Russian Journal of Physical Chemistry, **60** (8), 198

Translated from *Zhurnal Fizicheskoi Khimii*, **60**, 2079-2081 (1986)

U.D.C. 543.422.5 : 547.1

Determination of the Dipole Moments of Organic Molecules in the Electronic Ground State by the Electrochromic Method

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

The dipole moments of rod-shaped organic molecules in their electronic ground state have been determined by relative measurements of electrochromism. The method is shown to be applicable to various types of organic molecule which absorb in the visible and u.v. regions.

The dipole moments of molecules in the electronic ground state are usually measured by the dielectric method.[1] The electrochromism method,[2] based on optical measurements of the orientation polarisation of molecules, can also be used. Because of the high sensitivity of optical methods the orientation polarisation can be measured reliably even in sparingly soluble substances, i.e. at very low concentrations, if the solutions have a high extinction coefficient.[3]

We have previously developed a method[4] of determining the dipole moments of molecules in an electronically excited state by a computer calculation (from the electrochromism spectra of a given sample) of the ratio of two components depending on μ_g and μ_e (where μ_g and μ_e are the dipole moments of the molecule in the ground and the excited state). It is found that the ratio μ_e/μ_g is independent of the electric field intensity, of the sample thickness, of the polarisation of the light, and of the operating mode of the apparatus.[5] To calculate μ_e we need data on the dipole moment of the molecules in the ground state, μ_g, which are often not available. In order to fill this gap we propose a comparative method of determining the dipole moment of molecules in the ground state μ_g which involves the use of a standard substance with a known value of μ_g^*. It could be of value not only as a means of complementing the above method[4] but also in its own right.

The overall electrochromism spectrum is the sum of increments in optical density ΔD contributed by the various electro-optic effects:[5]

$$\Delta D_{\theta=90^\circ}=(\Delta D_1+\Delta D_2+\Delta D_3+\Delta D_4)_{\theta=90^\circ},$$

where ΔD_1 is the orientation effect, ΔD_2 is the cross effect, and ΔD_3 and ΔD_4 are the Stark effects, i.e.

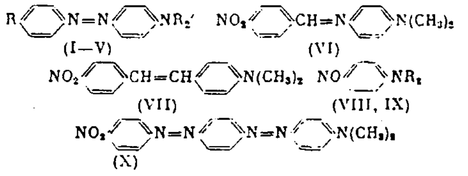
$$\Delta D_1=\frac{1}{30}\left(\frac{\mu_g F}{kT}\right)^2(1-3\cos^2\gamma)(1-3\cos^2\theta)D, \tag{1}$$

$$\Delta D_2=\frac{1}{5}\frac{\mu_g F^2}{hckT}\{((\mu_e\cos\beta-\mu_g)[2-\cos^2\theta-\cos^2\gamma(1-3\cos^2\theta)]+$$

$$+\mu_e\sin\beta\cdot\cos\varkappa\cdot\sin\gamma\cdot\cos\gamma(1-3\cos^2\theta))\}\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}}.$$

Here D is the optical density, $\bar{\nu}$ is the wave number, $\theta = (e, F)$ is the angle between the direction of the electric vector of the light beam with unit vector **e** and that of the electric field **F**, which can be set in the range 55–90°, the angle $\gamma = (\mu_g, m)$ is formed by the dipole moment of the molecule in the ground state μ_g and the moment of the transition with unit vector **m**, $\beta = (\mu_g, \mu_e)$ is the angle between the directions of the vectors μ_g and μ_e, and κ is the angle between the projections of μ_e and **m** on a plane perpendicular to **F**. The quantities ΔD_3 and ΔD_4 can be ignored in our case because the dipole moments of our molecules are relatively large and the electrochromism signals ΔD_1 and ΔD_2 are greater than the contributions from the Stark effects by 1.5–2 orders of magnitude. The orientation contribution (1) can therefore be separated from the overall electrochromism spectrum as the product $\mu_g^2(1-3\cos^2\gamma)$.

In the present study we examined the elongated rod-like molecules



R=H(I, II), NO_2(III), Br(IV), CH_3–CO–NH(V), C_2H_5(VIII), CH_3(IX); R′=CH_3(I, III–V), C_2H_5(II)

It follows from symmetry considerations that the dipole moment of the ground state μ_g and the unit vector of the transition moment **m** have the same direction. Therefore Eqn.(1) takes the form

$$\Delta D_{1\,\theta=90^\circ}=-\frac{1}{15}\left(\frac{\mu_g F}{kT}\right)^2 D. \tag{2}$$

For two molecules, one of which is used as a standard, we obtain from Eqn.(2)

$$\mu_g=\mu_g^*\Big/\left(\frac{D}{\Delta D_1}\frac{\Delta D_1^*}{D^*}\right)^{1/2}.$$

This approach assumes that the quantity μ_g^* is reliably known. We used dimethylaminoazobenzene (I) as the reference molecule because its dipole moment is given in standard tabulations.[6] This molecule has also been used as a standard in dielectric measurements[7] and in our previous work on electrochromism.[4]

In the more general case of non-rod-like molecules the angle γ must be measured in a separate experiment.

The experimental compounds I–X were purified in a chromatographic column packed with Al_2O_3. The measurements were made with toluene solutions of 10^{-3} M concentration. The absorption spectra were recorded on a Perkin Elmer spectrophotometer, and the electrochromism spectra on the apparatus already described.[5] The present procedure differed from that of our previous work[4] in requiring a correction for the spectrum produced by the operation of the apparatus.[5] The relative error in the determination of μ_g was less than 5% for a confidence level of 0.95.

The following values of the dipole moment were obtained (3.33×10^{30} C m^{-1}) for molecules I–X:

Molecule	I	II	III	IV	V	VI	VII	VIII	IX	X
This work	3.22± 0.12	4.33 ±0.12	8.09 ±0.13	5.47 ±0.11	1.59 ±0.09	6.63 ±0.13	7.29 ±0.13	7.15 ±0.24	5.72 ±0.05	7.09 ±0.16
Published data	3.22 [6. 7]	3.15 [6]	8.00 [9]	5.1 [8]	–	6.6 [9]	7.1 [9, 10]	7.15 [6]	6.9 [9]	–

Our values of μ_g agree well with the published values.[6–10]

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

REFERENCES

1. V.I.Minkin, O.A.Osipov, and Yu.A.Zhdanov, "Dipol'nye Momenty v Organicheskoi Khimii" (Dipole Moments in Organic Chemistry), Izd.Khimiya, Leningrad, 1968, 248 pp.
2. W.Liptay, Z.Elektrochem., 1979, 80(3), 207.
3. A.Kriebel and H.Labhart, Z.phys.Chem., 1974, 92(1/2), 247.
4. A.N.Shchapov, A.I.Kornilov, R.M.Basaev, and F.P.Chernyakovskii, Zhur.Fiz.Khim., 1979, 53(10), 2568 [Russ.J.Phys.Chem., 1979(10)].
5. F.P.Chernyakovskii, Uspekhi Khim., 1979, 48(3), 563 [Russ.Chem.Rev., 1979(3)].
6. O.A.Osipov and V.I.Minkin, "Spravochnik po Dipol'nym Momentam" (Dipole Moments Handbook), Izd.Vysshaya Shkola, Moscow, 1965, 264 pp.
7. T.W.Campbell, D.A.Young, and M.T.Rogers, J.Amer. Chem.Soc., 1951, 73(12), 5789.
8. F.P.Chernyakovskii and A.V.Ryazanova, in "Uchenye Zapiski Yaroslavskogo Tekhnologicheskogo Instituta" (Scientific Memoirs of the Yaroslavl' Technological Institute), Yaroslavl', 1971, Vol.26, pp.51–54.
9. W.Liptay, in "Excited States", Academic Press, New York–London, 1974, Vol.1, pp.129–229.
10. H.Labhart, Adv.Chem.Phys., 1967, 13, 179.

Yaroslavl' Polytechnic Institute
Zhdanov Leningrad
State University

Received
3rd December 1985