STUDY OF CONFORMATION OF SOME EPOXIDATED CYCLOHEXANES

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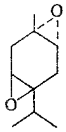
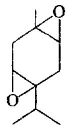
Six-membered rings with two planar groupings, which are formed by double bonds or by condensation with small flat rings in the 1,4 positions, can exist only in the conformations of a bathtub, which are characterized by a variable angle of bending. When the polarization and anisotropy of the polarizability of such compounds are studied a number of important problems, dealing with their spatial structure, is touched upon. Thus, when discussing the dipole moments (DM) for the derivatives and analogs of trans-tricyclo-$[5.1.0.0^{3,5}]$octane it was assumed that the central six-membered ring is planar [1, 2]. However, resort to the methods of double refraction in an electrical field (Kerr effect) and the Rayleigh scattering of light made it possible to conclude that the cyclohexane ring exhibits substantial curvature [3]. While studying some derivatives of the cis-series it was unexpectedly found that the syn – syn bathtub conformation is stable even in such a sterically overloaded molecule as Δ^3-carene β-oxide [4-6]. A similar structure was also established for the oxide of 4-cyclohexene-1,2-dicarboxylic anhydride, which has a cis-configuration [7].

When the studies were extended to other compounds of analogous structure it seemed of special interest to study pairs of isomers with a cis- and trans-orientation of two identical small rings relative to the six-membered ring. We examined the polarity and polarizability of the trans-(I) and cis-(II) γ-terpinene dioxides [8].



(I)



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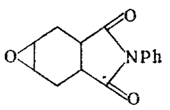
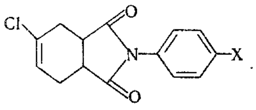
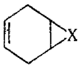


(III)



(IV), (V)



(VI), (VII)

For (I) it is necessary to find the degree of curvature of the cyclohexane ring. Such a possibility ensues from a comparison of the experimental DM (in benzene 1.34 [8] and in CCl_4 0.99 D) and those calculated for various spatial structures. (An examination of the molecular anisotropy of the polarizability is made difficult due to the possible rotation of the irregular isopropyl group.) The main problem is interpreting the DM when measured in solutions and the value of the atomic polarization [1, 3]. Following the considerations given in [3], a comparison was made of the DM, Kerr constants (KC), and Rayleigh scattering of light. The molar KC of (I) is equal to $7.0 \cdot 10^{-12}$, which corresponds to the sum of the anisotropic and dipole terms $\theta_1 + \theta_2 = 1.674 \cdot 10^{-35}$. The molecular anisotropy, found from the degree of depolarization of scattered light, $\gamma^2 = 3.708$ Å^6, can be used directly to calculate θ_1 ($\theta_1 = 0.204 \cdot 10^{-35}$). Consequently, the KC is determined mainly by the dipole term $\theta_2 = 1.470 \cdot 10^{-35}$, which is possible only when the group

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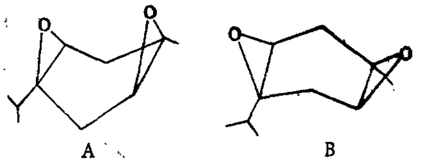

Fig. 1

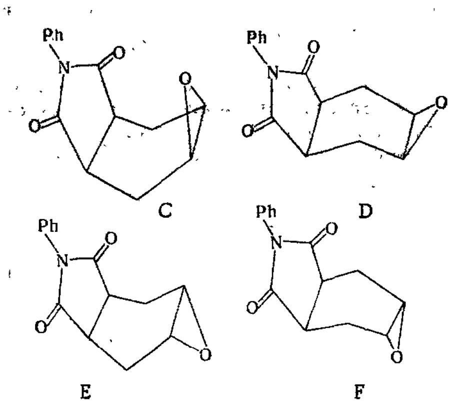

Fig. 2

Fig. 1. Possible conformations of cis-γ-terpinene dioxide.

Fig. 2. Possible spatial structures of (III): C and D) cis; E and F) trans.

moments of the epoxide rings are noncollinear, i.e., when the cyclohexane ring has a substantial noncoplanarity, as in the case of trans-1,4-cyclohexadiene dioxide [3]. When using the parameters given in [3], the experimental DM of 0.99 D corresponds to a dihedral angle of 150° between the planes in which the atoms of the six-membered ring lie, which is close to the results of 150-160° for the tricyclooctanes and cyclohexadiene dioxide [3].

Under the condition of retaining the degree of curvature of the central ring, two stable conformations, syn – syn (A) and anti – anti (B), can be depicted for (II) (Fig. 1). The experimental DM (in benzene 4.37 [8] and in CCl_4 4.26 D) is close to the possible maximum 4.16 D, which is achieved when the planes of the two three-membered rings lie in parallel. This is possible only in conformation A, where the cyclohexane ring has a curvature angle of 156°.

As was mentioned above, a cyclohexane ring that is cis-1,4 condensed with an oxide and a dimethylcyclopropane ring [4-6], or an oxide and a five-membered anhydride ring [7], has a similar shape. Structures of the latter type are formed as the result of the stereochemically rare cis-epoxidation of 4,5-disubstituted cyclohexanes [7, 9, 10]. The predominant cis-epoxidation of cyclohexenedicarboxylic acid N-phenylethylimide [10] made it possible to expect a cis-configuration for (III). In any case, due to the nonidentity of the fragments condensed with the central ring, two conformations of the molecule are possible (Fig. 2).

The DM of the imide ring is equal to the experimental value of 1.69 D for N-phenylsuccinimide [11], and it is oriented along the axis of symmetry of the imide ring [12]. In structures D – D the angle between these DM and the moment of the oxide ring, with an angle of 120° between the planes of the imide ring and the adjacent bonds, and the other geometric parameters the same as in [7], is equal to 102°, while in structure C it is 18°. The experimental value of 3.62 D corresponds to an angle of 15° between the dipoles. As a result, we obtain a cis-configuration and a syn – syn conformation for bathtub (III), the same as for the corresponding anhydrides [7].

In this connection it is interesting to examine the conformation of the six-membered ring in the imides of 4-cyclohexene-1,2-dicarboxylic acid. Based on the DM and KC, an equilibrium of the syn and anti bathtub was established for their anhydrides, with a predominance of the former [7, 13]. The insertion of a chlorine atom at the double bond has little effect on the position of the equilibrium, but it does permit using the DM method to determine the structure. Their determination and the calculations by the additive vector scheme were made for the N-phenyl-(IV) and N-p-chlorophenylimides (V) of 1-chlorocyclohexene-4,5-dicarboxylic acid. The group moment of the N-p-chlorophenylimide ring, equal to the experimental DM value of 3.32 D for the corresponding succinimide [11], was used for (V). The calculations were made for the syn and anti bathtub conformations, the structure of which is the same as in the analogous anhydrides [13]. The calculation results, the experimental DM, and the amount of the syn form in each case, which was calculated using Eq. (1), are given in Table 1.

$$\mu^2_{\text{syn}}\cdot n_{\text{syn}}+\mu^2_{\text{anti}}\cdot n_{\text{anti}}=\mu^2_{\text{expt}} \qquad (1)$$

TABLE 1. Dipole Moments (D) of Imides of Chlorocyclohexenedicarboxylic Acid

Compound	Conformation (calculation)		Experiment	syn
	syn	anti		
(III)	3,03	1,36	2,40	0,54
(IV)	4,23	0,85	3,30	0,59

TABLE 2. Polarity and Polarizability of Dihalobicycloheptenes

Compound	Conformation (calculation)		Experiment
	syn	anti	
(VI) μ, D	2,03	1,60	2,14
$_mK\cdot10^{12}$	21,0	35,0	23,0
(VII) μ, D	2,30	1,90	1,97
$_mK\cdot10^{12}$	38,0	65,0	38,0

TABLE 3. Dipole Moments and Kerr Constants

Compound	$\alpha\varepsilon_0$	β	γ	δ	μ, D	$_mK\cdot10^{12}$
(I)	1,208	—0,450	0,044	4,667	0,99	7,0
(II)	21,149	—0,449	0,072	—196,72	4,26	—263,0
(III)	—	—	—	—	3,62	—
(IV)	2,547	—	0,154	—	2,40	—
(V)	4,514	—	0,525	—	3,30	—
(VI)	5,781	0,456	0,238	18,937	2,14	23,0
(VII)	3.615	0,715	0,303	19,944	1,97	38,0

The good agreement of n_{syn} for the two compounds (a chlorine atom in the p-position of the benzene ring does not affect the conformational equilibrium [14]) confirms the validity of the parameters used in the calculation. The free energies of the two conformers are nearly equal; only a very slight preference of the syn-bathtub can be noted. This preference is expressed more stongly for the corresponding more polar anhydride [13], although the steric conditions are the same. Evidently, the relative stability in the diaxial (syn) and diequatorial (anti) conformations is different for different rings that are condensed with the cyclohexane ring. If equilibrium is observed for polar five-membered planar rings, then the cyclopropane fragment in 3-carene completely stabilizes the syn-bathtub [15, 16]. For comparison we examined the structure of the cyclohexane fragment in molecules that contain a three-membered ring with polar substituents: 7,7-dichloro-(VI) and 7,7-dibromobicyclo [4,1,0]-3-heptene (VII). The DM and molar KC were calculated for two of the conformers. Here we used the geometry of the carbon skeleton that was determined by electron diffraction for 3-carene [15], and the parameters of the gem-dihalo fragments taken from [17]. The calculation results and the experimental data are given in Table 2.

We will mention that a difference in the orientation of a weakly polar unsaturated grouping does not create a difference in the DM that is sufficient to identify their structure. A greater difference was observed for the KC of two conformers, in which connection the values calculated for the syn-bathtub coincide with the experimental values. To obtain unequivocal results it is necessary to study compounds that contain polar substituents at the double bond.

EXPERIMENTAL METHOD

The trans-(I) and cis-(II) γ-terpinene dioxides were obtained by the epoxidation of γ-terpinene with peroxybenzimidic acid [8]. 4,5-Epoxycyclohexane-1,2-dicarboxylic acid N-phenylimide (III) was obtained in 80% yield by the oxidation of the corresponding unsaturated imide with peracetic acid, mp 220-222°. Found: C 68.75; H 5.70; N 6.00%. $C_{14}H_{13}NO_3$. Calculated: C 69.12; H 5.38; N 5.75%. Adducts (IV) and (V) were synthesized by the diene condensation of chloroprene with the N-phenyl- and N-p-chlorophenylimides of maleic acid. The yield of (IV) was 60%, and mp 109°. Found: C 69.98; H 4.52; N 4.48; Cl 10.82%. $C_{14}H_{12}NO_2Cl$. Calculated: C 71.10; H 4.77; N 4.14; Cl 10.51%. The yield of (V) was 55%, and mp 162°. Found: C 64.40; H 3.57; N 4.08; Cl 19.50%. $C_{14}H_{11}NO_2Cl_2$. Calculated: C 64.68; H 3.80; N 3.77; Cl 19.12%. Compounds (VI) and (VII) were synthesized as described in [18, 19].

The DM and molar KC were determined in CCl_4 at 20° the same as described in [3, 7]. The results of the measurements are given in Table 3. For (I) the molecular anisotropy from the data of Rayleigh scattering under the same conditions is: $A = 0.023$, $D = -0.776$, $\delta^2_\infty = 1.327\cdot10^{-3}$.

CONCLUSIONS

1. The cyclohexane ring, 1,4-condensed with two small rings, exists in two forms: in a nonplanar form with a trans-orientation of the rings, and in the conformation of a syn – syn bathtub with a cis-orientation.

2. The N-phenylimide of cis-4-cyclohexene-1,2-dicarboxylic acid is epoxidated in the cis-position.

3. In solutions the imides of cyclohexenedicarboxylic acids are represented by equilibrium mixtures of the syn- and anti-bathtub conformations.

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