DIPOLE MOMENTS AND MOLAR KERR CONSTANTS OF
ADDUCTS OF DIENE SYNTHESIS OF BENZOQUINONE
WITH CYCLIC DIENES

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Continuing investigations of bicyclic unsaturated compounds and their epoxy derivatives [1-3], we studied adducts of the diene synthesis of p-benzoquinone with cyclopentadiene and cyclohexadiene-1,3 (monoadducts Ia, b and bisadducts Iia, b), using data on the polarization and polarizability of the molecules.

The configuration of cyclopentadiene and benzoquinone derivatives has now been established. The possibility of intramolecular photochemical cyclization of the adducts (Ia), (II) is evidence of an endo-orientation of the molecules of the dienophile and diene; moreover, the bisadduct has an endo-trans-endo-structure [4 (p. 293)-6]. The latter conclusion is confirmed by the results of an X-ray diffraction study of the corresponding tetrahydro-derivative [7]. The stereochemistry of the diene synthesis of p-benzoquinone with cyclohexadiene has not been investigated. However, it has been shown that endo-addition occurs in analogous diene syntheses of p-benzoquinone with 1-methoxycyclohexadiene-1,3 [8] and cyclohexadiene with 2,3-dimethyl-5,8-quinoxalinedione [9]. The closeness of the NMR spectra of compound (b) and its homologs to the spectra of the corresponding derivatives of cyclopentadiene has also permitted us to assume an endo-structure of the monoadducts in these cases [10]. Thus, the indirect evidence gives a basis for expecting the fulfillment of the general rule of endo-orientation of the diene and dienophile in the case of diene synthesis of p-benzoquinone and 1,3-cyclohexadiene, according to the principle of "maximum accumulation of unsaturation" [4, p. 41].

The most interesting and little investigated is the problem of the conformation of the six-membered ring - cyclohexenedione ring in monoadducts or cyclohexenedione in bisadducts. The available data are rather contradictory. It has been found that the tetrahydro-derivative of the bisadduct of cyclopentadiene (Iia) has a flat central ring in the crystalline state [7]. The possibility of a planar structure has also been proposed for the enedione ring of monoadducts, where conjugation should stabilize the coplanar arrangement of the three double bonds [10]. However, even in methylenenaphthoquinone, which possesses a large conjugated system, the corresponding six-membered
ring, according to the x-ray diffraction data [11], has a nonplanar structure. Evidently, in considering the conformation of molecules in solutions, one cannot rely upon the results of crystallographic investigations, since in each individual case the influence of the crystal lattice may determine deviations from the form of the free molecules. For the monoadduct of benzquinone with cyclopentadiene, a substantial dipole moment of 1.39 D has been found [12], indicating nonplanarity of the dione ring. An angle between keto-groups of 15° corresponds to the experimental value with a moment of the C=O bond 2.79 D and neglecting weak dipoles. As a result of the approximations used in the calculation, this result can be considered only approximate.

It should be mentioned that the ring formed in mono- or bisadducts of diene synthesis of the p-benzoquinone molecule, being nonplanar, can exist only in the boat conformation, since groups including a carbon-carbon double bond (4-5-6-1, Fig. 1) or a bond contained in the bridge of a bicyclic system (1-2-3-4), should be coplanar. Moreover, a different arrangement with respect to the bicyclic system is possible for the bonds of the dione ring 4-5, 5-6, and 6-1 (see Fig. 1). In the case of an anti-orientation, they are found to be distant from one of its bridges, but an approach of the atoms of the bicyclic system and keto groups arises; in the syn-conformation, steric interactions of the atoms 5 and 6 with the closest atoms of the fragment formed by the diene molecule are possible. These atoms may be contained in an unsaturated bridge in the case of endo-orientation of the diene and dienophile or methylene or ethylene bridge in the case of an exo-structure (see Fig. 1). The presence of an equilibrium mixture of syn and anti-forms, together with the possibility of existence of a flat dione ring, has been proposed for the monoadducts [10].

To confirm and verify the available data on the configuration of adducts of p-benzoquinone with cyclic dienes and determine the conformation of their molecules, as well as to verify the applicability of the methods of dipole moments and the Kerr effect to compounds whose molecules in different steric forms (isomeric or conformer) differ only in the orientation of the hydrocarbon portions containing no strong dipoles, we compared the measured values of the dipole moments \( \mu \) and the molar Kerr constants \( m_K \) of compounds of types (I) and (II) with those calculated according to an additive scheme for the possible structures. In the calculation we used the geometrical parameters of the bicyclic systems — bicycloheptene and bicyclooctene — cited in previous studies [1, 2]. The dihedral angle formed by the plane 1-2-3-4 (Fig. 1) and the plane of the bridge of the norbornene system, including the 2-3 bond, were assumed equal to 125.67°, as in the tetrahydro-derivative of the bisadduct (IIa) [7]. Since the analogous angle in the norbornide, containing a condensed norbornene system and five-membered imide ring, has practically the same value of 125° [13], this parameter may be considered independent of the substituents and determining the direction of the endo-oriented bonds of the ethylene bridge of the bicycloheptene system. Since there are no accurate structural data for adducts of cyclohexadiene, in accord with the hypothesis of normal values of the valence angles [2], we consider the dihedral angle between the plane 1-2-3-4 and the bridge of the bicyclooctene system equal to 120°. To calculate the dipole moments we used an additive scheme, based on the moments of the carbon-hydrogen bond calculated from the intensities of the vibrational bands [14]:

\[
\begin{align*}
\mu(C_{sp^3}-H) & = -0.28 \text{ D}, \\
\mu(C_{sp^2}-H) & = -0.70 \text{ D}.
\end{align*}
\]

In this case the moment of the \( C_{sp^3}-C_{sp^2} \) bond is equal to 0.78 D; the moment of the C=O bond can be calculated from the experimental dipole moment of cyclohexanone or cyclopentanone 3.00 D [5] and is equal to 1.94 D. However, the presence of a conjugated system of bonds \( O=C-C=C=O \) of the monoadducts gives a basis for expecting a change in the bond moment; the moment of the C=O bond calculated on the basis of the data for methyl vinyl ketone \( \mu = 2.98 \text{ D} \) [15]) (evidently including the moment of conjugation) is equal to 2.08 D. Both these values were used in the calculations. As it follows from the data obtained earlier [1, 2, 16, 17], the dipole moments of substituted bicylenes are insufficiently accurately described by vector summation of all the dipoles of the molecule, including the weak dipoles of the \( C_{sp^3}-C_{sp^2} \) and C-H bonds, although they undoubtedly make their own contribution to the resultant moments of the molecules. Therefore in the calculation the summary moments of the hydrocarbon bridges of the bicyclic systems, calculated from the experimental data for pairs of exo–endo-isomers [1, 2, 17], were used; in the orientation of the intramolecular coordinate axes used in [1, 2], for the bicycloheptene system \( \mu_x = -0.20, \mu_y = 0.05, \mu_z = -0.13 \text{ D} \) [2].

In the calculation of the molar Kerr constants it was assumed that the C-H bonds are isotropically polarizable, \( b_L = b_T = b_V = 0.64 \text{ Å}^3 \); correspondingly all the carbon-carbon bonds, regardless of