STUDY OF THE ELECTRONIC SPECTRA OF SYDNONES AND SYDNONEIMINES

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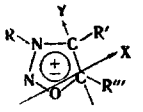
The absorption spectrum of 3-methylsydnone and the luminescence spectra of 3-methyl- and 3-phenylsydnone and 3-methylsydnoneimine hydrochloride were interpreted on the basis of calculations by the Pariser–Parr–Pople method with allowance for a correction for the solvent effect.

The long-wave band in the absorption spectra of sydnones (I) and sydnoneimines (II), the maxima of which, depending on the substituents, range from 286 to 380 nm (log ε 3.60-4.40), have been assumed to be due to a π–π* transition [1-3].



I R″=O; II R″=$NH_2^+Cl^-$

The nature of the shortwave band at 190-210 nm (log ε 3.44-4.21) recently discovered [2] for 3-alkyl derivatives has not been established.

The results of calculations of sydnone by the Pariser–Parr–Pople method, which we accomplished from the program in [4] with the parameters in [5, 6] and the heteroring geometry estimated by the method in [7], are presented in Table 1.

The values

$$\Delta E = E_{H_2O}^{\pi-\pi^*} - E_{decane}^{\pi-\pi^*} = \frac{1}{8066 a_0^3} \cdot [500(\mu_e^2 - \mu_g^2) - 9300(\mu_g \mu_e \cos\varphi - \mu_g^2)], \quad (1)$$

which characterize the changes in the excitation energies on replacement of a polar solvent (H_2O) by a nonpolar solvent (decane), were calculated from the calculated dipole moments of the ground (μ_g) and excited (μ_{ex}) states and the Onsager radius (a_0 = 2.5 Å) [1]. Equation (1) was derived from the ratios linking the change in the energies of the excited states with the corresponding parameters of the solvents and the investigated molecules [1]. According to the calculated values, the spectrum of sydnone, in addition to the absorption band corresponding to the $S^*_1 \leftarrow S_0$ transition, should be characterized by two absorption bands at 190-230 nm corresponding to excitation of this molecule to the S^*_2 and S^*_3 states. In this case, if in the vapor state or in nonpolar solvents the energies of the indicated excited states with respect to the energy of the ground state (S_0) should, judging from the calculated values, be close in magnitude, they should differ appreciably in polar solvents, and the shift of the absorption bands corresponding to transition to the S^*_2 state should be bathochromic on passing from a nonpolar solvent to a polar solvent, and the bands corresponding to the transition to the S^*_3 state, like the bands corresponding to the $S^*_1 \leftarrow S^*_0$ transition, should be hypsochromic. It may be assumed that the observed shortwave band, which is shifted to the long-wave region on replacement of a polar solvent by a nonpolar

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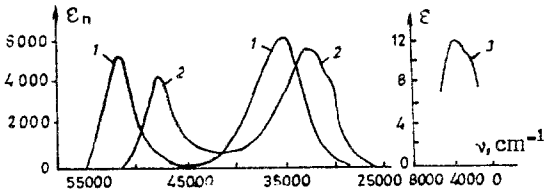

Fig. 1. Absorption spectra of 3-methylsydnone in water (1), decane (2), and methyl iodide (3).

TABLE 1. Calculated * (with allowance for the interaction of all of the singly excited configurations) Energies (E) and Dipole Moments ($\mu^{\pi+\sigma}$)† of the Excited States, Oscillator Forces (f),‡ and Directions of the Moments of the Transitions (ω) clockwise with respect to the Y axis) and Δ E Values [Eq. (1)] of Sydnone (a_0 = 2.5 Å)

MO		E, eV	f	φ°	$\mu^{\pi+\sigma_D}$	φ (μ)	ΔE, eV	MKV vector
	S_0				6,4	165		
Φ_6	S^*_1	4,13	0,53	271	5,2	169	0,5	0,99 (5←4)
Φ_5	S^*_2	6,54	0,04	153	9,5	148	−1,3	0,91 (6←4) −0,40 (5←3)
Φ_4	S^*_3	6,65	0,25	342	3,9	213	1,1	0,40 (6←4) +0,94 (5←3)
Φ_3	T^*_1	0,80		270	5,5	168	0,4	0,99 (5←4)

*The $\gamma_{\mu\nu}$ integrals were calculated from the Pariser—Parr formula.
†The μ^{σ} values were calculated by the Del Re method [11].
‡The $f_{exp}^{H_2O}$ values for transitions to the S^*_1 and S^*_3 states for sydnone are 0.45 and 0.22, respectively, and the f_{exp}^{decane} values are 0.44 and 0.22.

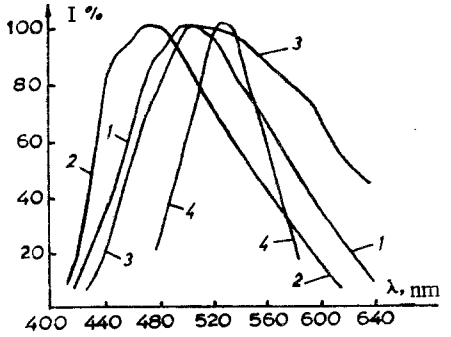

Fig. 2. Luminescence spectra of 3-methylsydnone (1), 3-phenylsydnone (2), and 3-methylsydoneimine hydrochloride (3) in water and of 3-phenylsydnone in decane (4) at 77°K.

solvent, corresponds to excitation (π—π^*) to the S^*_3 state, and this is confirmed by the good agreement between the oscillator force of the transition calculated by the method [8] and the force determined from the spectrum (Table 1). The band corresponding to excitation of sydnone to the S^*_2, state should, judging from the calculated values, be of low intensity and therefore probably does not appear in the spectrum.

Using the indications in [9, 10] regarding the possibility of the identification of absorption bands corresponding to T^*_1—S_0 transitions for some carbocycles and heterocycles, we observed that an absorption band at 2700-4400 cm^{-1} (Fig. 1), the intensity of which is proportional to the concentration of sydnone and dissolved oxygen, appears in the absorption spectra of a number of sydnones dissolved in CH_3I after oxygen is passed through the solutions. When dissolved oxygen is absent, this band is not observed even in concentrated

solutions of sydnones. The energy of the T^*_1 state of 3-methylsydnone ($\sim$ 0.5 eV) determined from the spectrum is in good agreement with the calculated value (Table 1).

Data on the luminescence of liquid or solid dilute solutions of sydnones and sydnone-imines are not available in the literature. We have found that weak pale-blue luminescence corresponds to dilute ($c \sim 10^{-3}$ M) solutions of 3-methylsydnone, 3-phenylsydnone, and 3-methylsydnonimine hydrochloride in water during irradiation with an SVD-120A mercury–quartz lamp with a UFS-3 light filter (ISP-51 apparatus with a photoelectric adapter) (Fig. 2). The strong bathochromic shift of the luminescence bands with respect to the corresponding absorption bands may be due, on the one hand, to a change in the geometry of the molecules in equilibrium states S^*_1 and, on the other hand, to disruption of the Boltzmann distribution of the unit cells that include the molecules of the investigated compounds and the solvent with respect to the energies of interaction of the molecules in these cells [12].

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POLYMETHINE DYES — 4-SUBSTITUTED FURO[2,3-b]- AND SELENOPHENO[2,3-b]PYRIDINE DERIVATIVES

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Polymethine dyes that are 4-substituted furo[2, 3-b]pyridine and selenopheno-[2, 3-b]pyridine derivatives were synthesized. It was shown that replacement of the vinylene group in the benzene ring of a 4-quinoline heteroresidue in the cyanine dyes by an oxygen or selenium atom causes a greater hypsochromic shift in their absorption maxima than replacement by a sulfur atom.

Polymethine dyes that are 4-substituted thienopyridine derivatives (I) were previously studied [1-2]. It was shown that replacement of the vinylene group by a sulfur atom in the benzene ring of a 4-quinoline heteroresidue in the cyanine dyes leads to a sharp hypsochromic shift of their absorption maxima. In this connection, it seemed of interest to synthesize polymethine dyes of the cyanine and merocyanine series, as well as p-dimethyl-

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