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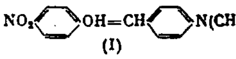
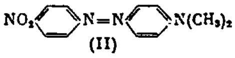
Determination of the Dipole Moments of the Ground and Electronically Excited States and of the Direction of the Electronic Moment of the Transition in Hydrogen-bonded Complexes by Methods Based on Electrochromism

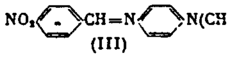
G.S.Denisov, A.I.Kornilov, O.V.Khranina, and F.P.Chernyakovskii

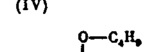
A method for the determination of the direction of the electronic moment of the transition on excitation of molecules has been developed. Taking into account the angle γ, the dipole moments of the ground and first electronically excited states of hydrogen-bonded complexes have been measured.

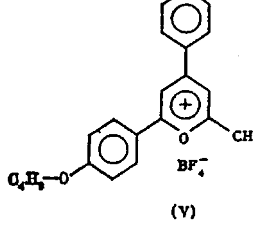
In previous studies [1-3] we proposed a method for the determination of the dipole moments of organic molecules in the ground (μ_g) and electronically excited (μ_e) states based on electro-optical measurements. The method uses a standard substance with well-known electro-optical characteristics and is free from many significant disadvantages characteristic of absolute methods of measurement. The measurements are limited to molecules in which, by virtue of symmetry conditions, the angle γ between the dipole moment of the ground state μ_g and the direction of the electronic moment of the transition m is zero. Under these conditions, the direction of the orientational dipolar polarisation, arising in the electric field, coincides with the optical symmetry axis of the solution. This significantly simplifies the conditions of the measurement and the method of calculation. In a more general case, it is essential to measure γ for all molecules and to take it into account in the calculation of μ_g and μ_e. In the present communication a method is proposed for the determination of the angle γ and of the dipole moments taking into account the value of γ. The results have been extended to the hydrogen-bonded complexes (VI)-(VIII).

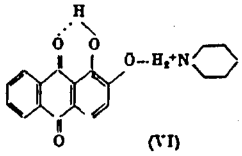

(I)

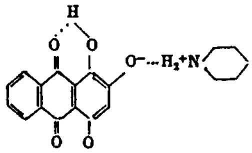

(II)


(III)


(IV)

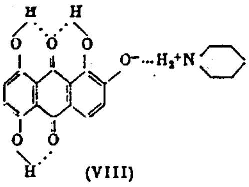

(V)


(VI)


(VII)

The electrochromism method exhibits a high selectivity, based on the possibility of the separate recording of the electrochromism spectra[4] at the wavelengths corresponding to the bands of the free molecules, hydrogen-bonded complexes, and complexes in which a proton has been transferred. As a result of this, the electrochromism method is free from the difficulties arising in the determination of the dipole moments of complexes by dielectric methods in which the polarisations of all the mixture components are recorded simultaneously.[5]

The application of an electric field F with a strength of $\sim 10^5$ V cm to a solution of polar molecules produces orientational electric polarisation of the solution and at the same time anisotropic distribution of the directions of the electronic moments of the transition. Thus the dichroism p, whose magnitude depends on the angle γ in the molecules, can be determined from measurements of the optical density of the solution:


(VIII)

where $D_{\parallel}$ and $D_{\perp}$ are the optical densities of the solution measured with the aid of a light beam whose polarisation vector e makes an angle $\theta = (\mathbf{e}, \mathbf{F})$ with the direction of the field F. The subscripts $\parallel$ and $\perp$ correspond to $\theta = 0°$ and $90°$.

Instead of optical densities, in the method based on electrochromism one records their increments induced by the orientation of the dipoles by the field. They are referred to below as the electrochromism spectra ΔD. Neglecting the small effects associated with the electronic polarisability, the following expressions were obtained from Liptay's theory[6] in conjunction with Chernyakovskii's study:[4]

$$\Delta D = \Delta D_1 + \Delta D_2 = AD + B\bar{\nu}\frac{\partial}{\partial\bar{\nu}}(D/\bar{\nu}), \tag{1}$$

where

$$A = \frac{a^2}{30}(1-3\cos^2\gamma)(1-\cos^2\theta), \tag{2}$$

$$B = \frac{ab}{5}\{(\mu_e\cos\beta-\mu_g)[2-\cos^2\theta-\cos^2\gamma(1-3\cos^2\theta)]+$$
$$+\mu_e\sin\beta\cos\varkappa\sin\gamma\cos\gamma(1-3\cos^2\theta)\},$$
$$a = \mu_g F/kT, \qquad b = F/hc. \tag{3}$$

The following notation has been used in Eqns.(1)-(3): D is the optical density, $\bar{\nu}$ the wavenumber, $\beta = (\widehat{\mu_g, \mu_e})$, κ the angle between the projections of μ_e and $\mathbf{m}$ on to a plane perpendicular to **F**. Assuming that **m**||$\Delta\mu$, where $\Delta\mu = \mu_e - \mu_g$, we find that

$$B = \frac{ab}{5}\Delta\mu \cos\gamma[2-\cos^2\theta + (1-2\cos^2\gamma)(1-3\cos^2\theta)].$$

From the electrochromism spectra, we obtain

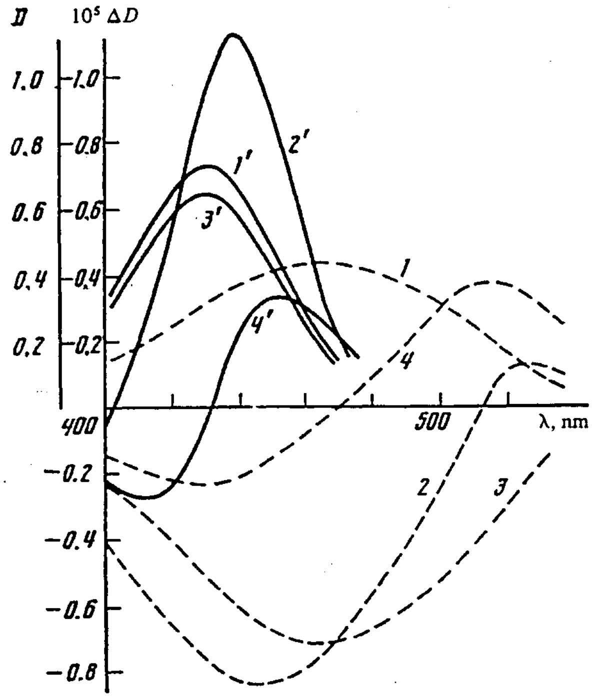
$$\cos^2\gamma = 2 - {}^{5}/_{3}\,\Delta D_{2(\theta=90^\circ)}/\Delta D_{2(\theta=55^\circ)}. \tag{4}$$

The Figure illustrates the absorption spectra D of solutions of compounds (II) and (V) and the electrochromism spectra ΔD, ΔD_1, and ΔD_2 for $\theta = 90°$. The spectra for $\theta = 55°$ are not illustrated in order not to complicate the Figure. From the overall form of $\Delta D_{(\theta = 90°)}$ alone, without isolating ΔD_1, it is possible to estimate γ in the range $90° > \gamma > 0°$, because, according to Eqn.(2), ΔD_1 changes sign at $\gamma = 55°$. The Table presents the values of $\cos\gamma$ and γ calculated by Eqn. (4) as well as the dipole moments of the molecules and complexes calculated by the methods already described[1-3] (but this time with allowance for the angle γ obtained in the present study) by means of the formulae:

$$\mu_g = \mu_g^* \left[\frac{\Delta D_1 D^*}{\Delta D_1^* D}\,\frac{(1-3\cos^2\gamma^*)}{(1-3\cos^2\gamma)}\right]^{1/2}, \tag{5}$$

$$\Delta\mu = -\frac{\mu_g}{3}\,\frac{hc}{kT}\,\frac{D}{\bar{\nu}\frac{\partial}{\partial\bar{\nu}}(D/\bar{\nu})}\,\frac{\Delta D_{2(\theta=90^\circ)}}{\Delta D_{1(\theta=90^\circ)}}\,\frac{(1-3\cos^2\gamma)}{\cos\gamma(3-2\cos^2\gamma)}. \tag{6}$$

In the calculation of μ_g, the dimethylaminoazobenzene molecule was used as the standard. Its parameters in Eqn.(5) have been designated by an asterisk.



The absorption D (curves *1* and *1'*) and electrochromism ΔD (curves *2* and *2'*), ΔD_1 (curves *3* and *3'*), and ΔD_2 (curves *4* and *4'*) spectra of compound (II) in toluene (curves *1–4*) and of compound (V) in dioxan (curves *1'–4'*). For the explanation of the Figure, see text.

Compounds (I)–(III) have been thoroughly investigated[7-9] and have been used to test the method proposed. A satisfactory agreement has been observed between the values of γ, μ_g, and μ_e for these molecules and the values obtained in other studies (see Table) The relative error in the measurement of $\cos\gamma$, μ_g, and μ_e does not exceed 5% for a reliability coefficient of 0.95.

The angles γ and the dipole moments of the molecules and complexes (in units of 33.3×10^{-30} C m).

Molecule	λ^{max}, nm	cos γ	γ, deg	μ_g, D	μ_e, D
			Toluene		
I	435	1.00±0.01	0.0 [7]	7.3±0.2; 7.1 [7]	34,3±0.3; 32 [8]
II	465	1.00±0.01	0.0 [7]	8.1±0.2; 8.0 [7]	25.6±0.2; 25 [7]
III	450	1.00±0.01	0.0 [7]	6.6±0.2; 6,6 [7]	33.9±0.5; 29.6 [9]
IV	460	0.98±0.01	11	5.8±0.1	34.6±0.5
			Dioxan		
V	430	0.46±0.02	63	20.0±0.1	18.7±0.1
VI	550	0.86±0.01	30	4.2±0.1	37.6±0.4
VII	540	0.89±0.01	27	5.6±0.7	15.1±0.4
VIII	550	0.91±0.01	25	5.8±0.3	31.7±0.4

Note. Numbers in square brackets denote references (Ed. of Translation).

Compounds (I)–(IV) were purified on a chromatographic column filled with Al_2O_3 and compounds (V)–(VIII) were purified by recrystallisation. Piperidine was used as the proton acceptor in the complexes and the solvents were toluene and dioxan. The dried liquids were redistilled before use. The concentration of the solution was $\sim 10^{-3}$ M. The absorption and electrochromism spectra were recorded on the apparatus already described.[4,5] The overall electrochromism ΔD spectra were separated into the contributions ΔD_1 and ΔD_2 with the aid of a computer.

The determination of the direction of the electronic moment of the transition is necessary for the calculation of μ_g and μ_e for various molecules. The knowledge of these quantities for complexes with and without transfer of a proton makes it possible to determine from their electrochromism spectra the angle between the dipole moments of the components of the complex. This yields new information about the geometry of hydrogen-bonded complexes.

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