C3—C4	1.364 (7)
N11—H11	0.88	C3—H3	0.95
N12—C11	1.285 (5)	C4—C5	1.375 (6)
C11—C12	1.447 (6)	C4—H4	0.95
C11—H11A	0.95	C5—C6	1.378 (6)
C12—O11	1.215 (5)	C5—H5	0.95
C12—H12	0.95	C6—H6	0.95
C2—C3	1.398 (6)		
C2—C1—N11	123.3 (4)	O22—N2—O21	121.5 (4)
C6—C1—N11	119.9 (4)	O22—N2—C2	119.4 (4)
C6—C1—C2	116.8 (4)	O21—N2—C2	119.1 (4)
N12—N11—C1	119.4 (4)	C4—C3—C2	120.6 (4)
N12—N11—H11	120.3	C4—C3—H3	119.7
C1—N11—H11	120.3	C2—C3—H3	119.7
C11—N12—N11	118.6 (4)	C3—C4—C5	119.2 (4)
N12—C11—C12	116.4 (4)	C3—C4—H4	120.4
N12—C11—H11A	121.8	C5—C4—H4	120.4
C12—C11—H11A	121.8	C4—C5—C6	121.2 (5)
O11—C12—C11	123.7 (4)	C4—C5—H5	119.4
O11—C12—H12	118.1	C6—C5—H5	119.4
C11—C12—H12	118.1	C5—C6—C1	121.4 (4)
C3—C2—C1	120.8 (4)	C5—C6—H6	119.3
C1—C2—N2	122.5 (4)	C1—C6—H6	119.3
C3—C2—N2	116.7 (4)		
C6—C1—N11—N12	-2.0 (6)	C1—C2—N2—O22	172.4 (4)
C2—C1—N11—N12	177.4 (4)	C3—C2—N2—O21	171.3 (4)
C1—N11—N12—C11	-174.3 (4)	C1—C2—N2—O21	-7.7 (6)
N11—N12—C11—C12	177.7 (3)	C1—C2—C3—C4	-0.3 (7)
N12—C11—C12—O11	-172.8 (4)	N2—C2—C3—C4	-179.3 (4)
N11—C1—C2—C3	-178.1 (4)	C2—C3—C4—C5	-1.2 (7)
C6—C1—C2—C3	1.3 (6)	C3—C4—C5—C6	1.7 (7)
N11—C1—C2—N2	0.9 (7)	C4—C5—C6—C1	-0.7 (7)
C6—C1—C2—N2	-179.8 (4)	N11—C1—C6—C5	178.6 (4)
C3—C2—N2—O22	-8.6 (6)	C2—C1—C6—C5	-0.8 (6)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N11—H11 \cdots O21	0.88	2.01	2.629 (5)	126
N11—H11 \cdots O21 ⁱ	0.88	2.50	3.327 (5)	157
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