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DIPOLE MOMENTS AND UV SPECTRA OF SOME TWO-RING CYCLIC SULFIDES

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UDC 547.818:543.52'422.6

The dipole moments and UV spectra of 17 compounds of the 5,6-tetramethylene- and 5,6-trimethylenethiapyran series and their saturated analogs were measured. The dipole moments of the investigated compounds range from 1.2 to 2.0 D. The effect of the size of the saturated side ring and the position of the unsaturated bonds in the sulfur-containing heteroring on the dipole moments is demonstrated. The UV spectra of the compounds with, respectively, five- and six-membered saturated side rings are virtually identical. The position of the bands is determined primarily by the structure of the heteroring.

The structures of cyclic sulfides have been previously investigated [1-3]. In the present research we measured the dipole moments and UV spectra of a number of 5,6-tetramethylene- and 5,6-trimethylenthiapyrans and their saturated analogs (see Table 1). It seemed of interest to establish the effect of the size of the saturated side ring and the position of the unsaturated bonds in the sulfur-containing heteroring on the polar and spectral properties of the sulfides.

The dipole moments of all of the investigated compounds range from 1.2 to 2.0 D. However, these relatively small differences make it possible to establish some general principles of the effect of substituents on the polar properties of the two-ring cyclic sulfides.

First of all, one's attention is drawn to the fact that the dipole moments of the compounds with six-membered side rings (I, III, V, XI, and XIII) are ~0.2-0.3 D higher than the dipole moments of the corresponding compounds with five-membered rings (II, IV, VI, XII, and XIV). The reason for the observed differences may be the different geometries of the sulfur-containing rings in 5,6-trimethylene- and, respectively, 5,6-tetramethylene derivatives, as well as the different contributions of the side rings to the overall dipole moment of the molecule. Judging from the fact that the UV spectra of compounds with, respectively, five- and six-membered side rings are virtually identical (see Table 1), it may be concluded that the character of the electronic interaction and, evidently, the geometry of the sulfur-con-

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TABLE 1. Polar and Spectral Properties of Sulfides

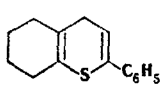
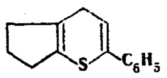
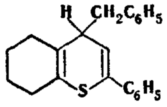
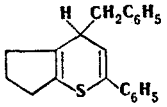
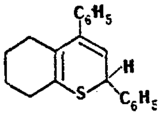
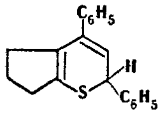
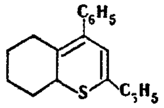
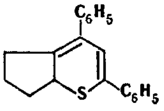
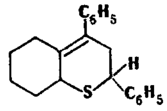
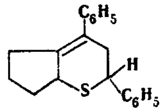
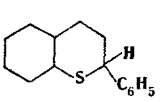
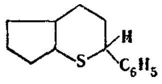
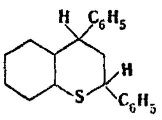
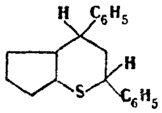
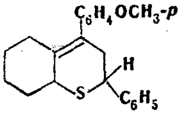
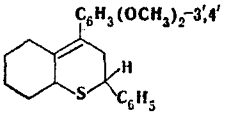
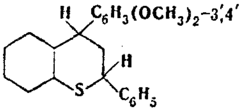
Compound	Formula	mp	P_∞	R_D	μ_D	λ_{max} (lg ε)
1	2	3	4	5	6	7
I		49—51	140,61	70,61*	1,83	198 (4,6), 240 (4,2), 295sh (3,2)
II		54—55	115,16	65,89*	1,55	198 (4,5), 235 (4,1), 297 (3,0)
III		59,5—60,5	151,66	99,03	1,60	190 (4,9), 203 sh (4,5), 240 (4,2), 292 (3,3)
IV		51—52	129,76	94,41	1,31	189 (5,0), 203 sh (4,7), 240 (4,3), 297 (3,3)
V		89—90,5	140,18	99,75*	1,40	225 (4,3), 237 (4,2), 298 (3,1)
VI		86—87	124,19	95,45*	1,18	220 (4,2), 234 (4,3), 296 (3,2)
VII		79—81	139,17	97,83*	1,42	252 (4,2), 360 (3,9)
VIII		104—106	133,41	93,78*	1,39	258 (4,2), 353 (3,7)
IX		106—108	146,34	94,87	1,58	209 (4,3), 212 sh (4,3), 238 (3,9), 258 sh (3,7), 263 sh (3,6)†
X		88—89	145,55	90,27	1,63	207 (4,3), 213 sh (4,3), 235 sh (3,9), 258 (3,6), 263 sh (3,6), 268 sh (3,6)†
XI		57—59	146,68	71,35	1,91	191 (4,7), 206 (4,1), 246 sh (2,4), 253 (2,4), 259 (2,4), 265 (2,2)
XII		37—38	121,48	66,76	1,63	207 (4,1), 246 sh (2,4), 253 (2,3), 259 (2,3), 265 (2,2)†

TABLE 1. (Continued).

1	2	3	4	5	6	7
XIII		125—126,5	163,79	95,34	1,82	191 (5,2), 206 (4,4), 247sh (2,6), 253 (2,7), 259 (2,7), 265 (2,5)
XIV		115—116	138,04	90,72	1,51	191 (5,1), 206 (4,4), 246 (2,6), 253 (2,6), 259 (2,7), 264 (2,5)
XV		127—128	183,42	101,13*	1,98	210 (4,3), 215—230 sh (4,3), 277 sh (3,5), 285 (3,4)
XVI		139—140,5	189,48	107,40	1,99	203 (4,6), 230 sh (4,1), 264 (3,5), 285 (3,6), 289 (3,6), 295 sh (3,5), 301 sh (3,4)
XVII		141—142	187,57	107,86	1,96	202 (4,4), 230 (3,6), 260 infl 277 (3,1), 281 (3,1), 287 (3,0)

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*This is the experimental value.

†Recorded at 200-400 nm.

taining ring in them are also identical. The observed differences are most likely due primarily to the different dipole moments of the five- and six-membered side rings.

It is interesting to note that the introduction of a benzyl substituent in the 4 position of the thiapyran ring leads to an identical decrease (0.23 and 0.24 D) in the dipole moments of compounds with both six-membered (I and III) and five-membered (II and IV) side rings. This fact also to some extent confirms the identical geometries of the sulfur-containing rings in these compounds. It should be added that the transition from γ-thiapyran derivatives to α-thiapyran derivatives is accompanied by approximately identical decreases in the dipole moments of compounds with both six-membered (I and V) and five-membered (II and VI) rings.

A comparison of the dipole moments of the compounds of the saturated series (XI-XIV) with the corresponding compounds with unsaturated heterorings makes it possible to establish the effect of the position of the unsaturated bonds in the ring on the polar properties of the molecules. Thus the dipole moments of the γ-thiapyran derivatives (I and II) are only 0.3-0.4 D lower than the values for the corresponding saturated compounds (XIII and XIV). These differences may be associated both with a change in the conjugation conditions and with a change in the geometry of the heteroring on passing from α-thiapyran derivatives to γ-thiapyran derivatives.

EXPERIMENTAL

All of the substances were synthesized and purified by the methods described in [4-7]. The dipole moments in benzene at 25°C were measured by the Debye method. The experimental data were extrapolated with respect to the Hedestrand formula. The UV spectra of hexane solutions of the compounds were recorded at 190-400 nm with a Perkin—Elmer 450 spectrophotometer. The results are presented in Table 1, in which P_∞ is the molar polarization, R_D is the molar refraction, and μ_D is the dipole moment (in debyes) found from the formula $\mu = 0.22(P_\infty - R_D)^{1/2}$. The R_D values for a number of the compounds were measured (as noted in Table 1), whereas the others were calculated by an additive scheme.

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MASS SPECTRA OF 1- AND 2^a-SUBSTITUTED 1,3,5,7-TETRAMETHYL-2,4,6,8-TETRATHIAADAMANTANES

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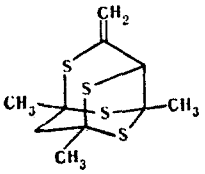
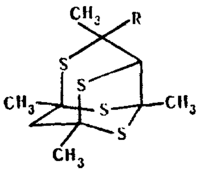
A comparative analysis was made of the mass spectra of monosubstituted 1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantanes (TMTTA). It is shown that the pathways of monomolecular fragmentation depend on the character of the substituent and the isomeric form of the TMTTA. The principal lines in the mass spectra of the investigated compounds indicate the occurrence of competitive processes of fragmentation of the molecular ions (M^+) with detachment of the substituent from the M^+ ion or with cleavage of the cellular structure. The first process makes it possible to form a judgement regarding the mechanism of the fragmentation of the molecular ion and the site of primary localization of the charge on the fragment ions as a function of the donor–acceptor properties of the substituents, and the second process enables one to form a judgement regarding the character of the fragmentation of the cellular structures of the various isomeric forms.

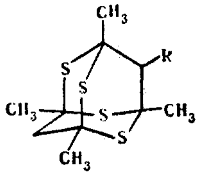
The mass spectra of hydroxythiaadamantanes, 1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane (TMTTA) [1-3], and mono-, di-, tri-, and tetrasubstituted adamantanes [4, 5] have been described. In the present research we studied the mass spectra of 1- and 2^a-substituted TMTTA derivatives that correspond to two isomeric forms — the proto (A) and thia (B) forms.



I (A)



A



B

II $R=NHC_6H_5$; III $R=NH(CH_2)_2OH$; IV $R=O(CH_2)_2OH$; V $R=SCOCH_3$; VI $R=SC_4H_9$; VII $R=SCH_2OH$; VIII $R=OH$; IX $R=OCOC_6H_5$; X $R=OCOC(CH_3)=CH_2$; XI $R=OCOCH_3$; XII $R=SCOCH_3$; XIII $R=Br$; XIV $R=Cl$

The hypothetical compositions of the principal fragments and the relative intensities (in percent of the total ion current) of the most characteristic lines in the mass spectra of the investigated compounds with respect to the single-isotope compounds are presented in Table 1.

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