Orthorhombic
$P2_12_12_1$
$a = 9.185\,(1)$ Å
$b = 12.052\,(1)$ Å
$c = 18.899\,(1)$ Å
$V = 2092.1\,(2)$ Å^3
$Z = 4$
$D_x = 1.357$ Mg m^{-3}
D_m not measured

Cell parameters from 32
    reflections
$\theta = 12\text{–}45°$
$\mu = 1.809$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.4 \times 0.3 \times 0.2$ mm
Colourless

Data collection

Siemens *P4* diffractometer
$\theta/2\theta$ scan
Absorption correction:
    ψ scan (North *et al.*,
    1968)
    $T_{min} = 0.472$, $T_{max} = 0.696$
3644 measured reflections
1739 independent reflections
    (plus 1417 Friedel-related
    reflections)

2496 reflections with
    $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 69.28°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = -22 \rightarrow 22$
3 standard reflections
    every 97 reflections
    intensity decay: $<0.5\%$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.161$
$S = 1.057$
3156 reflections
268 parameters
H atoms treated by a
    mixture of independent
    and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 1.0523P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.020$

$\Delta\rho_{max} = 0.344$ e Å^{-3}
$\Delta\rho_{min} = -0.238$ e Å^{-3}
Extinction correction:
    SHELXL97 (Sheldrick,
    1997)
Extinction coefficient:
    0.0058 (6)
Scattering factors from
    *International Tables for
    Crystallography* (Vol. C)
Absolute structure: Flack
    (1983)
Flack parameter = $-0.03\,(4)$

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

N2—C3	1.416 (8)	C5—C4	1.497 (7)
N2—C1	1.462 (6)	C4—C3	1.474 (9)
N2—C2	1.461 (6)	C1—C21	1.551 (7)
C10—C1	1.542 (6)	C1—C20	1.544 (6)
C3—N2—C1	119.3 (4)	N2—C1—C10	110.2 (4)
C3—N2—C2	113.9 (4)	F2—C21—F3	106.0 (4)
C1—N2—C2	120.0 (4)	F2—C21—F1	106.0 (4)
C5—C10—C1	121.8 (4)	F3—C21—F1	105.0 (4)
C10—C5—C4	121.3 (4)	F2—C21—C1	113.0 (4)
C3—C4—C5	113.1 (5)	F3—C21—C1	113.7 (4)
N2—C3—C4	112.9 (6)	F1—C21—C1	112.5 (4)
C1—C10—C5—C4	1.3 (7)	C2—N2—C1—C20	51.4 (6)
C10—C5—C4—C3	16.0 (8)	C5—C10—C1—N2	7.6 (6)
C1—N2—C3—C4	56.9 (8)	C5—C10—C1—C21	−113.9 (5)
C5—C4—C3—N2	−42.8 (8)	C9—C10—C1—C21	66.6 (5)
C3—N2—C1—C10	−37.1 (7)	C5—C10—C1—C20	129.4 (5)
C3—N2—C1—C21	82.5 (6)	C21—C1—C20—S1	−179.4 (3)
C2—N2—C1—C21	−66.7 (6)	O3—S1—C11—C16	−15.2 (5)
C3—N2—C1—C20	−159.4 (6)	C20—S1—C11—C16	−126.0 (4)

H atoms were located at calculated positions and refined in the riding mode.

Data collection: *XSCANS* (Siemens, 1997). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular

graphics: *SHELXTL-Plus* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*97.

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1-Acetyl-2-(3,3-dimethyl-2-butylidene)-hydrazine: a monoclinic crystal structure with local orthorhombic pseudosymmetry

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Abstract

The crystal packing of the title molecule, 2'-(3,3-dimethylbut-2-ylidene)acetohydrazide, $C_8H_{16}N_2O$, shows layers with local pseudo-orthorhombic symmetry. The two independent molecules are related by a local noncrystallographic glide plane perpendicular to the a axis. The glide planes only act within a layer with a thickness of half the c cell parameter, resulting in an overall monoclinic symmetry for the structure.

Comment

·The structure of the title molecule, (I), contains two crystallographically independent molecules. The dimensions of both molecules are almost identical; the only significant differences between the molecules are rotational differences of $\sim 2°$ about the amide C—N bonds and of $\sim 3°$ about the C3—C5 and the corresponding C11—C13 bonds. The two independent molecules are related by a non-crystallographic glide plane perpendicular to the a axis, with a translation vector of $\mathbf{b}/2$. This glide plane is not continuous in the direction perpendicular to the (001) plane, but only acts within a layer with a thickness of half the c cell parameter (see Fig. 2). The symmetry within this layer is approximately orthorhombic. Neighbouring layers are displaced by 0.70 Å in the a direction, leading to a monoclinic overall symmetry for the three-dimensional crystal structure. Without these displacements, the structure would be orthorhombic with space group $Pbca$, but with rather short intermolecular H···H contacts (as short as 2.23 Å) between neighbouring layers. A quantitative measure of the exactness of the pseudosymmetry operation is given by the deviation of the atomic positions from the hypothetical coordinates calculated by the local pseudo-glide plane. This deviation is 0.073 Å averaged over all 22 non-H atoms; if the methyl C atoms of the $tert$-butyl group are excluded, it is reduced to 0.043 Å.

(I)
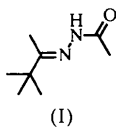
Pseudosymmetry in organic crystal structures has been discussed by Zorky (1996). Using the nomenclature from that work, the layers in the title compound belong to structural class $P_{l(XY)}2_1/b$, $Z = 4$ (1).

The angle between the plane of the C=N double bond and the plane of the N-acetyl group is 15.2 (2)°
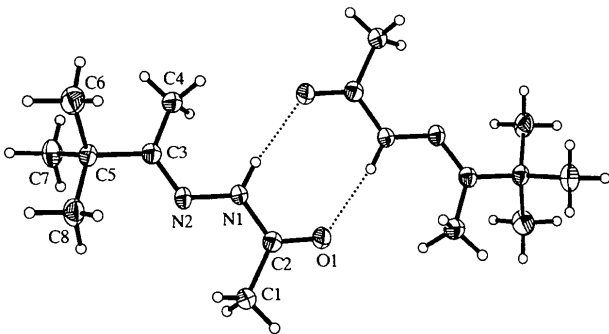

Fig. 1. The molecular structures of the hydrogen-bonded dimers of (a) molecule 1 of (I) and (b) molecule 2 of (I), with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

for molecule 1 and 12.4 (2)° for molecule 2. The shortest intramolecular contact distances are N2···H1C [2.46 (2) Å] and N4···H9C [2.48 (2) Å], and these approach the van der Waals contact distance of 2.5 Å between nitrogen and hydrogen. Both molecules form centrosymmetric dimers by hydrogen bonding between the amide groups (Table 1). Additional intermolecular O···H distances are ~ 2.60 Å or longer and thus contribute only very weakly to the crystal packing.
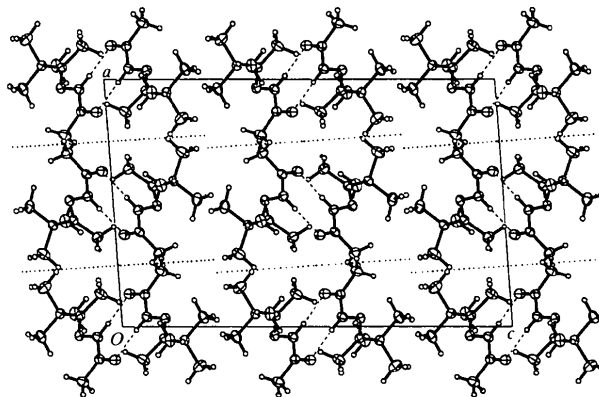

Fig. 2. The crystal packing of (I) shown down the b axis. The pseudo-glide planes are indicated by dotted lines.

All crystal structures of acetylhydrazone-containing compounds reported in the literature are for metal-bonded structures (Domiano *et al.*, 1983; Curtis *et al.*, 1984; Ianelli *et al.*, 1996; Summers *et al.*, 1996). These structures contain *trans* amide bonds rather than the *cis* amide bond observed in the title compound.

Experimental

The title compound was prepared according to Jefferson & Warkentin (1992). The compound was recrystallized from a solution in hexane/diethyl ether. Several crystals of the title compound were found to be twinned about the pseudo-symmetry plane. The crystal used for the data collection, however, was not affected by twinning.

Crystal data

$C_8H_{16}N_2O$	Mo $K\alpha$ radiation
$M_r = 156.23$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 261
$P2_1/c$	reflections
$a = 12.5516(15)$ Å	$\theta = 3–23°$
$b = 7.6362(7)$ Å	$\mu = 0.073$ mm^{-1}
$c = 19.828(2)$ Å	$T = 134$ K
$\beta = 94.049(11)°$	Thick plate
$V = 1895.7(4)$ Å^3	$1.00 \times 0.65 \times 0.20$ mm
$Z = 8$	Colourless
$D_x = 1.095$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART diffractometer	$R_{int} = 0.028$
	$\theta_{max} = 30.13°$
ω scans	$h = -17 \rightarrow 16$
Absorption correction:	$k = -10 \rightarrow 10$
empirical (*SADABS*;	$l = -27 \rightarrow 26$
Sheldrick, 1996a)	365 standard reflections
$T_{min} = 0.861$, $T_{max} = 1.000$	frequency: 540 min
31 151 measured reflections	intensity decay: none
5043 independent reflections	
4935 reflections with	
$I > 0$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.355$ e Å^{-3}
$R = 0.063$	$\Delta\rho_{min} = -0.192$ e Å^{-3}
$wR = 0.053$	Extinction correction:
$S = 1.283$	isotropic (*MolEN*; Fair,
4935 reflections	1990)
328 parameters	Extinction coefficient:
H atoms refined isotropically	2.5 (4) × 10^{-6}
$w = 4F_o^2/[\sigma^2(F_o^2)$	Scattering factors from *Inter-*
$+ 0.0009F_o^4]$	*national Tables for X-ray*
$(\Delta/\sigma)_{max} = 0.010$	*Crystallography* (Vol. IV)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H01$\cdots$O1'	0.89 (1)	2.06 (1)	2.938 (1)	170 (1)
N3—H03$\cdots$O2"	0.89 (1)	2.08 (1)	2.970 (1)	170 (1)

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $-x, 2 - y, -z$.

The measured reflections were corrected for absorption and for systematic variations in the uniformity of the X-ray beam using *SADABS* (Sheldrick, 1996a). H atoms were taken from a difference synthesis and were refined with isotropic displacement parameters.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS* in *SHELXTL* (Sheldrick, 1996b). Program(s) used to refine structure: *LSFM* in *MolEN* (Fair, 1990). Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *CIF* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1301). Services for accessing these data are described at the back of the journal.

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1-Methyl-4-(N-methylnitramino)pyridinium bromide

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Abstract

The structure of the title compound, $C_7H_{10}N_3O_2^+ \cdot Br^-$, is composed of 1-methyl-4-(N-methylnitramino)pyridinium cations and bromide anions, with normal electrostatic interactions. The cations are present in the nitramino form. The N—NO$_2$ nitramino group is twisted 51.5 (4)° out of the plane of the aromatic ring.

Comment

N-Methyl-N-(4-pyridyl)nitramine, (1), is a typical secondary aromatic nitramine which can be rearranged to 4-methylamino-3-nitropyridine when heated in an inert solvent. N-(4-Pyridyl)nitramine, (2), behaves analogously, but the rearrangement requires more severe conditions and results in much lower yield (Daszkiewicz *et al.*, 1997). X-ray studies have revealed that primary pyridylnitramines such as (2) exist in the nitrimino tautomeric form (Krygowski *et al.*, 1996). The difference in susceptibility of (1) and (2) to the rearrangement may be due to differences in their molecular structures. In a typical secondary aromatic nitramine, the plane of the N—NO$_2$ group is twisted ca 70° out of the ring plane along the Ar—N bond (Ejsmont *et al.*, 1998; Anulewicz *et al.*, 1993). In (3), the N—NO$_2$ group is nearly coplanar with the pyridine ring. Despite this difference, the geometries of both the ring and the N—NO$_2$ substituent are not disturbed to the degree implied by the nitrimine formulation (Bujak *et al.*, 1998). The pyridine N atom in (1) retains its nucleophilic character, hence the preparation of (4) is straightforward. We have examined its molecular structure to compare it with the structure of