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Hydrogen-bonding interactions in thiosemicarbazones of carboxylic acids: structure of 2-ketobutyric acid thiosemicarbazone hemihydrate

Permalink
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Journal
Acta Crystallographica Section C: Structural Chemistry, 47(11)

ISSN
0108-2701

Authors
Sonawane, P
Chikate, R
Kumbhar, A
et al.

Publication Date
1991-11-15

DOI
10.1107/s0108270191005450

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A comparison of the crystal structure of Acm reported by Mathew & Palenik (1974) with that of MAcm, shows the following remarkable facts:

(1) The N(3)—N(4) distance [1·374 (3) Å in MAcm, 1·372 (3) Å in Acm] does not change despite the presence of a methyl group bonded to N(4) in MAcm.

(2) The S(6)—N(8) bond length is significantly shorter in MAcm [1·575 (2) Å] than in Acm [1·594 (3) Å].

(3) The C(2)—N(3)—N(4), N(3)—N(4)—C(5) and C(5)—N(11)—C(12) angles are modified in MAcm compared to Acm probably due to differences in the C(5)—N(4) and C(5)—N(11) bonds.

(4) The hydrogen-bond system is clearly different in both structures, as could be expected since, on the one hand, there is one less H atom available and on the other, the methyl substituent on N(4) prevents the formation of hydrogen bonds by the N(3) and N(4) ring atoms. Thus, only one significant hydrogen bond is observed from MAcm in contrast to the three (involving the N-thiadiazole atoms as well) exhibited by Acm.

We greatly appreciate financial support from CICYT(FAR 88-502).

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Acta Cryst. (1991). C**47**, 2379–2381

Hydrogen-Bonding Interactions in Thiosemicarbazones of Carboxylic Acids: Structure of 2-Ketobutyric Acid Thiosemicarbazone Hemihydrate

BY PRAMILA SONAWANE, RAJEEV CHIKATE, AVINASH KUMBHAR AND SUBHASH PADHYE

Department of Chemistry, University of Poona, Pune 411 007, *India*

AND ROBERT J. DOEDENS

Department of Chemistry, University of California, Irvine, California 92717, *USA*

(*Received* 3 *December* 1990; *accepted* 3 *May* 1991)

Abstract. 2-Thiosemicarbazonobutanoic acid hemihydrate, $C_5H_9N_3O_2S.0{\cdot}5H_2O$, $M_r = 184{\cdot}22$, triclinic, $P\bar{1}$, $a = 8{\cdot}163\ (2)$, $b = 8{\cdot}868\ (2)$, $c = 12{\cdot}438\ (2)$ Å, $\alpha = 72{\cdot}99\ (2)$, $\beta = 79{\cdot}47\ (2)$, $\gamma = 84{\cdot}06\ (2)°$, $V = 845{\cdot}3\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}447$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 0{\cdot}332$ mm^{-1}, $F(000) = 392$, $T = 296$ K, $R = 0{\cdot}038$ for 3830 independent reflections with $I > 3\sigma(I)$. Three hydrogen bonds link the two crystallographically independent molecules in a pairwise fashion. The two molecules both have *E* configurations about each C—N and N—N bond, but differ by nearly 180° in the orientation of the —COOH group.

Introduction. The structure of the title compound was determined in order to provide a point of comparison with a series of complexes of trivalent transition metal ions in which it is present as a ligand in its singly and doubly deprotonated forms. One such metal complex of a closely related ligand has already been reported (Timken, Wilson & Hendrickson, 1985).

Experimental. The compound was prepared as described by Sah & Daniels (1950). Large rhombic-shaped plates were grown by slow evaporation of a saturated solution in boiling water. Data were collected on a Nicolet/Siemens *R3m/V* diffractometer from a fragment of dimensions $0{\cdot}60 \times 0{\cdot}50 \times 0{\cdot}33$ mm that had been cut from a larger crystal. Unit-cell parameters were obtained from the setting angles of 32 reflections with $30 \le 2\theta \le 40°$. $\theta/2\theta$ scans. Data collected for $4 \le 2\theta \le 60°$ with $0 \le h \le 11$, $-12 \le k \le 12$, $-16 \le l \le 17$. No absorption

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correction. Three standard reflections (235, 045, 412) measured after each 97 data; max. variation ± 2%. Total of 5065 reflections measured; 3830 with $I > 3{\cdot}0(I)$. Structure solved by direct methods (*MITHRIL*; Gilmore, 1983). Other calculations employed a local modification of the *UCLA Crystallographic Computing Package* (Strouse, 1981) and the molecular graphic portions of *SHELXTL-Plus*88 (Sheldrick, 1988). Refinement based on F converged to $R = 0{\cdot}038$, $wR = 0{\cdot}058$, $S = 1{\cdot}78$. Standard deviations estimated as described by Doedens & Ibers (1967) with $p = 0{\cdot}05$; $w = 4F_o^2/\sigma^2(F_o^2)$. Max. shift in final cycle = $0{\cdot}57\sigma$; max. peak on final difference Fourier map = 0·50 e Å^{-3}. Scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The ethyl group in one of the two independent molecules was disordered. Two alternative orientations for this group were included in the refinement with multiplicities fixed at 0·667 and 0·333 on the basis of relative peak heights on a difference Fourier map. Refinement included anisotropic thermal parameters for all non-H atoms. H atoms were located on difference Fourier maps and refined with isotropic thermal parameters, with the exception of H atoms associated with the disordered ethyl groups, which were held in fixed idealized positions with C—H = 0·95 Å and $U_{iso} = 0{\cdot}063$ Å^2. The total number of parameters refined was 286.

Discussion. Atomic parameters are listed in Table 1,* while Table 2 contains bond distances and angles. A view of the two crystallographically independent molecules is shown in Fig. 1. These two molecules have the same configuration of the semicarbazide chain (*E* stereochemistry about the central C—N and N—N bonds) but differ in the orientation of the carboxylic acid residue [torsion angles: N(2)—C(2)—C(3)—O(2) = 180·0, N(12)—C(12)—C(13)—O(12) = 6·6°]. The only significant bond-length difference between the two molecules involves the C—O bond to the protonated oxygen [C(3)—O(2) = 1·315 (2), C(13)—O(12) = 1·332 (2) Å]. Other bond distances and angles are consistent with expectations (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) and indicative of electron delocalization along the thiosemicarbazide chain.

As shown in Fig. 1, the two crystallographically independent molecules are linked together by three hydrogen bonds – two N—H···O interactions and one O—H···O bond. These hydrogen bonds presumably provide the driving force for the difference in

* Lists of structure factors, thermal parameters and hydrogen coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54227 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is the mean of the eigenvalues of the U tensor.

	x	y	z	U_{eq}
C(1)	0·36969 (18)	0·32873 (16)	0·66848 (12)	320 (9)
C(2)	0·15767 (26)	0·64571 (20)	0·49754 (14)	506 (13)
C(3)	0·11366 (20)	0·68199 (17)	0·38063 (12)	356 (10)
C(4*a*)	0·07472 (40)	0·74740 (31)	0·57572 (21)	392 (18)
C(4*b*)	0·17383 (73)	0·78975 (51)	0·54501 (39)	320 (32)
C(5*a*)	0·19767 (44)	0·86873 (36)	0·56391 (26)	578 (25)
C(5*b*)	−0·00246 (73)	0·79139 (66)	0·61533 (44)	478 (40)
C(11)	0·80463 (18)	0·38086 (15)	0·00627 (11)	299 (9)
C(12)	0·61631 (17)	0·71873 (15)	−0·16407 (11)	281 (8)
C(13)	0·59171 (20)	0·77300 (17)	−0·28596 (12)	356 (10)
C(14)	0·56442 (18)	0·83184 (16)	−0·09440 (12)	312 (9)
C(15)	0·70985 (25)	0·92572 (22)	−0·09484 (17)	460 (13)
N(1)	0·28826 (19)	0·47168 (15)	0·63261 (11)	395 (10)
N(2)	0·24196 (16)	0·51506 (14)	0·52758 (10)	334 (8)
N(3)	0·40302 (19)	0·24075 (16)	0·59735 (11)	405 (10)
N(11)	0·71831 (16)	0·52312 (13)	−0·02445 (10)	312 (8)
N(12)	0·68899 (15)	0·58088 (13)	−0·13398 (9)	301 (8)
N(13)	0·85467 (20)	0·30826 (16)	−0·07345 (11)	428 (10)
O(1)	0·15102 (16)	0·59753 (13)	0·31862 (9)	445 (9)
O(2)	0·02704 (19)	0·81738 (14)	0·35378 (10)	548 (10)
O(3)	0·91086 (17)	0·92895 (15)	0·15857 (10)	428 (9)
O(11)	0·54069 (18)	0·90500 (13)	−0·32962 (10)	513 (9)
O(12)	0·63005 (19)	0·67141 (15)	−0·34833 (10)	533 (10)
S(1)	0·42046 (6)	0·27253 (5)	0·80041 (3)	441 (3)
S(11)	0·83764 (6)	0·30748 (4)	0·14188 (3)	414 (3)

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(1)—S(1)	1·685 (1)	C(11)—S(11)	1·682 (1)
C(1)—N(1)	1·361 (2)	C(11)—N(11)	1·366 (2)
C(1)—N(3)	1·318 (2)	C(11)—N(13)	1·317 (2)
C(2)—N(2)	1·277 (2)	C(12)—N(12)	1·284 (2)
C(2)—C(3)	1·497 (2)	C(12)—C(13)	1·495 (2)
C(2)—C(4*a*)	1·537 (3)	C(12)—C(14)	1·491 (2)
C(2)—C(4*b*)	1·582 (5)		
C(3)—O(1)	1·206 (2)	C(13)—O(11)	1·204 (2)
C(3)—O(2)	1·315 (2)	C(13)—O(12)	1·332 (2)
C(4*a*)—C(5*a*)	1·505 (4)	C(14)—C(15)	1·517 (2)
C(4*b*)—C(5*b*)	1·542 (8)		
N(1)—N(2)	1·362 (2)	N(11)—N(12)	1·364 (2)

S(1)—C(1)—N(1)	118·96 (11)	S(11)—C(11)—N(11)	118·99 (10)
S(1)—C(1)—N(3)	123·58 (11)	S(11)—C(11)—N(13)	124·05 (11)
N(1)—C(1)—N(3)	117·45 (13)	N(11)—C(11)—N(13)	116·95 (12)
N(2)—C(2)—C(3)	113·97 (13)	N(12)—C(12)—C(13)	114·73 (11)
N(2)—C(2)—C(4*a*)	126·11 (15)	N(12)—C(12)—C(14)	127·78 (12)
N(2)—C(2)—C(4*b*)	122·01 (21)		
C(3)—C(2)—C(4*a*)	118·92 (14)	C(13)—C(12)—C(14)	117·38 (11)
C(3)—C(2)—C(4*b*)	117·67 (19)		
C(2)—C(3)—O(1)	124·59 (13)	C(12)—C(13)—O(11)	122·43 (13)
C(2)—C(3)—O(2)	111·63 (12)	C(12)—C(13)—O(12)	118·37 (12)
O(1)—C(3)—O(2)	123·77 (13)	O(11)—C(13)—O(12)	119·18 (13)
C(2)—C(4*a*)—C(5*a*)	105·81 (25)	C(12)—C(14)—C(15)	111·04 (13)
C(2)—C(4*b*)—C(5*b*)	98·25 (40)		
C(1)—N(1)—N(2)	119·09 (12)	C(11)—N(11)—N(12)	118·84 (11)
C(2)—N(2)—N(1)	118·38 (12)	C(12)—N(12)—N(11)	118·54 (11)

Possible hydrogen-bonding contacts, with A—H···B angles*

O(1)···H(12^{i})	2·11 (2), 147 (2)	O(12)···H(3n^{i})	2·14 (2), 167 (2)
O(1)···H(13n^{i})	2·07 (2), 160 (2)	S(1)···H(3a^{iii})	2·46 (2), 165 (2)
O(3)···H(2^{ii})	1·70 (3), 153 (2)	S(1)···H(11n^{iii})	2·82 (2), 178 (2)
O(3)···H(13m^{vi})	2·32 (2), 142 (2)	S(11)···H(3b^{iv})	2·62 (3), 155 (2)
O(11)···H(3m^{v})	2·14 (2), 168 (2)	S(11)···H(1n^{iii})	2·93 (2), 177 (2)

Symmetry codes: (i) $1-x, 1-y, z$; (ii) $1+x, y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, y-1, z$; (v) $x, 1+y, z-1$; (vi) $2-x, 1-y, z$.

* For each potential hydrogen-bond donor, the shortest contact to a potential acceptor is tabulated, subject to the constraint that the A—H···B angle is ≥ 140°. Distances are not normalized. The number designating an H atom corresponds to that of the atom to which it is bound. The letter *n* or *m* denotes a hydrogen bound to nitrogen; other H atoms are bound to oxygen.

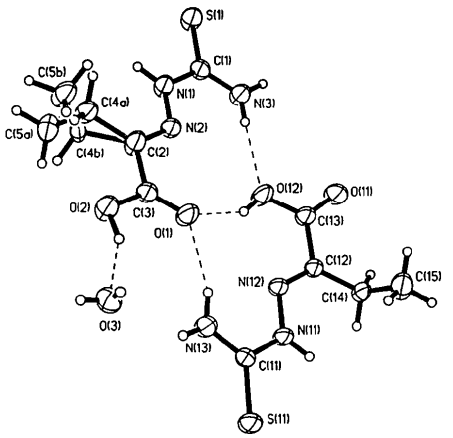

Fig. 1. View of the hydrogen-bonded pair of molecules constituting the asymmetric unit. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level. Both orientations of the disordered ethyl group are shown.

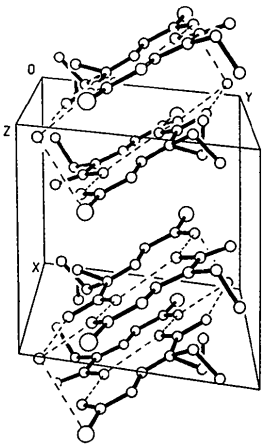

Fig. 2. View of the unit-cell contents.

the conformations of the two molecules. Additional hydrogen bonds connect this pair of molecules to the water of hydration and to other molecules. Details of the potential hydrogen-bonding interactions are included in Table 2. A number of these interactions are shown in Fig. 2, which depicts the unit-cell contents.

A search of the Cambridge Structural Database (Allen *et al.*, 1979) reveals numerous thiosemicarbazones, but none that are derivatives of simple monocarboxylic acids. Pyruvic acid thiosemicarbazone also crystallizes as a hemihydrate (Timken, Wilson & Hendrickson, 1985) and may well have a similar crystal structure.

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Acta Cryst. (1991). C**47**, 2381–2383

Structure of *N*,*N*-Dimethyl[2-(2-ethoxyphenylcarbamoyloxy)-2-methylpropyl]-ammonium Chloride

BY VIKTOR KETTMANN AND EVA FREŠOVÁ

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Odbojarov 10, 83232 *Bratislava, Czechoslovakia*

AND FRIDRICH GREGÁŇ

Department of Organic Chemistry, Faculty of Pharmacy, Comenius University, Odbojarov 10, 83232 *Bratislava, Czechoslovakia*

(*Received* 21 *February* 1991; *accepted* 23 *April* 1991)

Abstract. $C_{15}H_{25}N_2O_3^+.Cl^-$, $M_r = 316{\cdot}9$, monoclinic, $P2_1/c$, $a = 13{\cdot}228\ (9)$, $b = 11{\cdot}065\ (8)$, $c = 11{\cdot}556\ (10)$ Å, $\beta = 96{\cdot}32\ (7)°$, $V = 1681\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}25\ (1)$, $D_x = 1{\cdot}252$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}22$ mm^{-1}, $F(000) = 652$, $T = 293$ K, final $R = 0{\cdot}045$ for 2708 unique observed reflections. The structure consists of discrete cations connected in pairs by hydrogen-bonded chloride

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