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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF THE α-PINENE OXIDE MOLECULE

Earlier (^{1}), in studying α-pinene oxide by the method of proton magnetic resonance, a conformational formula for α-pinene oxide was proposed. It was shown that one of the gem-dimethyl groups interacts with the oxide ring, whereas the second does not interact with it. As for the conformation of the cyclohexene oxide ring in the α-pinene oxide molecule, it was accepted, according to literature data, as a half-chair, analogous to cyclohexene oxide (^{2}).

Fig. 1

The aim of the present work is an electron-diffraction study of the structure of the α-pinene oxide molecule. Electron-diffraction patterns of the vapor of the compound under investigation were obtained on an EG-100A electron-diffraction apparatus (^{3}). In the work an additional diffusion pump DMN-20 was used, located near the evaporator nozzle for more effective removal of the vapor of the substance being studied. In recording the electron-diffraction patterns an s^2 sector was used. From the vapors of α-pinene oxide, 15 series of electron-diffraction patterns were obtained at different nozzle—plate distances (188 and 418 mm) and at accelerating electron voltages of 40 and 60 kV. The interpretation of the electron-diffraction patterns was carried out on the basis of visual estimation of intensity by the radial-distribution method and by the method of successive approximations according to the equations*:

$$rD(r) = \sum sI(s)\exp(-as^2)\sin sr\,\Delta s, \tag{1}$$

where

$$s = \frac{4\pi}{\lambda}\sin\frac{\vartheta}{2},$$

λ is the electron wavelength, ϑ is the scattering angle,

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

* The calculations were carried out on the M-3 electronic computer by L. F. Shatrukov, to whom we express our gratitude.

$I(s)$ is the scattering intensity, $\exp(-as^2_{\max}) = 0.1$; $\Delta s = 0.2\ \text{Å}^{-1}$, and

$$I(s) = \sum_i \sum_j nZ_i Z_j \exp\left(-\frac{1}{2} l^2_{ij} s^2\right) \frac{\sin sr_{ij}}{sr_{ij}}, \tag{2}$$

where Z_i and Z_j are the nuclear charges of atoms i and j, l_{ij} is the root-mean-square amplitude of thermal vibrations. The values of $l^2_{ij}/2$ were taken as follows: 0.0020 Å^2 for C—C and C—O distances between bonded atoms, 0.0040 Å^2 for $\mathrm{C} \cdots \mathrm{H}$ distances between nearest nonbonded atoms,

Fig. 2

0.0032 Å^2 for $\mathrm{C} \cdots \mathrm{C}$ and $\mathrm{C} \cdots \mathrm{O}$ distances between nearest nonbonded atoms, 0.0040 Å^2 and 0.0060 Å^2 for $\mathrm{C} \cdots \mathrm{C}$, $\mathrm{C} \cdots \mathrm{O}$, and $\mathrm{C} \cdots \mathrm{H}$ distances between nonbonded atoms separated by two and three atoms.

Figure 1 shows the radial distribution curve constructed from the experimental intensity curve with extrapolation of $I(s)$ in the region $s = 0$–$2.6\ \text{Å}^{-1}$ by the theoretical intensity curve. The radial distribution curve $rD(r)$ has five peaks that may be regarded as structural: 1.09, 1.54, 2.16, 2.58, and 4.09 Å. The first peak on the $rD(r)$ curve was assigned to C—H distances, the second to C—O and C—C distances, the third peak at $r = 2.16$ Å to $\mathrm{C} \cdots \mathrm{H}$ and $\mathrm{C}_{3(4)} \cdots \mathrm{C}_{6(5)}$ distances, the fourth—an extremely complex peak—was assigned mainly to $\mathrm{C} \cdots \mathrm{C}$ and $\mathrm{C} \cdots \mathrm{O}$ distances separated by one carbon atom. The position of this peak ($r = 2.58$) made it possible to estimate the valence angle C—C—C, which was subsequently refined by constructing theoretical curves. The region of the $rD(r)$ curve from 2.6-3.5 Å corresponds to longer $\mathrm{C} \cdots \mathrm{C}$ and $\mathrm{C} \cdots \mathrm{O}$ distances, whose atoms are separated by two and even three carbon atoms. The peak at $r = 4.09$ Å was assigned to the distances $\mathrm{C}_6 \cdots \mathrm{C}_{10}$, $\mathrm{C}_4 \cdots \mathrm{C}_{10}$, $\mathrm{C}_7 \cdots \mathrm{C}_{10}$, $\mathrm{C}_8 \cdots \mathrm{C}_{10}$ (see Fig. 2a).

Fig. 3

Formally, the model of the molecule of α-pinene oxide may be represented as a combination of a dimethylcyclobutane ring and 2:3-epoxybutylene. It is known from literature data$^{(4-7)}$ that the carbon atoms of cyclobutane do not lie in one plane. The angle between two planes in the cyclobutane molecule and its derivatives is 150-160°. Taking the angles $C_1{-}C_2{-}C_3$, $C_1{-}C_7{-}C_6$, $C_7{-}C_1{-}C_2$, $C_8{-}C_4{-}C_9$, $C_{10}{-}C_2{-}C_8$, and $C_1{-}C_2{-}C_{10}$

equal to 112-114° (from the data of the radial-distribution curve), theoretical intensity curves were calculated for various angles α and β (α is the angle between the planes $C_3C_4C_6$ and $C_3C_5C_6$; β is the angle between the planes C_1OC_2 and $C_1C_2C_7$). The best agreement with the experimental intensity curve is given by theoretical curve *i* (model *a*, Fig. 2, Fig. 3, and Table 1), the parameters of which are given in Table 2. For comparison, Fig. 1 gives the theoretical radial-distribution curve calculated from the curve $I(s)$ for model *i*. From the comparison it is seen that, on the whole, both curves agree satisfactorily. The section of the curve $rD(r)$ in the region 2.0-2.2 was calculated without the exponential term in equation (1), in order to determine the position of the peak in this region.

Table 1

Comparison of the experimental and theoretical intensity curves (curve *i*)

Max.	Min.	s_{theor}	s_{expt}	$\frac{s_{\text{theor}}}{s_{\text{expt}}}$
1		2.96	2.96	1.000
	2	3.98	4.00	0.995
2		5.36	5.30	1.011
	3	6.86	6.80	1.009
3		8.32	8.00	(1.040)
	4	9.11	8.88	1.026
4		9.82	9.65	1.018
	5	11.33	11.40	0.994
5		12.94	12.93	1.001
	6	14.56	14.25	1.022
6		15.08	15.02	1.004
	7	15.90	16.07	0.990
7		17.76	17.85	0.995
	8	19.27	19.25	1.001
8		21.04	20.80	1.011
Average value				1.006
Mean deviation				$±$0.009

It is interesting to note the following. The carbon atom C_{10} is in an approximately equatorial position. If the angle β is increased to 180° and more, then the oxygen atom and the methyl group will become "crowded," and as a result the CH_3 group will tend to move into an axial position. But then it will be “crowded” because of the position of the gem-dimethyl group. It is sufficient to point out that the distance C_8 C_{10} in this case will be about 1.9 Å, and the molecule will experience additional steric strain.

Construction of theoretical intensity curves for models in which the angle β is 116, 130, 150°, etc., confirmed this supposition. None of the theoretical curves (for example, curves *a*, *b*, *c*, and *g* in Fig. 3) agrees with the experimental one.

A model was also tested (model *b*, Fig. 2) in which the atoms C_1, C_2, C_3 and C_6 and C_7 are coplanar, but the theoretical intensity curve for this model (curve *d*, Fig. 3) does not agree with the experimental curve. In paper (2) there is an indication that the bonds C_1–C_7, C_1–C_2, C_2–C_3 in cyclohexene oxide lie in one plane, the atom C_5 is below, and the atom C_6 above this plane. One might suppose that such a motif would also be retained in the α-pinene oxide molecule. However, construction of such a model (model *c*, Fig. 2) showed that the distances C_2 C_4 and C_5 C_7 would be approximately equal to 2.3 Å (a considerable shortening of the C C distance compared with the value 2.58 Å). If these distances are taken

Table 2

Parameters of the theoretical curves*

Curve**	C_8 C_{10}, Å	C_1–C_2–C_3 C_1–C_7–C_6	C_2–C_1–C_7	C_8–C_4–C_9	α	β
a	2.16	112	112	114	160	116
b	2.16	114	112	114	140	116
c	2.16	114	112	114	140	130
g	2.16	114	112	114	140	150
*d****	2.12	114	112	114	140	108
e	2.16	112	112	114	146	105
zh	2.13	112	112	114	152	106
z	2.13	112	112	114	152	100
i	2.13	112	112	114	146	103

* For all the curves listed in the table, the values are $r(C—H) = 1.08$ Å, $r(C—C) = 1.55$ Å, $r(C—O) = 1.44$ Å. Shortest distances C H = 2.16 Å, C_{10}–C_2–C_1 = C_{10}–C_2–C_3 = 112.

** Table 2 and Fig. 3 give some of the calculated curves.

*** Atoms C_1, C_2, C_3, C_6, and C_7 are coplanar.

equal to ~ 2.5 Å (this corresponds to a $C—C—C$ angle of ~ 109°), then the $C_4 \ldots C_5$ distance will be less than 2.0 Å, which is unlikely. And indeed, the theoretical intensity curve (curve e in Fig. 3) agrees poorly with the experimental curve.

Thus, as a result of the electron-diffraction study of the structure of the molecule of α-pinene oxide, the configuration of the molecule was determined (model a, Fig. 2) with the following parameters: $r(C—H) = 1.09$ Å (assumed), $r(C—C) = 1.56 \pm 0.02$ Å, $r(C—O) = 1.45$ Å (assumed),

$$\angle C_1—C_2—C_3 = \angle C_1—C_7—C_6 = \angle C_7—C_1—C_2 = \angle C_{10}—C_2—C_1 =$$

$$= \angle C_{10}—C_2—C_3 = 112 \pm 3^\circ, \quad \angle C_3—C_4—C_6 = \angle C_3—C_5—C_6 = 87^\circ,$$

$$\angle C_8—C_4—C_9 = 114 \pm 3^\circ, \quad \alpha = 146 \pm 8^\circ, \quad \beta = 103 \pm 10^\circ, \quad \angle C—C—H = 109^\circ$$

(assumed).

It is interesting to note that in the molecule of α-pinene oxide there are no large deviations of the $C—C—C$ valence angles from the tetrahedral value, except in the cyclobutane ring (incidentally, in octachloro- and octafluorocyclobutane the $C—C—C$ angles are 87—89°); i.e., the configuration of the molecule found has the minimum spatial hindrance among those tested. The magnitude of the angle $\beta = 103^\circ$ agrees well with the corresponding angle (98.1°) in the molecule of cyclopentene oxide (^{8}).

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REFERENCES

1. B. A. Arbuzov, Z. G. Isaeva, Yu. Yu. Samitov, DAN, **137**, 589 (1961).
2. V. Ottar, Acta chem. scand., **1**, 283 (1947).
3. N. P. Levkin, Yu. M. Kushnir, Izv. AN SSSR, ser. fiz., **23**, 531 (1959).
4. J. D. Dunitz, V. Schomaker, J. Chem. Phys., **20**, 1703 (1952).
5. T. B. Owen, J. L. Hoard, Acta crystallogr., **4**, 172 (1951).
6. H. P. Lemaire, R. L. Livingston, J. Am. Chem. Soc., **74**, 5732 (1952).

7. W. G. Rothschild, B. P. Dailey, J. Chem. Phys., **36**, 2931 (1962).
8. G. Erlandsson, Arkiv Fysik, **9**, 341 (1955).

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