CRYSTAL AND MOLECULAR STRUCTURE OF 2-(p-TOLYLIMINO)-4-METHYL-4-ETHYL-5-METHYLENETHIAZOLIDINE

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It was found by an x-ray diffraction study of 2-(p-tolylimino)-4-methyl-4-ethyl-5-methylenethiazolidine that the thiazolidine molecules in the crystal are joined together to form centrosymmetric dimers due to the formation of N—H...N hydrogen bonds. The structure of the dimer and the bond lengths and angles of the thiazolidine are presented. The study confirmed the imino structure of the investigated compound. The pathway of fragmentation of the alkyl groups attached to C_4 during mass-spectroscopic analysis was analyzed thoroughly.

The problems involved in the amino-imine tautomerism of heterocyclic amines, particularly 2-aminothiazoline, have been discussed in a number of papers [1-6]. Depending on the nature of the substituents attached to the exocyclic nitrogen atom, the nature of the heteroring, and the character of the solvent in the case of solutions, as well as a number of other factors, the indicated compounds may exist in the amino or imino form or as mixtures of both tautomeric forms.

On the basis of the results of spectroscopic studies we proposed that 2-(p-tolylimino)-4-methyl-4-ethyl-5-methylenethiazolidine (I) has an imino structure in the crystalline form [3]. However, since the results of spectral methods are susceptible to the effect of a large number of various factors [1, 2] and do not always make it possible to unambiguously

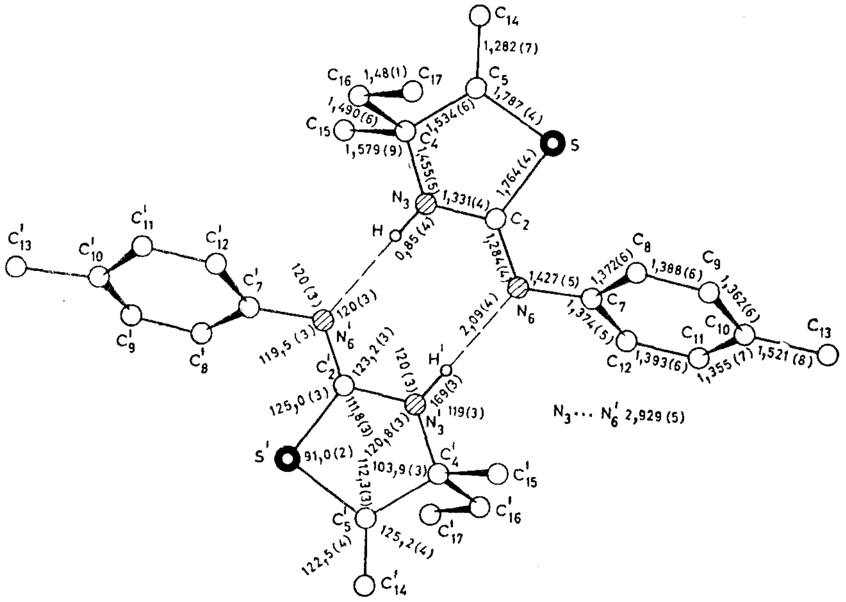

Fig. 1. Structure of the I dimer in the crystalline state with the bond lengths and angles (the dash lines indicate the hydrogen bonds).

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TABLE 1. Coordinates of the Nonhydrogen Atoms ($\cdot 10^4$)

Atom	x	y	z	Atom	x	y	z
S	3465 (1)	4994 (1)	8115 (2)	C_{10}	2916 (4)	8807 (4)	11158 (6)
C_2	1856 (3)	5054 (3)	6801 (5)	C_{11}	3015 (5)	9168 (4)	9266 (7)
N_3	1343 (3)	4111 (3)	5529 (5)	C_{12}	2482 (5)	8222 (4)	7878 (7)
C_4	2052 (4)	3139 (4)	5409 (6)	C_{13}	3493 (7)	9870 (7)	12631 (10)
C_5	3400 (4)	3603 (4)	6836 (7)	C_{14}	4382 (5)	3071 (6)	7122 (10)
N_6	1254 (3)	5916 (3)	6991 (4)	C_{15}	2358 (11)	3252 (11)	3273 (10)
C_7	1860 (3)	6869 (3)	8427 (6)	C_{16}	1162 (5)	1725 (5)	5942 (11)
C_8	1743 (4)	6501 (4)	10338 (6)	C_{17}	830 (7)	1499 (7)	7935 (12)
C_9	2273 (4)	7469 (4)	11686 (6)				

TABLE 2. Coordinates of the Hydrogen Atoms ($\cdot 10^3$)

Atom	x	y	z	Atom	x	y	z
$H(N_3)$	53 (4)	401 (3)	488 (6)	$H'(C_{14})$	423 (5)	223 (5)	602 (7)
$H(C_8)$	136 (4)	563 (4)	76 (5)	$H(C_{15})$	147 (5)	275 (4)	247 (8)
$H(C_9)$	215 (4)	714 (4)	311 (7)	$H'(C_{15})$	281 (6)	271 (7)	309 (10)
$H(C_{11})$	348 (4;	7 (4)	882 (6)	$H''(C_{15})$	269 (8)	401 (6)	297 (11)
$H(C_{12})$	261 (4)	851 (4)	654 (6)	$H(C_{16})$	25 (5)	154 (4)	482 (7)
$H(C_{13})$	392 (5)	73 (5)	190 (7)	$H'(C_{16})$	164 (5)	108 (5)	570 (7)
$H'(C_{13})$	274 (5)	1006 (5)	320 (8)	$H(C_{17})$	40 (7)	224 (7)	826 (10)
$H''(C_{13})$	374 (7)	938 (7)	378 (11)	$H'(C_{17})$	25 (10)	54 (10)	817 (14)
$H(C_{14})$	479 (6)	663 (5)	174 (8)	$H''(C_{17})$	185 (7)	174 (5)	910 (8)

solve the structural problems, we subjected I to x-ray diffraction analysis to unambiguously establish its structure in the crystalline form.

The x-ray diffraction study confirmed the assumption of an imino structure for I. The I molecules in the crystal are joined by N—H...N hydrogen bonds to give centrosymmetric dimers. The structure of the dimer and the bond lengths and angles in the molecule are presented in Fig. 1.

The position of the objectively localized 3-H atom bonded to the endocyclic nitrogen atom constitutes unambiguous evidence in favor of the imino structure of I. In addition, the formation of a strong N—H...N hydrogen bond [N_3—H 0.85(4) Å, 3-H...N'_6 2.09(5) Å, angle N_3—H—N'_6 169(3)°], the length of which [2.929(5) Å] is appreciably shorter than the average distance (2.98 Å) for H bonds of this type obtained in [7] on the basis of a statistical treatment of the results of numerous structural investigations, in this case evidently reflects the potentially tautomeric character of the I molecule. The lengths of the C_2—N_3 and C_2=N_6 bonds in the I molecule are, respectively, smaller and greater than the lengths of the analogous bonds [1.392(7) and 1.250(6) Å] in 2-(2,6-dimethylphenyl)imino-3-(2-methylbenzoyl)triazolidine (II) [4], which has an imino structure and in which the possibility of amino-imine tautomerism is excluded because of the presence of a substituent attached to the endocyclic nitrogen atom.

The thiazolidine ring in the I molecule is virtually planar (the maximum deviation of the C_4 atom is 0.03 Å); the N_6 atom lies in the plane of the ring, while the C_{14} atom deviates appreciably (by −0.07 Å) from it. The lengths of the bonds in the heteroring basically have their usual values. The length of the S—C_2 bond is in agreement with the values found (1.753-1.772 Å) for the analogous S—C(sp^2) bonds in aminothiazoline derivatives [4]. The second bond in which a sulfur atom participates (S—C_5) is not much longer than the S—C_2 bond; however, its length is nevertheless somewhat shorter than the lengths of the analogous bonds in aminothiazolidines (1.800-1.840 Å [4]) with an sp^3-hybridized C_5 atom.

The phenyl ring forms a dihedral angle of 76° with the mean square plane of the thiazolidine ring. Thus the possibility of conjugation of the C_2=N_6 bond and the π-electron system of the phenyl ring is excluded. The length of the N_6—C_7 bond is close to the length of the analogous bond in the II molecule.

Intensive thermal motion of the peripheral atoms in a molecule usually leads to apparent shortening of the terminal bonds. Thus the C_5—C_{14}, C_4—C_{16}, and C_{16}—C_{17} distances in the I molecule are shortened relative to the standard lengths of the C_{sp^2}=C_{sp^2} and C_{sp^3}—C_{sp^3} bonds. At the same time, the C_4—C_{15} bond is elongated appreciably; this possibly reflects its known lability. It was noted during a mass-spectroscopic study [6] that 2-aminothiazoline derivatives readily lose a 4-alkyl group in the case of fragmentation under the influence of electron impact. In addition, in conformity with the general conclusions drawn in [6] for the analogus 2-aminothiazoline derivatives, in the mass-spectroscopic analysis of I one observes first and foremost the detachment of the bulkier, i.e., ethyl, substituent, despite the apparent greater lability of the methyl group (C_4—C_{15} 1.579 Å as compared with C_4—C_{16} 1.490 Å). It is possible that this is associated with the fact that the unpaired electron in the uncharged radical is stabilized more easily in the longer hydrocarbon chain as a result of rearrangement or subsequent fragmentation [8].

EXPERIMENTAL

2-(p-Tolylimino)-4-methyl-4-ethyl-5-methylenethiazolidine (I) was obtained by the method in [3] and had mp 130°C. The mass spectrum of I was recorded with an MI-1305 spectrometer at an ionizing voltage of 70 eV and an accelerating voltage of 2000 V. The peaks had the following m/z values (the relative intensities in percent are given in parentheses): 246 (10), 217 (100), 132 (17), 100 (29), 91 (19), 65 (13), 41 (15), and 32 (12). (The ion peaks with relative intensities higher than 10% are presented.)

The I crystals were triclinic with the following parameters at +20°C: a = 10.264(1), b = 10.448(1), c = 7.0781(1) Å, α = 82.47(2), β = 100.12(2), γ = 109.77(1)°, V = 701.1(3) Å^3, d_{calc} = 1.17 g/cm^3, Z = 2, and space group $P\bar{1}$

The parameters of the cell and the intensities of 1393 reflections with $F^2 \geqslant 2\sigma$ were measured with a four-circle Hilger-Watts automatic diffractometer (λCu K_α, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leqslant 66°$). The structure was elucidated by a direct method and was refined by the total matrix method of least squares, initially within the isotropic approximation and subsequently within the anisotropic approximation. All of the H atoms, including the H atom bonded to the heteroring N atom, were revealed in differential synthesis and were included in the refinement within the isotropic approximation. The final R factor was 0.0522 (R_w = 0.0570). The calculations were made with an Eclipse S/200 computer by means of modified EXTL programs.* The coordinates of the nonhydrogen atoms are presented in Table 1, while the coordinates of the hydrogen atoms are presented in Table 2.

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*The programs were modified in the laboratory of x-ray diffraction analysis of the Institute of Heteroorganic Compounds by A. I. Yanovskii and R. G. Gerr.