INTRAMOLECULAR INTERACTION IN ARYLDIHYDROTHIOPHENE 1,1-DIOXIDES

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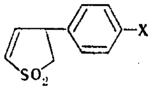
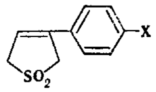
The peculiarities of the intramolecular interaction in unsaturated five-membered cyclic sulfones as a function of their structures were studied on the basis of an analysis of the electronic absorption spectra of single crystals of isomeric β-aryldihydrothiophene 1,1-dioxides at 4.2°K, the IR spectra of the molecules at 298°K, and the results of x-ray diffraction analysis of 3-phenyl-4,5-dihydrothiophene 1,1-dioxide. In addition to the inductive effect, conjugation of the SO_2 group with the π-electron system of 3-phenyl-4,5-dihydrothiophene 1,1-dioxide, which is manifested most appreciably in the excited electronic state, was observed.

We have previously reported [1] that 4-aryl-4,5-dihydrothiophene 1,1-dioxides (I) are converted to the isomeric 3-aryl-2,5-dihydrothiophene 1,1-dioxides (II) and 3-aryl-4,5-dihydrothiophene 1,1-dioxides (III) in aqueous and alcohol solutions of bases.


I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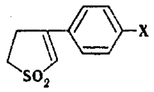
III

I–III a $X=H$; b $X=OCH_3$; c $X=NH_2$

Compounds IIb,c, which contain electron-donor substituents in the para position of the phenyl ring, are practically irreversibly isomerized to IIIb,c. The reaction is reversible for unsubstituted phenyldihydrothiophene 1,1-dioxides IIa and IIIa, but the equilibrium is shifted to favor isomer IIIa, which attests to its greater thermodynamic stability. It is known [2] that 2,5-dihydrothiophene 1,1-dioxide is more stable than 4,5-dihydrothiophene 1,1-dioxide. The observed increase in the stability of 3-aryl-4,5-dihydrothiophene 1,1-dioxides (IIIa-c) is consequently due to interaction of the C_6H_4X substituent with the sulfonyl group. In the present research we made an attempt to study the nature of this interaction.

It has been shown in the case of a large number of alkyl- and halo-substituted benzenes [3] that the low-temperature electronic absorption spectra of molecular crystals can be used for the study of the nature of an intramolecular interaction. Aryldihydrothiophene 1,1-dioxides have not been previously investigated in this manner.

It follows from an analysis of the electronic spectra obtained in this research (Table 1) that the spectra of the isomeric phenyldihydrothiophene 1,1-dioxides differ appreciably from one another with respect to the position of the purely electronic transition in reciprocal centimeters ($\Delta\nu_{00}$) and their relative intensities [$I_{00}/(I_{00} + \nu_{6B})$, where I_{00} is the intensity of the purely electronic band, and $I_{00} + \nu_{6B}$ is the intensity of the band due to an electronic vibrational transition with the participation of an incompletely symmetrical vibration].

According to the spectra, two crystalline modifications are observed for 4-phenyl-4,5-dihydrothiophene 1,1-dioxide (Ia). Their spectra are shifted relative to one another by 250 cm^{-1} and are located in approximately the same region as the spectrum of the hydrocarbon analog, isopropylbenzene [3] [ν_{00} = 37,335, $I_{00}/(I_{00} + \nu_{6B})$ = 3 : 1]. The bands of the purely electronic transition in the spectra of both crystalline modifications (37,450 cm^{-1}, 37,200 cm^{-1}) are weakened (Table 1) as compared with the bands of the electronic vibrational

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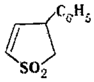
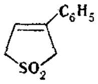
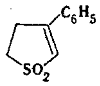
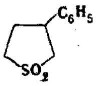
TABLE 1. Spectral Characteristics of Phenyldihydrothiophene

Compound	Molecular structure	Electronic spectra			IR spectra, $\nu_{S=O}$	
		ν_{00}	$\Delta\nu_{00}$	$I_{00}/I_{00}+\nu_{6B}$	*s*	*as*
I a		37 450† 37 200†	390 640	1 : 5 1 : 3		
II a		34 174	3666	6 : 1	1115 1130	1310
III a		33 100	4740	1 : 5	1125	1285
IV		37 270		1 : 3	1140	1300

†The data pertain to different crystalline modifications.

transition ($I_{00} + \nu_{6B}$).† The spectrum of isomer Ia is similar with respect to its structure and the position and intensity of its bands to the spectrum of 3-phenylthiolane 1,1-dioxide (IV, Table 1).

The spectrum of crystals of 3-phenyl-2,5-dihydrothiophene 1,1-dioxide (IIa) is shifted considerably to the long-wave region relative to the spectrum of crystals of isomer Ia and lies in the region of absorption of the hydrocarbon analog, styrene [3] [ν_{00} = 34,218 cm^{-1}, $I_{00}/(I_{00} + \nu_{6B})$ = 6 : 1]. As in the case of styrene, the relative intensity of the purely electronic band of 3-phenyl-2,5-dihydrothiophene 1,1-dioxide is 6 : 1.

The absorption of crystals of the IIIa isomer is shifted by 1000 cm^{-1} to the long-wave region relative to the absorption of the IIa isomer. The intensity of the purely electronic band is weakened appreciably as compared with the electronic vibrational band due to excitation of the incompletely symmetrical vibration. A pronounced shift of 4860 cm^{-1} (ν_{00} of Ic = 32,100 cm^{-1}, ν_{00} of IIIc = 27,240 cm^{-1}) of the beginning of absorption to the long-wave region is observed when donor substituents (NH_2, for example) are introduced in the para position of the phenyl ring in the series of I and III isomers.

It follows from the above general analysis of the spectra that their absorption in the near-UV region is primarily due to excitation of the 6 π-electron system of the benzene ring. In the case of I and IV the small shift of the spectra relative to the spectrum of benzene ($\Delta\nu_{00}$) and the low relative intensity of the purely electronic band (Table 1), in analogy with the spectral data for isopropylbenzene, provide evidence that a five-membered ring with a double bond remote from the phenyl ring distorts the π-electron cloud of the benzene ring extremely insignificantly. At the same time, an appreciable effect of the five-membered ring on the properties of the π-electron cloud of the phenyl ring is observed from the spectra (Table 1) for the isomeric phenyldihydrothiophene 1,1-dioxides IIa and IIIa. For example, the frequency of the purely electronic band in the spectrum of 3-phenyl-2,5-dihydrothiophene 1,1-dioxide differs by only 44 cm^{-1} from the analogous band in the spectrum of styrene (ν_{00} = 34,218 cm^{-1}) and is similar to it in intensity. Hence it can be concluded that the carbon–carbon double bond in the five-membered ring is conjugated with the 6 π-electron system of the benzene ring, as in the case of the styrene molecule [3]. In the case of 3-phenyl-4,5-dihydrothiophene 1,1-dioxide, in which the double bond of the five-membered ring is found between the benzene ring and the SO_2 group, the shift of the purely electronic band is increased by another 1000 cm^{-1} as compared with the spectrum of 3-phenyl-2,5-dihydrothiophene 1,1-dioxide; in this case the intensity of the purely electronic band decreases appreciably as compared with isomer IIa. The indicated spectral data constitute evidence for the direct effect of the SO_2 group on the π-electron system of the molecule.

According to the Petrashky theory developed for the spectra of substituted benzenes, the intensity of the purely electronic absorption bands and the position of their spectra depend on the inductive effect and the conjugation of the substituents with the benzene ring. However, because of the fact that the dependences of the enumerated spectral characteristics on the difference in the various electronic levels differ, it can be roughly

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†It has been previously noted [3] that the intensity of the $I_{00} + \nu_{6B}$ transition remains practically unchanged in a series of monosubstituted benzene derivatives.

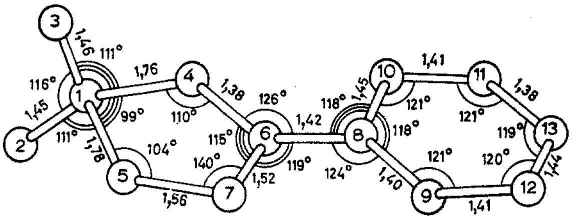

Fig. 1. Geometry of the 3-phenyl-2-sulfolene molecule.

assumed that the intensity of the purely electronic transition is primarily determined by the inductive effect, whereas both effects contribute to the relative shift of the spectra with a certain predominance of the conjugation effect. The latter circumstance is connected with the fact that conjugation makes the principal contribution to the shift of the spectral of the compounds due to the most substantial change of the energy of the excited electron level. With allowance for these theoretical considerations, the decrease in intensity in the case of 3-phenyl-4,5-dihydrothiophene 1,1-dioxide can be explained by manifestation of the negative inductive effect of the sulfonyl group and the donor–acceptor interaction (which acts in the same direction) of the sulfur atom with the π electrons of the carbon- carbon double bond of the five-membered ring the IIa isomer molecule. Owing to this, the electron cloud is withdrawn from the carbon–carbon double bond in the direction of the sulfur atom, and the polarization of the π-electron cloud decreases; this is also responsible for the decrease in intensity of the purely electronic band in the spectrum of 3-phenyl-4,5-dihydrothiophene 1,1-dioxide as compared with the spectrum of 3-phenyl-2,5- dihydrothiophene 1,1-dioxide.

The additional shift of the spectrum of isomer IIIa to the long-wave region relative to the spectrum of benzene ($\Delta\nu_{00}$), which is greater than that observed for the spectra of isomer IIa, makes it possible to assume that in the excited state of the SO_2 group, in addition to manifesting an inductive effect, also participates in appreciable conjugation with the π-electron cloud of the molecule owing to the vacant 3d orbitals of the sulfur atom or the antibonding σ^* orbital. The data from a study of the IR spectra of the compounds provide evidence in favor of this interaction in the ground electronic state. From a comparison of the IR spectra of the isomeric phenyldihydrothiophene 1,1-dioxides (I–III) and 3-phenylthiolane 1,1-dioxides (IV) (Table 1) it is apparent that the frequencies of the vibrations of the S–O bond of the IIIa isomer are 10–20 cm^{-1} lower than those of the Ia and IIa isomers and saturated sulfone IV. This decrease in the frequencies can be explained, in analogy with earlier studies [5, 6], by an increase in the electronegativity of the sulfur atom owing to its interaction with the carbon–carbon double band and the decrease in the polarity of the S–O bond. With allowance for the most recent studies [7], conjugation, which is small in comparison with the inductive effect in the ground state and is manifested appreciably in the excited state, also evidently makes a small contribution to this shift.

In order to add more depth to our ideas regarding the interaction of the SO_2 group with the π-electron system in the 3-phenyl-4,5-dihydrothiophene 1,1-dioxide molecule, we subjected it to x-ray diffraction analysis.

According to the results of x-ray diffraction analysis, the crystals of the IIIa isomer belong to the $P2_1/C$ space group and have four molecules in the unit cell. The six-membered and five-membered rings of the molecule are coplanar. Sulfur is found at the apex of a somewhat distorted tetrahedron, which is formed, on the one hand, by the bonds between sulfur and the two carbon atoms of the five-membered ring (the angle between them is 99°) lying in a single plane and, on the other, by the bonds between sulfur and the two oxygen atoms, the angle between which is 116°. The S–C bond lengths in the five-membered ring are 1.76 and 1.78 Å. The S–O bond length is 1.46 Å. It is considerably less than the length of the covalent S–O single bond (1.70 Å) calculated from the covalent radii [8]. The length of the carbon–carbon double bond in the five-membered ring is 1.38 Å. The C–C bond between the five-membered and six-membered rings (1.42 Å) is considerably shorter than the C–C single bond. This molecular geometry attests to conjugation of the five-membered and phenyl rings. The lengths of the S–O bonds in the investigated compounds and in analogous structures [9] coincide and agree with the data in [10] on the nature of the S–O bond in sulfones. The difference in the S–C bond lengths in the five-membered ring is within the limits of the accuracy of the measurements (0.02 Å). Despite this, the primary formation of sulfones IIIa and IIIc in the isomerization of Ia,c and IIa,c can be explained only by interaction of the C_6H_5 and $C_6H_4NH_2$ substituents with the SO_2 group through the carbon–carbon double bond. A comparison of the spectra of crystals of IIIa and IIIc in the excited electronic state experimentally confirms the donor–acceptor character of this interaction.

EXPERIMENTAL

The isomeric aryldihydrothiophene 1,1-dioxides were synthesized by the method in [11]. The crystals for the electronic spectra were grown from melts in a thin-layer quartz cuvette.

The electronic spectra of the crystals were photographed with an ISP-28 spectrograph in polarized light at 4.2°K by the method described in [3].

The lattice parameters and the space group of the IIIa crystal were determined from the rotational x-ray diffraction patterns and reciprocal lattice patterns and were refined with a DARM-2.0 diffractometer. The set of integral intensities was generated with a DARM-2.0 diffractometer. A total of 1240 independent reflections was measured. No correction for absorption was introduced. The structure was decoded by direct methods [12]. The bond lengths and valence angles are presented for R-0.114.

LITERATURE CITED

1. T. É. Bezmenova, S. M. Lukashov, V. P. Tantsyura, T. S. Lutsii, A. F. Rekasheva, and T. D. Zaika, Khim. Geterotsikl. Soedin., No. 8, 1072 (1975).
2. C. D. Broaddus, J. Am. Chem. Soc., 88, 3863 (1966).
3. V. L. Broude, G. V. Klimusheva, A. L. Liberman, M. I. Onoprienko, A. F. Prikhot'ko, and A. I. Shatenshtein, Absorption Spectra of Molecular Crystals [in Russian], Vol. 1, Naukova Dumka, Kiev (1965), p. 11.
4. J. Petruska, J. Chem. Phys., 34, 1111 (1961).
5. E. N. Prilezhaeva, L. V. Tsymbal, O. N. Domanina, T. N. Shkurina, and M. F. Shostakovskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 3, 724 (1960).
7. E. C. Muller and A. Schweig, Tetrahedron, 29, 3973 (1973).
8. R. I. Gillespie and E. A. Robinson, Can. J. Chem., 41, 2074 (1963).
9. Yu. A. Kolesnik and V. V. Kozlov, Usp. Khim., 37, 1192 (1968).
10. N. Kharasch (editor) [no title given], Vol. 2, Pergamon Press, New York (1966), p. 1.
11. Yu. N. Usenko, S. M. Lukashov, and T. É. Bezmenova, Khim. Geterotsikl. Soedin., No. 11, 1489 (1972).
12. V. N. Andrianov, Z. Sh. Safina, and B. L. Tarnopol'skaya, Rentgen-70. Automated System of Programs for X-Ray Diffraction Calculations [in Russian], Izd. Akad. Nauk SSSR, Chernogolovka (1970), p. 3.

SOME TRANSFORMATIONS OF α,ω-BIS(1,3-THIAZAN-2-THION-4-ON-3-YL)ALKANES

B. S. Zimenkovskii and N. M. Turkevich

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The reaction of α,ω-bis(1,3-thiazan-2-thion-4-on-3-yl)alkanes with hydrazine gives the corresponding α,ω-di(4-thiosemicarbazido)alkanes, which are readily acylated. Subsequent dehydration of the acylation products gives the corresponding 5,5'-dialkyl-α,ω-bis(2,3-dihydro-1,2,4-triazole-3-thion-4-yl)alkanes, which are converted to 5,5'-dialkyl-α,ω-bis(1,2,4-triazol-4-yl)alkanes by known methods. The UV and IR spectral data are presented.

Compounds having bactericidal, chemotherapeutic, and cytostatic activity have recently been observed among 1,2,4-triazole derivatives [1-3]. Some triazoles have found technical application [4, 5]. In view of the practical significance of this class of compounds, we set out to synthesize some bistriazolinethiones.

One of the well-known methods for the preparation of 3-mercapto-1,2,4-triazoles consists in acylation of thiosemicarbazide [6] and subsequent dehydration of the product. We carried out the hydrazinolysis in n-butyl alcohol or in an aqueous alkali solution of α,ω-bis(1,3-thiazan-2-thion-4-on-3-yl)alkanes (I) synthesized via a simplified method [7, 8] to give the corresponding α,ω-di(4-thiosemicarbazido)alkanes (II) (Table 1), which are the starting compounds for the synthesis of bistriazole-3-thiones. Similar compounds have been described in the literature, but they were obtained by a fundamentally different method and in lower yields [9].

Compounds II are relatively easily acylated by glacial acetic acid and benzoyl chloride in dry pyridine. In the case of the first reagent α,ω-bis(1-acyl-4-thiosemicarbazido)alkanes (IIIa) are formed smoothly. The use of acetic anhydride as the acylating agent leads to oils that are difficult to purify.

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