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1-Acetyl-5-benzyl-2-methylthio-5*H*-imidazol-4-one

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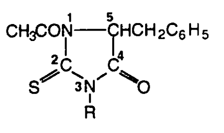
Abstract

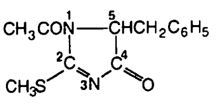
Atoms of the imidazolone ring in the title compound, $C_{13}H_{14}N_2O_2S$, are approximately coplanar. The N(1) acetyl group lies close to the plane while the C(2) methylthio substituent is twisted by about 7° from it. The imidazolone and phenyl rings face each other, the dihedral angle between their perpendiculars being 53.4 (3)°.

Comment

The methylation of 1-acetyl-5-benzyl-2-thioxoimidazolidin-4-one [*N*-acetylphenylalanine thiohydantoin (1), $R = \text{H}$] by means of diazomethane has been studied, and the reaction, experimental details of which will be reported elsewhere, found to give two isomers, namely the *N*-methyl isomer [(1), $R = \text{CH}_3$] and the *S*-methyl isomer (2). The structure of the former isomer was established by means of its ^{1}H NMR spectrum (the relevant spectroscopic data will be presented elsewhere) as 1-acetyl-5-benzyl-3-methyl-2-thioxoimidazolidin-4-one [(1), $R = \text{CH}_3$]. The structure of the latter isomer was shown by X-ray analysis to be 1-acetyl-5-benzyl-2-methylthio-5*H*-imidazol-4-one (2).



(1)



(2)

The atoms of the imidazolone ring are coplanar to within 0.038 (5) Å, but there is a slight degree of ring pucker, as reflected in the ring torsion angles (Table 2); the acetyl group at N(1) lies close to the ring plane [torsion angle C(5)—N(1)—C(1′)—C(1″) 2.6 (4)°], while the S—CH_3 group at C(2) is twisted by about 7° from it. The benzyl group at C(5) adopts an orientation relative to the imidazolone moiety as defined by the torsion angles C(4)—C(5)—C(5′)—C(6′) of 57.1 (3)° and C(5)—C(5′)—C(6′)—C(7′) of 81.9 (3)°. The two rings face each other, the dihedral angle between their perpendiculars being 53.4 (3)° (see Fig. 2). When compared with other 2-thiohydantoin derivatives (Lempert, Nyitrai, Zauer, Kálmán, Argay, Duisenberg & Sohar, 1973; Kiéc-Kononowicz, Zejc, Mikolajczyk, Zatorski, Karolak-

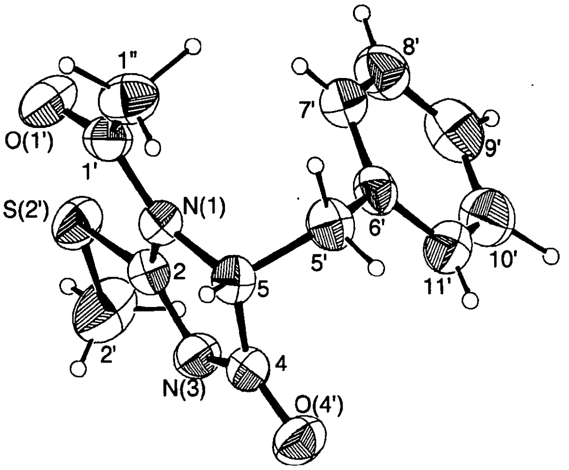


Fig. 1. Perspective view of (2) (3*R* enantiomer) with displacement ellipsoids scaled to 50% probability. The C symbol for C atoms is omitted and H atoms are denoted by spheres of arbitrary radii.

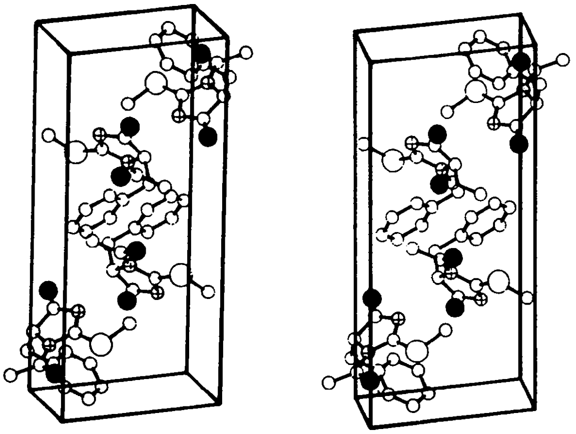


Fig. 2. Stereoview of the crystal packing, projected along **a** with the *b* axis vertical.

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Wojciechowska & Wieczorek, 1980; Karolak-Wojciechowska, Mikolajczyk, Zatorski, Kiéc-Kononowicz & Zejc, 1985; Camerman, Camerman & Duncanson, 1981; Kwiatkowski, Karolak-Wojciechowska & Kiéc-Kononowicz, 1991), revealed by a search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983), the N—C bond lengths, N(1)—C(2), N(3)—C(2), N(3)—C(4) and N(1)—C(5), in the imidazolone ring, with values of 1.391 (3), 1.312 (3), 1.389 (2) and 1.474 (3) Å, respectively, indicate a lesser extent of electron-charge delocalization than is generally observed for 2-thiohydantoin structures. The lengths of the exocyclic $C(sp^2)$—S and $C(sp^3)$—S bonds, 1.725 (4) and 1.798 (4) Å, respectively, and the angle subtended at the S atom, 99.7 (2)°, are as expected.

There being no hydrogen-bonding donors in the structure, the molecules are held together in the crystal by van der Waals interactions only. There are no abnormally short intermolecular contacts. The molecular packing, illustrated in Fig. 2, shows that there is no close overlap of the π-electron systems.

Experimental

Crystal data

$C_{13}H_{14}N_2O_2S$
$M_r = 262.3$
Monoclinic
$P2_1/c$
$a = 8.811$ (1) Å
$b = 17.768$ (2) Å
$c = 9.426$ (1) Å
$\beta = 115.20$ (1)°
$V = 1335.2$ (6) Å^3
$Z = 4$
$D_x = 1.305$ Mg m^{-3}
$D_m = 1.295$ (5) Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 21$–$41°$
$\mu = 2.08$ mm^{-1}
$T = 292$ (1) K
Prismatic
0.395 × 0.395 × 0.290 mm
Colourless
Crystal source: *n*-heptane/methylene chloride mixture

Data collection

Rigaku AFC diffractometer
ω-2θ scans [rate 2° min^{-1}; $\Delta\omega = (1.2 + 0.5\tan\theta)°$]
Absorption correction: analytical
$T_{min} = 0.445$, $T_{max} = 0.460$
2494 measured reflections
2272 independent reflections
1662 observed reflections [$I \geq 2\sigma(I)$]

$R_{int} = 0.012$
$\theta_{max} = 65°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 11$
3 standard reflections (122, 0$\bar{5}$2, $\bar{3}\bar{1}$2) monitored every 50 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.037$
$wR = 0.052$
$S = 1.88$
1662 reflections
222 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.0005F_o^2]$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: isotropic $F^* = F(1 - gF^2/\sin\theta)$
Extinction coefficient: $g = 3.9$ (2) × 10^{-6}
Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
N(1)	0.3721 (2)	−0.1531 (1)	0.0398 (2)	3.36 (5)
C(2)	0.4554 (3)	−0.1876 (1)	0.1851 (3)	3.42 (5)
N(3)	0.3654 (2)	−0.2357 (1)	0.2224 (2)	3.64 (5)
C(4)	0.2068 (3)	−0.2361 (1)	0.0982 (3)	3.46 (5)
C(5)	0.1960 (3)	−0.1781 (1)	−0.0243 (3)	3.38 (5)
C(1′)	0.4471 (3)	−0.1078 (1)	−0.0329 (3)	4.01 (6)
O(1′)	0.5951 (2)	−0.0938 (1)	0.0333 (2)	5.24 (5)
C(1″)	0.3367 (4)	−0.0781 (2)	−0.1921 (4)	5.04 (8)
S(2′)	0.66164 (7)	−0.16683 (4)	0.30622 (8)	4.28 (2)
C(2′)	0.6839 (4)	−0.2183 (3)	0.4782 (4)	5.87 (9)
O(4)	0.0910 (2)	−0.2753 (1)	0.0908 (2)	4.52 (5)
C(5′)	0.0722 (3)	−0.1155 (1)	−0.0319 (3)	3.73 (6)
C(6′)	0.1174 (3)	−0.0766 (1)	0.1245 (3)	3.49 (5)
C(7′)	0.2369 (3)	−0.0198 (1)	0.1744 (3)	4.18 (7)
C(8′)	0.2809 (4)	0.0144 (2)	0.3163 (4)	4.92 (8)
C(9′)	0.2064 (4)	−0.0076 (2)	0.4141 (4)	5.47 (8)
C(10′)	0.0868 (4)	−0.0632 (2)	0.3649 (4)	5.71 (9)
C(11′)	0.0422 (4)	−0.0977 (2)	0.2205 (4)	4.66 (7)

Table 2. *Selected geometric parameters* (Å, °)

N(1)—C(2)	1.391 (3)	C(1′)—O(1′)	1.208 (3)
N(1)—C(5)	1.474 (3)	C(1′)—C(1″)	1.494 (4)
C(2)—N(3)	1.312 (3)	C(2)—S(2′)	1.725 (2)
N(3)—C(4)	1.389 (2)	S(2′)—C(2′)	1.798 (4)
C(4)—C(5)	1.520 (4)	C(4)—O(4)	1.213 (3)
N(1)—C(1′)	1.393 (4)	C(5)—C(5′)	1.538 (3)
C(2)—N(1)—C(5)	107.0 (2)	O(1′)—C(1′)—C(1″)	123.0 (2)
N(1)—C(2)—N(3)	115.2 (2)	N(1)—C(2)—S(2′)	121.5 (2)
C(2)—N(3)—C(4)	106.5 (2)	N(3)—C(2)—S(2′)	123.3 (2)
N(3)—C(4)—C(5)	110.6 (2)	C(2)—S(2′)—C(2′)	99.7 (2)
N(1)—C(5)—C(4)	100.3 (2)	N(3)—C(4)—O(4)	124.8 (2)
C(2)—N(1)—C(1′)	125.3 (2)	C(5)—C(4)—O(4)	124.5 (2)
C(5)—N(1)—C(1′)	127.6 (2)	N(1)—C(5)—C(5′)	113.8 (2)
N(1)—C(1′)—C(1″)	117.1 (2)	C(4)—C(5)—C(5′)	109.8 (2)
N(1)—C(1′)—O(1′)	119.9 (2)	C(5)—C(5′)—C(6′)	113.3 (2)
N(1)—C(2)—N(3)—C(4)	−0.5 (3)		
C(2)—N(3)—C(4)—C(5)	−3.9 (3)		
N(3)—C(4)—C(5)—N(1)	6.3 (2)		
C(4)—C(5)—N(1)—C(2)	−6.2 (2)		
C(5)—N(1)—C(2)—N(3)	4.7 (3)		
N(3)—C(2)—N(1)—C(1′)	−171.3 (2)		
C(2)—N(1)—C(1′)—O(1′)	−2.6 (4)		
C(5)—N(1)—C(1′)—C(1″)	2.6 (4)		
N(3)—C(2)—S(2′)—C(2′)	−6.4 (3)		
C(2)—N(3)—C(4)—O(4)	178.6 (2)		
C(4)—C(5)—C(5′)—C(6′)	57.1 (3)		
C(5)—C(5′)—C(6′)—C(7′)	81.9 (3)		

Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined using *SHELX76* (Sheldrick, 1976). H-atom sites were located by difference synthesis; H-atom co-ordinates and the individual isotropic diaplacement parameters were refined. Refinement was by full-matrix least squares with anisotropic displacement parameters given to the S, O, N and C atoms. The figures were prepared from the output of *ORTEP*II (Johnson, 1976). Major calculations were performed on a VAX 8800 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71843 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1047]

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Guanidinium Nitrate

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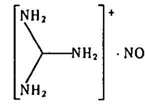
Abstract

Crystals of $C(NH_2)_3^+.NO_3^-$ are built of sheets of guanidinium and nitrate ions linked by N—H···O hydrogen bonds of length 2.945 (6), 2.962 (8) and 2.968 (6) Å. The sheets are perpendicular to the crystallographic mirror planes; the C and N(1) atoms of the guanidinium cations, and the N and O(1) atoms of the nitrate anions, lie on these planes. It appears that pronounced changes of the crystal shape, observed at the first-order phase transition of guanidinium nitrate crystals at 296 K, are connected with shear shifts of the sheets in the crystal lattice.

Comment

In the most recent article, the crystals of guanidinium nitrate (hereafter GN) were reported to exhibit unusual properties connected with two phase transitions observed in this substance (Szafrański, 1992). The low-temperature phase, GN1, on heating at T_{12} = 296 K, undergoes a transition to phase GN2; the second phase transition occurs at T_{23} = 384 K, where the crystals transform to the GN3 phase. The transition between the GN1 and GN2 phases has first-order character and is associated with a 20° temperature hysteresis between 276 and 296 K; the phase transition GN2–GN3 has a continuous character. One of the most interesting features of the GN1–GN2 transformation is the abrupt change in crystal dimensions; in certain directions the parameters expand or contract by nearly 45% of their initial length. The other interesting properties of the GN crystals at this phase transition were observed in calorimetric, dilatometric and dielectric measurements (Szafrański, 1992; Szafrański, Czarnecki, Dollhopf, Höhne, Brackenhofer & Nawrocik, 1993). The main aim of the present study was to determine the crystal data and the structure of the GN1 phase, which are necessary for interpretation of these phenomena. Crystals containing guanidinium cations are known to exhibit various types of molecular motions, like rotations or other forms of disorder of the cations (*e.g.* Grottel & Pająk, 1984; Grottel, Kozak, Małuszyńska & Pająk, 1992; Gima, Furukawa & Nakamura, 1984; Ratcliffe, 1985), and a cationic self diffusion was considered in order to explain the mechanism of the phase transition in guanidinium perchloate crystals (Titova & Rosolovskij, 1965; Pająk, Grottel & Kozioł, 1982). In no other guanidinium salt is a phase transition similar to that associated with the GN1–GN2 transformation reported.



GN

The GN1 crystals are built of guanidinium and nitrate ions hydrogen bonded into sheets along crystallographic planes (001), as shown in Fig. 1. The sheets are perpendicular to the mirror planes. The C and N(1) atoms of the cations and the N and O(1)