Dedicated to the memory of academician T.I. Malinowsky.

THE CRYSTAL AND MOLECULAR STRUCTURE OF THIOSEMICARBAZONE α - AMINOACETOPHENONE HYDROCHLORIDE

B.Ya. Antosyak[1], L.F. Chapurina[2] and C.I. Turta[2]

[1]Institute of Applied Physics, Academy of Sciences of Moldova, 5, Academiei str., MD-2028, Chisinau, Republic of Moldova
[2]Institute of Chemistry, Academy of Sciences of Moldova, 3, Academiei str., MD-2028, Chisinau, Republic of Moldova
(Received 19 December 2006)

Abstract

The crystal structure of $C_9H_{13}N_4SCl$ is reported. Compound crystallizes in the triclinic system, space group *P*-1, *a*=15.455(7), *b*=8.768(7), *c*=9.187(9) Å, α=101.92(3), β=87.10(4), γ=79.20(3)º, V=1191.33(7) Å^3, Z=4. The structure consists of two independent cations $[C_9H_{13}N_4S]^+$ and two independent anions Cl^-. H-bonds and π-π interactions joined the charged species into the complex network.

Introduction

The investigation of the molecular and crystal structures of semi- and thiosemicarbazones has been initiated in Moldova by academician T.I. Malinowsky. Derivatives of thiosemicarbazones were found to possess potential antiviral, anticancer [1-6] and antimicotic activity. The inculcation of different functional groups in the molecule of carbohydrazones influences essentially their properties. For better understanding of relationships between structure and biological activity of these compounds, it seemed worthwhile to determine the structure of new thiosemicarbazones. Thus we have focused on an analysis of the structural behaviour of the novel thiosemicarbazone based on its three-dimensional structure obtained on the basis of X-ray structure determination.

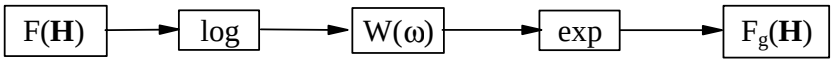
Experimental

The title compound has been obtained by the interaction of thiosemicarbazide hydrochloride with α-aminoacetophenone. The crystals suitable for X-ray analysis were obtained by slow evaporation of water solution at room temperature.

Crystal structure determination

The preliminary X-ray examination established the crystal system and cell dimensions. The compound is crystallised in the centrosymmetric space group *P*-1, and the subsequent analysis confirmed this. Accurate cell dimensions were obtained using a single-crystal DAR-UMB diffractometer fitted with graphite monochromator and CuK_α radiation. The intensities of 2434 unique reflections with $I \geq 2\sigma(I)$ were recorded and corrected for Lorentz and polarization effects but no absorption correction was applied.

All attempts to solve the structure by direct methods using standard procedure of the SHELX-76 program [7] were unsuccessful. The structure was determined by direct methods after preliminary processing their spectra by homomorphic filter proposed in [8]. According to [8] the homomorphic filter scheme is



Then output signal has the form

$$F_g(\mathbf{H}) = F(\mathbf{H})^{W(\omega)} ,$$

where the formula for the high frequency filter is $W(\omega) = a - bc^{-\omega}$, $\omega = \mathbf{H}/\mathbf{H}_{max}$ (**H** is the vector of the reciprocal lattice). The coefficients a, b, c had the values 1.2, 0.7 and 1000, respectively. The F_g(**H**) coefficients for direct methods were successfully used and initial non-hydrogen atomic coordinates for the structure were obtained from Fourier syntheses using the multi-solution methods of SHELX-76. H atoms of NH, NH_2, NH_3 and CH_2 groups were located on a difference Fourier synthesis. The hydrogen atoms of ammonium groups were refined in an approximation of rigid group. Phenyl rings were constrained as regular hexagons with C - C = 1.395 Å, and phenyl H atoms put in calculated positions. Positional and thermal parameters were refined by full-matrix least-square procedures with anisotropic temperature factors for all non-H atoms and isotropic ones for H atoms. Final *R* = 0.088. Atomic coordinates and isotropic thermal parameters are listed in Table 1.

Table 1. Atomic coordinates ($Åx10^{-4}$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for compound (I).

Atom	Molecule A				Molecule B			
	x	y	z	U(eq)	x	y	z	U(eq)
Cl(1)	5061(2)	2451(3)	5404(3)	52(2)				
Cl(2)	4964(2)	2210(3)	-922(3)	49(3)				
S(1)	2051(2)	1346(3)	9055(3)	61(4)	7259(2)	5588(3)	-3156(3)	52(3)
N(1)	2442(6)	815(11)	6172(9)	42(4)	7173(6)	4970(10)	-471(9)	42(4)
N(2)	2961(5)	765(9)	4893(9)	35(5)	6800(6)	4355(10)	-8939(9)	45(1)
N(3)	3519(7)	1633(16)	7566(14)	54(7)	6204(6)	3968(11)	-2004(12)	50(8)
N(4)	4094(6)	687(11)	2601(10)	48(5)	5800(6)	3874(11)	2856(10)	49(1)
C(1)	2718(6)	1279(13)	7549(10)	39(3)	6849(7)	4796(11)	-1826(11)	40(5)
C(2)	2642(6)	335(11)	3666(11)	35(5)	7248(7)	4127(12)	1727(11)	43(1)
C(3)	3213(6)	273(12)	2286(11)	40(5)	6790(7)	3535(4)	2869(12)	48(4)
C(4)	1805(5)	-186(9)	3447(8)	35(3)	1805(5)	4290(8)	1893(6)	38(9)
C(5)	1634(4)	-1476(9)	4004(8)	49(1)	1634(4)	3523(8)	751(6)	48(7)
C(6)	334(5)	-1971(9)	3793(8)	56(7)	834(5)	3634(8)	940(6)	62(2)
C(7)	204(5)	-1176(9)	3026(8)	57(4)	1805(5)	4511(8)	2272(6)	62(3)
C(8)	375(5)	113(9)	2470(8)	59(8)	1634(4)	5278(8)	3414(6)	53(6)
C(9)	1175(5)	608(9)	2681(8)	47(1)	8392(4)	5167(8)	3225(6)	47(1)

Discussion

The crystal of the title compound (I) is built of two independent thiosemicarbazone α-aminoacetophenone cations and two independent Cl anions linked by the network of hydrogen bonds. The general view of (I) is shown in Fig. 1.

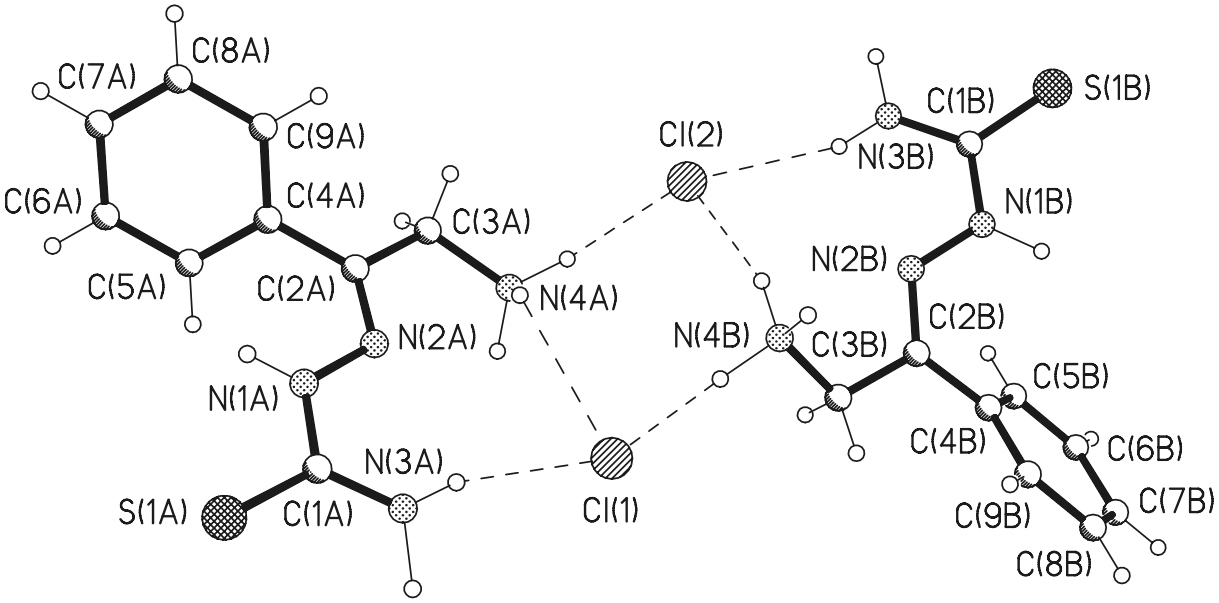


Fig. 1. A perspective view of the cations A, B and Cl anions, with the atom-numbering scheme.

Both A and B cations of the thiosemicarbazones represent non-planar units. If we compare the conformations, we find differences between two cations. The least-square planes between six-membered phenyl rings (planar within ±0.003 Å) and N(2)C(2)C(3)C(4) fragments (planar within ±0.02 Å) make a dihedral angle of 52.7º in A and 59.3º in B cation, respectively. Besides, the torsion angles around the C(1)-N(1), N(1)-N(2), N(2)-C(2) and C(2)-C(3) bonds in the A cation are in the range ±2.2º and indicate the planar conformation of the fragment. The respective angles in the B cation except N(2)-C(2)-C(3)-N(4) angle also fall in the same range. As for torsion angle N(2)-C(2)-C(3)-N(4) its value is equal to -21.7º and indicates a slightly twisted form for the chain N(1)-N(2)-C(2)-C(3)-N(4) in the B cation.

In the present compound the thiosemicarbazide moieties are planar. The sum of the angles around C(1) atoms in each of the cation is 360º and it corroborates the planarity of the thiosemicarbazide fragments. The thiosemicarbazide branch S(1)-C(1)-N(1)-N(2) is in anti-conformation, the corresponding torsion angle is 178.9 and 177.7º in A and B, correspondingly. The same conformation was found in 2-acetylpyridinium 4N-phenylthiosemicarbazone chloride [2], 2-(1-(thiosemicarbazono)ethyl)pyridinium chloride [3], (E)-2-acetylpyridine thiosemicarbazone hydrochloride [4], bis(pyridine-2-carbaldehyde thiosemicarbazone) dihydrochloride dihydrate [5] and 5-amino-4-methyl-1-isoquinoline-carbaldehyde [6] molecules. Only in the molecule of the pyridoxal methylthiosemicarbazone [1] the thiosemicarbazide skeleton has *cis*-configuration.

There are no intrinsic differences between the corresponding bonds and angles in both cations taking into account the standard deviations. The bond lengths and angles fall within the range typically observed in the above-mentioned structures and in the structure of pyridoxal methylthiosemicarbazone [1]. But in the compounds cited in [3, 4, 6] only the

C(1)-N(3) bond length is shortened up to 1.308, 1.314 and 1.275 Å, respectively. The bond length values indicate the presence of delocalization of π-electrons in the thiosemicarbazoneaminoacetone moieties of both cations.

A peculiar interest represents the crystal packing in the structure. In the present compound each organic thiosemicarbazone cation has one NH, NH_2, NH_3^+ and CH_2 groups that all are proton donor sites, and, except NH group, all are involved into the H-bonding system in the crystal.

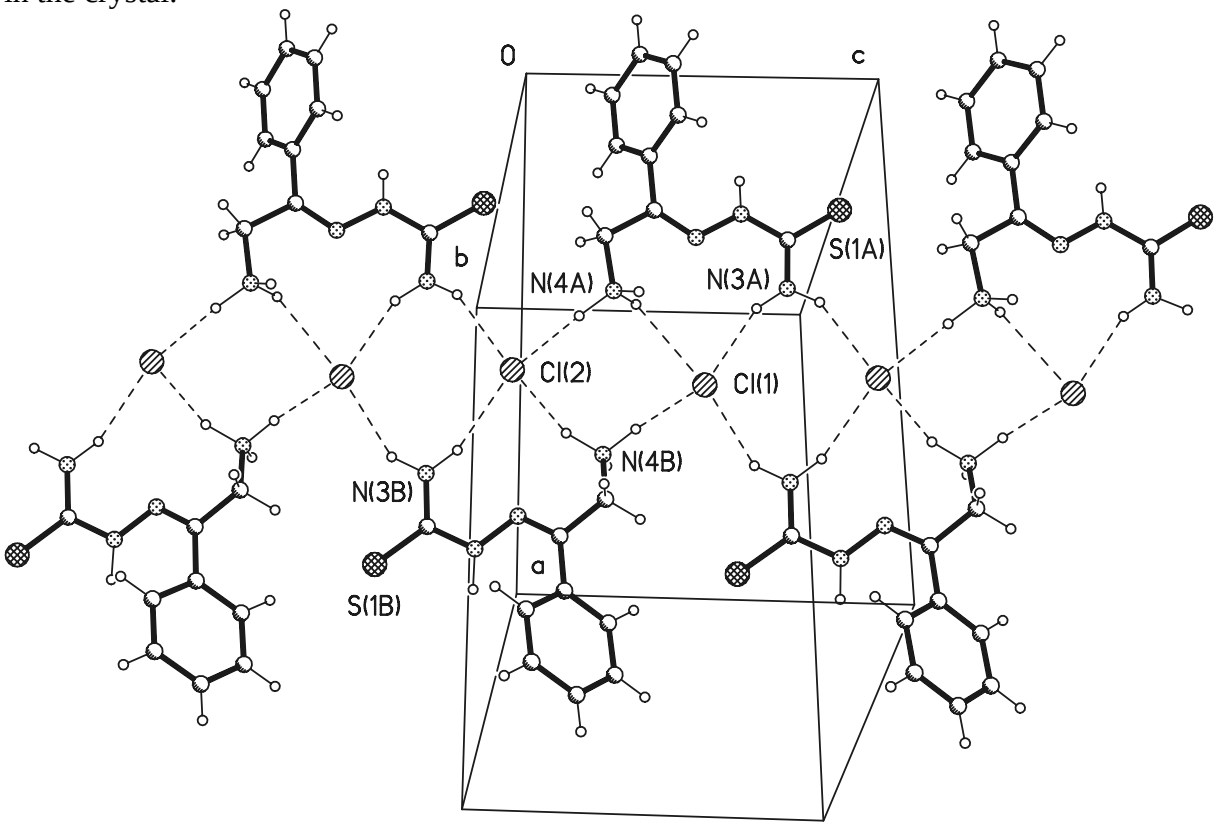


Fig. 2. The view of the tape $C_9H_{13}N_4SCl$ along *c* axis.

The charged units in (I) are linked by the combination of N-H···Cl, N-H···S and C-H···S hydrogen bonds. The Cl(1) anion acts as a five-center acceptor in the structure. It joins NH_3^+ and NH_2 groups of the A cation by the N(4A)···Cl(1) and N(3A)···Cl(1) hydrogen bonds (both equal to 3.30 Å) (Fig. 2). These two H-bonds close the ten-membered pseudo-cycle built on the seven-membered branch of the cation A, a feature often observed in the crystal structures of relative compounds [1-6]. The same chlorine atom acting as a bridge links the ammonium group of B cation [N(4B)···Cl(1) 3.13 Å] and amino-group of adjacent B cation [N(3B)*···Cl(1) 3.25 Å] which is generated by translation along *c* axis. In a similar manner, the Cl(2) anion acts as an acceptor towards the B cation and two A and A' cations. The values of the corresponding H-bonds are: N(4B)···Cl(2) 3.13, N(3B)···Cl(2) 3.41, and N(3A)···Cl(2) 3.32, N(4A)*···Cl(2) 3.26 Å, and they agree with the values for such structures [1-6]. The anions Cl(1) and Cl(2) deviate from the best plane of thiosemicarbazide moieties at 0.52 and -0.74 Å in the A and B cations, correspondingly. Thus, *via* H-bonds all these ions are joined in the tape running parallel to *ac* plane. Two these tapes related by inversion, run through each unit cell along *c* axis and these are linked by N-H···Cl hydrogen bonds. Atom N(4B) at (*x*, *y*, *z*) acts as a hydrogen-bonding donor to atom Cl(1)# at (1-*x*, 1-*y*, 1-*z*), and a propagation

of this interaction by translation and inversion generates a sheet (Fig. 3). This weak H-bond, equal to 3.28 Å, is slightly shorter than the sum of the Van der Waals radii for the N and Cl atoms (3.35 Å) and together with the N(4B)···Cl(1) intermolecular contact leads to a centrosymmetric parallelogram with the Cl(1)-N(4B)-Cl(1)# angle equal to 87.0º. Besides the mentioned above N-H…Cl interactions, N-H…S interactions contribute to the layer formation, N(4A)···S(1B)# 3.46, H(13A)···S(1B)# 2.65 Å, N(4A)-H(13A)···S(1B)# 131º.

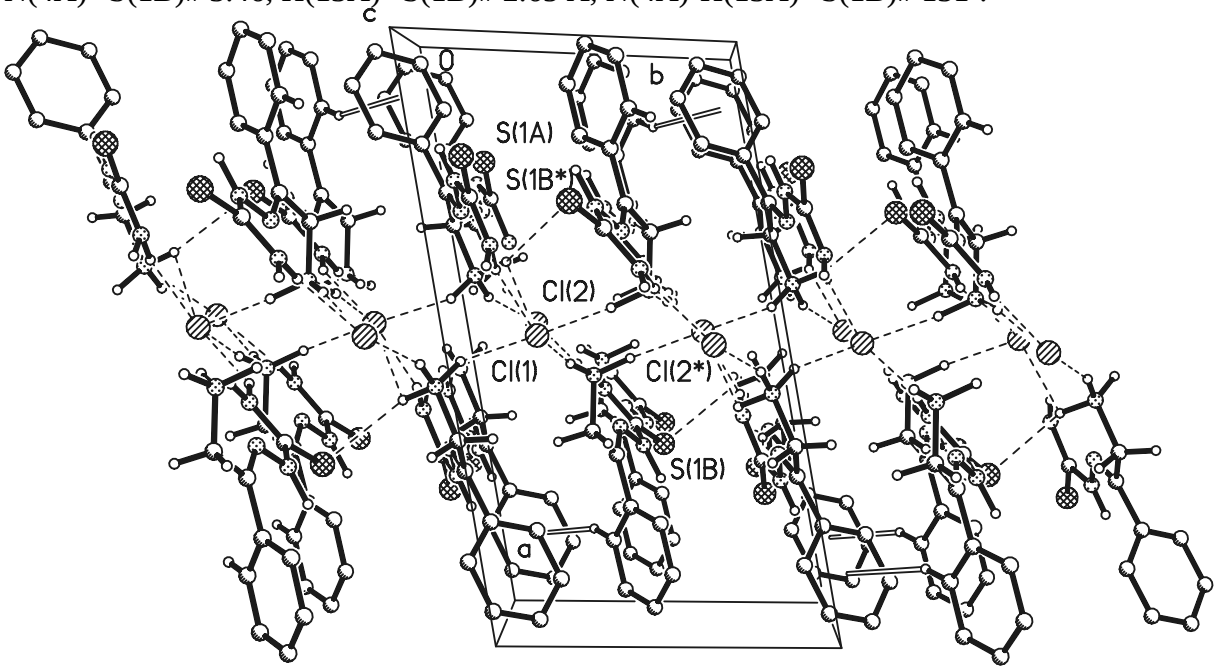


Fig. 3. The fragment of sheet in the crystal of (I). Only H-atoms participating in the important intermolecular interactions are shown. C-H···π interactions are shown by open lines.

Also within this sheet the cations are weakly linked by a C-H···π interaction, atom C(5) in the cation B (1-x, y, 1-z) acts as a hydrogen-bond donor, *via* atom H(5B), to the phenyl ring of the cation A (x, y, z) [C(5B)$···$C_g$ 3.95, H(5B)$···$C_g$ 3.04 Å, C(5B)$-H(5B)$···C_g 158º, where C_g is H-ring centroid] .

Conclusion

The structure is built of the charged species, the cations of thiosemicarbazone $[C_9H_{13}N_4S]^+$ and Cl^- anions. Two independent cations have different conformations. The bond lengths are typical for the similar structures. The Cl(1) and Cl(2) anions act as five-center acceptors in the structure and link the cations of thiosemicarbazone into the complex network by the combination of N-H···Cl, N-H···S and C-H···S hydrogen bonds.

Supplementary material

Crystallographic data for **1** has been deposited with the Cambridge Crystallographic Data Center, CCDC 632028. Copy of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] U. Abram, K.Ortner, R. Gust, K. Sommer, J. Chem. Soc., Dalton Trans., 735, (2000).
[2] D. Kovala-Demerti, V. Varagi, M. Demertis, C. Raptopoulou, A. Terris, Acta Cryst., Sect. C, 52, 2027, (1996).
[3] S. Abram, U. Abram, Acta Cryst., Sect. C, 53, 360, (1997).
[4] A. Kumbhar, P. Sonawane, S. Padhye, D.X. West, R.J. Butcher, J. Chem. Cryst., 27, 533, (1997).
[5] M.K. Urtiagu, M.I. Arroirtua, J. Garcia-Tojal, T. Rijo, Acta Cryst., Sect. C, 51, 2172, (1995).
[6] R. Kuroda, S. Neidle, D.E.V. Wilman, Acta Cryst., Sect. C, 40, 465, (1984).
[7] G.M. Sheldrick, University of Gοttingen, Germany,(1976).
[8] B.Ya. Antosyak, B.N. Biyushkin, T.I. Malinowsky, Doklady Akad. Nauk SSSR, 311, 3, 617, (1990).
[9] Chr. Janiak, J. Chem. Soc., Dalton Trans., 3885, (2000).