# INVESTIGATION OF THE STRUCTURE OF ADDUCTS OF DIENE SYNTHESIS OF BENZOQUINONE WITH ACYCLIC DIENES AND THEIR EPOXY DERIVATIVES

A. N. Vereshchagin, A. P. Anastas'eva, and B. A. Arbuzov

UDC 541.6:547.567+547.315.2

In a number of previous studies the configuration and conformation of molecules containing six-membered rings with planar groups of atoms, including the adducts of diene synthesis of p-benzoquinone with cyclic dienes and their oxides [1, 2], have been discussed. The cyclohexenedione or epoxycyclohexanedione ring in them is condensed with a bicyclic bridge system and has a boat conformation. The steric structure of molecules containing condensed rings, each of which has a flat fragment, was not investigated previously. Great structural variety is possible for them on account of the existence of rings in the form of a half-chair or boat, as well as cis- or trans-coupling of the rings. One of the simple methods of producing such compounds is the diene synthesis of p-benzoquinone with acyclic dienes, leading to hydrogenated derivatives of naphthoquinone [mono-adducts (I)] or anthraquinone [bis-adducts (II)] [3]. The epoxidation of derivatives of butadiene (Ia) and (IIa) has also been described [4]; the results give a basis for believing that in the case of (Ia), oxidation proceeds at the unconjugated double bond, with the formation of (III)



The presence of polar carbonyl groups in the adducts and their oxides makes these compounds extremely convenient for investigation by the methods of dipole moments and the Kerr effect. We have synthesized epoxides of mono- and bis-adducts of isoprene and dimethylbutadiene (IIIb, c) and (IVb, c). In attempts to produce monoxides of bis-adducts using equimolar amounts of peracetic acid, complex mixtures of products, containing chiefly the dioxides (IV), were isolated, in contrast to the reactions in which bis-adducts of cyclic dienes participate [2]. In this case, the epoxidation of one double bond has no appreciable influence on the reactivity of the second.



	Calculated parameter	Conformation (see Fig. 1)						
Com- pound		1	2	3	4	5		
Ia	$\mu, D$	0,45	1,62	2,40	1,53	1,38		
Ib	$\mu, D$	0,41	1,72	2,11	1,65	1,58		
Ic	$\mu, D$ $mK \cdot 10^{12}$	0,35 11	1,79 -132 -132	1,79 -41	1,79 39	1,79 55		

The structure of the monoxides (III) is confirmed by the IR spectra. The IR spectra contain the bands of the valence vibrations of the carbonyl 1680 cm<sup>-1</sup>, characteristic of conjugated ketones and quinones, as well as the bands  $\nu(C=C)$ , displaced into



Fig.1. Possible conformations of molecules of the mono-adducts of benzoquinone (I).

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.7, pp. 1420-1425, July, 1971. Original article submitted September 8, 1969.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

	Config- uration	Calculated diameter	Conformation (see Fig. 2)						
Com- pound			1	2	3	4	5		
IIIa	cis	μ, D	3,09 405	3,52	2,96	2,63	1,63		
	trans	$\mu, D$ $\mu, 10^{12}$	1,24 22	0,89	2,03 -31	1,78 46	3,37 378		
IIIb	cis	$\mu, D$	3,09	3,52	2,96	2,63	1,63		
	trans	$\mu, D$ $mK \cdot 10^{12}$	1,24 20	0,89 36	2,03 36	1,78 -26	3,37 		

TABLE 2. Calculated Dipole Moments and Kerr Constants of Oxides of the Mono-Adducts of Quinone (III)



Fig.2. Possible steric structures of oxides of the mono-adducts (III).

the region characteristic of conjugated olefins  $(1600-1605 \text{ cm}^{-1})$  [5]. For the product of oxidation at the conjugated double bond, we should have expected the appearance of the band of the valence vibrations of the C = C bond at 1660 cm<sup>-1</sup> (cis-1,2-disubstituted bond) and a smaller shift of the band  $\nu$ (C = O) from the frequency 1715 cm<sup>-1</sup>, characteristic of saturated ketones [6]. The absorption bands of carbonyl 1710-1719 cm<sup>-1</sup> in the spectra of dioxides of the bis-adducts (IV) are situated in this region; the overtones 3402-3048 cm<sup>-1</sup> appear in all cases [5]. There are also overtones in the spectra of the monoxides (III), but as a result of conjugation, they also have reduced frequencies 3350-3360 cm<sup>-1</sup>. In the spectra of the oxides obtained, there are bands characteristic of the epoxide ring 834-847 and 1240-1250 cm<sup>-1</sup>.

Conformation of Hydrided Derivatives of Naphthoquinone. The molecules of the mono-adducts (I), under the condition of cis-coupling [3], can exist in a conformation with two cyclohexene rings in the form of a half-chair or boat; in the latter case, the different orientation of the olefin fragment is responsible for the possibility of four steric structures (Fig. 1). In the conformation 1, the geometry of the rings was assumed according to [7]; the carbonyl groups were considered to lie in the plane of the  $C_{Sp^3} - C_{Sp^2}$  and  $C_{Sp^2} - C_{Sp^2}$  bonds and to be oriented along the bisectrix of the angle between them. The geometry of the cyclohexene and cyclohexenedione rings in the form of a boat was considered earlier [1, 8]. In the calculation we used the scheme of vector additivity of the moments and tensor additivity of the axes of the ellipsoids of polarizability of the bonds and groups, cited in [1]. The molecules were oriented in the system

of coordinates as shown in Fig.1. Summation gives the calculated moments and Kerr constants cited in Table 1.

The experimentally determined dipole moments of the adducts (Ia), (Ib), and (Ic) were equal to 0.40, 0.33, and 0.76 D, the molar Kerr constants to 101, 130, and  $128 \cdot 10^{-12}$ , respectively. A comparison with the calculated moments (see Table 1) definitely indicates that in the molecules of the mono-adducts, the sixmembered rings take the form of a half-chair, just as in the other investigated compounds of the cyclohexene series. Only the Kerr constants calculated for this structure, just like the experimental values, have a positive sign; however, the discrepancy in absolute value is substantial.

Conformation of Oxides of Mono-Adducts of Quinone. The stereochemistry of the oxidation of the adducts (I) was not investigated earlier, nor was the conformation of the molecules of the epoxides (III) formed. The only attempt to determine the steric structure of certain derivatives of quinones on the basis of the PMR spectra [6] was unsuccessful, evidently as a result of a lack of consideration of the coplanarity of the bonds in the rings. In the oxidation of the mono-adducts (I), an oxygen atom can be introduced from the side of the neighboring ring or from the opposite side, forming cis- or trans-oxides (III). We investigated derivatives of divinyl and isoprene (IIIa) and (IIIb). The dipole moment and Kerr constant of (IIIc) were not measured as a result of the very low solubility of the product in  $CCl_4$ . The same pertains to the dioxide (IVc). The bicyclic system in each case can have the same conformations as the molecules of the initial adducts; the possible steric structures of the oxides are given in Fig.2. In calculations of the dipole moments and Kerr constants, it was assumed that the epoxide ring forms an angle of  $102^{\circ}$  with the plane of the C-C bonds adjoining it, just as in cyclohexene oxide [9], and that the geometry of the skeleton of the molecule is

### TABLE 3. Synthesized Epoxy Derivatives

Compound	Yield,%	Mp, ℃	Found, %		Calculated, %	
			С	Н	С	Н
<ul> <li>2,5-Dioxo-8:9-epoxy-8-methylbicyclo-[4, 4, 0]-3-decene (IIIb).</li> <li>2,5-Dioxo-8:9-epoxy-8,9-dimethylbicyclo-[4, 4, 0]-3-decene (IIIc).</li> <li>2,9-Dioxo-5:6, 12:13-diepoxy-5,12-dimethyltricyclo-[8, 4, 0, 0<sup>3:8</sup>]-textedecane (Vb).</li> </ul>	65	102	68 <b>.</b> 64	6.35	68.73	6.29
	60	145	69.63	6.92	69.88	6.84
2,9-Dioxo-5:6, 12:13-diepoxy-5, 6, 12, 13-tetramethyltricy-	40	225	69.32	7.25	69.54	7.30
clo-[8, 4, 0, 0 <sup>3,8</sup> ]-tetradecane (Vc)	60		71.22	8.02	71.02	7.95

TABLE 4. Dipole Moments and Molar Kerr Constants of the Investigated Compounds

Com- pound	ae <sub>o</sub>	β	Y	δ	μ, D	m <sup>K•1012</sup>
Ia Ib Ic Ila Ilb Ilc IIIa IIIb Va Vb	0,761 0,558 0,912 1,176 0,875 0,597 1,922 2,787 1,931 1,104	$\begin{array}{c} 0,705\\ 0,194\\ 0,116\\ 0,227\\ 0,305\\ 0,333\\ 0,855\\ 0,597\\ 0,881\\ 0,775\\ \end{array}$	$\begin{array}{c} 0,434\\ 0,441\\ 0,073\\ 0,564\\ 0,628\\ 0,077\\ 0,122\\ 0,002\\ 0,407\\ 0,331 \end{array}$	$\begin{array}{c} 82,184\\ 99,000\\ 90,750\\ 100,728\\ 74,934\\ 71,661\\66,310\\105,321\\ 13,485\\ 17,838\end{array}$	0,40 0,33 0,76 0,80 0,53 0,60 1,51 1,66 1,78 1,30	$\begin{array}{c} 101\\ 130\\ 128\\ 163\\ 136\\ 147\\ -139\\ -237\\ 36\\ 74 \end{array}$

not changed significantly when the double bond is replaced by an oxide ring. The parameters of polarizability of the epoxide ring and neighboring C-Cbonds used in the calculations are cited in [2]. The orientation of the system of coordinates is shown in Fig. 2. Since the polarity of ethylene oxide and its homologs is practically constant, the calculated dipole moments of the epoxy-derivatives (IIIa) and (IIIb) are equal (Table 2). Data on the anisotropy of the polarizability of the conformers, obtained by tensor summation of the ellipsoids of the bonds and groups, are cited in Table 2.

The experimentally determined dipole moment of the derivative of butadiene (IIIa) is equal to 1.51 D, that of isoprene (IIIb) 1.66 D; the molar Kerr constants are -139 and  $-237 \cdot 10^{-12}$ . A comparison of them with those calculated (Table 2) permits us to conclude that the oxides have a trans-configuration. Actually, of the moments calculated for the cis-structure, only the moment of the conformation 5 agrees with the experiment (all the others have considerably larger values), but for this form the Kerr constants are positive, which contradicts the experimental data.

A consideration of the theoretical parameters of the trans-structures shows that the molecules cannot exist entirely in form 1 (half-chair-half-chair), since the Kerr constants calculated for it are positive. Only conformations 5 have negative constants of sufficient magnitude (below the experimental values). Thus, a form possessing the following characteristic structural features participates in the equilibrium: the epoxy cyclohexane ring has a boat conformation, as was previously found for terpinolene oxide [10] and cis-dicyanocyclohexene oxide [11]. Moreover, the  $C_{sp^3} - C_{sp^3}$  bonds have a syn-orientation with respect to the epoxide ring; the double bond in the other ring also has a syn-orientation with respect to the epoxided ring. Such a structure is analogous to that found for mono-adducts of p-benzoquinone with cyclic dienes and their monoxides [1,2]. An explanation for its stability can be found in a consideration of the mutual arrangement of the bonds. A calculation of the energy of orientation of the orbitals, corresponding to rotation around the bonds adjoining the oxide ring, considering the bending of the bonds of the latter [12], gives 3.3 kcal/mole for the half-chair 1, 0.1 kcal/mole for the syn-boats 2 and 5, and 4.7 kcal/mole for the anti-boats 3 and 4. In addition, the boat forms possess an energy corresponding to the shielded conformation of the bond common to the two rings (~2.9 kcal/mole). Thus, in epoxycyclohexanes a cis-boat may be no less energetically stable than a half-chair. In the case under consideration, the latter should be somewhat destabilized on account of the axial position of one of the carbonyl groups (see Fig. 2). At the same time, conformations 3 and 4 (anti-boat) should possess a supplementary energy of Van der Waals repulsion of the atoms of the two six-membered rings. The moment and Kerr constants, calculated for conformations 5, significantly exceed the experimental values. Consequently, this form exists at equilibrium with a less polar form. Moments lower than the experimental values were calculated for the conformations 1 (half-chair-half-chair) and 2. It is impossible to select between them; the possibility remains that a conformational equilibrium is established among the three steric structures. The dipole moments correspond to a content of  $\sim 10-20\%$  of form 5 in both cases.

<u>Conformation of Bis-Adducts of p-Benzoquinone</u>. The question of the conformation of bis-adducts of p-benzoquinone with acyclic dienes (II) and their epoxy-derivatives (V) is more complex. The central ring in them has a 1,4-cyclohexanedione structure, for which a twist-form with noncolinear carbonyl groups was found (the angle between them is 152-156°) [13-15]. On the basis of the dipole moments, the same conformation has been proposed for substituted cyclohexanediones, including perhydroanthraquinones, structurally similar to the investigated bis-adducts [14]. A certain decrease in the moments (to 1D) may be evidence of an approach to the undistorted twist-form. Unquestionably, the closeness of the dipole moments cannot be an unambiguous confirmation of the structure; for example, in perhydro-5:8-methanonaphtho-quinone, the dione ring cannot exist in a twist-conformation, although its moment is close to the moment of cyclohexanedione (1.47 and 1.31 D [14]). The dipole moments of the bis-adducts (IIIa-c) are equal to 0.80, 0.53, and 0.60 D, respectively. If we assume that the central ring in them has the same conformation as 1,4-cyclohexanedione, then with a value of the C = O dipoles of 3.15 D (from the data of [14]), the moments correspond to an angle between them of 165-170°. It is evident that the structural changes even of fragments far removed from the central ring have an appreciable influence on its steric structure.

The introduction of two oxygen atoms (for an annular-trans-configuration of the carbon skeleton) can lead to a cis-cis, trans-trans, or trans-cis structure



The dipole moments were calculated using molecular models, on the assumption that the central ring has a distorted twist-form. A molecule with a cis-trans arrangement of the oxygen atoms can exist in two conformations. In the calculation we used the total moments of the two carbonyl groups, equal to the experimental dipole moments of the bis-adducts (IIa) and (Ib), and the group moment of the epoxide ring 2.08 D (the experimental dipole moment of cyclohexene oxide [16]). Calculation shows that the cis-cis and trans -trans structures should have moments of  $\sim 2.0-2.5$  D (selection between them is impossible) the trans -cis structure should have a dipole moment of  $\sim 3.0$  or 3.6 D. The experimental dipole moments of the diepoxides (Va) and (Vb) are lower than those calculated (1.30 and 1.78 D). Evidently the conformation of two methyl groups produces an appreciable distortion of the structure. The Kerr constants of bis-adducts of the quinone (II) and their oxides (V) were not discussed as a result of the great indeterminacy of the steric arrangement of the atoms.

#### EXPERIMENTAL

Adducts of p-benzoquinone with butadiene, isoprene, dimethylbutadiene, and oxides of butadiene derivatives were produced according to the methods of [4, 17-21]. The adducts had the following melting points: (Ia) 56°, according to the data of [17]: 58°; (Ib) 82-83°, according to the data of [18]: 79°; (Ic) 116°, according to the data of [19]: 116°; (IIa) 151°, according to the data of [20]: 154-155°; (IIb) 169-170°, according to the data of [21]: 170-171°; (IIc) 195°, according to the data of [17]: 194°, [22]: 202-203°; (IIIa) 94-95°, according to the data of [4]: 96-97°; (Va) 179°, according to the data of [4]: 185-186°.

Epoxy derivatives of adducts of isoprene and dimethylbutadiene were synthesized analogously [4]. The yields of the reactions, melting points of the products, and data of the analyses are cited in Table 3.

The dipole moments and molar Kerr constants were determined analogously [23]. The coefficients of the calculation equations and resultant data are cited in Table 4. The measurements for the adducts (I) and (II) were performed in  $CCl_4$ , and for the epoxides (III) and (V) in dioxane.

#### CONCLUSIONS

1. The dipole moments and molar Kerr constants of mono- and bis-adducts of p-benzoquinone with butadiene, isoprene, dimethylbutadiene, and some of their epoxy derivatives were determined.

2. Epoxidation of the mono-adducts gives trans-oxides; the mono-adducts exist in a half-chair-half-chair conformation; for their monoxides one of the stable conformations is the boat-boat conformation.

## LITERATURE CITED

- 1. B. A. Arbuzov, L. A. Grozina, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2370 (1969).
- 2. B.A.Arbuzov, L.A.Grozina, and A.N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2377 (1969).
- 3. A.S.Onishchenko, Diene Synthesis [in Russian], Izd-vo AN SSSR (1963), pp. 39, 108, 112, 144.
- 4. B. A. Arbuzov, Z. G. Isaeva, and E. G. Kamaev, Uch. Zap. Kazansk. Un-ta, 110, No. 9, 175 (1950).
- 5. K. Nakanisi, Infrared Spectra and Structure of Organic Compounds [Russian translation], Mir (1965), p. 51.
- 6. M. F. Ansell, J. W. Lown, D. W. Turner, and D. A. Wilson, J. Chem. Soc., 3036 (1963).
- 7. E.J. Corey and R.A. Sneen, J. Amer. Chem. Soc., 77, 2505 (1955).
- 8. A. N. Vereshchagin, A. P. Anastas'eva, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 995 (1970).
- 9. Tables of Interatomic Distances and Configurations, L.E. Sutton (editor), London (1958).
- 10. B.A.Arbuzov, R.P.Arshinova, S.G. Vul'fson, I.S.Andreeva, and A.N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 1960 (1970).
- 11. A. N. Vereshchagin, A. P. Anastas'eva, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 752 (1971).
- 12. A.N. Vereshchagin and O.N. Nuretdinova, Izv. Akad. Nauk SSSR, Ser. Khim., 1715 (1970).
- 13. P. Groth and O. Hassel, Proc. Chem. Soc., 218 (1963).
- 14. A. Mossel, C. Romers, and E. Havinga, Tetrahedron Letters, 1247 (1963).
- 15. N. L. Allinger and L. A. Freiberg, J. Amer. Chem. Soc., 83, 5028 (1961).
- 16. A. N. Vereshchagin, A. P. Anastas'eva, and S. G. Vul'fson, Izv. Akad. Nauk SSSR, Ser. Khim., 559 (1969).
- 17. Swiss Patent No. 143258-264, Chem. Zbl., 1, 2937 (1931).
- 18. A. A. Demidov and A. P. Terent'ev, Uch. Zap. Mosk. Un-ta, 21, 237 (1941).
- 19. M. Lora-Tamayo and J. L. Leon, J. Chem. Soc., 1499 (1948).
- 20. K. Alder and G. Stein, Ann., 501, 247 (1933); Chem. Abstrs., 27, 2441 (1933).
- 21. O. Diels and K. Alder, Ber., 62, 2337 (1929).
- 22. G. T. Morgan and E. A. Coulson, J. Chem. Soc., 2329 (1931).
- 23. A.N. Vereshchagin and L.A. Grozina, Teoret. i Éksperim. Khimiya, 4, 361 (1968).