Kerr constants and dipole moments of aminobenzoic acids in dioxane

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Aminobenzoic acids in dioxane have been investigated by dipole moment and Kerr effect methods. *m*-Aminobenzoic acid exists in a solution mainly (~60 %) in the *syn*-form. In *p*-aminobenzoic acid, conjugation flattens the pyramidal configuration of the nitrogen atom, which is even more flattened in *o*-aminobenzoic acid owing to an intramolecular hydrogen bond.

Key words: aminobenzoic acids, structure; Kerr constants; dipole moment; polarizability; interaction moment.

The structures of aromatic carboxylic acids have been studied by different physicochemical methods. However, some aspects of the relation between the structure of these molecules in solutions and their electrical properties have not been conclusively elucidated. This work continues the series of studies performed previously for benzoic acid.[1]

Among the substituted benzoic acids, aminobenzoic acids are of special interest. Primarily, this is due to the fact that the carboxyl group is an electron acceptor, and the amino group is a strong electron donor. Thus, intramolecular electronic interactions should manifest themselves most clearly. The comparative analysis of *para*, *ortho*, and *meta* isomers is of special interest. As is known,[2—4] that benzoic acid in dioxane exists in the form of a monomer owing to the suppression of self-association and the formation of hydrogen complexes. Assuming similar behavior of aminobenzoic acids, we used dioxane as the solvent. For studying these acids in solutions, we employed the methods of dipole moments and electric birefringence (Kerr effect).

The theoretical Kerr constant (${}_mK$) can be split into two components: the anisotropic component (Q_1) and the dipole component (Q_2)

$${}_mK = \frac{2\Pi N_A}{9}(Q_1 + Q_2), \qquad (1)$$

Q_1 is determined by the anisotropy of the optical polarizability of the molecule (b_{ij}) and the ratio of its electronic (P_e) and atomic (P_a) polarizabilities

$$Q_1 = \frac{1}{45kT}\left(\frac{P_e + P_a}{P_a}\right)[(b_{ii} - b_{jj})^2 + 6\,b_{ij}^2], \qquad (2)$$

and Q_2 is expressed in terms of the product of the components of the polarizability tensor (b_{ij}) and the electric dipole moment vector (μ_i)

$$Q_2 = \frac{1}{45k^2T^2}[2\,m_i^2(b_{ii} - b_{jj} - b_{kk}) + 6\,m_i^2 b_{ij}], \qquad (3)$$

where m_i are the components of the vector μ_i.

The Kerr effect and the method of dipole moments have been previously used for studying the electronic structure of such conjugated molecules as substituted dimethylanilines.[5] The introduction of an acceptor to the *para* position of aniline and its *N*-alkyl derivatives was found to cause a noticeable flattening of the structure, whereas donor substituents enhance the pyramidal configuration of the nitrogen atom. As an estimate of the degree of nonplanarity, we used the value m_z, which corresponds to the contribution of the dimethylamino group to the z component of the dipole moment. (In *N,N*-dimethylaniline, m_z = 0.42 D; in *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, m_z = 0.83 D; and in *p*-nitro-*N,N*-dimethylaniline, m_z = 0.)

Kerr constants were calculated using the following components of the molecular tensors (b_i/Å^3): $b_1 = b_2$ = 10.55, b_3 = 6.71 for Ph;[6] b_1 = 18.74, b_2 = 14.89, b_3 = 9.27 for benzoic acid, and the axes that correspond to b_1 and b_2 form the angles 5° and 95°, respectively, with the bond C_{arom}—C(O) (*cf.* Ref. 1); b_1 = 14.74, b_2 = 11.65, and b_3 = 8.18 for aniline.[6]

The dipole moment (μ) was calculated within the simple additive scheme: for benzoic acid,[3] μ = 1.73 D and φ = 74° (φ is the angle between the dipole moment vector and the C_{arom}—C(sp^2) bond); for aniline,[7] μ = 1.76 D and φ = 48.5° (φ is the angle between the dipole moment vector and the rotation axis). As a second approximation, the moment of interaction was introduced for the *para* and *ortho* derivatives (the superadditive contribution due to the interaction of the donor-acceptor groups).

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Table 1. Experimental dipole moments (μ_{exp}) and Kerr constants ($_mK_{exp}$) in dioxane

Compound	α	β	γ	δ	μ_{exp}/D	$_mK_{exp} \cdot 10^{-12}$/esu
1	6.8792	0.1934	0.1144	100.09	2.59±0.07	150±36
2	1.7158	0.1553	0.1265	41.21	1.17±0.27	69±25
3	10.4890	0.2287	0.1311	502.23	3.31±0.10	770±51

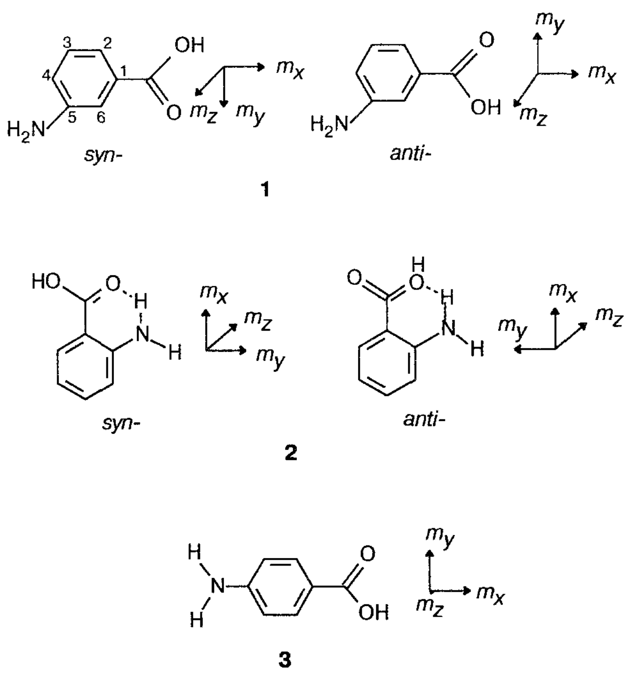
Note. Compounds **1**, **2**, and **3** are *m*-, *o*-, and *p*-aminobenzoic acid, respectively; the parameters α, β, γ, and δ are the contributions to the dipole moment of permittivity, density, refractive index, and the birefringence constant, respectively (*cf.* Ref. 6).

Experimental

In this study, reagent grade commercial samples of aminobenzoic acids were used, which were purified by double recrystallization from 10 % and 20 % aqueous ethanol.

Molar Kerr constants were measured at 25 °C with the setup described in Ref. 7. Experimental Kerr constants and dipole moments are listed in Table 1.

Scheme 1



1

2

3

Results and Discussion

In *m*-aminobenzoic acid, the mutual effect of the functional groups must be rather weak and predominantly inductive. Conjugation may occur in the case of the amino groups in the *ortho* and *para* positions relative to the carboxyl group. *m*-Aminobenzoic acid can occur in *syn* and *anti* forms (Scheme 1). As expected, the calculations of the dipole moment and the Kerr constant for *m*-aminobenzoic acid using the simple additive scheme gave consistent results (Table 2) with nearly equal amounts of *syn* and *anti* isomers. According to the data of both methods, *m*-aminobenzoic acid in solution is ~60 % *syn* conformer.

For *p*-aminobenzoic acid, like for *m*-aminobenzoic acid, the validity of the simple additive scheme must be verified. The additive dipole moment of *p*-aminobenzoic acid is calculated as the sum of the dipole moments of aniline and benzoic acid. The value thus obtained (2.68 D) differs substantially from the experimental value (μ_{exp} = 3.31 D). The Kerr constant calculated using the additive dipole moment ($146 \cdot 10^{-12}$ esu) also differs from the experimental value. Since *p*-aminobenzoic acid exhibits strong direct polar conjugation, the moment of

Table 2. Calculated dipole moments (μ_{theor}) and Kerr constants ($_mK_{theor}$)

Compound	*A*				*B*				*C*			
	syn-	*n*	*anti-*	*n*	*syn-*	*n*	*anti-*	*n*	*syn-*	*n*	*anti-*	*n*
				μ_{theor}/D								
1	3.16	0.6	1.81	0.4								
2	1.48	1	3.16	0	1.08	1	4.05	0	1.27	1	3.57	0
				$_mK_{theor} \cdot 10^{-12}$/esu								
1	286	0.6	−70	0.4								
2	−113	0.3	161	0.7	−25	1	812	0	55	1	775	0

Note. ***A***, additive scheme; ***B***, the moment of interaction along the C_{arom}—COOH bond; ***C***, the moment of interaction along the C_{arom}—N bond; *n* is the conformer fraction in the mixture.

interaction along the C(1)—C(4) axis of the phenylene ring (see Scheme 1) should be taken into account. The *y* and *z* components of the dipole moments were determined using the additive scheme, and its *x* component was determined from the experimental data taking into account the superadditive contribution due to the conjugation effect. However, in this case the theoretical Kerr constant also differs from the experimental value ($594 \cdot 10^{-12}$ esu). It has been known[5] that direct polar conjugation results in a decrease in the vertical component of the dipole moment m_z and in an increase in the m_x component directed along the C(1)—C(4) axis. The extent of the increase in m_x and the decrease in m_z can be estimated by solving the inverse problem. From the experimental data using relationships (1)—(3), the values m_x = 2.7 D and m_z = 0.8 D were determined, which differ significantly from those calculated using the simple additive scheme (m_x = 1.64 D and m_z = 1.32 D). Thus, direct polar conjugation causes a substantial reconstruction of the dipole moment ellipsoid. However, the amino group is not flattened completely.

o-Aminobenzoic (anthranilic) acid, like *m*-aminobenzoic acid, occurs in *syn* and *anti* forms (see Scheme 1). The dipole moments and Kerr constants of both forms and their ratio in solution calculated by the simple additive scheme are contradictory (see Table 2). It is evident that conjugation together with the intramolecular hydrogen bond in anthranilic acid also flattens the pyramidal configuration of the nitrogen atom. We calculated the Kerr constant and the dipole moment taking into account the moment of interaction, which, in anthranilic acid, can be directed along one of the bonds C_{arom}—COOH or C_{arom}—N. As can be seen from Table 2, both variants of the calculation indicate that the molecules of anthranilic acid in dioxane occur predominantly in the *syn* form. Unfortunately, the available data gives no way of selecting the direction of the moment of interaction yet.

References

1. A. P. Timosheva, S. G. Abdullina, Yu. G. Kondrashina, and S. G. Vul'fson, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1069 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 838 (Engl. Transl.)].
2. O. O. Exner and V. Eqchlicka, *Chem. Comm.*, 1965, **30**, 639.
3. P. M. Brooks and M. E. Hobbs, *J. Am. Chem. Soc.*, 1940, **62**, 2851.
4. C. I. Beguin and T. Janmann, *Helv. Chim. Acta*, 1958, **41**, 1376.
5. G. Ya. Cheryukanova, S. G. Vul'fson, G. A. Chmutova, and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1180 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, **23** (Engl. Transl.)].
6. A. N. Vereshchagin, *Polyarizuemost' molekul* [*Polarizability of Molecules*], Nauka, Moscow, 1980 (in Russian).
7. V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, *Dipol'nye momenty v organicheskoi khimii* [*Dipole Moments in Organic Chemistry*], Khimiya, Leningrad, 1968 (in Russian).

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