# Chemistry

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1965

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## Abstract

## Full Text

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# Electron-Diffraction Study of the Structure of Molecules of $\Delta^3$-Carene Oxide

For $\Delta^3$-carene oxide two stereoisomers are known: the $\alpha$- and $\beta$-isomers. Both isomers boil at a temperature of $\sim 170^\circ$ and have $[\alpha]_D = +13.9$ and $[\alpha]_D = -1.40$ for the $\alpha$- and $\beta$-isomers, respectively. The two isomers can interconvert only with rupture of one C—O bond ([1]). In the present work an attempt has been made to determine the structure of these molecules.

The electron-diffraction investigation was carried out on an EG-100A electron diffractograph at various electron-accelerating voltages. The electron-diffraction patterns were interpreted by the radial-distribution method and by the method of successive approximations. The experimental intensity curves were obtained by photometry of electron-diffraction patterns of the vapors. However, because of the great complexity of the peaks on the radial-distribution curve (Fig. 1), the values $b_{ij} = 1/2l_{ij}^2$ (where $l_{ij}$ are the root-mean-square amplitudes of thermal vibrations of the atoms) entering into the equation $I_{\text{theor}}(s)$ were adopted on the basis of literature data. The quantities $b_{ij}$ were taken equal to: 0.0005 Å$^2$ for C—C and C—O distances; 0.0020 Å$^2$ for C . . . C and C . . . O distances between nonbonded atoms separated by one carbon atom; 0.0026, 0.0030, and 0.0040 Å$^2$ for C . . . C and C . . . O distances between nonbonded atoms separated, respectively, by two, three, and four atoms; 0.0026 and 0.0050 Å$^2$ for C—H and C . . . H (in CCH) distances, and, finally, 0.0062 Å$^2$ for the remaining C . . . H distances.

The conformation of the stereoisomers of $\Delta^3$-carene oxide had previously been studied by proton magnetic resonance ([2]). In that work it was established that the $\alpha$-form has a conformation in which one of the gem-dimethyl groups is located near the epoxy group, i.e., the cis form was proposed. For the $\beta$-form the trans form was adopted, in which there is no interaction of the protons of the methyl group with the epoxy ring. Similar results were also obtained in work ([3]). Of the possible spatial models of $\Delta^3$-carene oxide, the possible models are those shown in Fig. 2. In models I and II the cyclohexane ring has the form of a boat; in models IV and V, respectively, the form of a chair and a half-chair. In model III the atoms of the six-membered ring are coplanar. A model of a "twisted" boat is also possible (see, for example, ([4], [5])).

Fig. 1

Figure 1: Fig. 1

Fig. 2: structural models of the $\alpha$-form and $\beta$-form

Figure 2: Fig. 2: structural models of the $\alpha$-form and $\beta$-form

**Fig. 1**

In interpreting the experimental intensity curves of both forms of $\Delta^3$-carene oxide, all the indicated molecular models were considered. In accordance with the data of the radial-distribution curve, in constructing the theoretical intensity curves the valence angles C–C–C were ···

in the six-membered ring were varied from 114 to 120°. The angles $\alpha$ and $\beta$ were also varied ($\alpha$ and $\beta$ are the angles between the planes of the three-membered rings and the corresponding adjacent planes of the six-membered ring), which is equivalent to changing the distances $C_5 \ldots C_7$ and $O \ldots C_2$. It should be noted that, as was to be expected, the experimental intensity curves (and, correspondingly, the radial distribution curves) of the $\alpha$- and $\beta$-forms of $\Delta^3$-carene oxide are similar. An essential point in interpreting the electron diffraction patterns was the data of works ([2,3]). The theoretical intensity curves of models in which the cyclohexane ring has the chair and half-chair forms in the $\alpha$-isomer (analogous results were also obtained for the $\beta$-isomer) agree rather unsatisfactorily with the experimental curve (curves $a$, $b$, and $v$, Fig. 3). The parameters of the theoretical intensity curves presented in Fig. 3 are given in Table 1. For the half-chair model (curve $z$) the values of the angles $C_5H_4C_3$, $C_4C_3C_2$, and $C_3C_2C_1$ in the cyclohexane ring were taken as 118.5, 116, and 109.5°, respectively. The angles $OC_4C_3$ and $C_7C_4C_3$ were taken as 112 and 113°, respectively. It should be noted that spatial hindrances are observed in these models. Thus, the hydrogen atoms in the methyl group ($C_8$) and in the methylene group ($C_3$) are at distances of less than 2.0 Å. These spatial hindrances could have been reduced to a minimum by increasing the angle $\alpha$. However, serious difficulties then arise in interpreting the radial distribution curve. The value of $C_5 \ldots C_7$ would then be greater than 3.4 Å. Moreover, the theoretical intensity curves in this case are clearly not in agreement with the experimental curve (Fig. 3 gives only those curves which best correspond to the experimental curve).

**Fig. 2**

**Table 1**

**Parameters of the theoretical curves***

| Curve | $C-C$, Å | $C-O$, Å | $\angle CCC$ in the ring | $C \dots C_2$, Å | $C \dots C_5$, Å | $C_7 \dots C_4$, Å | Curve | $C-C$, Å | $C-O$, Å | $\angle CCC$ in the ring | $C \dots C_2$, Å | $C \dots C_5$, Å | $C_7 \dots C_4$, Å |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *a* | 1.53 | 1.42 | 118° | 3.45 | 3.45 | 2.55 | *e* | 1.53 | 1.42 | 118° | 3.40 | 3.40 | 2.55 |
| *b* | 1.54 | 1.44 | 114° | 3.40 | 3.40 | 2.56 | *zh* | 1.53 | 1.42 | 118° | 3.43 | 3.44 | 2.55 |
| *v* | 1.54 | 1.42 | 120° | 3.35 | 3.35 | 2.55 | *z* | 1.53 | 1.42 | 119° | 3.40 | 3.40 | 2.56 |
| *d* | 1.54 | 1.42 | 120° | 3.40 | 3.35 | 2.59 | *i* | 1.53 | 1.42 | 119° | 3.38 | 3.38 | 2.57 |

* For all curves $\angle C_8C_7C_9 = 118°$, $r(C-H) = 1.10$ Å, $r(C \dots H) = 2.14$ Å (in the CCH group).

The spatial hindrances in models of types IV and V can be reduced by taking the six-membered ring to be planar. In this case the distances between the indicated hydrogen atoms, with a reasonable interpretation of the radial distribution curve, are 2.1-2.2 Å, which is still less

sums of the van der Waals radii. The theoretical intensity curves for such a model (curves *g* and *d*, Fig. 3) agree rather satisfactorily with the experimental curve, except for minimum 7. It should be noted that the regions of $I_{\text{theor}}(s)$ most sensitive to changes in the parameters are the region of $s$ from 14.0 to 15.0 $Å^{-1}$ and the region of minimum 7.

Of the possible models of the molecule of $\Delta^3$-carene oxide, the remaining one is the model in which the cyclohexane ring has the bath form. As calculations of the theoretical intensity curves have shown, model I (curves *z* and *i*) agrees best with the experimental curve, although model II (curves *e* and *zh*) cannot be rejected on the basis of the electron-diffraction experiment alone. It is curious to note that the best agreement with the experimental data is observed for such models in which the angle C–C–C in the six-membered ring is 118-119°, i.e., the deviation of the cyclohexane skeleton from a planar arrangement is small. None of the theoretical intensity curves with a C–C–C angle equal to 112-116° agrees with the experimental data. Such an increase in the valence angle is apparently connected with the action of three-membered rings. Thus, in the cyclopropane ring the angle H–C–C is 120° ([6]), and in propylene oxide ([7]) the angle C–C –C is 144°. A natural question arises as to why the angles $C_2C_3C_4$ ($C_5C_6C_1$) are then increased to 119°, although one would expect them to be 111-112°. Evidently, in this case the interaction of the nonbonded atoms $C_7$ and $C_8$ with atoms $C_4$ and $C_5$ is manifested, since the distances $C_7 \dots C_{4(5)}$ and $C_8 \dots C_{4(5)}$ are respectively equal to 3.4 and 3.3 Å, which is 0.2-0.3 Å less than the sum of the van der Waals radii of carbon. At smaller values of the angles $C_2C_3C_4$ ($C_5C_6C_1$) the latter would decrease still more. The increase in the distances $C_7 \dots C_{4(5)}$ and $C_8 \dots C_{4(5)}$ by changing the angles $\alpha$ and $\beta$ would be hindered by the hydrogen atoms at atoms $C_1$ and $C_2$ and by the methyl group of the epoxide ring. In this connection the results of work ([8]) are of interest, in which the authors, on the basis of measurements and calculations of dipole moments,

Fig. 3

Figure 3: Fig. 3

came to the conclusion that in derivatives of tricyclo-(5.1.0.0. 3, 5)-octane the cyclohexane ring is almost planar. Although, as indicated above, on the basis of the electron-diffraction data (Table 2) it is impossible to choose between models I and II, nevertheless, in our opinion, model I is more preferable for the following reasons. Model II is energetically less favorable, since the hydrogen atoms of the methyl group ($C_8$) and of the methylene groups ($C_3$ and $C_6$) are at a distance of 1.8–2.0 Å, which is considerably less than the sum of the van der Waals radii of hydrogen (2.4). Such steric difficulties are absent in model I, in which the corresponding distances are 2.4 Å. And, finally, we tested a model of a "twisted" bath. On the basis of comparison of the corresponding intensity curves this model was excluded.

**Fig. 3**

Thus, as a result of the investigation carried out, the structure of the molecules of the $\alpha$- and $\beta$-forms of $\Delta^3$-carene oxide has been determined with the following parameters (model I):

**Table 2**

**Results of electron-diffraction pattern measurements**

| Max. | Int. | $\alpha$-form (model I), $s_{exp}$ | $s_{theor}/s_{exp}$ (curve $u$) | $\beta$-form (model I), $s_{exp}$ | $\beta$-form (model I), $s_{theor}/s_{exp}$ | Max. | Int. | $\alpha$-form (model I), $s_{exp}$ | $s_{theor}/s_{exp}$ (curve $u$) | $\beta$-form (model I), $s_{exp}$ | $\beta$-form (model I), $s_{theor}/s_{exp}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 2.97 | (0.875) | 2.66 | (0.940) | 6 | 5 | 14.21 | 0.993 | 14.22 | 0.999 |
| | | 3.96 | (0.912) | 3.75 | 1.003 | | | 14.78 | 0.982 | 14.85 | 0.991 |
| 2 | 2 | 5.42 | 1.000 | 5.40 | 0.998 | | 6 | 16.02 | 0.991 | 15.92 | 1.003 |
| | | 6.91 | 1.001 | 7.01 | 0.997 | 7 | | 17.72 | 0.985 | 17.70 | 0.989 |
| 3 | 3 | 8.24 | 0.987 | 7.98 | 1.004 | | 7 | 20.00 | 1.001 | 19.90 | 0.988 |
| | | 9.00 | 0.978 | 8.76 | 0.994 | 8 | | 22.21 | 0.991 | 22.12 | 0.999 |
| 4 | 4 | 9.94 | 0.991 | 9.86 | 1.002 | | 8 | 23.65 | 0.995 | 23.78 | 0.990 |
| | | 11.37 | 0.992 | 11.29 | 1.004 | 9 | | 25.64 | 0.996 | 25.48 | 0.996 |
| 5 | | 13.07 | 0.995 | 13.02 | 0.996 | | | | Mean value 0.992± 0.005 | | 0.997± 0.004 |

**$\alpha$-form**

$$r(\mathrm{C-H}) = 1.09 \text{ Å} \quad \text{(accepted)}, \qquad r(\mathrm{C-O}) = 1.41 \text{ Å} \quad \text{(accepted)},$$

$$r(\mathrm{C-C}) = 1.52 \pm 0.02 \text{ Å}, \qquad \text{angle CCC (in the ring)} = 119 \pm 2^\circ,$$

$$\text{angles } \alpha = 117 \pm 4^\circ \text{ and } \beta = 121 \pm 5^\circ, \qquad \angle\mathrm{CCH} \text{ (in } \mathrm{CH_3}) = 108^\circ \text{ (accepted)},$$

$$\angle\mathrm{HCH} \text{ (in } \mathrm{CH_2}) = 106^\circ \text{ (accepted)}, \qquad \angle\mathrm{C_8C_7C_9} = 118 \pm 3^\circ, \qquad \angle\mathrm{C_{10}C_3C_4} = 113^\circ.$$

**$\beta$-form**

$$r(\mathrm{C-H}) = 1.10 \text{ Å} \quad \text{(accepted)}, \qquad r(\mathrm{C-C}) = 1.42 \text{ Å} \quad \text{(accepted)},$$

$$r(\mathrm{C-C}) = 1.53 \pm 0.02 \text{ Å}, \qquad \text{angle CCC (in the ring)} = 119 \pm 2^\circ, \qquad \alpha = 118 \pm 4^\circ,$$

$$\beta = 106 \pm 5^\circ, \qquad \angle\mathrm{C_8C_8C_9} = 118 \pm 3^\circ, \qquad \angle\mathrm{C_{10}C_5C_4} = 114^\circ, \qquad \angle\mathrm{CCH} = 108^\circ$$

$$\text{(in } \mathrm{CH_3}), \qquad \angle\mathrm{HCH} = 106^\circ \text{ (in } \mathrm{CH_2}).$$

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Received
27 I 1965

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*Note: Figure translations are in progress. See original paper for figures.*