DIPOLE MOMENTS, MOLAR KERR CONSTANTS, AND THREE-DIMENSIONAL STRUCTURE OF SOME 4,5-DIHYDRO-1,3,5-DITHIAZINES

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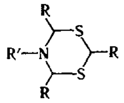
The three-dimensional structure of some 4,5-dihydro-1,3,5-dithiazine derivatives was investigated by means of dipole moments and the Kerr effect. The presence of equilibrium boat and chair forms in the conformational mixture is proposed for the 2,4,6-trimethyl and 2,4,-5,6-tetramethyl derivatives. Energy data that confirm the possibility of anomalous conformations are presented.

The predominant conformation of cyclohexane systems is the chair form with equatorial orientation of the substituents. Replacement of a methylene group of the ring by a heteroatom does not have a substantial effect on the conformational properties of the system. However, heterocycles have a number of peculiarities [1] that are often responsible for conformational anomalies. The nature of the ring may be the reason why the molecules exist in flexible forms. As noted in [2], the introduction into the ring of two heteroatoms (the sulfur atom, for example) that do not have sp^3 bonds promotes the existence of flexible forms in the conformational equilibrium. In this connection, it seemed of interest to thoroughly analyze the 4,5-dihydro-1,3,5-dithiazine system:

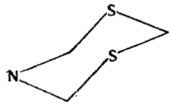


I-III

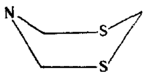
I $R=CH_3, R'=H$; II $R=R'=CH_3$; III $R=H, R'=CH_3$

We investigated the structure of these compounds using the method of dipole moments (DM), the Kerr effect, and PMR spectroscopy.*

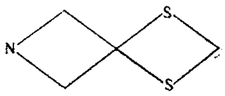
The following ring conformations can be considered for 4,5-dihydro-1,3,5-dithiazines: chair (A), symmetrical boat (B), and a symmetrical twist form (C) with different orientations of the substituents attached to the carbon and nitrogen atoms:



A



B



C

An analysis of the PMR spectra of I and II makes it possible to consider the methyl groups in the 4 and 6 positions to be equivalent. In view of this, we did not examine the unsymmetrical conformations of the boat and twist forms, and we also excluded the case of trans orientation of the methyl groups in the 4

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* The analysis of the PMR spectra will be given in a separate communication.

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TABLE 1. Calculated and Experimental DM and Kerr Constants of 2,4,6-Trimethyl- and 2,4,5,6-Tetramethyl-4,5-dihydro-1,3,5-dithiazines (I, II)

Compound	Calculated parameters	cis, cis				cis, trans				trans-4,6-$(CH_3)_2$, twist		Exptl. values
		chair, eee		boat, eea		chair, eea		boat, eee				
		N—R (*e*)	N—R (*a*)	N—R (*e*)	N—R (*a*)	N—R (*e*)	N—R (*a*)	N—R (*e*)	N—R (*a*)	trans	cis	
I	DM	2,92	0,90	2,69	1,52	2,92	0,90	2,69	1,52	2,01	2,01	1,4
	$_mK \cdot 10^{12}$	−24	−8	−6	+8	−22	−1	45	−31	−1	−30	9
II	DM	2,59	1,43	2,15	1,29	2,59	1,43	2,15	1,29	1,52	1,52	1,60
	$_mK \cdot 10^{12}$	−35	12	7	21	−8	6	40	2	15	1	22

TABLE 2. Calculated and Experimental DM and Kerr Constants of N-Methyl-4,5-dihydro-1,3,5-dithiazine

Calculated parameters	Chair		Boat		Twist	Exptl. data
	$N—CH_3$ (*e*)	$N—CH_3$ (*a*)	$N—CH_3$ (*e*)	$N—CH_3$ (*a*)		
DM	2,59	1,43	2,15	1,29	1,52	1,50
$_mK \cdot 10^{12}$	−13	−4,2	11	−1,5	−4,4	−3,7

TABLE 3. Dipole Moments and Molar Kerr Constants of the Investigated Compounds

Compound	$\alpha\varepsilon_0$	β	γ	δ	μ, *D*	$_mK \cdot 10^{12}$
I	2,717	−0,460	0,113	6,691	1,45	9,2
II	3,517	−0,461	0,119	16,764	1,60	21,8
III	3,825	−0,465	−0,124	−4,167	1,50	−3,7

and 6 positions of conformations A and B. Equivalency of these groups is possible for a trans orientation in the twist form and for a cis orientation in the chair and boat conformations. The case of a mixture of conformers (A, B, and C) is therefore excluded. The case with a diaxial orientation of the methyl groups in the 4 and 6 positions, which we did not consider, is also disadvantageous for the chair conformation.

The DM were calculated via an additive scheme using the following bond moments: $m_{C_{sp^2}-H} = -0.28$ D, $m_{C-N} = 0.53$ D, $m_{N-H} = -1.35$ [3], and $m_{C-S} = 0.95$ (from the experimental moment for ethyl sulfide). The CNC and NCS valence angles were assumed to be tetrahedral with angle CSC 98°, angle SCS 112°, bond length C−N 1.47 Å, and bond length C−S 1.81 Å [4].

Data on the components of the polarizability tensors of the bonds from [5] were used to calculate the Kerr constants. The longitudinal (b_L) and transverse (b_T) bond polarizabilities (in cubed angstroms) were calculated to be as follows: C−C 0.99, 0.27; C−S 1.88, 1.69; C−N 0.57, 0.69; N−H 0.50, 0.83. The C−H bond was assumed to be isotropically polarizable. The diagonal (b_{ii}) and nondiagonal (b_{ij}) components of the molecular ellipsoids were found by tensor summation of these values. The molar Kerr constants were calculated from the equations [5]

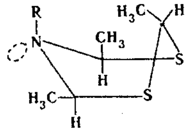
$$45kT\theta_1 = \frac{P_D}{P_E}\left[\sum (b_{ii}-b_{jj})^2 + 6\sum b_{ij}^2\right],$$

$$45k^2T^2\theta_2 = \sum \mu_i^2(2b_{ii}-b_{jj}-b_{kk}) + 6\sum \mu_i\mu_j b_{ij},$$

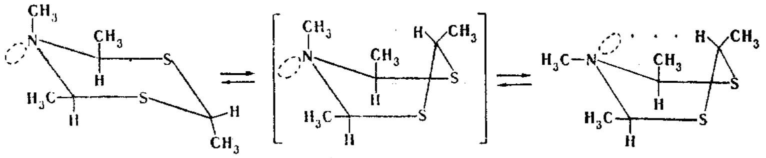
$$_mK = \frac{2\pi N}{9}(\theta_1+\theta_2)$$

The calculated and experimental DM and Kerr constants of the trimethyl and tetramethyl derivatives (I and II) are presented in Table 1. The cases of cis orientation of the CH_3 group relative to the methyl groups in the 4 and 6 positions (cis, cis) in the chair (eee) and boat (eea) conformations and of trans orientation of the CH_3 group relative to the same groups (cis, trans) in the chair (eea) and boat (eee) conformations were examined. An equatorial [N−R (e)] or axial [N−R (a)] orientation of the substituent attached to the nitrogen atom is possible for each conformer (A and B). The values for the cis and trans orientations of the 2-CH_3 group relative to the 4-CH_3 group were calculated for a trans orientation of the 4-CH_3 and 6-CH_3 groups in the twist conformation.

The experimental DM and ${}_mK$ values for I and II make it possible to exclude the twist conformation with a trans orientation of the methyl groups in the 4 and 6 positions. The values calculated for the B (eea) form with N−R (a) are closest to the experimental values.



B (eea)



A (eea) B (eee)

However, this conformation is unlikely because of bowsprit interactions. Thus the conformations possible for a cis, cis orientation are unacceptable. A positive ${}_mK$ value is observed for the B (eee), N−R (e) form for the cis, trans configuration, but the absolute values of ${}_mK$ and DM calculated for this structure considerably exceed the experimental values of these parameters. This form should consequently be found in a mixture with the other form with low DM and ${}_mK$ values. Only A (eea), N−R (a) can be a form of this sort. An estimate of the fraction of the individual conformers in an equilibrium mixture gives the following values: 0.2 B for I (from ${}_mK$ and DM), and 0.4 B (from ${}_mK$) and 0.3 B (from DM) for II. However, we suppose that it will be possible to draw a definite conclusion regarding the presence of the boat form in the conformational equilibrium only after an investigation of the PMR spectra at various temperatures.

In the case of III (Table 2), good agreement is observed for both the chair and twist conformations. An analysis of the PMR spectra recorded at low temperatures makes it possible to make the correct choice.

The following question arises: what are the factors that destabilize the chair form? It is absolutely clear that the reason for the increased flexibility of these systems is the presence of three heteroatoms. An axial orientation of the 2-CH_3 group is not entirely favorable. For this reason, using the Hill equation [6], we determined the sum of the van der Waals energies of the paired interactions of the 2-CH_3 group with the 4-C and 6-C atoms and with the axial protons attached to these atoms – $E_V = 1.84$ kcal/mole. In addition, as a result of the shorter C−N distance as compared with the C−S distance in this ring, one side of the molecule is more constricted. This deformation leads to an increase in the syn-axial interaction of the protons in the 4 and 6 positions. An estimate of this interaction by the Hill method gives 0.47 kcal/mole. The transition of conformations A and B is associated with surmounting the rotational barrier, the magnitude of which in the sulfides is 2.13 kcal/mole [7]. The overall barrier for two bonds is 4.26 kcal/mole. In contrast to cyclohexane systems, the possibility of interaction between the hybridized unshared pair of electrons of the nitrogen atom at the bow of the boat and the hydrogen atom in the 2 position (the attraction effect) cannot be excluded in the B conformation of dihydrothiazines. A comparison of the energy data presented demonstrates that the difference in energies between the chair form (A) and the boat form (B) for the trans, cis configuration of I and II is ~2 kcal/mole, which is considerably lower than for cyclohexane systems. The presence of nonchairlike forms in the conformational mixture should therefore be more likely for heterocycles of the dihydrodithiazine type.

EXPERIMENTAL

Compounds I-III were synthesized by the methods in [8-10] and had melting points that were in agreement with the literature values. The dipole moments and molar Kerr constants were measured as in [11] in carbon tetrachloride at 25°. The coefficients of the computational equations and the results are presented in Table 3.

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