STRUCTURE OF THE 2-MERCAPTO-3-THENYLIDENE-CYCLOHEXYLAMINE MOLECULE IN THE CRYSTALLINE STATE

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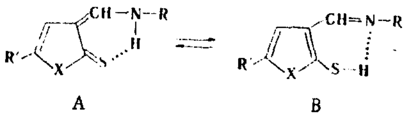
The crystal structure of $C_{11}H_{14}NS_2$ was determined by means of a diffractometric experiment (λ MoKα, by the method of least squares within the anisotropic approximation, R = 0.051 with respect to 1685 reflections). The crystals are monoclinic with a = 14.953, b = 12.663, c = 6.222 Å, γ = 91.69°, Z = 4, and space group $P2_1$; the crystal cell contains two independent molecules having identical structures. The distribution of the bond lengths in the molecule provides evidence for the contribution of two tautomeric forms – 2-mercapto-3-thenylidenecyclohexylamine and 3-cyclohexylaminomethylenethiolene-2-thione – to the structure and for statistical delocalization of the H atom between the S and N atoms of the molecule.

The synthesis and properties of ligands of a new type – mercaptoaldimines of the thiophene, furan, and benzo[b]thiophene series cumulative data on which are presented in [1], have been described in recent years. In a number of cases these compounds have interesting and useful properties such as, for example, inhibitors of the oxidation of hydrocarbons [2] or agents to fight deep-rooted mycoses [3]. They also serve as starting compounds in the synthesis of chelate compounds and a number of condensed heterocyclic systems.

It has been established by IR and PMR spectroscopy that one of the peculiarities of mercaptoaldimines is the fact that in solution they exist in the form of an equilibrium mixture of tautomers, in which the equilibrium is shifted to favor tautomeric form A [4-7].



X = O or S; R' – H, Alk

In mercaptoaldimines the migration of an H atom between the two reaction centers evidently takes place via an intramolecular mechanism, since the PMR spectra of these compounds indicate a strong intramolecular hydrogen bond [4, 5].

An x-ray diffraction study of some chelate compounds based on N-substituted mercaptoaldimines of the thiophene series showed that their structures cannot be described within the framework of canonical formulas [8, 9]. In this connection it seemed of interest to ascertain which of the forms – A or B – is realized in the ligand molecule in the solid state. With this end in mind, we made an x-ray diffraction study of 2-mercapto-3-thenylidenecyclohexylamine ($C_{11}H_{14}NS_2$), which exists in the 3-cyclohexylaminomethylenethiol-4-ene-2-thione form in solution.

The $C_{11}H_{14}NS_2$ crystals are monoclinic with a = 14.953(1), b = 12.663(1), c = 6.2220(4) Å, γ = 91.69(1)°, V = 1177.7(3) Å^3, d_{meas} = 1.24, d_{calc} = 1.24 g/cm^3, Z = 4, and space group $P2_1$; the crystal contains two crystallographically independent molecules. The x-ray diffraction experiment (1685 $F^2 > 1\sigma$) was obtained with a Hilger–Watts four-circle automatic diffractometer with λ Mo K$_\alpha$ emission, a graphite monochromator, ω scanning, and θ_{max} = 57°.

The structure was decoded by a direct method and was refined by the method of least squares within the anisotropic approximation to R = 0.067. All of the hydrogen atoms except the two bonded to the nitrogen (in

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TABLE 1. Coordinates of the Atoms and Isotropic Temperature Parameters of the Hydrogen Atoms (B_j, Å^2) in the $C_{11}H_{14}NS_2$ Structure

Atom	x	y	z	B_j	Atom	x	y	z	B_j
		Molecule A					Molecule B		
S(1)	0,8566 (1)	0,6357 (1)	0,1072 (3)	—	S(1′)	0,6628 (1)	0,1278 (1)	0,9092 (3)	—
S(2)	1,0323 (1)	0,7405 (1)	0,2147 (3)	—	S(2′)	0,4938 (1)	0,2371 (1)	0,8096 (3)	—
N	0,8231 (2)	0,5089 (3)	0,5086 (7)	—	N′	0,6828 (3)	0,0004 (3)	0,5054 (7)	—
C(1)	0,9440 (3)	0,6554 (3)	0,2758 (8)	—	C(1′)	0,5753 (3)	0,1504 (3)	0,7412 (9)	—
C(2)	0,9586 (3)	0,6115 (3)	0,4844 (8)	—	C(2′)	0,5566 (3)	0,1072 (3)	0,5358 (8)	—
C(3)	1,0399 (3)	0,6499 (4)	0,5781 (11)	—	C(3′)	0,4764 (4)	0,1406 (4)	0,4465 (10)	—
C(4)	1,0866 (4)	0,7184 (5)	0,4560 (15)	—	C(4′)	0,4354 (3)	0,2179 (4)	0,5702 (12)	—
C(5)	0,8984 (3)	0,5410 (4)	0,5876 (8)	—	C(5′)	0,6093 (3)	0,0342 (4)	0,4286 (9)	—
C(6)	0,7579 (3)	0,4367 (4)	0,6158 (10)	—	C(6′)	0,7415 (4)	−0,0755 (5)	0,3914 (12)	—
C(7)	0,7328 (5)	0,3472 (5)	0,4724 (14)	—	C(7′)	0,8304 (6)	−0,0182 (6)	0,3369 (15)	—
C(8)	0,6812 (6)	0,3831 (6)	0,2797 (13)	—	C(8′)	0,8859 (6)	0,0031 (8)	0,5359 (25)	—
C(9)	0,6003 (4)	0,4468 (8)	0,3478 (15)	—	C(9′)	0,8801 (6)	−0,1035 (8)	0,6920 (17)	—
C(10)	0,6280 (4)	0,5372 (6)	0,4979 (16)	—	C(10′)	0,7961 (5)	−0,1524 (6)	0,7036 (19)	—
C(11)	0,6783 (4)	0,4991 (5)	0,6857 (12)	—	C(11′)	0,7483 (5)	−0,1667 (6)	0,5182 (19)	—
H(3)	1,058 (4)	0,628 (4)	0,705 (12)	5 (2)	H(3′)	0,452 (4)	0,115 (5)	0,329 (12)	6 (2)
H(4)	1,144 (4)	0,755 (5)	0,496 (11)	5 (2)	H(4′)	0,384 (3)	0,264 (4)	0,554 (10)	3 (1)
H(5)	0,916 (3)	0,512 (4)	0,682 (11)	4 (2)	H(5′)	0,589 (4)	0,001 (4)	0,291 (11)	5 (2)
H(6)	0,788 (5)	0,405 (5)	0,698 (14)	9 (2)	H(6′)	0,688 (4)	−0,102 (4)	0,258 (12)	7 (3)
H(71)	0,698 (3)	0,289 (4)	0,550 (10)	6 (2)	H(71′)	0,855 (3)	−0,068 (5)	0,255 (13)	4 (1)
H(72)	0,788 (4)	0,305 (5)	0,438 (13)	6 (2)	H(72′)	0,830 (4)	0,021 (5)	0,259 (12)	7 (3)
H(81)	0,659 (5)	0,326 (5)	0,171 (15)	9(3)	H(81′)	0,940 (3)	−0,010 (3)	0,561 (9)	3 (2)
H(82)	0,720 (4)	0,421 (4)	0,178 (12)	4 (2)	H(82′)	0,875 (5)	−0,064 (6)	0,633 (17)	10 (4)
H(91)	0,554 (5)	0,388 (6)	0,466 (17)	10 (3)	H(91′)	0,927 (4)	−0,160 (5)	0,633 (14)	7 (3)
H(92)	0,576 (5)	0,463 (6)	0,250 (16)	9 (3)	H(92′)	0,900 (6)	−0,080 (7)	0,855 (17)	10 (4)
H(101)	0,573 (4)	0,588 (5)	0,558 (14)	8 (2)	H(101′)	0,815 (5)	−0,243 (6)	0,717 (15)	10 (4)
H(102)	0,669 (4)	0,582 (5)	0,458 (12)	4 (2)	H(102′)	0,757 (4)	−0,106 (5)	0,806 (12)	10 (4)
H(111)	0,641 (4)	0,435 (5)	0,755 (14)	9 (3)	H(111′)	0,684 (5)	−0,193 (6)	0,581 (17)	10 (4)
H(112)	0,697 (5)	0,581 (6)	0,752 (15)	10 (4)	H(112′)	0,780 (5)	−0,222 (6)	0,428 (19)	10 (4)

TABLE 2. Anisotropic Temperature Parameters of the Atoms in the $C_{11}H_{14}NS_2$ Structure*

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$S_{(1)}$	86 (1)	103 (1)	237 (4)	−2 (2)	0 (4)	58 (4)
$S_{(1')}$	75 (1)	101 (1)	272 (4)	4 (2)	−1 (4)	−52 (4)
$S_{(2)}$	79 (1)	82 (1)	549 (8)	−19 (2)	149 (5)	12 (5)
$S_{(2')}$	71 (1)	84 (1)	482 (7)	13 (2)	103 (4)	−26 (5)
N	48 (2)	100 (4)	273 (14)	−9 (5)	−28 (11)	52 (13)
N′	60 (3)	101 (4)	305 (16)	18 (5)	12 (12)	−93 (14)
$C_{(1)}$	64 (3)	64 (4)	32 (2)	6 (5)	68 (14)	−19 (14)
$C_{(1')}$	58 (3)	64 (4)	334 (20)	−5 (5)	36 (14)	25 (15)
$C_{(2)}$	53 (3)	75 (4)	259 (18)	14 (5)	−9 (12)	−43 (14)
$C_{(2')}$	57 (3)	77 (4)	268 (18)	−13 (5)	−1 (12)	16 (14)
$C_{(3)}$	52 (3)	103 (5)	457 (26)	3 (6)	−8 (16)	−92 (21)
$C_{(3')}$	66 (4)	102 (5)	400 (27)	−10 (7)	−17 (17)	48 (20)
$C_{(4)}$	57 (3)	105 (6)	656 (44)	−10 (7)	53 (20)	−113 (27)
$C_{(4')}$	63 (4)	112 (6)	489 (32)	18 (7)	9 (19)	76 (24)
$C_{(5)}$	57 (3)	84 (4)	242 (16)	32 (6)	23 (13)	11 (15)
$C_{(5')}$	60 (3)	90 (5)	278 (17)	−19 (6)	39 (14)	−49 (16)
$C_{(6)}$	52 (3)	120 (5)	361 (21)	−3 (7)	−14 (15)	188 (19)
$C_{(6')}$	74 (4)	132 (7)	405 (26)	29 (8)	−1 (18)	−194 (23)
$C_{(7)}$	101 (5)	89 (6)	649 (41)	−17 (8)	126 (25)	17 (25)
$C_{(7')}$	125 (7)	147 (8)	640 (41)	127 (12)	367 (29)	136 (32)
$C_{(8)}$	143 (7)	172 (9)	433 (31)	−179 (14)	−78 (25)	−42 (29)
$C_{(8')}$	106 (6)	228 (16)	1312 (98)	−206 (17)	286 (41)	−670 (70)
$C_{(9)}$	77 (5)	274 (14)	668 (43)	−133 (13)	−264 (24)	449 (41)
$C_{(9')}$	120 (6)	217 (12)	752 (46)	−16 (13)	−300 (30)	−223 (40)
$C_{(10)}$	50 (3)	156 (8)	768 (46)	39 (8)	48 (21)	227 (33)
$C_{(10')}$	95 (6)	155 (7)	816 (47)	88 (11)	−103 (30)	122 (35)
$C_{(11)}$	67 (4)	155 (7)	420 (27)	−1 (8)	113 (18)	45 (24)
$C_{(11')}$	120 (6)	118 (7)	706 (53)	47 (11)	56 (32)	−79 (33)

*The anisotropic temperature factor is $T = \exp[-10^{-4}(B_{11}h^2 + \ldots + B_{12}hk + \ldots)]$.

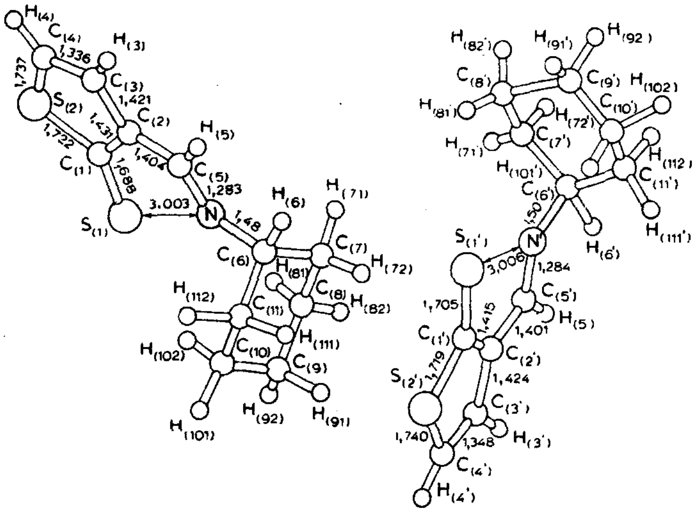

Fig. 1. Geometry of the 2-mercapto-3-thenylidenecyclohexylamine molecules in the crystalline state.

form A) or sulfur (in form B) atom were exposed by differential synthesis. Further refinement was carried out within the anisotropic approximation for the nonhydrogen atoms and within the isotropic approximation for the hydrogen atoms (R = 0.051). As usual, the calculated (at the end of the refinement) differential synthesis with exclusion of the long-range reflections ($\sin\theta/\lambda \leq 0.4$) did not expose the two absent hydrogen atoms, but markedly diffuse electron density maxima, the height of which does not exceed the height of the background maxima, were found in the regions between the S and N atoms in both molecules.

The coordinates of the atoms and the isotropic temperature parameters of the H atoms are presented in Table 1, and the anisotropic temperature parameters of the nonhydrogen atoms are presented in Table 2.

The structure of the molecules and the geometrical parameters of greatest importance for discussion are shown in Fig. 1. All of the bond lengths and valence angles are presented in Table 3. The C−C and C−S bond

TABLE 3. Bond Lengths d (Å) and Valence Angles ω (deg) in the $C_{11}H_{14}NS_2$ Structure

Bond	d	Bond	d	Bond	d	Bond	d
Molecule A				Molecule B			
$S_{(1)}$—$C_{(1)}$	1,688 (5)	$C_{(6)}$—$C_{(7)}$	1,482 (9)	$S_{(1')}$—$C_{(1')}$	1,705 (5)	$C_{(6')}$—$C_{(7')}$	1,534 (10)
$S_{(2)}$—$C_{(1)}$	1,722 (5)	$C_{(7)}$—$C_{(8)}$	1,503 (12)	$S_{(2')}$—$C_{(1')}$	1,719 (5)	$C_{(7')}$—$C_{(8')}$	1,510 (16)
$S_{(2)}$—$C_{(4)}$	1,734 (8)	$C_{(8)}$—$C_{(9)}$	1,534 (12)	$S_{(2')}$—$C_{(4')}$	1,740 (7)	$C_{(8')}$—$C_{(9')}$	1,663 (16)
$C_{(1)}$—$C_{(2)}$	1,431 (7)	$C_{(9)}$—$C_{(10)}$	1,525 (13)	$C_{(1')}$—$C_{(2')}$	1,415 (7)	$C_{(9')}$—$C_{(10')}$	1,386 (11)
$C_{(2)}$—$C_{(3)}$	1,421 (7)	$C_{(10)}$—$C_{(11)}$	1,478 (11)	$C_{(2')}$—$C_{(3')}$	1,424 (7)	$C_{(10')}$—$C_{(11')}$	1,366 (15)
$C_{(3)}$—$C_{(4)}$	1,336 (9)	$C_{(11)}$—$C_{(6)}$	1,511 (8)	$C_{(3')}$—$C_{(4')}$	1,348 (9)	$C_{(11')}$—$C_{(6')}$	1,405 (11)
$C_{(2)}$—$C_{(5)}$	1,404 (6)	Средн.	1,51	$C_{(2')}$—$C_{(5')}$	1,401 (7)	Средн.	1.48
N—$C_{(5)}$	1,286 (6)			N′—$C_{(5')}$	1,284 (6)		
N—$C_{(6)}$	1,477 (7)			N′—$C_{(6')}$	1,499 (8)		
Angle	ω	Angle	ω	Angle	ω	Angle	ω
$S_{(1)}C_{(1)}S_{(2)}$	122,1 (3)	$NC_{(6)}C_{(7)}$	110,4 (5)	$S_{(1')}C_{(1')}S_{(2')}$	121,2 (3)	$N'C_{(6')}C_{(7')}$	108,5 (5)
$S_{(1)}C_{(1)}C_{(2)}$	129,2 (3)	$NC_{(6)}C_{(11)}$	108,8 (4)	$S_{(1')}C_{(1')}C_{(2')}$	129,3 (4)	$N'C_{(6')}C_{(11')}$	108,6 (6)
$S_{(2)}C_{(1)}C_{(2)}$	108,7 (3)	$C_{(6)}C_{(7)}C_{(8)}$	111,7 (5)	$S_{(2')}C_{(1')}C_{(2')}$	109,5 (3)	$C_{(6')}C_{(7')}C_{(8')}$	111,5 (7)
$C_{(1)}S_{(2)}C_{(4)}$	93,6 (3)	$C_{(7)}C_{(8)}C_{(9)}$	111,0 (7)	$C_{(1')}S_{(2')}C_{(4')}$	93,5 (3)	$C_{(7')}C_{(8')}C_{(9')}$	108,6 (8)
$S_{(2)}C_{(4)}C_{(3)}$	111,0 (4)	$C_{(8)}C_{(9)}C_{(10)}$	111,3 (6)	$S_{(2')}C_{(4')}C_{(3')}$	110,2 (4)	$C_{(8')}C_{(9')}C_{(10')}$	114,7 (8)
$C_{(4)}C_{(3)}C_{(2)}$	114,6 (5)	$C_{(9)}C_{(10)}C_{(11)}$	111,7 (6)	$C_{(4')}C_{(3')}C_{(2')}$	114,6 (5)	$C_{(9')}C_{(10')}C_{(11')}$	118,6 (9)
$C_{(1)}C_{(2)}C_{(3)}$	112,2 (4)	$C_{(10)}C_{(11)}C_{(6)}$	111,0 (6)	$C_{(1')}C_{(2')}C_{(3')}$	112,1 (4)	$C_{(10')}C_{(11')}C_{(6')}$	114,6 (7)
$C_{(1)}C_{(2)}C_{(5)}$	124,1 (4)	$C_{(11)}C_{(6)}C_{(7)}$	112,9 (5)	$C_{(1')}C_{(2')}C_{(5')}$	125,1 (4)	$C_{(11')}C_{(6')}C_{(7')}$	115,5 (6)
$C_{(3)}C_{(2)}C_{(5)}$	123,7 (5)	Av.	111,1	$C_{(3')}C_{(2')}C_{(5')}$	122,7 (5)	Av.	112,6
$C_{(2)}C_{(5)}N$	124,4 (5)			$C_{(2')}C_{(5')}N'$	123,2 (5)		
$C_{(5)}NC_{(6)}$	125,5 (5)			$C_{(5')}N'C_{(6')}$	124,2 (5)		

TABLE 4. Equations of the Ax + By + Cz − D = 0 Planes of the Fragments of the Molecules, Deviations of the Atoms from These Planes (Å), and Torsion Angles (φ) in Cyclohexane in the $C_{11}H_{14}NS_2$ Structure

Plane	Atoms and their deviations from the plane	A	B	C	D
I	S(2) C(1) C(2) C(3) C(4) −0,0013 0,0012 −0,0005 −0,0008 0,0014 S(1)* C(5)* N* −0,03 −0,01 −0,083	0,5067	−0,7551	−0,4159	0,0495
II	N C(5) C(2) C(1) S(1) −0,006 0,007 −0,001 −0,005 0,004	0,477	−0,775	−0,415	−0,515
III	S(2′) C(1′) C(2′) C(3′) C(4′) −0,004 0,001 0,004 −0,008 0,008 S(1′)* C(5′)* N′* 0,02 0,02 −0,07	0,512	0,745	−0,427	3,824
IV	N C(5′) C(2′) C(1′) S(1′) 0,009 −0,012 0,003 0,006 −0,006	0,494	0,759	−0,425	3,700

Torsion angles	φ	Torsion angles	φ
$C_{(6)}C_{(7)}C_{(8)}C_{(9)}$	−53,5	$C_{(6')}C_{(7')}C_{(8')}C_{(9')}$	42,2
$C_{(7)}C_{(8)}C_{(9)}C_{(10)}$	53,1	$C_{(7')}C_{(8')}C_{(9')}C_{(10')}$	−40,4
$C_{(8)}C_{(9)}C_{(10)}C_{(11)}$	−54,8	$C_{(8')}C_{(9')}C_{(10')}C_{(11')}$	44,2
$C_{(9)}C_{(10)}C_{(11)}C_{(6)}$	54,8	$C_{(9')}C_{(10')}C_{(11')}C_{(6')}$	−50,4
$C_{(10)}C_{(11)}C_{(6)}C_{(7)}$	−55,6	$C_{(10')}C_{(11')}C_{(6')}C_{(7')}$	52,7
$C_{(11)}C_{(6)}C_{(7)}C_{(8)}$	55,0	$C_{(11')}C_{(6')}C_{(7')}C_{(8')}$	−51,4

*These atoms were not taken into account in the construction of the planes.

TABLE 5. Short Intermolecular Distances d (Å) in the $C_{11}H_{14}NS_2$ Structure*

Distance		d	Distance		d
$S_{(1)}\cdots C_{(5)}$	III	3,510	$C_{(1)}\cdots H_{(112')}$	II	2,97
$S_{(1)}\cdots C_{(10')}$	III	3,82	$C_{(1')}\cdots C_{(5')}$	V	3,76
$S_{(1)}\cdots H_{(5)}$	III	3,12	$C_{(1')}\cdots C_{(7')}$	I	3,78
$S_{(1)}\cdots H_{(101')}$	IV	2,90	$C_{(1')}\cdots H_{(7)}$	I	2,70
$S_{(1)}\cdots H_{(112')}$	I	2,72	$C_{(1')}\cdots H_{(112')}$	V	3,08
$S_{(1')}\cdots C_{(5')}$	III	3,51	$C_{(2)}\cdots C_{(5)}$	VII	3,82
$S_{(1')}\cdots H_{(5')}$	III	3,09	$C_{(2)}\cdots H_{(5)}$	VII	3,02
$S_{(1')}\cdots H_{(71)}$	I	3,00	$C_{(2)}\cdots H_{(91')}$	II	3,07
$S_{(1')}\cdots H_{(81)}$	III	2,98	$C_{(2')}\cdots H_{(5')}$	V	3,00
$S_{(2)}\cdots C_{(5)}$	VII	3,83	$C_{(3)}\cdots H_{(91')}$	II	3,07
$S_{(2)}\cdots C_{(8')}$	IV	3,67	$C_{(3')}\cdots H_{(5')}$	V	3,00
$S_{(2)}\cdots H_{(82')}$	VII	3,11	$C_{(4)}\cdots C_{(6)}$	VII	3,73
$S_{(2')}\cdots C_{(5')}$	V	3,80	$C_{(4)}\cdots H_{(91')}$	II	3,15
$S_{(2')}\cdots C_{(10)}$	VI	3,62	$C_{(4)}\cdots C_{(6')}$	V	3,73
$S_{(2')}\cdots H_{(5')}$	V	3,20	$C_{(4')}\cdots H_{(5')}$	V	3,09
$S_{(2')}\cdots H_{(101)}$	VI	2,98	$C_{(4')}\cdots H_{(91)}$	I	2,95
$N\cdots H_{(3)}$	VII	3,09	$C_{(5)}\cdots H_{(3)}$	VII	2,77
$N'\cdots H_{(3')}$	V	3,14	$C_{(5')}\cdots H_{(3')}$	V	3,23
$C_{(1)}\cdots C_{(5)}$	VII	3,67	$C_{(9)}\cdots H_{(101)}$	VI	3,12
$C_{(1)}\cdots H_{(5)}$	VII	3,05	$C_{(11')}\cdots H_{(102)}$	II	3,22
$C_{(1)}\cdots H_{(91')}$	II	3,14	$C_{(92)}\cdots H_{(101)}$	VI	2,57

*The short intermolecular distances between the atoms of the starting molecules (I), the coordinates of which are presented in the table, and the atoms of the molecules associated with them by the following symmetrical transformations are given in this table; plane II by a b translation, III by a c translation, IV by a b + c translation, V by the 2_1 [1/2 0 z] axis, VI by the 2_1 [1/2 1/2 z] axis, and VII by the 2_1 [1/2 1/2 z] axis.

lengths in the thiophene portion of the molecule and the length of the $C_{(5)}-N$ bond were obtained with good accuracy and coincide within the limits of 3σ in the two independent molecules. The geometrical parameters averaged over the two independent molecules are therefore used throughout the following discussion.

The thiophene ring is planar (Table 4), and the $S_{(2)}-C_{(1)}$ and $S_{(2)}-C_{(4)}$ bond lengths of 1.721 and 1.737 Å are only slightly shorter than in thiophene (1.714 Å) [10] and its derivatives [11] and appreciably shorter than the length of the S − C single bond (1.817 Å) [12]. The exocyclic $S_{(1)}-C_{(1)}$ bond (1.700 Å) is appreciably shorter than the endocyclic bonds but is still greater than the length of the S = C bond in the CS_2 molecule (1.553 Å) [10] and is close to the value found in thiazolinethione derivatives (1.688 Å [12] and 1.691 Å [13]). The $C_{(1)}-C_{(2)}$, $C_{(2)}-C_{(3)}$, and $C_{(3)}-C_{(4)}$ bond lengths in the heteroring are, respectively, 1.423, 1.423, and 1.342 Å, i.e., the latter bond is almost a double bond, whereas the other two are close to sesqui bonds. Alternation of the C−C bond lengths is found in thiophene itself: The two shorter bonds are 1.370 Å, and the longer bond is 1.423 Å. Thus the C−C bond lengths in the heteroring of the investigated molecule differ substantially from the lengths found in thiophene. The length of the $C_{(2)}-C_{(5)}$ bond is 1.403 Å and coincides with the length of the sesqui bond in benzene, whereas the length of the $C_{(5)}$−bond (1.284 Å) is somewhat greater as compared with the standard value for the double bond (1.255 Å [14]). The $S_{(1)}C_{(1)}C_{(2)}C_{(5)}N$ fragment of the molecule is planar and virtually coplanar with the thiophene ring.

Thus the distribution of the bond lengths provides evidence for contribution of both tautomeric forms and for the absence of predominance of one of them.

The intramolecular S...N distance [3.005(7) Å] is shortened considerably as compared with the sum of the vand der Waals radii (3.4 Å) and is less than the intermolecular S...N distance (3.299 Å) in the L-ergothioneine crystal [13], in which an S...H−N hydrogen bond is found. The character of the electron-density distribution constitutes evidence that the hydrogen atom is probably statistically delocalized between the S and N atoms, which is in agreement with the determined distribution of the bond lengths. The following constitutes yet another indirect piece of evidence for an intramolecular hydrogen bond. If there are potential hydrogen bond donors and acceptors in a molecule, intermolecular hydrogen bonds are usually formed in the crystal in the absence of intramolecular hydrogen bonds. However, an analysis of the intermolecular distances (Table 5) does not reveal short contacts between the S and N atoms, i.e., the crystal does not contain intermolecular hydrogen bonds of the indicated type.

It should be noted that in other prototropic systems also hydrogen bonding leads to the realization in the crystal of forms intermediate between two limiting forms with statistical delocalization of the H atom [15, 16].

The C−C bond lengths in the cyclohexane rings have considerable scatter; this is evidently associated with a certain degree of disorderliness of this fragment of the molecule. The greater diffuse character of the corresponding electron-density maxima and the higher values of the temperature parameters of the $C_{(7)}-C_{(11)}$ [$C_{(7')}-C_{(11')}$] atoms also indicate this. The cyclohexane rings have a chair conformation with torsion angles close to the usual values (Table 4). The $N-C_{(6)}$ bond length of 1.49 Å coincides with the standard value for a single bond (1.47 Å). The average length of the C−H bond is 1.03 Å, and the individual values vary from 0.74 to 1.25 Å.

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RING-CHAIN ISOMERISM OF N-MONOSUBSTITUTED 2-CYANOBENZENESULFONAMIDES*

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A number of N-monosubstituted 2-cyanobenzenesulfonamides (A) and their chain isomers – 2-substituted 3-iminobenzothiazoline 1,1-dioxides (B), which are formed as a result of intramolecular nucleophilic addition of the sulfonamido group to the C≡N bond – were synthesized by acylation of primary amines with 2-cyanobenzenesulfonyl chloride. The interconversions of the isomers – A → B under alkaline-catalysis conditions and B → A under thermal conditions – were accomplished for the first time. The influence of the electronic and steric effects of the substituent attached to the nitrogen atom on the relative stabilities of the open and chain isomers was ascertained. The A ⇌ B equilibrium constants in solutions in a mixture of dioxane and triethylamine were determined by IR spectroscopy.

It is known [2-4] that 2-cyanobenzenesulfonyl chloride (I) reacts with ammonia and primary amines to give 2-cyanobenzenesulfonamides (II), which undergo isomerization to 3-iminobenzisothiazoline 1,1-dioxides (III) when excess amine is present.

Since little study has been devoted to intramolecular nucleophilic addition of a sulfonamido group to polar multiple bonds [5-7], the aim of the present research was to study the influence of the electronic and steric effects of substituents attached to the nitrogen atom on the relative stabilities of isomers II and III and on the possibility of realization of their interconversions.

3-Iminobenzisothiazoline 1,1-dioxides IIIa, b, e, g, h (Table 1) were obtained in the reactions of chloride I with excess primary amine carried out in dioxane with subsequent dilution of the reaction mixture with water. As has been demonstrated for N-methylamide IIa [3], the initially formed amides II undergo isomerization to III under the influence of excess amine.

N-tert-Butyl- and N-(1-adamantyl)amides IIc, d (Table 2) and anilide IIf, which do not undergo isomerization under the reaction conditions, constitute exceptions to the above. Special experiments designed to effect the isomerization of these compounds under the influence of alkaline agents [a refluxing ethanol solution of triethylamine, an aqueous dioxane solution of potassium hydroxide, and CH_3SOCH_2Na in dimethyl sulfoxide (DMSO)] were also unsuccessful.

TABLE 1. 3-Iminobenzisothiazoline 1,1-Dioxides III

Compound	mp, °C	IR spectra, ν, cm⁻¹		Found, %				Empirical formula	Calculated, %				Yield, %
		C=N	N–H	C	H	N	S		C	H	N	S	
IIIa	166–167*	1655 br	3313	48,7	3,8	13,9	16,4	$C_8H_8N_2O_2S$	49,0	4,1	14,3	16,4	74
IIIb	147–148	1648	3303	53,2	5,5	12,5	14,6	$C_{10}H_{12}N_2O_2S$	53,6	5,4	12,5	14,3	94
IIIe	127–128	1659, 1654 sh 1647 sh	3303	61,9	4,5	10,2	11,9	$C_{14}H_{12}N_2O_2S$	61,8	4,4	10,3	11,8	95
IIIg	165–166	1664	3284	61,7	4,6	10,3	11,9	$C_{14}H_{12}N_2O_2S$	61,8	4,4	10,3	11,8	72
IIIh	166–167	1668	3267	58,5	4,3	9,7	11,3	$C_{14}H_{12}N_2O_3S$	58,3	4,2	9,7	11,1	87

*According to the data in [3], this compound has mp 165-166°C.

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