

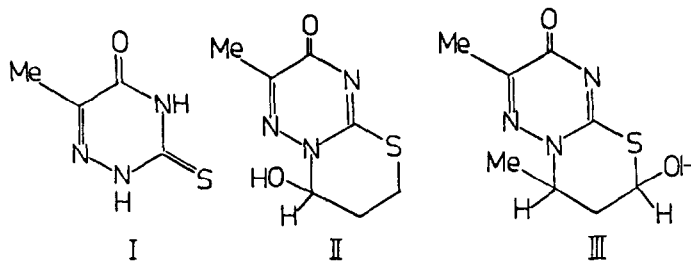
1,2,4-TRIAZINES AND CONDENSED DERIVATIVES, XXI<sup>1</sup>: ON THE FORMATION AND THE CRYSTAL STRUCTURE OF THE 2:1 ADDUCT OF 6-AZA-2-THIOTHYMININE AND TRIETHYL AMINE.

George P. Voutsas and Cleanthis C. Venetopoulos  
Department of Applied Physics, Aristotle University of  
Thessaloniki, Greece

Alajos Kálmán<sup>2</sup> and László Párkányi  
Central Research Institute for Chemistry of the Hungarian  
Academy of Sciences, H-1525, POB. 17., Hungary

Gyula Hornyák and Károly Lempert  
Department of Organic Chemistry, Technical University  
H-1111-Budapest, Gellért tér 4., Hungary

6-Aza-2-thiothymine (I) was found to furnish with acrolein and crotonaldehyde in the presence of triethyl amine the bicyclic products II and III respectively<sup>2</sup>. When I was allowed to react with the acetals of these aldehydes in the



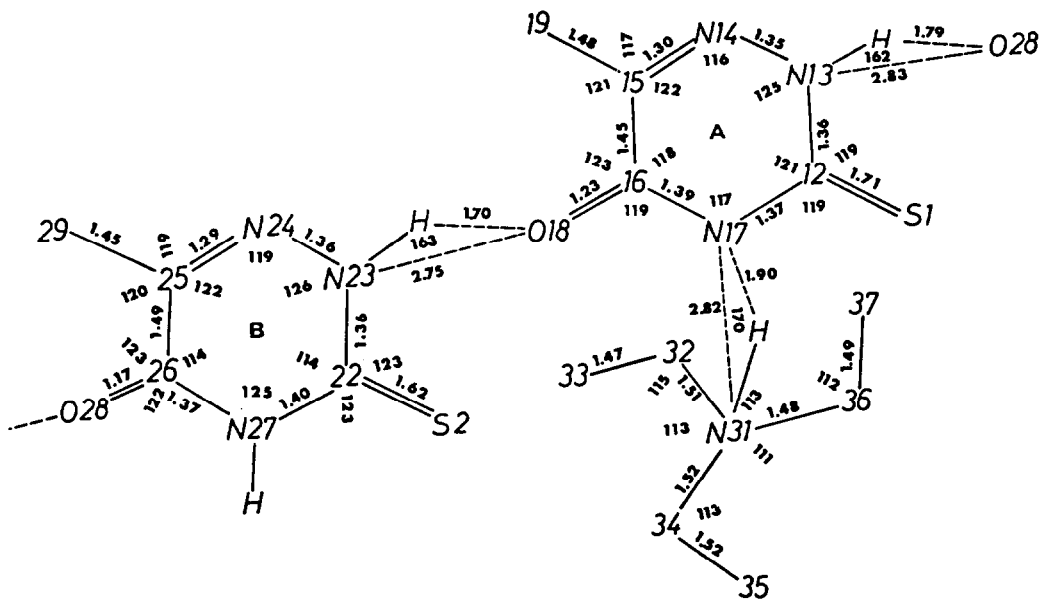
presence of triethyl amine, a new compound was obtained in both cases. The same compound was produced in 94% yield also when I and triethyl amine (applied either in stoichiometric amount or in excess) were refluxed in ethanol. The product proved to be a stable, crystalline 2:1 adduct [m.p. 168°C, from ethanol; correct N and S analyses. IR (KBr): 3300-2200 b; 1695 cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, reference DMSO-d<sub>5</sub> = 2.50 ppm): δ 1.1 t, 9H + 3.1 qu, 6H, J = 7.3 Hz, Et<sub>3</sub>; 2.0 s,

6H, Me<sub>2</sub>; 11.8 s, 4H, 4NH's]. Since neither IR nor <sup>1</sup>H-NMR spectra gave decisive structural information, the crystal and molecular structure of the adduct was determined by X-ray diffraction.

The structure was solved with MULTAN and refined to R = 0.083 for 1401 reflexions with  $F - 3\sigma(F) > 0$  out of 2041 intensities recorded on a Philips PW 1100 diffractometer with monochromated MoK $\alpha$  radiation<sup>3</sup>. The lattice parameters are:  $a = 12.000(2)$ ,  $b = 9.925(2)$ ,  $c = 8.555(1)$  Å,  $\alpha = 95.45(2)$ ,  $\beta = 97.61(2)$ ,  $\gamma = 104.71(2)^\circ$ ,  $V = 793.0$  Å<sup>3</sup>,  $D_c = 1.741$  g.cm<sup>-3</sup>,  $Z = 2$  for 2C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>OS.(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N. The fractional coordinates of the atoms are presented in the Table. Hydrogens bound to nitrogen atoms, except that belonging to N(23), were located in difference maps; the positions of the others were generated from assumed geometries.

X-ray analysis revealed that an ionized, i.e. deprotonated (A) and a neutral (B) 6-aza-2-thiothymine molecule share the asymmetric unit with a triethyl ammonium cation as shown by the schematic diagram of the structure. The triethyl ammonium cation with a slightly distorted tetrahedral configuration [the mean bond angle at N(31) is  $109 \pm 4^\circ$ ] is bound to the anion through an NH...N hydrogen bond in which the acceptor atom is N(17). The electron-withdrawing effect of the C=O and C=S groups increases the acidity of the nitrogen atom wedged between these two moieties. This effect enables N(17) in molecule A to lose its hydrogen atom to the triethyl amine molecule, forming simultaneously a strong hydrogen bond. The deprotonation of N(17) is also indicated by the diminished bond angle at N(17) compared to at N(27) in molecule B ( $117^\circ$  vs.  $125^\circ$ ) in accordance with the VSEPR theorem<sup>4</sup>. The ionization of ring A seems also to account for the considerably polarized C=O and C=S bonds accompanied by increased bond angles at C(12) and C(16) atoms relative to the corresponding bonds and angles in ring B. The geometry of the thiosemicarbazide moiety is different both in ring A and B and differs also from those found e.g. in 1-phenyl- and 4-phenyl-thiosemicarbazides<sup>5,6</sup>. Nevertheless, these observations do not shed light on the question why even an excess of triethyl amine can deprotonate only half of the 6-aza-2-thiothymine molecules in the crystal. Infinite chains of the alternating A and B molecules of 6-aza-2-thiothymine

A schematic diagram of the asymmetric unit showing atomic numbering (atoms are carbon unless indicated otherwise and only the relevant hydrogen atoms are shown), bond lengths and angles (for their standard deviations cf. ref. 3.).



Atomic coordinates ( $\times 10^4$  for non-hydrogen atoms with their e.s.d.'s in parentheses and  $\times 10^3$  for hydrogen atoms).

	x	y	z	x	y	z	
S(1)	7474(2)	7945(3)	4775(4)	H(13)	516	691	462
C(12)	6489(9)	8604(9)	5654(12)	H(19A)	433	1078	869
N(13)	5401(7)	7883(8)	5416(10)	H(19B)	359	898	858
N(14)	4543(7)	8255(8)	6082(10)	H(19C)	326	994	703
C(15)	4859(9)	9415(11)	7086(12)	H(23)	616	261	27
C(16)	6051(9)	10290(10)	7419(12)	H(27)	642	561	363
N(17)	6871(7)	9852(8)	6642(10)	H(29A)	253	1383	1184
O(18)	6357(6)	11397(7)	8335(9)	H(29B)	250	1208	1120
C(19)	3948(9)	9803(11)	7902(13)	H(29C)	247	1327	980
S(2)	7913(3)	4442(3)	1946(4)	H(31)	816	146	684
C(22)	6510(9)	4160(9)	1689(12)	H(32A)	1008	134	649
N(23)	5773(8)	3182(9)	540(11)	H(32B)	1035	311	617
N(24)	4590(8)	2858(9)	310(10)	H(33A)	1001	158	373
C(25)	4080(9)	3548(10)	1211(13)	H(33B)	890	244	381
C(26)	4762(9)	4703(10)	2479(14)	H(33C)	864	67	413
N(27)	5952(7)	4950(8)	2598(10)	H(34A)	777	301	515
O(28)	4332(7)	5404(7)	3256(10)	H(34B)	741	332	706
C(29)	2815(10)	3155(13)	1001(16)	H(35A)	840	552	617
N(31)	8757(7)	2292(8)	6987(9)	H(35B)	961	486	594
C(32)	9691(9)	2116(11)	6025(14)	H(35C)	925	517	785
C(33)	9284(11)	1672(12)	4307(12)	H(36A)	999	350	889
C(34)	8121(9)	3335(10)	6401(14)	H(36B)	855	296	930
C(35)	8902(11)	4830(10)	6606(17)	H(37A)	980	173	1067
C(36)	9205(11)	2645(12)	8710(13)	H(37B)	1013	110	884
C(37)	9478(14)	1427(14)	9416(19)	H(37C)	870	57	925

are bound together by two NH...O hydrogen bonds (their parameters are shown in the drawing). The fairly planar A and B rings make a dihedral angle of 14.2°.

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#### Notes and References

1. For Part XX., see J. Nyitrai, Gy. Domány, Gy. Simig, J. Fetter, K. Zauer and K. Lempert, Acta Chim. (Budapest), 97, 91 (1978).
2. Gy. Hornyák, L. Láng, K. Lempert and Gy. Menczel, Acta Chim. Acad. Sci. Hung., 61, 93 (1969).
3. Due to the low quality of the single crystals, a sample suitable for data collection of even limited accuracy, could only be selected after several fruitless attempts. Accordingly, the refinement had to be terminated at a relatively high R value. This accounts for the relatively high standard deviations of the bond lengths (0.01-0.02 Å) and angles (1-2°).
4. R.J. Gillespie, J. Chem. Educ., 40, 295 (1963).
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