In the previous articles of this series, we proposed a method of estimating the anisotropy of the polarizability of bonds and atom groups from data on the specific rotation of optically active molecules, and we used these results to find polarizability ellipsoids (PE) of cyclopropane and oxirane rings [1, 2]. This paper presents a calculation of the PE of the C=C double bond and the C=C bonds of the cyclobutane ring (CBR) from the optical rotation of pinene series compounds, α-pinene (I), trans-δ-pinene (II), and apopinene (III).

As preliminary analysis has shown, the correct use of the Kirkwood–Vol’kenshtein electrostatic model in optically active molecules requires a special accounting of optical rotation scatter within the scope of the theory.

Gyration Scatter. The equation relating the specific rotation \( [\alpha]_\lambda \) with the gyration \( g_\lambda \) [1]

\[
[\alpha]_\lambda = 2.880 \cdot 10^4 \frac{\pi^2 \lambda}{M \lambda^2} \left( \frac{n_k^2 + 2}{3} \right) g_\lambda
\]  

assumes that the latter is determined from the anisotropy of the polarizability of the oscillating bonds at the wavelength \( \lambda \) for which \([\alpha]_\lambda \) is calculated:

\[
g_\lambda = \frac{1}{6} \sum \gamma_{ik} v_{ik} T_{ik}
\]  

where \( T_{ik} \) is a parameter that describes the mutual orientation of the \( i \)-th and \( k \)-th bonds; \( \gamma = b_L - b_T \) (\( b_L \) and \( b_T \) are the longitudinal and transverse bond polarizabilities, respectively).

It is customary to plot a valence-optical diagram for the electron polarizabilities extrapolated to infinite wavelength (\( \lambda \to \infty, \nu \to 0 \)).

The relationship between the polarizability anisotropy found at a definite wavelength (\( \gamma_\lambda \)) and the anisotropy extrapolated to infinite wavelength (\( \gamma_\infty \)) is described by Eq. (3) [3]:

\[
\gamma_\lambda = \gamma_\infty \frac{\nu_\lambda^2}{\nu_\infty^2 - \nu^2} = \gamma_\infty \frac{\lambda^2}{\lambda_\infty^2 - \lambda^2}
\]  

where \( \nu \) is the frequency of the incident light; \( \nu_\infty \) is the resulting characteristic absorption frequency.

This gives us the scatter equation for the gyration \( g_\lambda \):

\[ g_\lambda = \frac{1}{6} \sum \frac{\lambda^2}{\lambda_\infty^2 - \lambda^2} \gamma_\infty \frac{\lambda^2}{\lambda_\infty^2 - \lambda^2} \gamma_{ik} T_{ik} \]  

Consequently, if the intensity of the chromophores in the molecule is comparable, it is
TABLE I. Refractive Indices, Molecular Refractions, and Lorentz Field Functions vs. Wavelength

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\lambda_o$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>488.1</td>
</tr>
<tr>
<td>$n^2$</td>
<td>1.4746</td>
</tr>
<tr>
<td>MR, cm$^3$</td>
<td>44.88</td>
</tr>
<tr>
<td>$(n^2+2)/3$</td>
<td>1.3845</td>
</tr>
</tbody>
</table>

necessary to account for the absorption of each bond. When $\lambda_0 \ll \lambda$ and $\lambda_0 \ll \lambda$, Eq. (4) is transformed to the original Eq. (2). If the molecule contains only one intense chromophore ($\lambda_0 \ll \lambda$), then

$$g = \frac{1}{6} \frac{\lambda^2}{\lambda^2 - \lambda_0^2} \sum \gamma_i \gamma_i \gamma_i T_{ik}$$

Substituting Eq. (5) in Eq. (1), we obtain

$$[\alpha] = 2.880 \times 10^4 \frac{n^2N_A}{M (\lambda^2 - \lambda_0^2)} \left( \frac{n_0^2 + 2}{3} \right) g'$$

(6)

In this equation, $g'$ is not a function of wavelength, unlike $g$ in Eq. (1). In this case, we should consider the scatter of the refractive index. However, our analysis of the data from [4] on the relationship between the mean and anisotropic polarizability of the molecules and wavelength showed that values of $\lambda_0$ obtained from refraction are significantly lower than those obtained from polarizability anisotropy, i.e., the scatter of the function $(n^2 + 1)/3$ is much lower than that of $\gamma$. (This problem and the reason for its appearance will be discussed in a separate paper.) As far as the Lorentz field function is concerned, its scatter, as the calculations show, should be still lower than the refraction scatter. In this connection, we determined the molecular refraction of liquid (I) at three wavelengths and extrapolated according to Eq. (7) [5, p. 13]

$$(MR_\infty)^{-1} = (MR_o)^{-1} - (\lambda_0^2/\lambda_0^2) \lambda^2$$

(7)

to infinite wavelength. The values obtained are shown in Table 1 and the value of $\lambda_0$ found was 95.9 nm.

As we can see, the function $(n^2 + 2)/3$ is practically independent of $\lambda$; therefore, the scatter of this term may be neglected. In this case, Eq. (6) is analogous to a single-term Druda equation [6, p. 74]:

$$[\alpha] = \frac{A}{\lambda^2 - \lambda_0^2}$$

(8)

Consequently, if the molecule has one strong electron transition, we can use Eq. (6).

We studied the optical rotation scatter of (I) in the form of the liquid itself and solutions of different concentrations in cyclohexane at five wavelengths in the 366 to 578-nm range. Cyclohexane is considered to be a sufficiently inert solvent (it is nonpolar and practically isotropic), i.e., possible solvent–solute interaction is reduced to a minimum. It is possible to rule out interactions between the solute molecules by using the data for dilute solutions and the best results are attained by extrapolation to infinite dilution:

$$\left( \frac{d[\alpha]}{dc} \right)_{c=0} \cdot 10^4 = 10^4 \lim_{c=0} \frac{[\alpha]_2}{c_2} = \infty [\alpha]_2$$

(9)

In this equation, the subscript 12 refers to the solution, 2 to the optically active substance; $[\alpha]_2$ is the observed angle of rotation of the solution, corrected to a length of 1 dm. The specific rotation $\omega [\alpha]_2$ is determined as the slope of the concentration function if that function is linear. When the function $[\alpha]_2(c_2)$ is curvilinear, $\omega [\alpha]_2$ is determined as the slope of the tangent at $c = 0$. When measurements are made in an optically inactive solvent, the point with coordinates $c = 0$ and $[\alpha]_2 = 0$ can be used as a supplement. We derive the quantity $\lim_{c=0} \lambda_0(c_2) = \omega [\alpha]_2$ by extrapolation. Table 2 lists values of $\lambda_0$ calculated from Eq. (8) and $\omega$ for solutions of (I) in C$_6$H$_{12}$. The value of $\omega [\alpha]_2$ found by Eq. (9) is