Reaction of Selenopyran V with CF_3CO_2H. A. A mixture of 0.75 g (2 mmoles) V, 12.5 ml CF_3CO_2H, and 5 ml abs. ether was stirred for 12 h under argon. The reaction mixture was diluted with 100 ml ether and treated as described in the reaction of Ia to yield 0.55 g (58%) IVc and 0.2 g (27%) IIIa.

B. A sample of 2 ml abs. CF_3CO_2H was added to a solution of 0.6 g (1.6 mmole) V in 10 ml dry benzene. After 3 h, the reaction mixture was treated as in method A to give 0.43 g (57%) IVc and 0.15 g (25%) IIIa.

Reaction of 2,4,6-Triphenyl-2,6-di(hydroseleno)-1-selenocyclohexane (IIa) with CF_3CO_2H. A sample of 2 ml CF_3CO_2H was added to a solution of 0.89 g (1.6 mmole) IIa in 10 ml dry benzene. The mixture was maintained for nine days at 20°C, diluted with 100 ml ether, and treated as in the reaction of Ia to yield 0.38 g (50%) IVc, 0.17 g (28%) IIIa, and 0.22 g (87%) elemental selenium.

Reaction of IIa with Boron Trifluoride Etherate. A sample of 2 ml $BF_3 \cdot Et_2O$ was added to a solution of 0.89 g (1.6 mmole) IIa in 10 ml dry benzene. The mixture was maintained at 20°C for four days and then diluted with 100 ml ether to yield 0.43 g (59%) 2,4,6-triphenylselenopyrilium tetrafluoroborate (IVe), 0.16 g (27%) IIIa, and 0.235 g (93%) elemental selenium.

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MOLECULAR AND CRYSTAL STRUCTURE OF 2-PARA-TOLUIMIDO-4,4-DIMETHYL-(4H)-1,3-THIAZINE

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S. T. Cholpankulova, and L. A. Tsoi

UDC 548.737:547.869:541.62

The imino structure of 2-p-toluimido-4,4-dimethyl-(4H)-1,3-thiazine (I) was demonstrated by x-ray diffraction structural analysis. Molecules of I in the crystal are linked by N—H···O hydrogen bonds in infinite chains. A shortened S···O intramolecular contact was found which corresponds to a secondary interaction. A mechanism was proposed for the thiazoline—thiazine rearrangement.

2-Acyliminothiazolines and 2-acyliminothiazines were obtained in the intramolecular cyclization of acylethynylthioureas and the possibility of the isomerization of the thiazoline to thiazines was discovered [1, 2]. The IR spectra of the compounds obtained show a shift to lower frequencies for the acyl substituent carbonyl group stretching vibrations. An attempt to relate this shift to intramolecular hydrogen bonding [2] did not account for the greater thermodynamic stability of the thiazine ring in comparison to the thiazoline ring upon isomerization. We carried out an x-ray diffraction structural analysis of 2-p-tolu-

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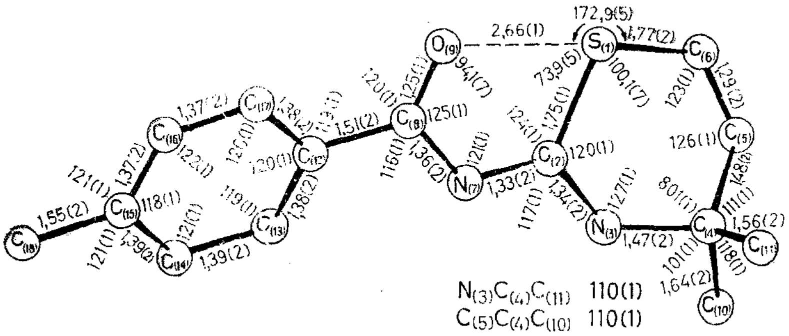

Fig. 1. Structure, bond lengths, and bond angles in I.

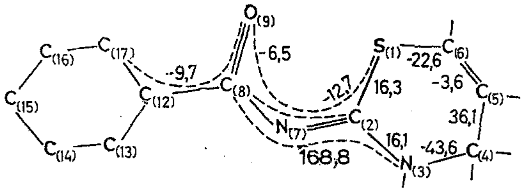

Fig. 2. Some torsional angles in I.

imido-4,4-dimethyl-(4H)-1,3-thiazine (I) in order to obtain an unequivocal structure determination.

The structure, bond lengths, and bond angles of I are shown in Fig. 1. On the whole, the molecule is nonplanar. Some of the torsional angles are given in Fig. 2. The thiazine ring has a conformation intermediate between a flattened, twisted boat and semichair. The torsional angles in the central $N_{(3)}C_{(2)}S_{(1)}N_{(7)}C_{(8)}O_{(9)}$ fragment do not exceed 13°. The molecule exists in the crystal in the imino form. The $H(N_{(3)})$ atom which is capable of migrating between two reaction sites ($N_{(3)}$ and $N_{(7)}$) is localized exclusively at $N_{(3)}$. Previously studied derivatives of 2-phenyliminothiazine have similar imino structure [3, 4]. The endocyclic $C_{(2)}$—$N_{(3)}$ bonds in these compounds (1.35 and 1.41 Å) are significantly longer than the exocyclic $C_{(2)}$—$N_{(7)}$ bonds (1.28 and 1.27 Å), and the bond angle at the cyclic nitrogen atom $N_{(3)}$ is somewhat expanded (127° and 129°). On the other hand, the endocyclic C—N bond in sulfamidothiazine which exists in the amino form (1.281 Å) [5] is significantly shorter than the exocyclic bond (1.381 Å). The angle at the cyclic nitrogen atom $N_{(3)}$ is only slightly expanded (122°) but the endocyclic angle at $C_{(2)}$ is markedly greater (128.1°).

On the other hand, not all the features typical for the imino form of aroyliminothiazines are encountered in I. Thus, in particular, the difference in the lengths of the $C_{(2)}$—N endo- and exocyclic bonds is lacking [1.34(2) and 1.33(2) Å]. A similar equalization of C—N bond lengths was previously found by Sólyom et al. [6] for 2-benzoylimino-4-methylperhydro-1,2,4-oxathiazine (IX) [in Table 1, 1.324(4) and 1.335(4) Å]. In both these molecules, an additional close contact is found, specifically, the shortened intramolecular S···O contact corresponding to an attractive interaction. Such an interaction was first discovered in 1961 by Mammi et al. [7] in crystals of 1,5-dimethyldithiofuraphthene (III). In contrast to the structure of 1,5-dimethyldithiothiaphthene [8, 9], in which both S—S bonds are equal in length (2.358 Å), the length of the S—S bond in the furaphthene analog (2.12 Å) is similar to the standard value for the S—S single bond (2.10 Å [10]), while the S—O bond (2.41 Å) is longer than the standard value for the covalent bond (1.67-1.70 Å [11]) but significantly shorter than the sum of the van der Waals radii for S and O (3.30 Å [12]). In recent years, a significant number of structures have been studied, in which an attractive S···O interaction was discovered [13-25]. Some of these examples are given in Table 1.

The distances for secondary S···O bonds fall in a rather broad range (from 2.03 to 2.80 Å). In all the structures presented (II-XVIII, Table 1), the configuration of the Y—S···O unit (Y = C, O, N, S) is close to linear. We should note that the short S···O contact is not required because of strong conjugation in the molecule since, for example, the conjugation in VII would also be retained with trans configuration relative to the C=N bond. The deformational electron density map in the crystal of 2-(2-chlorobenzoylimino)-1,3-thiazoli-

TABLE 1. Characteristic Interatomic Distances in Some Molecules with a Shortened S···O Intermolecular Contact[a]

Compound	Interatomic distances, Å			Reference
	a	*b*	*c*	
I	2,66 (1)	1,77 (2)	1,25 (1)	Present work
II	2,73	1,84	1,25	13
III	2,41	2,12	1,27	7
IV	2,720	1,825	1,205	14
V	2,684	1,826	1,225	15
VI	2,640	1,764	1,216	11
VII	2,604	1,770	1,228	16
VIII	2,305	1,659	1,243	17
IX	2,255	1,681	1,247	6
X	2,571; 2,515	2,080	1,200; 1,225	10
XI	2,509; 2,517	2,103	1,233—1,221	18
XII	2,327	2,110	1,258	19
XIII	2,255	2,126	1,269	20
XIV	2,78	1,52	1,29	21
XV	2,643; 2,658	1,781	1,207	22
XVI	2,644	1,781	1,215	23
XVII	2,44	1,65	1,24	24
XVIII	2,034	2,178	1,311	25

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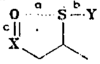
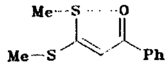
a





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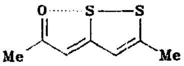

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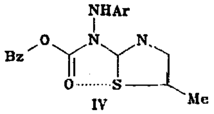

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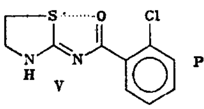

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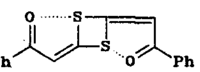

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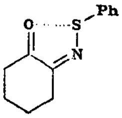

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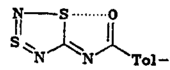

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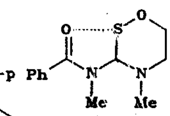

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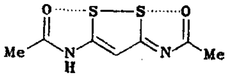

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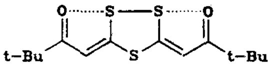

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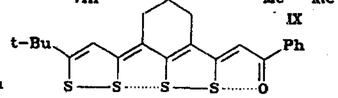

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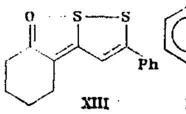

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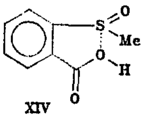

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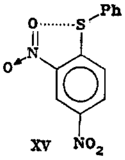

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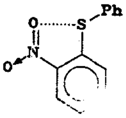

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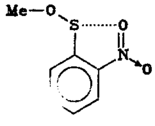

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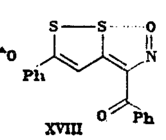


XVIII

dine (V) [15] also indicates the lack of strong steric repulsion between the S and O atoms. No perturbations due to such repulsions were found in this structure. On the other hand, bond peaks are also lacking in the region between the S and O atoms in this map. This lack may be the result of insufficient precision of this measurement since an electron density maximum was not found in the C—Cl bond.

Elongation of the X=O bond when the oxygen atom participates in the S···O interaction was found in almost all the molecules given in Table 1 (the standard C=O bond length is 1.215 Å [26] and the standard N=O bond length in nitro compounds is 1.14-1.24 Å [25]). This is also seen in the IR spectra of some of these compounds. Thus, in particular, the IR spectra of IX lack a carbonyl band in the characteristic region 1660-1800 cm^{-1} [6], while this band in VII [16] is shifted toward lower frequencies (1605 cm^{-1}) in comparison with the C=O group band in the spectrum of 1,2-benzoquinone (1664 cm^{-1}). The IR spectrum of XIII [20] both in the solid and in solution shows a bathochromic shift of the C=O group band to 1564 and 1568 cm^{-1} relative to νCO in cyclohexanone (1706 cm^{-1}).

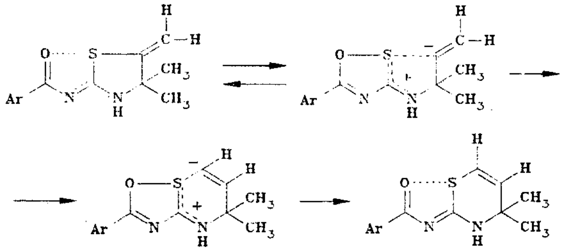
A reduction in the frequency of the carbonyl group band in I is found both in the solid state (1605 cm^{-1}) and in CCl_4 solution (1600-1620 cm^{-1}, 0.025 mole/liter), with extension of the C=O bond to 1.25(1) Å.

The S···O interaction also leads to an extension of the trans S—Y bond but only when the S···O distance is close to its lower limit (2.03-2.30 Å in XIII and XVIII). It is difficult to detect such extension of the S—N and S—O bonds in the structures of VIII and IX, in which the S···O distances (2.305 and 2.255 Å) are also close to this lower limit due to the lack of reliable S—N and S—O bond lengths.

No detailed analysis of the geometry of the secondary S···O interaction is given and no attempt was made to explain this effect in the works cited in Table 1. Only Johnson and Paul [25] noted that this interaction is "established due to the d and p orbitals and the geometry of the O···S—Y fragment is in accord with this conclusion." Apparently, these authors were referred to the σ-interaction of the vacant d_{z^2} orbital of the sulfur atom and the sp^2 orbital of the unshared electron pair of the oxygen atom. In I, as in most of the structures given in Table 1, both oxygen unshared electrom pairs occupy hybrid sp^2 orbitals and they are in the plane of the bonds of $C_{(8)}$ in I. One of these orbitals [$sp^2(1)$] is used to form a hydrogen bond, $N_{(3)}$—H···$O_{(9)}$ (see below), while the other orbital [$sp^2(2)$] is directed toward the sulfur atom. For this geometry of the indicated molecular fragment, the following interactions are possible: 1) σ-interaction of the vacant d_{z^2} orbital of the sulfur atom with the $sp^2(2)$ orbital of the unshared electron pair of the oxygen atom (σ-interaction, see above), 2) n—σ* interaction of the $sp^2(2)$ orbital with the antibonding orbital of the S—C bond (σ-interaction), and 3) n—π* interaction of the p orbital of the sulfur unshared electron pair with the antibonding orbital of the C=O π-bond (π-interaction).

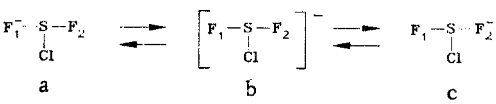
According to Epiotis et al. [27], type-3 interactions are stronger in organic compounds than type-2 interactions. The extension of the C=O and N=O bonds found for almost all the cases given in Table 1 may be the result of some antibonding character due to a type-3 interaction. Extension of the S—Y bond occurs only for very short S···O distances of about 2 Å, i.e., apparently, only the transfer of electron density to the antibonding orbital of the S—Y bond (in accord with a type-2 interaction) may be accomplished at such distances.

This S···O interaction, which is found both in aroylaminothiazines and in aroylaminothiazolidines, in apparently responsible for the following solid-phase reaction:



I

The first step in this reaction is intramolecular nucleophilic S_N2 attack of the carbonyl oxygen on the sulfur atom. The rather rigid conformation of I (see Fig. 2) provides suitable transition state geometry, in which the molecule is already predisposed to rearrange into the transition state due to approximation of its active segments. Hence, interest was found in CNDO/2 calculations of potential energy surface cross sections of the simpler reaction [28]:



These calculations showed that the axial orientation of $F^-_{(1)}$ relative to one of the ligands (in this case, the more electronegative $F_{(2)}$) in the plane of the molecule attacked is established even at extremely large distances (4-5 Å). Similar results were obtained by the expanded Hückel method. In addition, these calculations showed that the T-shaped structures b may be not simply transition states but rather stable intermediates. Analogous T-shaped structures in other nucleophilic substitution reactions at a divalent sulfur atom are more or less stable intermediates and not transition states. The symmetrical thiothiaphthenes with T-shaped configuration of the central sulfur atoms are such examples [8, 9]. The structures given in Table 1, in which complete equalization of the axial bonds of the sulfur atom is lacking may be considered as intermediate steps of nucleophilic substitution at the sulfur atom.

The determination of the remaining steps of the solid-phase isomerization of I, in accord with the mechanism given above, requires further study. In particular, an x-ray diffraction structural study of a thiazolidine derivative analogous to I and the calculation of the molecular packing energy in crystals of these compounds are needed.

N—H···N hydrogen bonds usually exist in crystals of heterocyclic acylamines and aroylamines; proton migration is accomplished along these bonds in potentially prototropic systems

TABLE 2. Atomic Coordinates ($\times 10^4$, $\times 10^3$ for H atoms) and Equivalent Isotropic Temperature Factors (Å^2) of Non-Hydrogen Atoms in I[a]

Atom	x	y	z	B_{eq}^{iso}
$S_{(1)}$	182 (3)	9190 (2)	3917 (3)	6,3 (1)
$O_{(9)}$	−1380 (8)	8000 (6)	4554 (7)	5,9 (3)
$N_{(3)}$	48 (10)	8236 (7)	1790 (9)	5,6 (4)
$N_{(7)}$	−1499 (10)	7722 (7)	2503 (8)	5,3 (4)
$C_{(2)}$	−474 (13)	8314 (8)	2664 (11)	5,7 (6)
$C_{(4)}$	1346 (15)	8634 (11)	1907 (14)	7,6 (7)
$C_{(5)}$	1488 (16)	9652 (12)	2433 (15)	8,4 (7)
$C_{(6)}$	1080 (14)	9955 (10)	3289 (14)	7,4 (6)
$C_{(8)}$	−1941 (11)	7629 (8)	3449 (12)	4,9 (4)
$C_{(10)}$	1090 (20)	8679 (14)	379 (16)	11,6 (9)
$C_{(11)}$	2510 (17)	7960 (13)	2832 (18)	11,2 (8)
$C_{(12)}$	−3171 (11)	6985 (8)	3117 (11)	5,1 (4)
$C_{(13)}$	−3896 (13)	6657 (9)	1861 (11)	6,1 (5)
$C_{(14)}$	−5001 (13)	6042 (10)	1589 (12)	7,2 (6)
$C_{(15)}$	−5372 (14)	5744 (10)	2568 (17)	7,9 (6)
$C_{(16)}$	−4622 (15)	6086 (11)	3804 (14)	7,6 (6)
$C_{(17)}$	−3536 (13)	6696 (10)	4090 (11)	6,6 (5)
$C_{(18)}$	−6551 (15)	5015 (13)	2274 (16)	11,3 (8)

Atom[b]	x	y	z
$H_{(3)}$	−52	790	96
$H_{(5)}$	198	1020	205
$H_{(6)}$	129	1073	364
$H_{(13)}$	−361	692	107
$H_{(14)}$	−559	579	58
$H_{(16)}$	−491	583	460
$H_{(17)}$	−295	695	508

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[a] The coordinates of the hydrogen atom were calculated using the results of the final refinement.

[b] $B_{eq}^{iso} = 1/3 \sum_{i,j} B_{ij} a^*_i a^*_j (\vec{a}_i \cdot \vec{a}_j)$.

[29, 30]. There are no such hydrogen bonds in the molecular structure of I. Instead, we find $N_{(3)}$—H···$O_{(9)}$ hydrogen bonds in the crystal which connect the molecules in infinite chains (O···N, 2.88 Å O···H, 1.91 Å, the N—H···O angle is 167°).

Although the bond lengths in I were determined with rather large error margins (0.01-0.02 Å), the scatter of chemically equivalent parameters or their departure from standard values generally do not exceed 1σ (this is found for the terminal methyl groups which experience considerable thermal motion, see Table 2) and, in particular, the scatter of the bond lengths in the benzene ring is 1.37-1.39 Å. Thus, the above conclusions concerning the molecular geometry of I and its interrelationship with the chemical behavior of this compound may be considered well established.

EXPERIMENTAL

A sample of 2-p-toluimido-4,4-dimethyl-(4H)-1,3-thiazine (I) was obtained according to our previous work [1], mp 76°C. The IR spectrum of thiazine I in a KBr pellet taken on a UR-20 spectrometer shows bands for νC=O at 1605 cm^{-1} and for νC=C at 1600 cm^{-1}.

The unit cell parameters for monoclinic crystals of I at +20°C: a = 10.970(2), b = 13.4591(5), c = 11.339(2) Å, β = 114.82(1)°, V = 1519.5 Å^3, d_{calc} = 1.14 g/cm^3, z = 4, space group $P2_1/c$.

The unit cell parameters and 1283 independent reflections with I > 2σ were measured on an automatic four-circle Hilger—Watts diffractometer with λMoKα radiation, graphite monochromator, θ/2θ scanning, and $2\theta_{max}$ = 67°. The structure was solved by the direct method using the MULTAN program and refined by the method of least squares in the full-matrix anisotropic approximation. The hydrogen atoms of the benzene ring and the heterocyclic system were found in the difference map, including the hydrogen atom at the cyclic nitrogen atom $N_{(3)}$. A total of 12-15 washed-out peaks were found near methyl group carbons $C_{(10)}$, $C_{(11)}$, and $C_{(18)}$, which indicates rotational disorderedness of these groups. There were no electron density peaks in the region 0.5-1.3 Å from $N_{(7)}$.

Further refinement was carried out by the method of least squares taking account of the contribution of the localized hydrogen atoms with fixed positional and isotropic temperature factors (B^{iso} = 7 Å^2). The final R = 0.086 (R_w = 0.095) for 959 reflections with $F^2 \geq 3\sigma$.

Table 2 gives the coordinates for all the atoms and isotropic equivalent temperature factors of the nonhydrogen atoms.

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