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A re-examination of supramolecular aggregation in two polymorphs of acetone 2,4-dinitrophenylhydrazone

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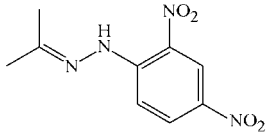
The structure of the triclinic polymorph of acetone 2,4-dinitrophenylhydrazone, $C_9H_{10}N_4O_4$, has been redetermined from diffraction data collected at 120 (2) K; the molecules are linked by C—H···O hydrogen bonds into centrosymmetric $R_2^2(10)$ dimers which are themselves linked into a chain by an aromatic π–π stacking interaction. In the monoclinic polymorph, which crystallizes with $Z' = 2$ in the space group $P2_1/n$, one type of molecule forms dimers exactly as in the triclinic polymorph, while the other forms $C(6)$ chains.

Comment

Some years ago, the structure of the triclinic polymorph of acetone 2,4-dinitrophenylhydrazone, (I), was reported from diffraction data collected at 296 K (Fronczek, 1994); the author noted the occurrence of an intramolecular N—H···O hydrogen bond, but did not report any direction-specific intermolecular interactions. More recently, the Cambridge Structural Database (CSD; Allen, 2002) has recorded the atomic coordinates for an otherwise unpublished monoclinic polymorph, (II) (CSD refcode LEBGEE01; Gelbrich, 2005). We have now taken the opportunity to redetermine the structure of triclinic polymorph (I), using diffraction data



(I) Triclinic polymorph
(II) Monoclinic polymorph

collected at 120 (2) K, and to examine in detail the supramolecular structure of monoclinic polymorph (II) using the atomic coordinates retrieved from the CSD. Neither of these previous reports employed an atom-labelling scheme consistent with the chemical nomenclature; we have employed a chemically consistent scheme in the new determination for polymorph (I), while retaining the original atom-labelling scheme for polymorph (II).

For polymorph (I) (Fig. 1), the somewhat larger low-temperature data set (1957 reflections labelled observed *versus* 1629 at 296 K) has provided a more precise determination of the structure, associated with a lower R value (0.041 *versus* 0.058). The unit-cell dimensions, space group and atomic coordinates indicate that no phase change has occurred between 296 and 120 K, but examination of the atom coordinates shows that the molecules are, in fact, linked by paired C—H···O hydrogen bonds (Table 1) into centrosymmetric dimers which, in turn, are linked into chains by an aromatic π–π stacking interaction; the molecule also has an intramolecular N—H···O hydrogen bond, as reported by Fronczek (1994). Aryl atom C5 in the molecule at (x, y, z) acts as a hydrogen-bond donor to nitro atom O42 in the molecule at $(-x, -y, 1 - z)$, thus generating by inversion a centrosymmetric $R_2^2(10)$ (Bernstein *et al.*, 1995) dimer centred at $(0, 0, \frac{1}{2})$. In addition, there is a π–π stacking interaction between the aryl rings of the molecules at (x, y, z) and $(1 - x, -y, 1 - z)$.

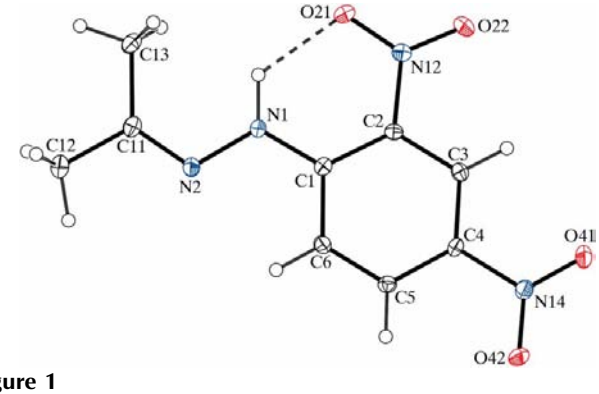


Figure 1
A molecule of triclinic polymorph (I), showing the atom-labelling scheme and the intramolecular hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 30% probability level.

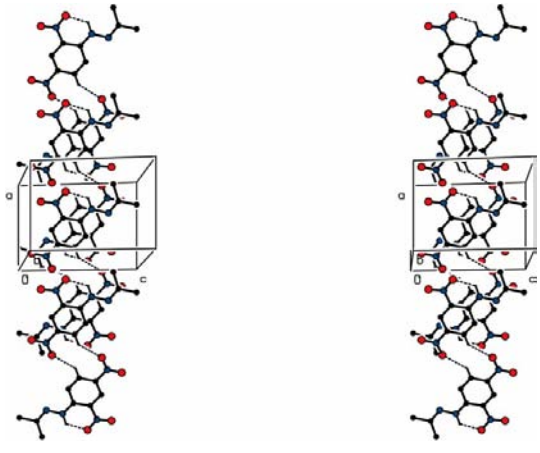


Figure 2
A stereoview of part of the crystal structure of polymorph (I), showing the formation of a π-stacked chain of hydrogen-bonded dimers along [100]. For clarity, H atoms bonded to C atoms but not involved in the motifs shown have been omitted.

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These rings are strictly parallel with an interplanar spacing of 3.361 (2) Å; the ring-centroid separation is 3.6123 (9) Å, corresponding to a ring-centroid offset of 1.323 (2) Å. Propagation by inversion of these two interactions then generates a π-stacked chain of hydrogen-bonded dimers running parallel to the [100] direction (Fig. 2).

The monoclinic polymorph crystallizes with $Z' = 2$ in the space group $P2_1/n$ (Gelbrich, 2005), and Fig. 3 shows the original atom-labelling scheme; the molecules containing atoms N1 and N2 are designated here as types 1 and 2, respectively. Each of the independent molecules adopts a conformation identical to that in polymorph (I) and each contains an intramolecular N—H···O hydrogen bond (Table 1). The molecules of type 1 are linked by paired C—H···O hydrogen bonds into cyclic centrosymmetric $R_2^2(10)$ dimers (Fig. 4*a*), while the molecules of type 2 are linked by a single C—H···O hydrogen bond into $C(6)$ chains running parallel to the [010] direction and generated by the 2_1 screw axis along $(-\frac{1}{4}, y, \frac{1}{4})$ (Fig. 4*b*). Thus, the aggregation of the type 1 molecules in polymorph (II) exactly matches that in polymorph (I), while the aggregation of the type 2 molecules is entirely different. There are no direction-specific interactions

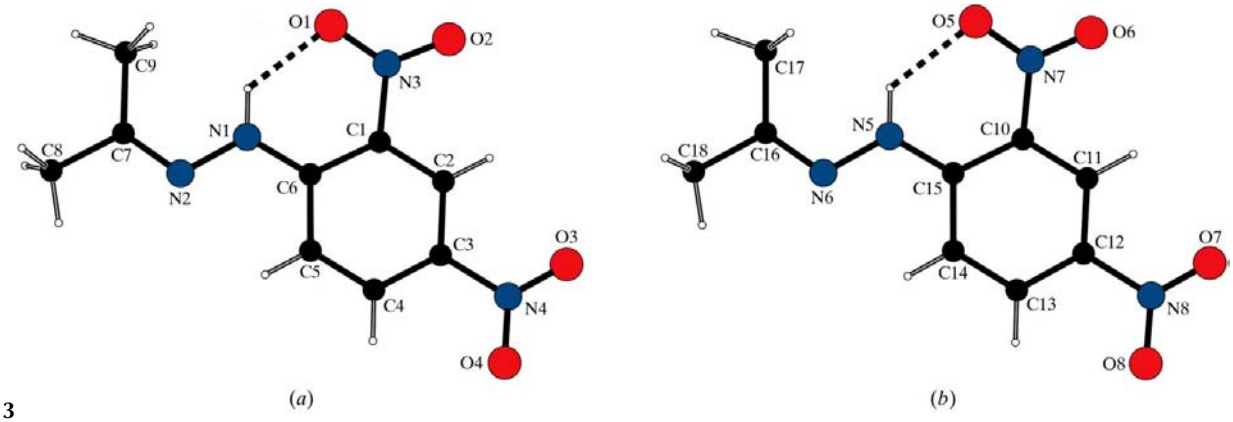

Figure 3
The two independent molecules of monoclinic polymorph (II) (CSD refcode LEBGEE01; Gelbrich, 2005), showing the original atom-labelling scheme of (*a*) molecule 1 and (*b*) molecule 2. The atoms are drawn as spheres with arbitrary radii.

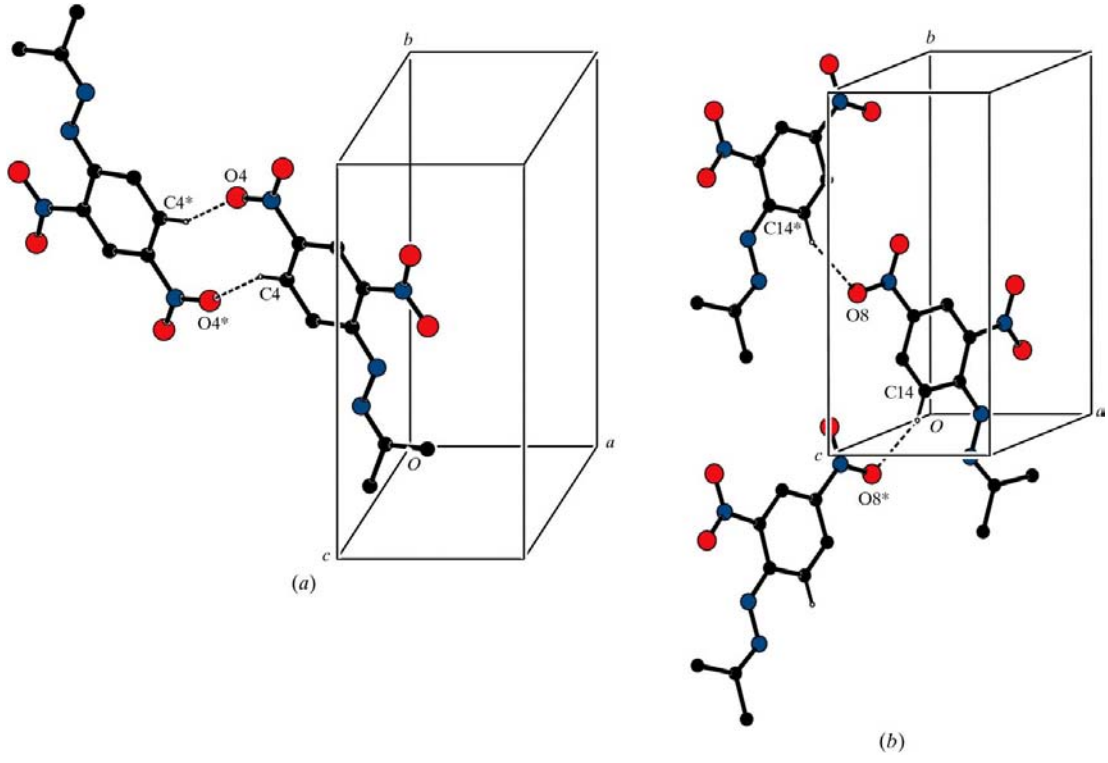

Figure 4
Parts of the crystal structure of monoclinic polymorph (II) (CSD refcode LEBGEE01; Gelbrich, 2005) showing (*a*) type 1 molecules linked into a centrosymmetric $R_2^2(10)$ dimer, where the atoms marked with an asterisk (*) are at the symmetry position $(-2 - x, 1 - y, z)$, and (*b*) type 2 molecules linked into a $C(6)$ chain along [010], where the 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. The original atomic coordinates and atom labels have been used and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

of any type between the aggregates; in particular, there are none between the dimers of type 1 molecules and the chains of type 2 molecules.

Experimental

2,4-Dinitrohydrazine (3 mmol) was dissolved in acetone (30 ml) and the solution was then heated under reflux for 1 h. The resulting solution was cooled and the excess solvent was removed under reduced pressure. The solid product, *viz*. polymorph (I), was crystallized from ethanol (m.p. 399–400 K).

Crystal data

$C_9H_{10}N_4O_4$
M_r = 238.21
Triclinic, $P\overline{1}$
a = 7.0932 (3) Å
b = 8.2032 (4) Å
c = 10.0526 (4) Å
α = 66.613 (2)°
β = 88.822 (3)°
γ = 77.387 (3)°
V = 522.49 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 120 (2) K
0.40 × 0.40 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.964, T_{max} = 0.998
12000 measured reflections
2393 independent reflections
1957 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.117
S = 1.04
2393 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Hydrogen-bond parameters (Å, °) for polymorph (I) at 120 K and for polymorph (II) at 150 K.

Polymorph	D—H···A	D—H	H···A	D···A	D—H···A
(I)	N1—H1···O21	0.97	1.91	2.5994 (15)	125
	C5—H5···O42^{i}	0.95	2.45	3.2660 (16)	144
(II)	N1—H1···O1	0.88	1.95	2.592 (3)	129
	N5—H11···O5	0.88	1.98	2.618 (3)	129
	C4—H3···O4^{ii}	0.95	2.40	3.281 (4)	154
	C14—H14···O8^{iii}	0.95	2.42	3.279 (4)	150

Note: original atom numbering is used for polymorph (II). Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x-2, -y+1, -z$; (iii) $-x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

All H atoms in (I) were located in difference maps and then allowed to ride in geometrically idealized positions, with C—H distances of 0.95 (aromatic) or 0.98 Å (methyl) and an N—H distance of 0.97 Å, and with $U_{iso}(H) = kU_{eq}$(carrier), where k = 1.5 for the methyl groups and k = 1.2 for all other H atoms. Three reflections (001, 100 and $\overline{1}01$), whose intensities had been attenuated by the beam-stop, were omitted from the final refinements.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3098). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Fronczek, F. R. (1994). *Acta Cryst.* C**50**, 122–124.
Gelbrich, T. (2005). Private communication (refcode LEBGEE01). CCDC, Union Road, Cambridge, England.
Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
McArdle, P. (2003). *OSCAIL for Windows*. Version 1.0. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
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). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.