Brief Communications

The structure of 6,6′-biquinolyl and its dication in solution

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Conformational analysis of 6,6'-biquinolyl and its dication was performed using dipole moments and data from electric and magnetic birefringence. The rotation angles between the quinoline rings for the *cis*- and *trans*-conformers in solution are ~50°. The emergence of positive charges on both heteroaromatic rings does not result in noticeable changes in the spatial structure.

Key words: 6,6′-biquinolyl, dication, structure, Kerr and Cotton—Mouton constants, dipole moment.

Previously[1] we offered a method for the investigation of the conformational behavior of binuclear aromatic ions in solutions, which was used for determining the conformations of 2,2′- and 4,4′-bipyridyls and their salts.[2] The conformation of such molecules is entirely determined by the rotation angle between the rings. In the present work we carried out the conformational analysis of 6,6′-biquinolyl (**1**) and its dication (**2**) by the methods of electric and magnetic birefringence (the Kerr and Cotton—Mouton effects) using data on dipole moments.

It has been of interest to follow the effect of conjugation between the quinoline rings, which leads to the flattening of the structure and prevents the mutual repulsion of the *ortho*-hydrogen atoms, on the conformation of the molecule. On going from the neutral molecule to the dication, the rotation angle between the rings may become substantially larger due to the excessive positive charge.[3]

Experimental

A commercial sample of **1** was purified by recrystallization until its physical characteristics were identical to those reported in the literature. The sample of **2** was obtained by dissolution of **1** in an acid. Molar Cotton—Mouton constants ($_mC$), Kerr constants ($_mK$), and dipole moments (μ) for **1** were determined by the known procedures.[1,4] $_mC$ for compound **2** was determined in a 20 % solution of HCl. All of the measurements were carried out at 25 °C. Refraction indices for the solutions were obtained on a PR-2 Pulfrich refractometer. Densities of the solutions were determined by pycnometry.

Results and Discussion

The spatial structure of biquinolyls and their salts in solutions has not been determined. Most of the data available were obtained by X-ray diffraction analysis. 2,2′- and 8,8′-biquinolyl in the crystalline state were

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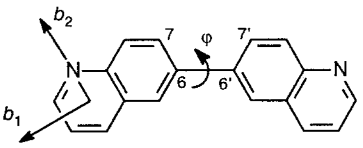
found to exist as conformers with the rings rotated relative to the *trans*-form by 0° and 96.8°, respectively.[5,6]

Most of the attention has been paid to the investigation of the carbon analogs of biquinolyls, binaphthyls, which have been studied by a set of various physical methods. It has been found that 1,1′- and 2,2′-binaphthyls exist in solution as conformers with rotation angles $\varphi = 90°$ and $0°$, respectively.[7,8]

In the calculations of the theoretical ${}_mC$ for compounds **1** and **2**, and ${}_mK$ and μ for **1** as a function of the 7—6—6′—7′ torsion angle (φ), we used the values of the polarizability ellipsoids (b_i) and the magnetic susceptibility (k_i) of the quinoline[9] and quinolinium[10] rings as well as the value of μ for quinoline[11] directed along the b_1 axis (the scheme in which b_1 and b_2 are the main axes of the polarizability ellipsoid in the quinoline fragment, b_3 is normal to the plane of the aromatic ring, and the direction of the k_i axes is analogous):



The anisotropy of polarizability and magnetic susceptibility of the C(sp^2)—C(sp^2) bond was taken to be equal to $\Delta b = 1.5$ and $\Delta k = 7.4$.[2] In addition, for molecules like **1** one may expect substantial exaltation of the polarizability and magnetic susceptibility[7] due to π-electron delocalization. We defined the exaltation of polarizability, δb, as the difference between the total molecular polarizability determined from the molecular refraction R_d and the sum of polarizabilities of the constituents Σb_i, *i.e.*, as the following relationship:

$$\delta b = (9\varepsilon_0/N_a)R_d - \Sigma b_i,$$

where $R_d(1) = 93.0$ cm^3, $\Sigma b_i(1) = 93.9$ and $\delta b = 11.1$*; $R_d(2) = 89.1$ cm^3, $\Sigma b_i(2) = 92.5$ and $\delta b = 8.2$.

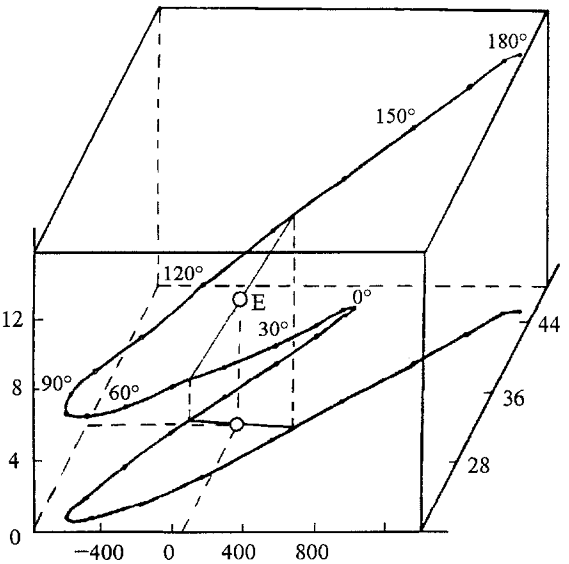


Fig. 1. Graphic determination of the conformation of 6,6′-biquinolyl based on the data from three methods.

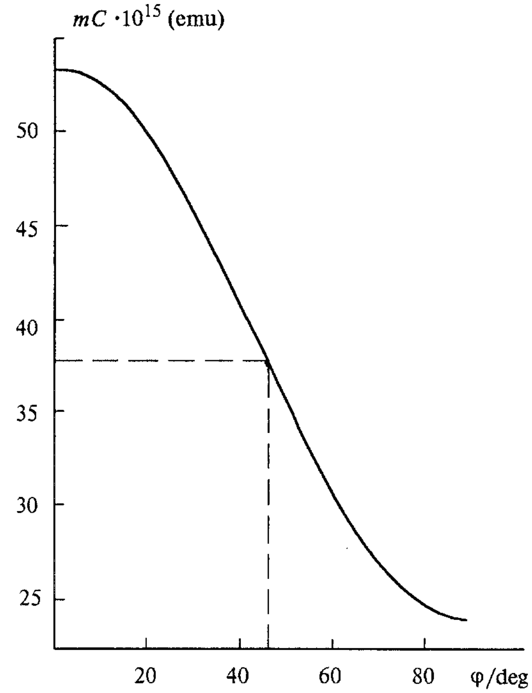


Fig. 2. Conformational dependence of 6,6′-biquinolyl dication.

The direction of δb along the bond between the quinoline rings was chosen as the most probable.

The most reliable and accurate results of the analysis of systems with two equilibrated conformers were obtained when three-dimensional plots were considered.[12] Figure 1 represents the μ^2—${}_mK$—${}_mC$ dependence for compound **1**. The locus of points corresponding to the parameters calculated for various φ angles is a complex curve. The chords that connect the corresponding points of the curve refer to the equilibria between the various conformers. The only chord that passes through the experimental point for **1** ($\mu = 2.67$ D, ${}_mC = 32.6 \cdot 10^{-15}$ emu, ${}_mK = 40 \cdot 10^{-12}$ esu), corresponds to the equilibrium between the *cis*- and *trans*-conformers in a 1:1 ratio with the ring rotated by 47°.

Figure 2 represents the dependence of ${}_mC$ on φ for compound **2**. Theoretical ${}_mC$ were determined as the average between ${}_mC_{\mathrm{teor}}(\varphi)$ and ${}_mC_{\mathrm{teor}}(180\text{-}\varphi)$ with the assumption that the pair-type equilibrium between the

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* Hereafter ${}_mP_i \cdot 10^{15}$ emu, $b_i \cdot 10^{24}$ cm^3.

cis- and *trans*-conformers with an equal rotation of the rings, as for the neutral molecule, is retained for the cation in solution. The experimental value ($_mC$ = $38 \cdot 10^{-15}$ emu) is in accord with the angle of 48°.

Thus, the transition of 6,6′-biquinolyl from the neutral form to its diprotonated form does not noticeably affect the conformation of the molecule.

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The experimental detection of a retro-Prince reaction exemplified by a homogeneous acid-catalyzed decomposition of isopentenols

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The occurrence of the retro-Prince reaction in the transformations of an equilibrium mixture of 2-methyl-3-buten-2-ol and 3-methyl-2-buten-1-ol in 24.9—49 % aqueous sulfuric acid at 25 °C has been experimentally proved.

Key words: acid catalysis; equilibrium mixture; isopentenols; Prince reaction.

Kinetic studies of the transformation of 2-methyl-3-buten-2-ol (**1**), 3-methyl-2-buten-1-ol (**2**), and 3-methyl-3-buten-1-ol (**3**)[1—3] in acidic media have shown that several consecutive reactions are involved and an equilibrium is established under the conditions studied.[3]

Previously[3] on the basis of kinetic and GLC data, a scheme was suggested for the transformations of an equilibrium mixture of alcohols **1** and **2** and isoprene (IP) in aqueous solutions of sulfuric acid (from 24.9 % to 49.76 %) at 25 °C.

The major reaction product under these conditions is 3-methylbutane-1,3-diol (**4**).

The reaction rates depend on the concentration of the catalyst (H_2SO_4). For example, in 25 % H_2SO_4 at 25 °C, the effective rate constants are 2.8 min^{-1} for isomerization of **1** into **2**, $9.5 \cdot 10^{-2}$ min^{-1} for dehydration of the **1** $\rightleftarrows$ **2** equilibrium mixture into IP, and $6.3 \cdot 10^{-2}$ min^{-1} for hydration of **3** into 4.

However, when compound **1** was the starting material, a material unbalance[3] was revealed: $C_0^{\mathbf{1}} = C^1 + C^2 + C^3 + C^4 + C^{IP} + C^X$, where $C_0^{\mathbf{1}}$ is the initial

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