The investigation of the steric orientation of aromatic radicals bonded to an oxirane ring is interesting from the standpoint of establishing the principles of internal rotation around carbon—carbon bonds adjoining the three membered ring, in particular, for elucidating the question of the steric possibilities of conjugation of aromatic systems with the orbitals of the bonds of these rings. It is known that phenylcyclopropane exists in a "bisector" conformation with orthogonal planes of the aryl and three-membered ring [1, 2], but the introduction of substituents causes appreciable distortions of the structure [3-6]. For heteroanalogs it might be expected that the disruption of symmetry of the three-membered ring will also lead to deviations from the "bisector" form. Precise structural data are available only for 1-(p-bromo-phenyl)-1,2-epoxycyclohexane in the crystalline phase [7]. The two-faced angle between the planes of the phenyl and oxide rings is equal to 83°, which corresponds to rotation by 14° from the bissector formed; unfortunately, the direction of the rotation is not indicated in [7].

There are no data for free molecules. The structure of compounds of this type has been insufficiently studied on account of the difficulty of the exact determination of the position of the aryl radicals in space. It has been shown in a number of studies that such data can be obtained on the basis of an analysis of the Kerr constants (KC), since aromatic systems possess substantial anisotropy of the polarizability [3, 6]. We used this method to study the conformation of aryloxiranes, with oxides of trans-stilbene and its derivatives (I)-(III) as examples:

The selection of these objects is dictated by the symmetry of the molecules, at least without consideration of the rotation of the phenyl radicals, and by the determined direction of the dipole moments (DM). In all cases in the calculation of the molar KC they were oriented along the axis of symmetry of the oxirane ring, and in absolute magnitude were considered equal to those determined experimentally. This minimizes the errors of calculation associated with the indeterminacy of the moments used. The calculations were performed using the geometrical parameters of the oxirane ring cited in [8] and the following components of the tensors of polarizability of the groups: the oxirane ring — $b_1$ (along the axis of symmetry) 1.41 Å³, $b_2$ (in the plane of the ring) 1.19 Å³, $b_3$ 2.15 Å³; the C—C bond adjoining it $b = 0.77$ Å³, $v_v = b_1 = 0.36$ Å³ [9], phenyl radical $b_1 = b_2 = 10.56$ Å³, $b_3 = 6.71$ Å³ [10], the C—CN group $b_1 = 4.03$ Å³, $b_3 = 1.54$ Å³ [10]; the C—H bonds were considered isotropically polarizable [10], and they were not considered in the calculation (with the exception of the C—H bonds included in the phenyl radicals).

In the calculation of the components of the molecular ellipsoids of polarizability, the components were summed over the axes of the system of coordinates, oriented as shown in Fig. 1. In this case the
Fig. 1. Orientation of diphenyloxirane molecules in the system of coordinates.

Fig. 2. Dependence of the Kerr constant of compound (I) on the rotation of the phenyls.

The contribution of the oxirane ring to the diagonal elements of the tensor of polarizability $b_{xx}$, $b_{yy}$, $b_{zz}$ is determined by the axes $b_1$, $b_2$, $b_3$, respectively. The contribution of each phenyl radical (together with the C–C bond) is expressed by the equations

\[
\begin{align*}
    b_{xx} &= 11.233 - 3.029 \cos^2 \varphi + 2.157 \sin \varphi \cos \varphi \\
    b_{yy} &= 0.207 + 1.948 \cos^2 \varphi - 2.152 \sin \varphi \cos \varphi \\
    b_{zz} &= 10.773 + 1.082 \cos^2 \varphi \\
    b_{xy} &= -2.74 + 2.182 \cos \varphi - 2.445 \sin \varphi \cos \varphi \\
    b_{xz} &= 0.667 - 0.610 \cos \varphi - 1.909 \sin \varphi \cos \varphi \\
    b_{yz} &= 1.792 - 1.620 \cos \varphi + 0.720 \sin \varphi \cos \varphi
\end{align*}
\]

The Kerr constant of compound (I) calculated on the basis of these values and the molecular DM is a function of the rotation of the phenyl radicals. The bissector conformation is taken as the initial position (see Fig. 1), and the positive direction is considered to be that in which the ortho-hydrogen atom found below the ring moves in the direction of the oxygen atom. Trans-oriented phenyl radicals do not interact sterically and have the same surroundings, which gives a basis for assuming an identity of their conformations.

The dependence of the calculated KC of compound (I) on the angle of rotation of the phenyls $\varphi$ is presented in Fig. 2. It coincides with the experimental value at $\varphi = 22$ and 122°. An analysis of the molecular structure shows that at $\varphi = 122^\circ$, the ortho-atoms interact strongly with the CH$_2$ group of the three-membered ring, which makes such a structure impossible. Consequently, a selection can be made in favor of the conformation characterized by rotation of the phenyls by 22° from the bissector orientation. To determine the factors responsible for it, we compared the energies of the conformers with $\varphi = 0$ and 22°, calculated considering steric interactions of the ortho-hydrogen atoms and carbon with the O, C, H$_1$, and H$_2$(cis) atoms according to the method of [11] and the electrostatic interactions (in the approximation of point dipoles) between the dipoles of the oxirane ring [9] and the C–H bond, on the one hand, and the C$_{sp^2}$–H bonds in the ortho-positions of the phenyl, on the other. For one phenyl of the molecule at $\varphi = 0^\circ$, the energy of steric interaction is $-1.23$ kcal/mole, that of electrostatic interaction $-0.14$ kcal/mole; at $\varphi = 22^\circ$ these energies are equal to $-1.57$ and $-0.36$ kcal/mole, respectively. Thus, the somewhat distorted conformation in comparison with the bissector conformation is 0.84 kcal/mole more profitable on account both of steric and of dipole interactions; moreover, the contribution of the latter to the energy change is the basic one.

In view of this, it is interesting to consider the steric structure of compound (II), in which the polarity of the substituent in the geminal positions to the phenyls is substantially increased, and the direction of the dipoles is changed. The configuration of the molecules was determined on the basis of the DM. For the cis-structure according to an additive scheme using the DM of the cyano group 3.38 D (from the experimental value 3.65 D for tert-butyl cyanide) we calculated a moment of 6.49 D, and for a trans-structure 0.49 D. The experimental value 0.32 D agrees with the latter. The molar KC as a function of the rotation of the phenyls is expressed by the equation

\[
\kappa K = 45.90 + 32.40 \sin \varphi \cos \varphi - 31.26 \cos^2 \varphi - 72.43 \cos^3 \varphi \sin \varphi + 24.93 \cos^4 \varphi
\]