Chemistry

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1964

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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

α-Pinene is one of the simplest unsaturated bicyclic terpenes of the pinane group. Its molecule, along with a six-membered ring, contains a cyclobutane ring, which was shown by the oxidation of α-pinene to pinonic and then to norpinic acid. α-Pinene is a liquid with a boiling point of 156°. Two optical isomers of α-pinene are known—the *d*- and *l*-isomers. The generally accepted conformational formula of α-pinene is given in Fig. 1. It was of interest to elucidate the nature of the arrangement of the carbon atoms C_1, C_2, C_3, C_6, and C_7, to determine the magnitudes of the valence angles, and also the angle α (α is the angle formed by the planes $C_3C_4C_6$ and $C_3C_5C_6$ in the cyclobutane ring). The present electron-diffraction study is devoted to this problem.

Fig. 1

Fig. 2

The electron-diffraction study of the structure of the α-pinene molecule was carried out on an EG-100 electron-diffraction apparatus. From α-pinene vapor, eight series of electron-diffraction patterns were obtained and measured using the sector method at electron accelerating voltages of 40 and 60 kV. The interpretation of the electron-diffraction patterns was carried out on the basis of a visual estimate of the intensity* of the diffraction pattern by the method of successive approximations and by the radial-distribution method according to the equations:

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

in which

Fig. 3

Figure 3: Fig. 3

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

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

$$I(s) = \sum_i \sum_j nZ_{iZ}j \exp(-b_{ij}s^2) \frac{\sin sr_{ij}}{sr_{ij}}, \tag{2}$$

* The region of the experimental curve s = 12.5–18.5 was constructed from photometric data.

where z_i and z_j are the nuclear charges of the i-th and j-th atoms, and b_{ij} is a quantity proportional to the mean-square amplitude of the vibrations of the atoms. Since the visual method was used, the values of b_{ij} were taken to be: 0.0005 Å^2

Fig. 3

for the distances C–C and C=C, 0.0012 Å^2 for the distances C–H and C···C between non-bonded atoms separated by one carbon atom, 0.0020 Å^2 for pairs of atoms separated by two, and 0.0030 Å^2 for pairs separated by three carbon atoms, and 0.0040–0.0050 Å^2 for the distances C···H.

Table 1

Parameters of the theoretical intensity curves

Parameters	Theoretical curves*	Theoretical curves*	Theoretical curves*	Theoretical curves*	Theoretical curves*	Theoretical curves*	Theoretical curves*	Theoretical curves*	Theoretical curves*
	1	2	3	4	5	6	7	8	9
r(C=C)	1.34	1.32	1.34	1.34	1.34	1.34	1.34	1.34	1.34
∠C_1—C_7—C_6 ∠C_1—C_2—C_3	112	111	114	112	112	112	112	112	112
∠C_2—C_1—C_7	118	120	116	118	118	118	118	118	118
∠C_8—C_4—C_9	112	114	114	114	114	114	111	116	114
∠C_1—C_2—C_{10}	125	127	127	126	126	126	126	126	126
α	146	146	146	154	140	148	146	146	146

* For all the curves indicated in the table, the distances C–H, C–C, and C···H are equal to 1.09, 1.54, and 2.15 Å, respectively.

The radial distribution curve (Fig. 2), constructed from the experimental intensity curve with extrapolation of $I(s)$ in the initial region by the best theoretical intensity curve, has peaks that may be regarded as structural at the following distances: 1.10, 1.54, 2.15, 3.89, and 5.0 Å. It was natural to assign the first two peaks, respectively, to the distances C–H and C–C (C=C); the third peak was assigned to the distances C···H in the C–C–H group and $C_{3(4)}$—$C_{6(5)}$. The fourth, very complex peak at 2.54 Å, was assigned mainly to the distances C··· C in

C–C–C group. The remaining peaks on the $rD(r)$ curve were assigned to larger C···C distances between valence-unbonded atoms.

The presence of a double bond in the α-pinene molecule somewhat facilitates the choice of a molecular model. Theoretical considerations, as well as abundant experimental material (see, for example, (^{1})) on the geometry of unsaturated compounds, indicate the coplanarity of atoms C_1, C_2, C_3, C_7, and C_{10}. The theoretical intensity curves proved to be sensitive to changes in the valence angles C_1—C_7—C_6 and C_1—C_2—C_3 (C_2—C_1—C_7), as is seen from Fig. 3 (curves 1, 2, and 3), which presents the theoretical intensity curves. The parameters of the theoretical curves in Fig. 3 are given in Table 1. To choose the best molecular model, the magnitudes of the C—C—C angles and α were varied (curves 4-9 in Fig. 3). The experimental intensity curve is best matched by curve 9. Table 2 gives a comparison of s_{expt} and s_{theor} for this curve. For comparison, a theoretical curve $rD(r)$ was calculated; it agrees satisfactorily with the experimental curve in Fig. 2. Thus, as a result of the electron-diffraction investigation carried out, experimental data were obtained on the structure of the α-pinene molecule with the following parameters: $r(C—H) = 1.09$ Å (assumed), $r(C = C) = 1.34$ Å (assumed), $r(C—C) = 1.54 \pm 0.02$ Å, angles C_1—C_2—C_3 (C_2—C_1—C_7) $= 118 \pm 3°$, C_1—C_7—C_6 $= 112 \pm 3°$, C_8—C_4—C_9 $= 114 \pm 3°$, $\alpha = 146 \pm 8°$, $r(C \ldots H) = 2.15$ Å (assumed from the radial distribution curve), $\angle C_1$—C_2—$C_{10} = 126°$.

Table 2

Comparison of the experimental and theoretical intensity curves (curve 9)

Max.	Min.	s_{expt}	s_{theor}	$\frac{s_{\text{theor}}}{s_{\text{expt}}}$
2	3	5.32	5.38	1.011
3	3	6.90	6.83	0.990
3	4	8.39	8.55	1.019
4	4	9.25	9.34	1.010
4	5	9.99	9.99	1.000
5	5	11.24	11.22	0.998
5	6	13.01	13.13	1.009
6	6	14.75	14.62	0.991

Max.	Min.	s_{expt}	s_{theor}	$\frac{s_{\text{theor}}}{s_{\text{expt}}}$
6	7	18.07	17.94	0.993
7	7	19.50	19.48	0.999
7	8	21.00	20.97	0.999
8	8	23.40	23.26	0.994
8	9	25.52	25.33	0.993
9	9	27.58	27.43	0.995
9	9	29.62	29.67	1.002
			Mean value	1.000
			Mean deviation	±0.007

Earlier (^{2}), in an electron-diffraction study of the structure of the α-pinene oxide molecule, it was shown that atoms C_2, C_3, C_6, and C_7 are coplanar. This is possibly connected with the presence of a cyclobutane ring in the α-pinene oxide molecule. An analogous picture is also observed in the α-pinene molecule. By analogy with the half-chair conformation of cyclohexane and its derivatives (^{3}), one might have expected a half-chair form of the $C_1C_2C_3C_4C_6C_7$ ring in the α-pinene molecule. In that case, however, there would be strong shortening of the $C_4 \ldots C_7$ and $C_2 \ldots C_5$ distances (to 2.3 Å). Apparently, the cyclobutane ring affects the arrangement of the remaining carbon atoms in such a way as to lead to coplanarity of atoms C_2, C_3, C_6, and C_7 in the molecule. The data obtained on the structure of the α-pinene molecule are consistent with the interpretation of the proton magnetic resonance spectrum of α-pinene (^{4,5}). In the latter works it was shown that the chemical shifts of the two gem-methyl groups are different, which indicates their different positions in the force field of the molecule.

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Received
11 V 1964

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