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Acetone 3-nitrophenylhydrazone, redetermined at 120 K: sheets built from N—H···O, C—H···O and C—H···N hydrogen bonds

Solange M. S. V. Wardell,[a] Marcus V. N. de Souza,[a] James L. Wardell,[b] John N. Low[c] and Christopher Glidewell[d]*

[a]Instituto de Tecnologia em Fármacos, Far-Manguinhos, FIOCRUZ, 21041-250 Rio de Janeiro, RJ, Brazil, [b]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]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 σ(C–C) = 0.003 Å
R factor = 0.058
wR factor = 0.146
Data-to-parameter ratio = 16.4

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

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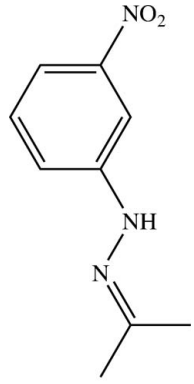
Molecules of the title compound, $C_9H_{11}N_3O_2$, are linked into sheets by a combination of N—H···O, C—H···O and C—H···N hydrogen bonds.

Comment

The structure of the title compound, (I) (Fig. 1), was determined many years ago [Cambridge Structural Database, Version 7.27 (Allen 2002) refcode NPHYAC; Menczel, 1969], using diffraction data collected at ambient temperature; no H atom coordinates were reported, and the structure was refined only to R = 0.169. We have now redetermined this structure using diffraction data collected at 120 K, and we report here the details of the supramolecular aggregation.



(I)

The molecules are linked into sheets by a combination of N—H···O, C—H···O and C—H···N hydrogen bonds (Table 1), and the sheet formation is readily analysed in terms of a hydrogen-bonded dimer as the basic building block. Atoms N1 and C2 in the molecule at (x, y, z) both act as hydrogen-bond donors to atom O31 in the molecule at ($\frac{3}{2}-x$, $\frac{1}{2}-y$, $1-z$), so forming a centrosymmetric dimer centred at ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{2}$) containing three edge-fused rings, one of $R_2^2(10)$ type (Bernstein *et al.*, 1995) flanked by two of $R_2^1(6)$ type (Fig. 2).

Atoms C5 in the molecules at (x, y, z) and ($\frac{3}{2}-x$, $\frac{1}{2}-y$, $1-z$), which form the dimer centred at ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{2}$), act as hydrogen-bond donors to atoms N2 in the molecules at ($\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) and (x, $-y$, $-\frac{1}{2}+z$), which lie in the dimers centred at ($\frac{3}{4}$, $\frac{3}{4}$, 1) and ($\frac{3}{4}$, $-\frac{1}{4}$, 0), respectively. Similarly, atoms N2 at (x, y, z) and ($\frac{3}{2}-x$, $\frac{1}{2}-y$, $1-z$) accept hydrogen bonds from atoms C5 in the molecules at ($\frac{3}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$) and (x, $1-y$, $-\frac{1}{2}+z$), which themselves form parts of the dimers centred at ($\frac{3}{4}$, $-\frac{1}{4}$, 1) and ($\frac{3}{4}$, $\frac{3}{4}$, 0), respectively. Hence each dimer is linked by C—H···N hydrogen bonds to four other dimers and

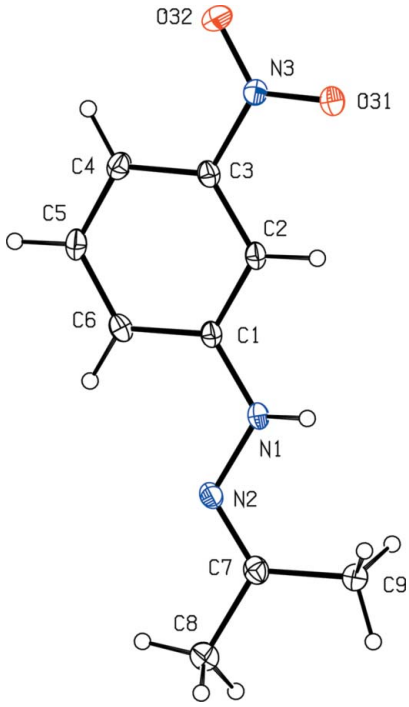


Figure 1
A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

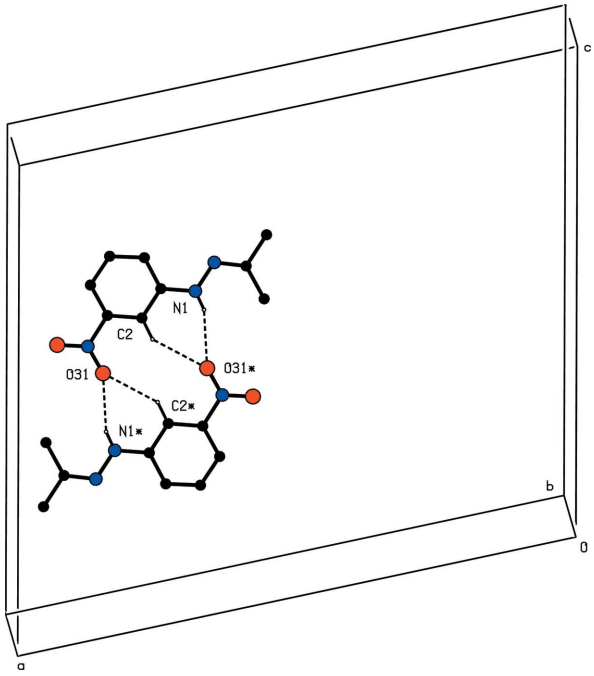


Figure 2
The molecular structure of (I), showing the formation of a centrosymmetric dimer containing three edge-fused hydrogen-bonded (dashed lines) rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. The atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

propagation of these interactions then generates a sheet parallel to (100) (Fig. 3).

This sheet is generated by centres of inversion with $x = \frac{3}{4}$, and it occupies the domain $0.5 < x < 1.0$; a second sheet, related to the first by the *C*-centring operation, is generated by

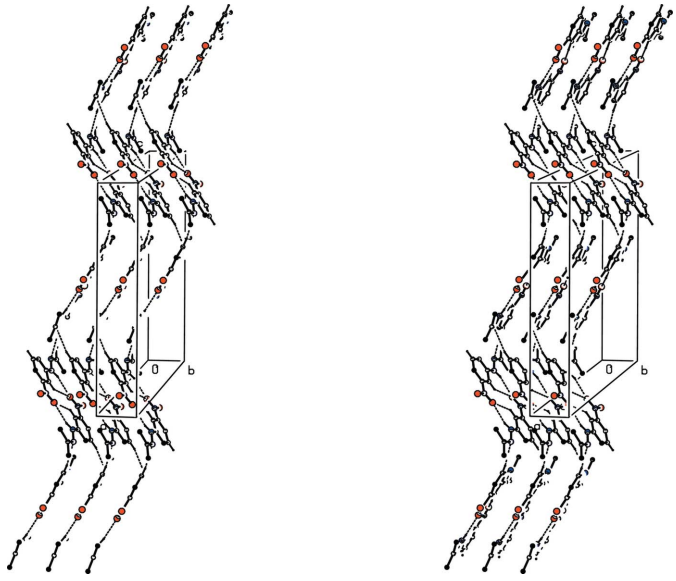


Figure 3
A stereoscopic view of part of the crystal structure of (I), showing the formation of a hydrogen-bonded (dashed lines) sheet parallel to (100). For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

centres of inversion with $x = \frac{1}{4}$, and it occupies the domain $0 < x < 0.5$; however, there are no direction-specific interactions between adjacent sheets.

Experimental

3-Nitrohydrazine hydrochloride (3 mmol) was dissolved in acetone (30 ml) and the solution was then heated under reflux for 1 h. The solution was cooled and the excess solvent was removed under reduced pressure. The resulting solid product, (I), was crystallized from ethanol.

Crystal data

$C_9H_{11}N_3O_2$
$M_r = 193.21$
Monoclinic, $C2/c$
$a = 22.7837\ (15)$ Å
$b = 3.8307\ (2)$ Å
$c = 21.7292\ (13)$ Å
$\beta = 100.129\ (3)^\circ$
$V = 1866.91\ (19)$ Å^3
$Z = 8$
$D_x = 1.375$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 120\ (2)$ K
Lath, colourless
0.20 × 0.06 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.977$, $T_{max} = 0.998$
10187 measured reflections
2117 independent reflections
1392 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 27.5^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.146$
$S = 1.03$
2117 reflections
129 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 1.9052P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O31^{i}	0.84	2.35	3.144 (2)	158
C2—H2···O31^{i}	0.95	2.49	3.305 (3)	143
C5—H5···N2^{ii}	0.95	2.61	3.546 (3)	167

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

All H atoms were located in difference maps and then treated as riding atoms with distances C—H = 0.95 Å or 0.98 Å and N—H = 0.84 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N).

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).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff of the Service for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

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supporting information

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Monoclinic, $C2/c$
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$c = 21.7292\ (13)$ Å
$\beta = 100.129\ (3)°$
$V = 1866.91\ (19)$ Å^3
$Z = 8$
$F(000) = 816$
$D_x = 1.375$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2405 reflections
$\theta = 2.9–27.5°$
$\mu = 0.10$ mm^{-1}
$T = 120$ K
Plate, colourless
0.20 × 0.06 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD 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)
$T_{min} = 0.977$, $T_{max} = 0.998$
10187 measured reflections
2117 independent reflections
1392 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.6°$
$h = -19\rightarrow28$
$k = -4\rightarrow4$
$l = -28\rightarrow28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.146$
$S = 1.03$
2117 reflections
129 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
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 1.9052P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.73046 (9)	0.6977 (5)	0.62467 (9)	0.0208 (5)
C2	0.76687 (9)	0.5776 (6)	0.58397 (9)	0.0219 (5)
C3	0.82780 (9)	0.6216 (6)	0.60016 (9)	0.0222 (5)
N3	0.86561 (8)	0.4855 (5)	0.55769 (8)	0.0247 (4)
O31	0.84193 (7)	0.3164 (5)	0.51155 (7)	0.0349 (4)
O32	0.91943 (7)	0.5383 (5)	0.56931 (7)	0.0379 (5)
C4	0.85489 (9)	0.7812 (6)	0.65520 (10)	0.0248 (5)
C5	0.81809 (10)	0.9004 (6)	0.69488 (10)	0.0261 (5)
C6	0.75668 (9)	0.8622 (5)	0.68035 (9)	0.0231 (5)
N1	0.66953 (7)	0.6555 (5)	0.60836 (8)	0.0252 (4)
N2	0.63415 (8)	0.7306 (5)	0.65204 (8)	0.0240 (4)
C7	0.57836 (10)	0.6671 (6)	0.63644 (10)	0.0259 (5)
C8	0.54023 (10)	0.7472 (7)	0.68419 (11)	0.0343 (6)
C9	0.54904 (9)	0.5192 (6)	0.57486 (10)	0.0279 (5)
H2	0.7501	0.4674	0.5457	0.026*
H4	0.8970	0.8073	0.6652	0.030*
H5	0.8352	1.0110	0.7329	0.031*
H6	0.7323	0.9479	0.7083	0.028*
H1	0.6569	0.5158	0.5792	0.030*
H8A	0.5645	0.8593	0.7205	0.041*
H8B	0.5233	0.5301	0.6973	0.041*
H8C	0.5079	0.9047	0.6660	0.041*
H9A	0.5556	0.6765	0.5411	0.033*
H9B	0.5062	0.4945	0.5744	0.033*
H9C	0.5662	0.2900	0.5688	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0254 (11)	0.0207 (11)	0.0158 (10)	−0.0018 (9)	0.0018 (8)	0.0009 (8)
C2	0.0276 (11)	0.0217 (11)	0.0154 (10)	−0.0027 (9)	0.0010 (8)	0.0008 (8)
C3	0.0271 (11)	0.0219 (11)	0.0176 (10)	−0.0009 (9)	0.0035 (8)	0.0016 (9)
N3	0.0238 (10)	0.0284 (11)	0.0213 (9)	−0.0023 (8)	0.0025 (7)	−0.0002 (8)
O31	0.0317 (9)	0.0481 (11)	0.0245 (8)	−0.0038 (8)	0.0043 (7)	−0.0110 (8)
O32	0.0213 (8)	0.0539 (12)	0.0382 (10)	−0.0046 (8)	0.0041 (7)	−0.0086 (8)
C4	0.0243 (11)	0.0247 (12)	0.0236 (11)	−0.0048 (9)	−0.0005 (9)	0.0010 (9)
C5	0.0329 (12)	0.0251 (12)	0.0181 (10)	−0.0049 (10)	−0.0021 (9)	−0.0010 (9)
C6	0.0312 (12)	0.0205 (11)	0.0184 (10)	0.0009 (9)	0.0060 (9)	0.0012 (9)
N1	0.0263 (10)	0.0314 (11)	0.0177 (9)	−0.0024 (8)	0.0031 (7)	−0.0074 (8)
N2	0.0266 (10)	0.0271 (10)	0.0185 (9)	0.0028 (8)	0.0049 (7)	0.0000 (8)
C7	0.0294 (12)	0.0258 (12)	0.0221 (11)	0.0044 (10)	0.0037 (9)	0.0032 (9)
C8	0.0318 (13)	0.0422 (15)	0.0296 (12)	0.0024 (11)	0.0075 (10)	−0.0021 (11)
C9	0.0262 (12)	0.0320 (14)	0.0250 (12)	−0.0017 (10)	0.0035 (9)	−0.0026 (10)

Geometric parameters (Å, º)

C1—N1	1.381 (2)	C6—H6	0.95
C1—C2	1.393 (3)	N1—N2	1.379 (2)
C1—C6	1.401 (3)	N1—H1	0.84
C2—C3	1.381 (3)	N2—C7	1.280 (3)
C2—H2	0.95	C7—C8	1.497 (3)
C3—C4	1.387 (3)	C7—C9	1.498 (3)
C3—N3	1.465 (3)	C8—H8A	0.98
N3—O32	1.224 (2)	C8—H8B	0.98
N3—O31	1.235 (2)	C8—H8C	0.98
C4—C5	1.382 (3)	C9—H9A	0.98
C4—H4	0.95	C9—H9B	0.98
C5—C6	1.387 (3)	C9—H9C	0.98
C5—H5	0.95		
N1—C1—C2	118.85 (18)	C1—C6—H6	119.9
N1—C1—C6	122.08 (19)	N2—N1—C1	118.80 (16)
C2—C1—C6	119.06 (19)	N2—N1—H1	119.1
C3—C2—C1	118.82 (19)	C1—N1—H1	117.7
C3—C2—H2	120.6	C7—N2—N1	116.84 (17)
C1—C2—H2	120.6	N2—C7—C8	116.60 (19)
C2—C3—C4	123.2 (2)	N2—C7—C9	125.06 (19)
C2—C3—N3	118.17 (18)	C8—C7—C9	118.34 (19)
C4—C3—N3	118.57 (19)	C7—C8—H8A	109.5
O32—N3—O31	122.21 (18)	C7—C8—H8B	109.5
O32—N3—C3	119.31 (17)	H8A—C8—H8B	109.5
O31—N3—C3	118.47 (17)	C7—C8—H8C	109.5
C5—C4—C3	117.2 (2)	H8A—C8—H8C	109.5
C5—C4—H4	121.4	H8B—C8—H8C	109.5
C3—C4—H4	121.4	C7—C9—H9A	109.5
C4—C5—C6	121.45 (19)	C7—C9—H9B	109.5
C4—C5—H5	119.3	H9A—C9—H9B	109.5
C6—C5—H5	119.3	C7—C9—H9C	109.5
C5—C6—C1	120.26 (19)	H9A—C9—H9C	109.5
C5—C6—H6	119.9	H9B—C9—H9C	109.5
N1—C1—C2—C3	179.65 (19)	C3—C4—C5—C6	0.0 (3)
C6—C1—C2—C3	0.6 (3)	C4—C5—C6—C1	0.5 (3)
C1—C2—C3—C4	−0.2 (3)	N1—C1—C6—C5	−179.77 (19)
C1—C2—C3—N3	178.36 (18)	C2—C1—C6—C5	−0.8 (3)
C2—C3—N3—O32	175.98 (19)	C2—C1—N1—N2	171.33 (18)
C4—C3—N3—O32	−5.4 (3)	C6—C1—N1—N2	−9.7 (3)
C2—C3—N3—O31	−4.9 (3)	C1—N1—N2—C7	−175.71 (19)
C4—C3—N3—O31	173.65 (19)	N1—N2—C7—C8	179.65 (18)
C2—C3—C4—C5	−0.2 (3)	N1—N2—C7—C9	−0.1 (3)
N3—C3—C4—C5	−178.69 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O31^{i}	0.84	2.35	3.144 (2)	158
C2—H2···O31^{i}	0.95	2.49	3.305 (3)	143
C5—H5···N2^{ii}	0.95	2.61	3.546 (3)	167

Symmetry codes: (i) −*x*+3/2, −*y*+1/2, −*z*+1; (ii) −*x*+3/2, *y*+1/2, −*z*+3/2.