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

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

[a]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

**Key indicators**
Single-crystal X-ray study
$T$ = 120 K
Mean $\sigma$(C–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.

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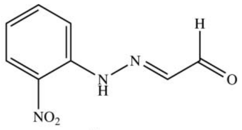
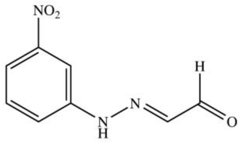
Molecules of the title compound, $C_8H_7N_3O_3$, are effectively planar and are linked into chains of edge-fused $R_2^2(12)$ and $R_4^4(24)$ rings by a combination of N—H···O and C—H···O hydrogen bonds.

## Comment

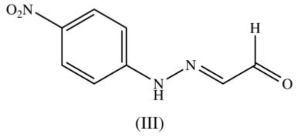
We report here the molecular and supramolecular structure of the title compound, (I), which completes the series of isomeric glyoxal nitrophenylhydrazones (I)–(III). These three isomers prove to adopt wholly different supramolecular structures. In isomer (II), the molecules are linked into simple *C*(6)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



(I)



(II)



(III)

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 H11···O21 contact (Table 2) is repulsive in nature.

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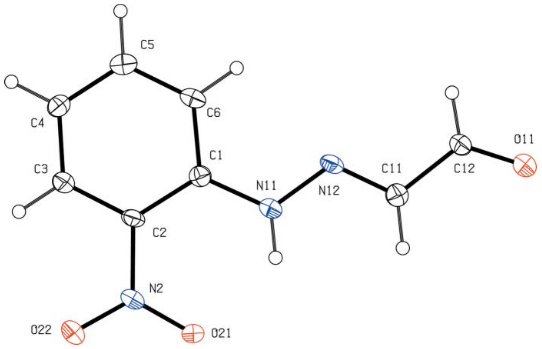

**Figure 1**
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

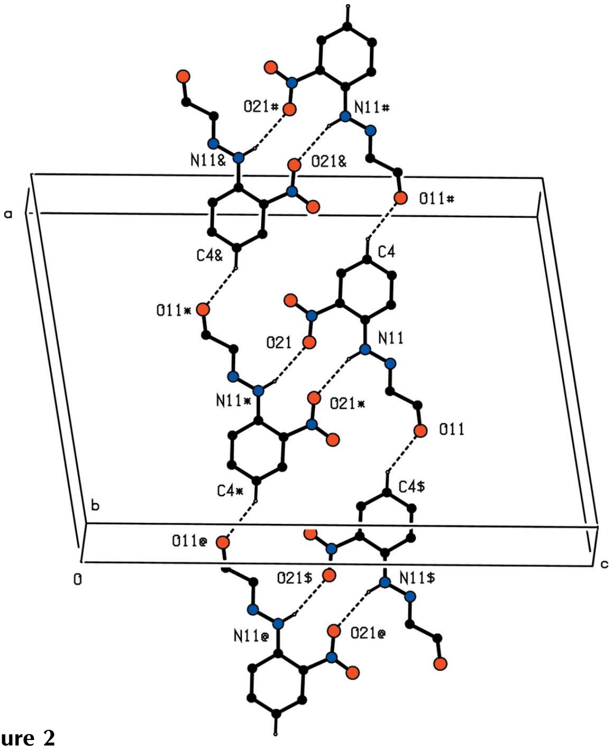

**Figure 2**
Part of the crystal structure of compound (I), showing the formation of a chain of edge-fused $R_2^2(12)$ and $R_4^4(24)$ rings along [130]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($), an ampersand (&) or an 'at' sign (@) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(\frac{1}{2} + x, \frac{3}{2} + y, z)$, $(-\frac{1}{2} + x, -\frac{3}{2} + y, z)$, $(\frac{3}{2} - x, \frac{5}{2} - y, 1 - z)$ 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 $(\frac{1}{2}n, -1 + \frac{3}{2}n, \frac{1}{2})$ ($n$ = zero or integer) and $R_4^4(24)$ rings centred at $(\frac{1}{4} + \frac{1}{2}n, -\frac{1}{4} + \frac{3}{2}n, \frac{1}{2})$ ($n$ = 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) Å
$b$ = 3.7723 (4) Å
$c$ = 23.896 (5) Å
$\beta$ = 96.429 (6)°
$V$ = 1672.4 (5) Å$^3$
$Z$ = 8
$D_x$ = 1.534 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu$ = 0.12 mm$^{-1}$
$T$ = 120 (2) K
Needle, orange
0.34 × 0.05 × 0.02 mm

### *Data collection*

Bruker Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ 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 $I > 2\sigma(I)$
$R_{\rm int}$ = 0.101
$\theta_{\max}$ = 27.6°

### *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 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.30 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| 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 (Å, °) for hydrogen bonds and short intramolecular contacts.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N11—H11···O21 | 0.88 | 2.01 | 2.629 (5) | 126 |
| N11—H11···O21$^{\rm i}$ | 0.88 | 2.50 | 3.327 (5) | 157 |
| C4—H4···O11$^{\rm ii}$ | 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 Å and N—H = 0.88 Å, and with

$U_{iso}(H) = 1.2U_{eq}(C,N)$. 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).

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