POLARIZABILITY ANISOTROPY OF MALEIC AND PHTHALIC ANHYDRIDES

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The polarizability of organic molecules is one of the fundamental physical properties that permit a study of mutual effects. In particular, it is well known that a relationship exists between the mean polarizability (molecular refraction) and the conjugation effects, which is expressed in the appearance of exaltation [1]. The spatial direction of such superadditive contributions has received incomparably less study. This is due to the need of determining the three major axes of the molecular polarizability ellipsoid using the methods of the Kerr effect and the depolarized Rayleigh scattering of light [2]. Here the orientation of the axes should be known, i.e., the existence of a definite symmetry of the molecule is required.

We examined the cyclic anhydrides, maleic (I) and phthalic (II) anhydrides, in which the CO—O—CO fragment is conjugated with either the double bond or the aromatic ring. The symmetry of the molecules determines the orientation of the major axes of the polarizability ellipsoids (Fig. 1). Previously, on the basis of determining the Kerr constants (KC) of (I) and (II) and comparing them with those calculated by the additive scheme, it was assumed that in both cases the exaltations of the polarizability are oriented along the b_2 axis [3]. If this could be close to the truth in the case of (I), then for (II) a noticeable exaltation of the b_1 axis should be observed due to conjugation with the aromatic ring, since in the general case the direction of exaltation coincides with the direction of electron shift [4]. The measurements [3] were made in benzene, i.e., under conditions where complex formation is possible, which affects the experimental values of the KC [5]. Consequently, we measured the dipole moments (DM), molecular refractions, molar KC ($_mK$), and molecular anisotropies using the data on the depolarization of the Rayleigh light scattering γ^2 of (I) and (II) in dioxane at 20°C. The results are given in Table 1; the values of the polarizability exaltations Δb are also indicated.

The DM, and especially the KC, are quite different from those found in [3], which confirms the existence of the benzene effect of the solvent. The experimental values were expressed via the value of the axes of the polarizability ellipsoids [2].

$$MR = 1.05\frac{4\pi N}{9}(b_1+b_2+b_3)$$

$$\gamma^2 = \Sigma(b_i-b_j)^2$$

$$_mK = \frac{2\pi N}{9}\left[\frac{1}{45kT}\frac{P_d}{P_e}\Sigma(b_i-b_j)^2+\frac{1}{45k^2T^2}\mu^2(2b_1-b_2-b_3)\right]$$

Solving the system of equations with respect to the unknown axes gives the results given in Table 2, together with the additive values [3].

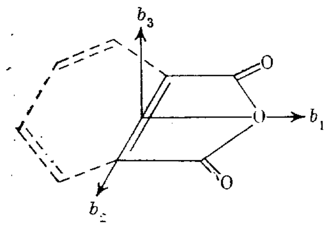

Fig. 1. Orientation of axes of polarizability ellipsoids of cyclic anhydrides.

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TABLE 1. Polarity and Polarizability Parameters of Studied Compounds

Compound	MR, cm³	Δb, Å³	μ, D	$_{m}K \cdot 10^{12}$	γ^2, Å⁶
(I)	21,10	1,15	4,22	−101	52,5
(II)	38,58	3,66	5,65	1701	168,9

TABLE 2. Axes of Polarizability Ellipsoids of Anhydrides,* Å³

Compound	b_1	b_2	b_3
(I)	7,87 (7,59)	10,54 (11,07)	4,30 (5,20)
(II)	15,78 (17,54)	16,38 (18,21)	8,32 (8,39)

*Additive values (the experimental values are given in parentheses).

The results for (I) are quite unexpected. As was postulated in [3], the polarizability along the b_1 axis does not increase, and even a certain depression is observed; exaltation of the b_2 axis is observed but it is slight. The main increase in the polarizability occurs along the b_3 axis, i.e., perpendicular to the plane of the conjugated system. It should be mentioned that a substantial exaltation of the mean polarizability was observed for the saturated five-membered anhydride ring [3], and a nonadditivity of the major axes of the polarizability ellipsoid [6]. Consequently, a deviation of the axes of the polarizability ellipsoid of (I) from the additive values cannot be interpreted as the manifestation of simple conjugation of the double bond with the carbonyl groups.

The picture is clearer in the case of (II). The perpendicular plane of the conjugated system, the b_3 axis, is close to that calculated in [3]. The polarizability exaltation is not directed perpendicular to the axis of symmetry, as was postulated in [3], but rather is distributed uniformly along the b_1 and b_2 axes. Taking into account the data for (I) and succinic anhydride [6], it is hardly possible to derive conclusions regarding the character of the interactions in (II) on the basis of comparison with the results of the additive summation of the ellipsoids of the individual bonds.

The determined parameters of the anhydride fragments should be used when calculating the polarizability anisotropy of the molecules containing them.

CONCLUSIONS

The polarizability ellipsoids of the maleic and phthalic anhydride molecules are characterized by substantial nonadditivity.

LITERATURE CITED

1. B. V. Ioffe, Refractometric Methods in Chemistry [in Russian], Khimiya (1974), p. 78.
2. R. J. W. LeFevre, Adv. Phys. Org. Chem., 3, 1 (1965).
3. R. J. W. LeFevre and A. Sundaram, J. Chem. Soc., 4009 (1962).
4. S. G. Vul'fson, G. L. Cheryukanova, G. A. Chmutova, and A. N. Vereshchagin, Dokl. Akad. Nauk SSSR, 212, 621 (1973).
5. R. S. Armstrong, M. J. Aroney, R. J. W. LeFevre, J. D. Saxby, and G. J. Wilkins, J. Chem. Soc. A, 2735 (1969).
6. B. A. Arbuzov, L. A. Grozina, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 548 (1969).