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SPECTRAL INVESTIGATION OF INTRAMOLECULAR INTERACTION IN SULFUR-ORGANIC COMPOUNDS

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Abstract—Earlier[1] it was reported that 4-aryl-4,5-dihydrothiophene-1,1-dioxides (I) are converted in aqueous and alcohol solution of bases to isomeric 3-aryl-2,5-dihydrothiophene dioxides (II) and 3-aryl-4,5-dihydrothiophene-1,1-dioxides (III) (Fig. 1).

In the presence of electron-donor substituents in the *p*-position of the phenyl ring, IIb, c compounds are practically irreversibly isomerised to III b, c. For unsubstituted phenyldihydrothiophene-1,1-dioxides IIa and IIIa the reaction proceeds riversibly but equilibrium is shifted towards isomer IIIa indicating its high thermodynamic stability. It is known[2] that 2,5-dihydrothiophene-1,1-dioxide is more stable than 4,5-dihydrothiophene-1,1-dioxide. Consequently, the observed stability increase of 3-aryl-4,5-dihydrothiophene-1,1-dioxides (IIIa-c) is due to interaction of the substituent C_6H_4X with the sulfonyl group. This paper investigates the nature of this interaction.

For a large number of alkyl- and halogeno substituted benzenes it was shown[3] that the nature of intramolecular interaction can be studied from measurement of the low-temperature electron absorption spectra of the molecular crystals.

Analysis of the observed electron spectra (Table 1) it follows that the spectra of isomeric phenyldihidrothiophene-1,1-dioxides differ markedly in the position of pure electron transition bands ($\Delta\nu_{00}$), their relative intensity ($I_{00}/I_{00} + \nu_{\sigma b}$, where I_{00} is the intensity of a pure electron band, and $I_{00} + \nu_{\sigma b}$ is the intensity of the band due to the vibronic transition involving nontotally symmetric vibrations).

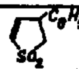
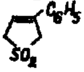
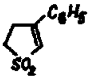
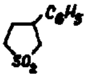
4-Phenyl-4,5-dihydrothiophene-1,1 dioxide (Ia) forms two crystal modifications with an interval between the bands of 250 cm^{-1}. These spectra are in the same region as the spectrum of the hydrocarbon analog iso-propylbenzene[3] ($\nu_{00} = 37335$ cm^{-1}, $I_{00}/I_{00+\nu_{\sigma b}} = 3:1$). Bands of the pure electron transition in the spectra of both crystal modifications (37450 cm^{-1}, 37200 cm^{-1}) are weaker (Table 1) than those of the vibronic transition ($00 + \nu_{\sigma b}$). It was reported earlier[3] that the intensity of the transition $I_{00} + \nu_{\sigma b}$ in the series of monosubstituted benzene does not change noticeably. The spectrum of isomer Ia has a structure similar to that of 3-phenylthiolan-1,1-dioxide (IV, Table 1).

The spectrum of 3-phenyl-2,5-dihydrothiophene-1,1-dioxide (IIa) is red-shifted considerably with respect to the isomer Ia and is in the absorption region of the hydrocarbon analog-styrene[3] ($\nu_{00} = 34218$ cm^{-1}, $I_{00}/I_{00+\nu_{\sigma b}} = 6:1$). The relative intensity of the pure electron band of IIa is 6:1, as in styrene.

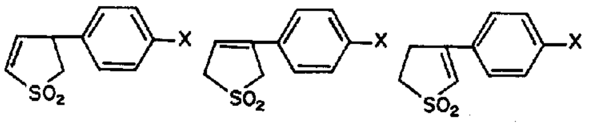
Absorption of the isomer IIIa is red-shifted by 1000 cm^{-1} with respect to the isomer IIa. The intensity of the pure electron band is markedly weaker than of the vibronic band due to excitation of non-totally symmetric vibrations. A series of isomers I, III with donor substituents, e.g. NH_2, in the *p*-position of the phenyl ring shows a sharp shift of the origin towards the long waves by 4860 cm^{-1} ($\nu_{00}I_c = 32100$ cm^{-1}, $\nu_{00}III_c = 27240$ cm^{-1}).

From the above general analysis of the spectra it follows that their absorption in the near UV is mainly due to excitation of the π-electron system of the benzene ring. For compounds I and IV, a small spectral shift with respect to the benzene spectrum ($\Delta\nu_{00}$) and low relative intensity of the pure electron band (Table 1) indicate that the 5-membered ring with double bond separated from phenyl distorts the symmetry of the

Table 1. Spectral characteristics of phenyldihydrothiophene-1, 1-dioxides

Compound	Molecule structure	Electron Spectra		
		ν_{00}	$\Delta\nu_{00}$	$I_{00} / I_{00+\nu_{\sigma b}}$
Ia		37450+) 37200+)	390 640	1:5 1:3
IIa		34174	3666	6:1
IIIa		33100	4740	1:5
IV		37270	570	1:3

+) Different Crystal Modifications



1 2 3

1–3 (a) X = H; (b) X = OCH_3; (c) X = NH_2

Fig. 1.

benzene cycle π-electron cloud only slightly. For isomeric phenyldihydrothiophene-1,1-dioxides IIa and IIIa the spectra show (Table 1) a noticeable influence of the 5-membered ring on the properties of the phenyl π-electron cloud. For instance, a pure electron band in the spectrum of 3-phenyl-2,5-dihydrothiophene-1,1-dioxide differs in frequency only by 44 cm^{-1} from a similar band in the spectrum of styrene ($\nu_{00} = 34218\ cm^{-1}$) and is the same in intensity. It can be concluded that the double carbon bond in the 5-membered ring is conjugate to 6π-electron system of the benzene ring as in the styrene molecule.[3] For 3-phenyl-4,5-dihydrothiophene-1,1-dioxide in which the double bond of the 5-membered cycle is between the benzene ring and the SO_2 group, the shift of the pure electron band increases by 1000 cm^{-1} as compared with 3-phenyl-2,5-dihydrothiophene-1,1-dioxide. The intensity of the pure electron band increases markedly as compared with the isomer IIa. The tabulated spectral data indicate a direct influence of the SO_2 group on the π-electron system of a molecule.

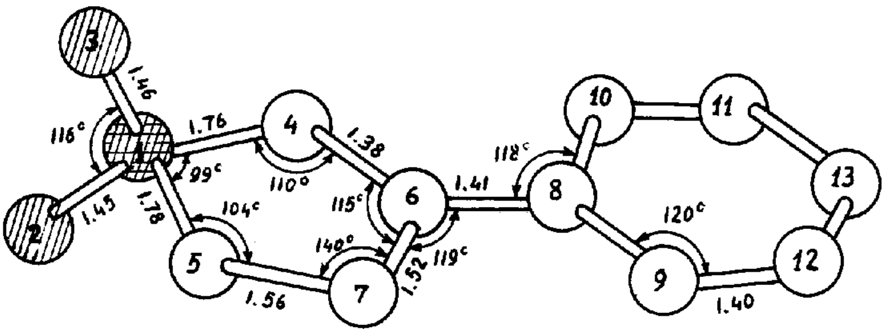
According to the theory of Petrushka[4], developed for the spectra of substituted benzenes, the intensity and position of the pure electron absorption bands depend on the inductive and conjugative effect of substituents to the benzene ring. However, because of unequal dependence of the spectral characteristics on the difference of diverse electron levels one can roughly consider that the intensity of the pure electron transition is largely determined by the inductive effect and the relative shift of the spectra is contributed from both effects with some preference conjugation. The latter circumstance arises because conjugation mainly influences the shift of the spectra due to the change in the energy of the excited electron level. Allowing for these theoretical considerations a decrease of the intensity in 3-phenyl-4,5-dihydrothiophene-1,1-dioxide can be explained in terms of the negative inductive effect of the sulfonyl group and donor-acceptor interaction of a S atom with π-electrons of the 5-membered cycle double C=C bond, acting in the same direction in a molecule of the isomer IIIa. Due to this the electron cloud shifts from the double carbon bond towards the S atom, polarisation of the π-electron cloud decreases, causing a lowering of the pure electron band intensity in the spectrum of 3-phenyl-4,5-dihydrothiophene-1,1-dioxide in comparison with 3-phenyl-2,5-dihydrothiophene 1,1-dioxide.

An additional shift of the band of the isomer IIIa, with respect to benzene ($\Delta\nu_{00}$), which is larger than for the isomer IIa, suggests that the SO_2 group in the excited state in addition to the inductive effect also shows a marked conjugative effect with the π-electron cloud due to the vacant 3d-orbital of the S atom or antibonding σ^*-orbital. This interaction in the ground electron state is evidenced by the IR spectra of the compounds. A comparison of the IR spectra of isomeric phenyldihydrothiophene-1,1-dioxide (I-III) and 3-phenylthiolane-1,1-dioxide (IV) reveals that the S–O bond vibration frequencies of the isomer IIIa are 10 to 20 cm^{-1} less than that of the isomers Ia, IIa and saturated sulphone IV. Such a lowering of the frequencies can be explained,[5,6] by an increase of the S atom electronegativity due to its interaction with the double carbon bond and a decrease of the S–O bond polarity. Accordingly,[7] it is believed that a small contribution to this shift comes also from the conjugative effect which is small compared to the inductive effect in the ground state and is pronounced in the excited state.

To elucidate the interaction of the SO_2 group with the π-electron system in the molecule of 3-phenyl-4,5-dihydrothiophene-1,1-dioxide, we performed X-ray investigations.

It was observed that crystals of the isomer IIIa belong to the space group $P2_1/C$ with four molecules in a unit cell. 6- and 5-membered rings of a molecule are coplanar. Sulfur is in the apex of a somewhat distorted tetrahedron formed by the sulphur bond with two C atoms of the 5-membered cycle (the angle between them is 99°) lying in one plane and by the sulphur bond with two O atoms with an angle 116°. The lengths of the S–C bonds in the 5-membered cycle are 1.76 and 1.78 Å and that of the S–O bond 1.46 Å. This band considerably shorter than that of the simple covalent S–O bond (1.70 Å) calculated from the values of the covalent radii.[8] The double C=C bond in the 5-membered cycle has the length 1.38 Å. The C–C bond between the 5-membered and 6-membered cycles is considerably shorter than the single C–C bond and is (1.42 Å). Such a geometry of the molecule indicates a conjugation of the 5-membered and phenyl rings. The S–O bond lengths in these compounds and similar structures[9] are the same and agree with the data for sulphones.[10] **The difference of the S–C bond lengths in the 5-membered ring is within the measurement accuracy (0.02 Å). In spite of such a small difference, sulphones IIIa and IIIb are formed by isomerisation of Ia, b and IIa due to interaction of substituents C_6H_5, $C_6H_4NH_2$ with the SO_2 group via the double C=C bond. Comparison of the spectra of crystals IIIa and IIIb in the excited electron state supports the donor-acceptor character of this interaction (Fig. 2).**

According to the X-ray data, the isomer Ia crystal belongs to the space group $P2_12_12_1$ with four molecules in a unit cell. The 6- and 5-membered rings are at an angle 35°. Sulfur is in the apex of the distorted tetrahedron with the same angle as in the structure IIIa. The double C=C bond in the 5-membered cycle has the length 1.39 Å. The length of the S–C bonds in the 5-membered cycle is 1.82 Å. The S–O bond length is the same as in the molecule of IIIa. The C–C bond between the 5-membered and 6-membered cycles is also somewhat reduced. Comparison between the structures of molecules Ia and IIIa shows that they differ mainly in a mutual arrangement of the 5- and 6-membered rings. For the isomer IIIa



1-S
2,3-O
4-13-C

Fig. 2.

both are in the same plane and in Ia are separated by an angle of 35°. This peculiarity explains the considerable changes in the spectral characteristics between Ia to IIIa.

EXPERIMENTAL

The electron spectra of the samples[11] were photographed on the spectrograph ISP-28 in the polarised light at 4.2 K using the method described.[3]

The lattice parameters and the space group of the compound IIIa were determined from the Weissenberg photographs and the set of integral intensities was made on DARM-2, 0 without correction for absorption. The number of measured independent reflections was 1240. The bond lengths and valence angles are given for R-0.114.

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