Molecular Structure Investigations by Electron Diffraction Method. I. The Molecular Structures of Isopropyl Alcohol and -Chloride

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Previous electron diffraction investigations of substituted paraffines, having the number of carbon atoms up to C_3 or C_4, gave various kinds of information about the structures of respective molecules, that is, reliable molecular parameters including the informations about the internal rotations in some kinds of molecules were obtained. In Table I, there are shown several data obtained recently by many authors. Nowadays, the investigations have been carried out using the visual method and also more quantitatively by the use of the apparatus having a sector.

TABLE I
THE LIST OF MOLECULAR CONSTANTS OF SEVERAL PARAFFINE DERIVATIVES FROM RECENT INVESTIGATIONS

Molecules	C-C (Å)	C-X (Å)	Other parameters	References
CH_3–CH_3	(C–H/C–C=1.115/1.54)		∠CCH=110.5°	(6)
CH_3–CH_2OH	1.54	C–O=1.48±0.04		(7)
CH_2Cl–CH_2OH	1.54	C–O=1.45 (1.43)	(Gauche form is predominant at room temperature.)	(8), (9)
CH_2Cl–CH_2Cl	1.49±0.03	C–Cl=1.78±0.01 C′···Cl=2.69±0.02,	(Gauche=27±5% at 22°C.)	(10)
CH_3–CCl_3	1.54±0.04	C–Cl=1.77_5±0.02		(11), (12), (13)
CH_3–CCl_2–CH_3	1.54±0.04	C–Cl=1.77_6±0.02,	∠ClCCl=109.5±2° ∠CCCl=109°±3°	(11)
CH_2Cl–$CHCl$–CH_3	1.56	C–Cl=1.79±0.035 C′···Cl=2.715±0.025,	∠CCCl=108±4°	(14)
CH_3–CF_3*	1.52±0.02	C–F=1.37±0.02		(15)
CF_3–CF_3*	1.45(±0.06)			(16)

*Origin of the deviations of molecular parameters seem to be somewhat different for fluorinated derivatives from that for other substituted paraffines.

There seem to be disagreements on several points of molecular parameters among a few examples shown in Table I. But whether these discrepancies are within a range of errors or whether they indicate real differences among the molecules could not be decided at present. As regards the C—C bond distances, for example, the value 1.54 Å has so far been usually considered to be reliable for saturated paraffines and their derivatives, but the value 1.49 Å has been obtained for 1,2-dichloroethane molecule[10], and 1.56 Å for 1,2-dichloropropane molecule[14]. The present author is trying to investigate some substituted paraffines as regards the C—C distances and other molecular parameters.

Isopropyl alcohol and -chloride molecules have been investigated, because the contribution of C—C atom-pairs to the intensity curves seems to predominate in these molecules over the cases of ethane derivatives. In this study, we may not ignore the question how the equilibrium positions of two methyl groups will contribute to the intensity curves. But in the reinvestigation of isopropyl chloride molecule[1], unfortunately, the problem of internal rotations of methyl groups has not been made clear by using the visual method.

Experimental Procedures

Commercial isopropyl alcohol was carefully dried on quick lime and distilled several times (boiling point: 82 °C). The chloride was synthesized[2] from purified alcohol and distilled carefully (b.p. 37°C).

The apparatus of electron diffraction is the one which was described in the previous report[3]. Eight maxima and five minima have been observed visually in the range $9<q<80$ for isopropyl alcohol, and twelve maxima and eight minima in the range $9<q<95$ for isopropyl chloride from ten or more photographic plates in both cases.

The experimental visual curve obtained for each case is shown in the top-most place of Fig. 3A and 3B respectively, and $q_{obs.}$'s, the corresponding observed q-values of maxima and minima, are shown in the third column in Table IV A and IV B.

The theoretical intensity curves for the assumed molecular models have been calculated by the use of the well-known formula[4]:

$$I=k\sum_i\sum_j Z_iZ_j/l_{ij}\cdot\left(\sin\frac{\pi}{10}ql_{ij}\right)\cdot\exp(-b'_{ij}q^2)$$

where $q=10\,s/\pi$, $s=(4\pi\sin\theta/2)/\lambda$, θ the scattering angle, and λ the wave length of the beam.

In constructing the assumed molecular models, the rotations of methyl groups about each C–C bond are considered. (The figures of molecular models are shown in Fig. 1, in which various parameters are given out.) That is, all the hydrogen atoms of methyl groups, which contribute to intensity curves as the variations of $C''\cdots H$ and $X''\cdots H$[*] distances, are taken into account[**].

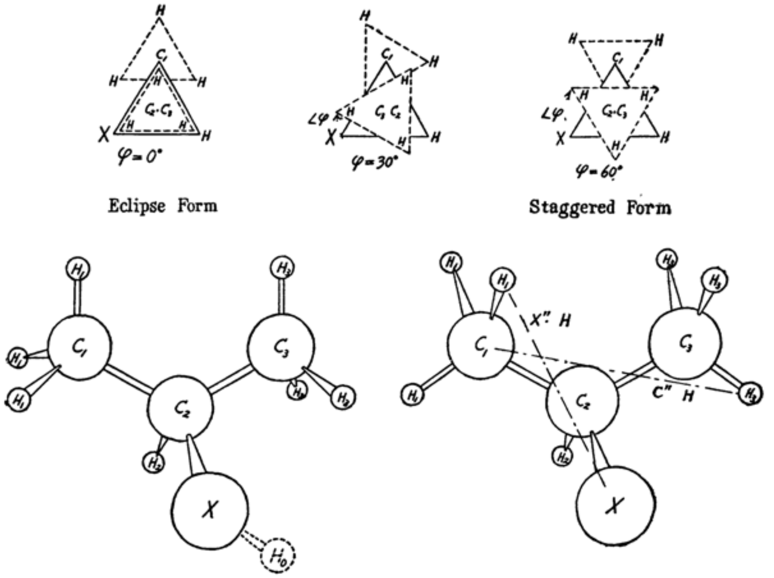

Fig. 1. Schematic models which show the interatomic configurations in relation to the rotations of methyl groups for isopropyl derivatives.

In case of isopropyl alcohol, the atom X is the hydroxyl oxygen and the hydroxyl hydrogen atom H_0 attached to the X atom, which are shown with dotted figure. In case of isopropyl chloride, X is the chlorine atom. One of the six $C''\cdots H$ and one of the six $X''\cdots H$ interatomic distances are hereby exemplified, and the meaning of the signs ($''$) and ($\cdots$) will be clear from this figure.

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[1] J. Y. Beach and D. P. Stevenson, *J. Am. Chem. Soc.*, **61**, 2643 (1939).

[2] "Organic Synthesis" Collective Vol. 1. p. 142 (1948), (Analogous method for *n*-Butyl Chloride.)

[3] T. Yuzawa and M. Yamaha, This Bulletin, **26**, (No. 8) 414 (1953).

[4] V. Schomaker and R. Spurr, *J. Am. Chem. Soc.*, **64**, 2693 (1942).

[*] The sign (...) shows the distance between two atoms which are non-bonded. The sign ($''$) shows that there are two other atoms in between along three successive bonds (assigned the mark of *two* dashes), e.g. $C''\ldots H$ shows one of the three $C_1''\ldots H_3$ distances in the case of C_1-C_2-C_3-H_3 as well as $C_3''\ldots H_1$ in C_3-C_2-C_1-H_1.

[**] The hydrogen atom H_0 attached to the oxygen atom of hydroxyl group is neglected, because the contributions of O-H_0, $C_2'\ldots H_0$ and those of farther distances between H_0 and other atoms to the intensity curves are negligibly small.

The variations of these distances in relation to the rotational angle φ of methyl group (the angle φ is conveniently taken from the C_1C_2X plane for $(\mathrm{methyl})_1$ group) are shown in Fig. 2 for each molecule. The contributions of these distances to the intensity curves are remarkable for the alcohol in the range $25<q<55$, where the influences of the thermal vibrations are comparatively small. For the chloride, on the contrary, these contributions appear in the range $q<35$ of the curve, where the exact estimation of the intensity relations is difficult.

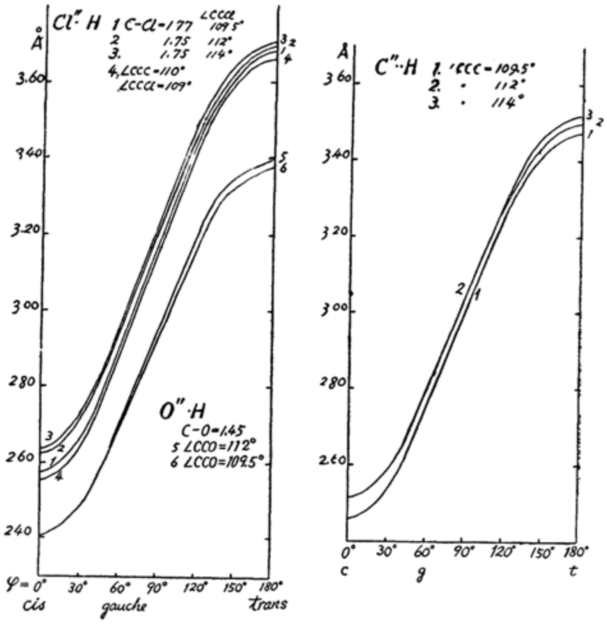

Fig. 2. The diagrams of interatomic distances C″...H, O″...H and Cl″...H versus the rotational angle φ. (In case of C—H=1.10)

Angle $\varphi=0°$, 60° and 180° correspond to cis, gauche and trans position respectively about the C—C bond.

The vibration factors b'_{ij} used in the formula are shown in Table II. For isopropyl

TABLE II

THE LIST OF THE APPROXIMATE VIBRATION FACTORS USED FOR THE CALCULATION OF INTENSITY CURVES

Atom pairs	nz_iz_j/l_{ij}**	Distances (Å)	$\langle l_{ij}^2\rangle_{Av}^{1/2}$	$b_{ij}=\pi/200\langle l^2_{ij}\rangle_{Av}$.	b'_{ij}
C—C	46	1.52—1.56	0.057	0.00015	0
C′...C	14	2.48—2.55	0.084	0.00035	0.00020
C—H	46	1.09—1.13	0.078 (0.064)*	0.00030	0.00015
C′...H	27	2.14—2.23	0.091 (0.086)*	0.00041	0.00025
C—Cl	58	1.75—1.80	0.061 (0.064)*	0.00018	0.00003
C′...Cl	75	2.68—2.75	0.068 (0.070)*	0.00023	0.00008
C—O	33	1.43—1.48	0.055^+	0.00015	0
C′...O	39	2.42—2.46	0.066^+	0.00022	0.00008
C″—H (cis, gauche) 6, 11					(0.00060)***
C″—H (120°, trans) 9, 4					(0.00040)***
Cl″...H (cis, gauche) 15, 28					(0.00076)***
Cl″...H (120°, trans) 24, 11					(0.00046)***
C″...H (cis, gauche) 8, 14					(0.00060)***
C″...H (120°, trans) 11, 6					(0.00040)***

Table II. *Reference (10)

**The values are to be some what changed from these values.

***Roughly assumed values.

$^+$Calculated with consideration of reference (5).

alcohol, the values have been assumed by the force constants calculated from vibration frequencies of ethyl alcohol[5]. For isopropyl chloride, the values have been assumed from the values suggested by J. Karle et al.[10].

(The valency agles ∠CCH and ∠HCH are assumed to be 109.5° throughout the investigation.)

Isopropyl Alcohol With the visual curve, the theoretical intensity curves are shown in Fig. 3A in accordance with the variations of assumed molecular models. As shown in Table III A, corresponding theoretical intensity curves to molecular constants of models are specified as follows:

1) For the groups of curves from A to C and D to F, the C–O distance increase successively in each group. The angles ∠CCC are 109.5°, 112° in the two groups respectively and other parameters, ∠CCO and rotational configurations, remain constant.

2) Curves assigned P, B, Q in order correspond to the increase of C–C distance with constant other parameters.

The $q_{obs.}$'s of the maxima and the minima

TABLE IIIA

THE LIST OF MOLECULAR MODELS AND CORRESPONDING ASSUMED MOLECULAR CONSTANTS FOR ISOPROPYL ALCOHOL

Models	C—C (Å)	C—O (Å)	∠CCC°	Configulation of two -CH_3 groups	$q/q_{obs.}$	
A	1.54	1 48	109.5	Eclipse	0.991_5	
B_E	〃	1.45	〃	〃	1.000_2	
C	〃	1.43	〃	〃	1.002_0	
D	〃	1.48	112	〃	—	
E	〃	1.45	〃	〃	0.995_1	
F	〃	1.43	〃	〃	—	
B_{30}	〃	1.45	109.5	$\varphi=30$	0.991_9	
B_S	〃	〃	〃	Staggered	0.998_3*	
P_E	1.52	1.45	109.5	Eclipse	1.012_5	
P_S	〃	〃	〃	Staggered	1.006_4*	
Q_E	1.56	〃	〃	Eclipse	0.990_6	
Q_S	〃	〃	〃	Staggered	0.987_2*	
X_E	1.54	1.45	109.5	Eclipse	0.997_6	(C-H = 1.13 Å)
Y_S	〃	〃	112	Staggered	—	(∠CCO = 112°)
Y_{30}	〃	〃	〃	$\varphi=30$	—	(〃)

* The 3rd and 5th maxima are not taken into account in these mean values.

TABLE IVA

OBSERVED q-VALUES AND CALCULATED $q/q_{obs.}$ VALUES FOR BETTER MOLECULAR MODELS OF ISOPROPYL ALCOHOL

Max.	Min.	$q_{obs.}$	wt.	A	B_E	B_{30}	C	E	X_E	B_S
	2	(14.39)								
2		18.43	1	1.010	1.023	1.004	1.028	1.010	1.031	0.982
	3	23.13	2	0.997	1.003	0.999	1.002	0.990	1.007	0.994
3		27.20	2	0.995	1.004	1.011	1.007	1.002	1.007	—*
shelf										
	4	(38.61)								
4		42.59	2	0.991	1.003	0.996	1.003	0.993	0.998	0.996
	5	48.21	2	0.991	1.000	0.975	0.998	0.994	0.994	(1.008)
5		52.36	1	0.974	0.980	0.951	0.985	0.976	0.974	—*
6		58.33	2	0.991	0.998	0.996	1.001	1.000	0.989	1.006
	7	63.79	1	0.979	0.992	0.991	0.992	—	0.986	0.995
7		68.33	1	—	0.995	0.988	—	—	0.985	0.995
8		(76.23)	(See Fig. 3A.)							
Weighted mean:				0.991_5	1.000_2	0.991_9	1.002_0	0.995_1	0.997_6	0.998_3
Wtd. mean sq. deviation:				0.008_3	0.008_2	0.015_0	1.008_7	0.008_8	—	—

*These values can not be taken into account since the features are different from that of visual one. (See Fig. 3A).

(abbreviated as "*q-values*" in this and next sections) of each curve in the cases 1) and 2), are slightly different from one another with the parameters mentioned, and the curves assigned B, including the subscripts, seem to be the most acceptable ones.

3) Curves assigned the same letters with different subscripts (e. g. B_E, B_{30}, B_S; P_E, P_S; Q_E, Q_S; and Y_E, Y_S) show the different rotational configurations of methyl groups with the same other parameters in each case, i. e. "E", "30" and "S" show the cases in which the angles φ are 0°, 30° and 60° respectively.

Through each group, for example B_E, B_{30} and B_S, the remarkable variations of the curves are shown by the features of the third maximum with the shelf-like maximum and the fifth maximum. The curves with subscripts "S" are at least to be rejected through these groups, and curves B_E and B_{30} are the acceptable ones. This selection seems to be confirmed, although the visual method used.+

4) The curves X_E and X_S, correspond to the case of C–H = 1.13 Å, and have shown slight disagreements in *q-values*. The curves Y correspond to the model having the both angles ∠CCC = ∠CCO = 112°, and are to be rejected because the *q-values* and the shapes of the fifth minimum and the fifth maximum are different obviously from the visual one.

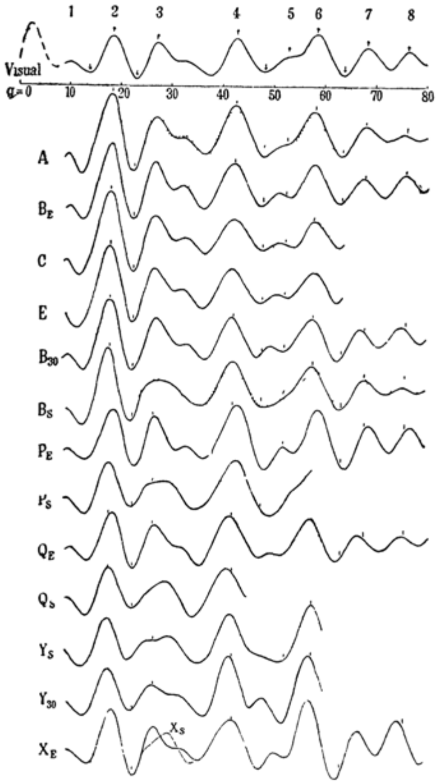

Fig. 3 A. Visual and theoretical intensity curves for isopropyl alcohol molecule.

Dotted curves on *A* and B_S correspond to the curves of each rigid model, and real curves *A* and B_S to the curves in which the vibration factors for each atomic distance as shown in Table II are taken into account. (In the other real curves, the factors are not taken into account for convenience, because the effects of the factors are not large enough to change the features of each maximum and minimum.)

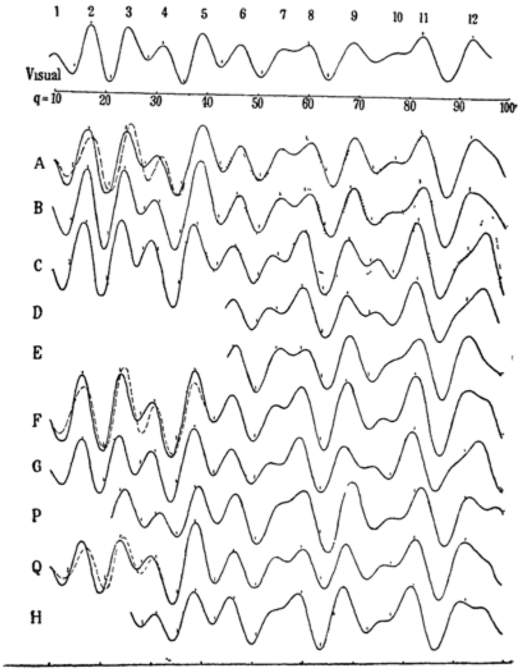

Fig. 3B. Visual and theoretical intensity curves for isopropyl chloride molecule.

Broken curves on A, F and Q in the range of $q<45$ correspond to each eclipse model, and all real curves in this *q*-range to each staggered model. Dotted curves on A, B and C in the range of $q>40$ correspond to the curves of each rigid model, and in all real curves from A to R in this *q*-range, the vibration factors are taken into account. The damping effects to the features of the curves seem to be remarkable in the range of $q>50$, especially the tenth maximum and the eleventh minimum.

+ In order to obtain the better visual curve, especially to confirm the intensity relation of the third maximum with the following shelf and the fifth small maximum, we have photographed by the use of a new apparatus, which has $1/s^2$ sector and the camera length about 11.82 cm., which has recently been constructed and is now in regulating. But since the microphotometry could not yet be applied, we have measured carefully by the visual method.

The influence of the vibration factors using the values above mentioned are shown with the dotted curves on the curves A and Bs.

The radial distribution curve was computed using the best visual intensity curve (see Fig. 4), The background line is almost smoothed out and the each peak of the curve seems to correspond almost correctly to each distance of all atom-pairs of the best model. The combinations of atomic distances O″ . . . H and C″ . . . H, corresponding to both the eclipse and staggered form of methyl groups seem to appear. From the feature of this curve, however, the fact can not be decided whether these might be the ghost maxima or not (marked with A, B and C in Fig. 4).

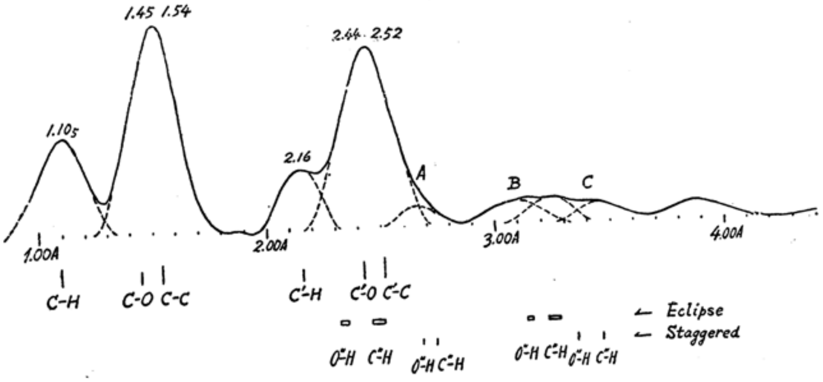

Fig. 4. Radial distribution curve for isopropyl alcohol molecule computed using the visual curve.

Under the curve, the interatomic distance corresponding to each peak is shown, and O″...H and C″...H distances are pointed out at lower levels. Interatomic distances, O″...H and C″...H, are to correspond to either level, (eclipse or staggered), in accordance with the variation of the rotational configurations. But the figures indicated by A, B and C are somewhat obscure.

Isopropyl Chloride.—The visual curve and theoretical intensity curves are shown in Fig. 3B. Molecular parameters used in obtaining each theoretical curve are listed in Table IIIB. The characteristic features of the curves, which change with the variations of corresponding parameters, and the interpretation and selection based on these features of intensity curves are specified as follows:

TABLE III B

THE MOLECULAR MODELS AND CORRESPONDING ASSUMED MOLECULAR CONSTANTS FOR ISOPROPYL CHLORIDE

Models	C—C (Å)	C—Cl (Å)	∠CCC°	∠CCCl°	$q/q_{obs.}$
A	1.54	1.75	109.5	109.5	1.006_0
B	〃	〃	112	109.5	1.006_8
C	〃	〃	112	112	0.989_0
D	〃	〃	114	112	(0.994_7)
E	1.54	1.77	112	108	(1.011_7)
F	〃	〃	109.5	109.5	1.002_5
G	〃	〃	114	112	0.984_6
P	1.52	1.77	109.5	109.5	(1.016_3)
Q	1.56	1.77	〃	〃	0.993_9
H	1.54	1.80	109.5	109.5	0.990_9

1) For the groups of curves from A to D and E to G, the angles ∠CCC and ∠CCCl increase in an orderly way in each group from A to D and E to G. The C-Cl distances are 1.75 Å and 1.77 Å respectively, and other parameters, C-C and rotational configurationes, remain constant.

When compared with those of the visual curve, nearly equal heights of the seventh

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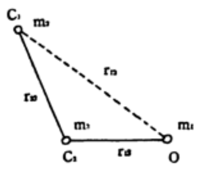

5) P. C. Cross and J. H. Van Vleck [*J. Chem. Phys.* **1**, 350 (1933)] have calculated that the parameters of the equation,

$$V=1/2[c_{13}(\Delta r_{13})^2+c_{23}(\Delta r_{23})^2+c_{12}(\Delta r_{12})^2],$$

are $c_{13}=4.0\times10^5$dyne/cm., $c_{23}=3.5\times10^5$, and $c_{12}=1.7\times10^5$dyne cm. respectively, where V is the potential function for the ethyl alcohol molecule (XXY type molecule), Δr_{ij}'s denote the displacements of interatomic distances as shown in the figure.

6) V. Schomaker et al., *J. Am. Chem. Soc.*, **73**, 1482 (1951).

7) M. Kimura, *J. Chem. Soc. Japan*. **71**, 18 (1950) (Japan).

8) O. Bastiansen, *Acta Chem. Scand.*, **3**, 415 (1949).

9) M. Kimura and M. Yamaha, the work was reported in the First Annual Meeting of the Chemical Society of Japan, April 3rd, 1948 (at Tokyo University, Tokyo).

10) J. Ainsworth and J. Karle, *J. Chem. Phys.*, **20**, 425 (1952).

TABLE IV B

OBSERVED q-VALUES AND CALCULATED q/q_{obs}. VALUES FOR BETTER MOLECULAR MODELS OF ISOPROPYL CHLORIDE

Max.	Min.	q_{obs}	wt.	A	B	C	F	Q
	2	(13.66)		(0.908)	(0.922)			(0.930)
2		16.55	1	1.003	1.009	0.982	1.015	0.997
	3	20.72	1	0.982	0.980	0.965	1.014	0.965
3		23.97	2	1.008	1.010	0.989	1.030	0.997
	4	28.10	1	0.982	0.980	0.959	1.012	0.966
4		30.82	2	0.980	0.980	0.964	1.003	0.972
	5	35.12	1	0.978	0.974	0.968	0.978	0.974
5		38.63	3	1.015	1.015	1.003	1.004	1.002
	6	42.59	2	1.021	1.017	0.997	0.997	1.006
6		46.25	3	1.012	1.012	0.995	0.995	1.002
	7	50.54	2	1.005	1.003	0.989	0.995	0.999
7		54.55	2	1.001	1.007	0.982	0.999	0.999
8		59.56	2	1.017	1.021	1.002	1.004	1.006
	9	63.60	2	1.022	1.022	1.008	1.009	1.011
9		68.60	3	1.010	1.013	0.997	1.001	0.997
	10	72.83	1	1.011	1.013	0.989	1.002	0.998
10		(77.31)	1	0.995	0.999	0.962	0.979	0.986
11		82.24	1	(1.010)	(1.010)	0.998	1.001	1.013
12		(92.33)		(1.007)	(1.007)	(1.045)	(1.001)	(0.996)
Weighted mean:				1.006_0	1.006_8	0.989_0	1.002_5	0.990_9
Wtd. mean sq. deviation:				0.012_9	0.013_6	0.014_4	0.010_9	0.013_9

and the eighth maxima, the small shelf-like tenth maximum on the eleventh maximum and the position of the twelveth maximum, the features in the curves A, B, E and F seem to be satisfactory. For angles ∠CCC and ∠CCCl≧112°, the features above pointed out become less satisfactory while further deviations occur, as shown in the curves D and G.

2) Curves P and Q, having constant C-Cl =1.77Å and ∠CCC=∠CCCl=109.5°, show the changes of *q-values* according to the variation of C-C distances, from 1.52Å to 1.56Å. The q/q_{obs}. values of curve Q are almost acceptable, but the values of P are so large that it seems to be out of the range of errors.

3) On the curves A, F and Q, the contributions of the rotational configurations of methyl groups appear in the range $10<q<35$. The broken curve on each curve corresponds to the eclipse form of each model, and real curves in the same q-range correspond to the staggered form. By the visual method, it is hardly possible to determine exactly the intensity ratio of the second to the third maxima, because of the coexistence of background in the q-range. So the difference of this ratio which appears in the theoretical intensity curves is not remarkable enough for us to distinguish it.

4) The effects of vibration factors are approximately taken into account in all the cases A to H. Dotted curves on A, B and C in the range $40<q$ show the curves in which these factors are neglected, i.e. they correspond to the rigid models. The damping effect agrees roughly with the visual curve in the intensity relations of maxima and minima in the range $q>60$, that is, the pictures from the curves including the factors seem to require the tenth maximum to be lower and the tenth and the eleventh minima to be shallower than the respective lines joining the mentioned adjacent features of the curves in which the factors are ignored.

Various molecular parameters obtained from this investigation seem nearly to agree with and confirm those from the previous data[1], in which the results were obtained from the observation of maxima and minima up to the range $q<50$, because the observation of this report has been obtained from wider range up to $q<95$, in which the variations of features of intensity relations are conspicuously clear in this range ($50<q<95$).

Results and Discussions

From these considerations above pointed out, the models corresponding to the curves B_S, P_S, Q_S, Y_S and Y_E for isopropyl alcohol and C, D, G, P and R for isopropyl chloride are at least to be rejected in our experiment.

We have obtained the final results as follows:

Isopropyl alcohol, C−O : 1.45±0.03Å, C−C : 1.54±0.02Å, ∠CCC≈∠CCO : 110±2.5° and the angle ∠CCO and ∠CCC are not equal to or larger than 112° simultaneously. And also the relative equilibrium position of the methyl groups against the central –CHOH group is not at least the rigorously staggered position.

Isopropyl chloride, C–Cl : 1.76±0.02Å, C–C : 1.55±0.02Å and ∠CCC≈∠CCCl : 109.5 ±1.5°.

These conclusions are reasonable, except in the case of the equilibrium position of methyl groups in the isopropyl alcohol molecule, compared with the structures of several related compounds of these molecules, but some discrepancies are found, for example, in comparison with the results of 1, 2-dichloropropane molecule by V. Schomaker et al.[14] which have shown the values 1.56Å and 1.79Å for C-C and C-Cl distances respectively.

From the results of this investigation, it seems to be hoped that we could obtain some aspects about the problems of methyl groups from the electron diffraction investigations, if we would choose adequate samples and could determine the intensity relations more quantitatively.

Summary

The molecular structures of isopropyl alcohol and -chloride have been investigated by the electron diffraction method. The atomic distances, C-O : 1.45±0.03Å, C-C : 1.54±0.02Å and valence angles,∠CCC≈∠CCO : 110°±2.5° are determined for the former molecule, and distances C-Cl : 1.76±0.02Å, C-C : 1.55±0.02Å and angles ∠CCC≈∠CCCl : 109.5±1.5° for the latter.

The approximate thermal vibration factors have been taken into account for the determination of the best molecular models. The rotational configurations of methyl groups have been considered, but the equilibrium position of two methyl groups cannot be determined conclusively, in spite of the fact that this effect upon the intensity curves are not to be ignored in the case of isopropyl alcohol molecule.

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