Molecular Structural Studies on Compounds Containing C—O Bond by Electron Diffraction. II. The Molecular Structure of Anhydrous Oxalic Acid[1]

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Introduction

A number of studies[2] have been carried out on the structure of carboxyl group by use of x-ray diffraction, electron diffraction and molecular spectra. However systematic conclusion has not yet been reached for the structure of a carboxyl group. Hence it seems to be desirable to have more abundant informations regarding the geometrical configuration of the group in order to discuss the character of carboxyl group by theoretical treatments. An oxalic acid molecule contains two carbonyl groups in a conjugated system $O=C\dot{-}C=O$. Therefore the structural determination will decide the degree of conjugation between the two carbonyl groups across the central $C-C$ bond.

In the present study we dealt with anhy-

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[1] Presented at the 5th annual meeting of the Chem. Soc. Japan held on April 4, 1952.

[2] Cf. O. Thomas, *J. Chem. Phys.*, **18**, 761 (1950); M. Davies and O. Thomas, "Discussion of the Faraday Soc." 335 (1950).

drous oxalic acid in order to investigate the two subject problems mentioned above, i.e. 1) the stereochemistry of the carboxyl group, 2) the degree of conjugation between the two carbonyl groups. Hendricks,[3] Cox et al.,[4] Robertson,[5,6] Brill et al.[7] and Ahmed et al.[8] have already determined the molecular structures of anhydrous oxalic acid and its dihydrate by x-ray diffraction. Their studies were also undertaken mainly to make clear the two problems mentioned above although the results of their analyses appear to be inconsistent as will be described later. According to their results there exists an intermolecular hydrogen bond in the crystal of dihydrate and the distance O−H···O has a value of about 2.50Å, which is considerably short. This suggests that the structure of a free molecule might be different appreciably from the molecular structure in the crystalline state.

Therefore we attempted to determine the structure of a free anhydrous molecule by gas electron diffraction method and to obtain informations on the properties of carbon-carbon and carbon-oxygen bonds as well as on the effect of a hydrogen bond upon these distances.

Experimental Results

The sample used in the present investigation was anhydrous oxalic acid prepared from oxalic acid dihydrate by heating at temperatures above its melting point and was purified by sublimation. Anhydrous oxalic acid readily sublimes on heating at temperatures above 100°C. The sample was sublimed at about 120°C in a high temperature nozzle.

Excellent photographs were taken using an electron wavelength of about 0.06 Å and a camera length of about 11 cm. The characteristic features of the photographs are represented by the visual curve V in Fig. 2, where the dotted portion is drawn by use of the theoretical intensity curves to be mentioned later. That the feature of photograph bears a close resemblance to that of dimethylglyoxal is reasonable on account of the similarity of molecular structure between them. The maxima and minima were measured on the photographs within $q=83$. These observed values are listed in Table I.

TABLE I

OBSERVED AND CALCULATED q VALUES

			model L		model J	
Max.	Min.	$q_{\text{obs.}}$	$q_{\text{calc.}}$	$q_{\text{calc.}}/q_{\text{obs.}}$	$q_{\text{calc.}}$	$q_{\text{calc.}}/q_{\text{obs.}}$
	2	14.91				
2		18.07	18.6	1.016	18.5	1.013
	3	21.60				
3		23.87	24.2	1.014	24.2	1.014
	4	26.30	26.0	0.989	26.2	0.995
4		28.94	29.6	1.022	29.6	1.022
	5	32.16	32.4	1.008	32.1	0.998
5		35.56	36.2	1.017	36.1	1.015
	6	40.80	41.6	1.018	41.8	1.025
6		45.40	45.9	1.012	46.0	1.013
	7	48.87	49.4	1.011	49.2	1.006
7		52.43	53.1	1.013	53.0	1.011
	8	56.18	57.0	1.016	56.4	1.005
8		58.93	60.2	1.021	59.9	1.017
	9	62.90	64.0	1.017	63.5	1.009
9		67.25	68.5	1.020	67.9	1.010
	10	71.13	72.4	1.018	72.1	1.013
10		74.34	75.8	1.021	75.4	1.014
	11	77.78	79.6	1.023	79.3	1.021
11		81.12	83.2	1.024	83.0	1.022
average				1.015		1.012
average deviation				0.005		0.006

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[3] S. B. Hendricks, *Z. Krist.*, **91**, 48 (1953).

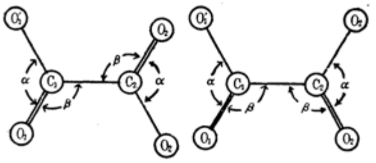
[4] E. G. Cox, M. W. Dougill and G. A. Jeffrey, *J. Chem. Soc.*, **1952**, 4854.

[5] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, **1936**, 1817.

[6] J. D. Dunitz and J. M. Robertson, *J. Chem. Soc.*, **1947**, 142.

[7] R. Brill, C. Herman and C. L. Peters, *Ann. Physik*, **42**, 357 (1947).

[8] F. R. Ahmed and D. W. J. Cruickshank, *Acta Cryst.*, **6**, 385 (1953).



trans form *cis* form

Fig. 1.

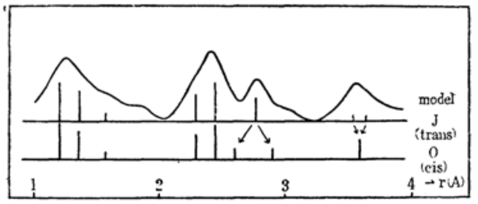


Fig. 2. The radial distribution curve for anhydrous oxalic acid.

The radial distribution curve was calculated by use of the formula

$$rD(r)=\sum_{q=1}^{q=\max.} I(q)\exp(-aq^2)\sin(\pi qr/10)$$

with $\exp(-aq^2_{\max.})=0.1$, and is shown in Fig. 2. The curve has maxima at 1.26, 2.40, 2.75 and 3.55 Å. Each peak may be regarded as made up of the contributions of several interatomic distances. The first peak may be interpreted as representing the bonded $C_1=O_1$ and C_1-O_1' distances, the second peak the non-bonded $C_1\cdots O_2'$, $C_1\cdots O_2$ and $O_1\cdots O_1'$, distances, and the third and the fourth peaks the non-bonded $O_1\cdots O_2'$, $O_1\cdots O_2$ and $O_1'\cdots O_2'$ (see Fig. 1). The last two peaks correspond to the long distances which are related to the rotational configuration about C–C axis. The existence of the third and fourth peaks shows that the four non-bonded O···O distances can be classified definitely into two groups. Accordingly the molecule seems to have, roughly speaking, either the *trans* form or the *cis* form. The sharp feature of the third peak seems to favor the trans form, because if the molecule takes the *cis* form, two equal distances $O_1'\cdots O_2$ and $O_1\cdots O_2'$ in the trans form will turn out to be two different distances $O_1\cdots O_2$ and $O_1'\cdots O_2'$. The possible O–O distances of trans (J) and cis (O) models are shown by bold lines in the radial distribution curve (Fig. 2).

The theoretical intensity curves were calculated with the following simplified equation,

$$I(q)=\sum_{i\neq j}\sum Z_iZ_j\sin(\pi qr_{ij}/10)/r_{ij}$$

Six parameters C=O, C–C, C–O, ∠α, ∠β and ∠γ (a twisted angle) are required for settling molecular forms. The effect of hydrogen atoms is negligibly small on the theoretical intensity curves except the O—H distance which was assumed to be 0.96 Å. If the distance C=O is assumed to be equal to 1.20 Å and the molecule is planar, the parameters involved are as follows C–C/C=O, C–O/C=O, ∠α and ∠β. Fifty three theoretical intensity curves were calculated for the models with the values ranging from 1.44 to 1.60 Å for C–C, from 1.30 to 1.40 Å for C—O, from 116° to 131° for ∠α and from 112° to 134° for ∠β. Some of them are reproduced in Fig. 3. in order to illustrate the variation of the relative positions and intensities of maxima and minima with the change of the parameters.

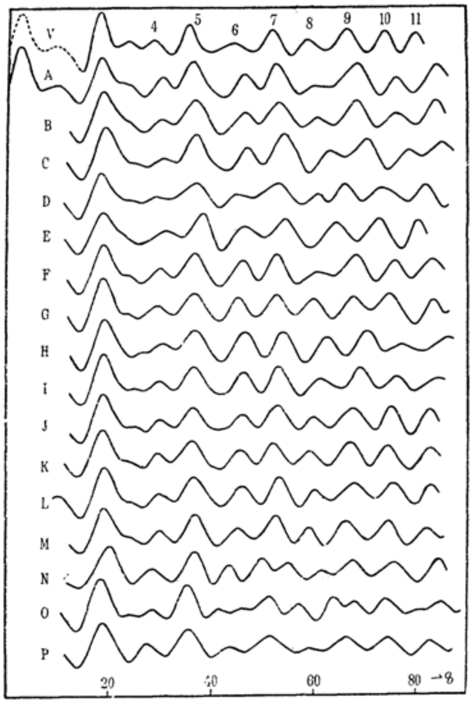


Fig. 3. The visual and theoretical intensity curves.

The models are listed in Table II. The curves A, B, D and E illustrate the effect of ∠β, the curves F and G that of C–O distance, the curves H, I and J that of C–C distance, and curves B, C, K and L that of ∠α. Our analysis could be facilitated by the fact that the calculated intensity curves are not very sensitive to the parameter ∠β. The curve J in Fig. 3, which is one of the best models, is in good agreement with the observed scattering curve, except that the agreement is not perfect in regard to both the height of the third maximum and the depth of the fifth minimum, which appears stronger on photographs than would be suggested by the calculated intensity curves. This discrepancy may be considered to be due merely to a difficulty in the examination of photographs by visual method. It is found that the models with C–C distance smaller (or larger) than that of the best model can also give the theoretical intensity curves in agreement with the visual curve, if the value of ∠α is decreased (or increased) from that of the best model (e.g. curve L in Fig. 2). These circumstances are shown schematically in Fig. 4. Therefore it is impossible to determine the C–C distance very accurately. Further the theoretical intensity curves were calculated for the models with various twisted angles about C–C axis (Cf. Curves M and N in Fig. 2.). If a twisted angle from the

TABLE II

MODELS FOR ANHYDROUS OXALIC ACID

Model	C=O(Å)	C—O(Å)	C−C(Å)	∠α(degree)	∠β(degree)	∠γ and configuration
A	1.20	1.30	1.48	122	123	planar, *trans*
B	〃	〃	〃	122	120	〃 〃
C	〃	〃	〃	125	〃	〃 〃
D	〃	1.35	1.56	〃	117.5	〃 〃
E	〃	〃	〃	〃	112	〃 〃
F	〃	1.33	1.52	123.5	123	〃 〃
G	〃	1.37	〃	〃	〃	〃 〃
H	〃	1.35	1.48	125	〃	〃 〃
I	〃	〃	1.52	〃	〃	〃 〃
J	〃	〃	1.56	〃	〃	〃 〃
K	〃	〃	1.52	122	〃	〃 〃
L	〃	〃	〃	123.5	〃	〃 〃
M	〃	〃	1.56	125	〃	twisted through 30° from the *trans* form.
N	〃	〃	〃	〃	〃	twisted through 60° from the *trans* form.
O	〃	〃	〃	〃	〃	planar, *cis*
P	〃	〃	〃	〃	〃	free rotation

trans form is less than about thirty degrees, it is possible to obtain theoretical intensity curves in agreement with the visual curve, because the two distances which vary with internal rotation, O_1-O_2' and O_1-O_2 or $O_1'-O_2'$ change in opposite directions so that the effect of the changes is partly compensated each other. However the models with a twisted angle greater than about 30° are unacceptable because the third maximum disappears in the theoretical curves. Therefore electron diffraction data can give no conclusive value of the twisted angle about the C−C axis up to 30°. The free rotational and *cis* models are also discarded because of the disappearance of the third maximum and because of the changes of the 6th and 9th maxima into double maxima respectively. The effect of intramolecular vibrations was taken into account for the interatomic distances except for those related to the internal rotation. The mean amplitudes used in the calculation were estimated using the values for oxalyl chloride.9) The results are practically the same as those obtained for the fixed models.

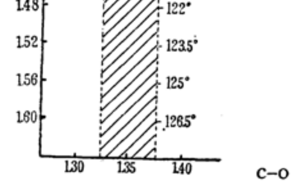


Fig. 4. Parameter chart for oxalic acid. The shaded part shows the region of parameters giving acceptable models when is assumed ∠β=123°.

The effect of the internal rotation can be found in the results obtained from the considerations of the theoretical intensity curves for the models with various twisted angles. But we could not obtain a definite conclusion for the rotational vibration because we must take into account at the same time both the twisted angle in equilibrium and the rotational vibration as well as internal vibrations.

Finally a quantitative comparison with the observed values was made for the maxima and the minima of the best theoretical intensity curves. The results are shown in Table I. For the 2nd and 3rd minima a comparison was not made on account of the inaccuracy of the observed values.

Thus the molecular structure of anhydrous oxalic acid was obtained as follows: C=O 1.22Å ±0.02 Å, C−O 1.37 Å±0.02 Å, C−C 1.54 Å±0.06 Å, ∠O=C−O 125°±3°, ∠O=C−C 122°±5°, and the *trans* form. But the deviation from the *trans* form is permissible within a twisted angle of about thirty degrees.

Although the existence of dimers as in formic acid10) might be improbable in the gaseous state, the theoretical intensity curves were calculated for the model dimerized in the same type as β form of anhydrous oxalic acid.3) When O···O distance is equal to about 2.70 Å, the dimerized model gives a theoretical intensity curve in fair agreement with the visual curve. Further investigation on this point, however, has not been carried out.

Discussion of Results

Our analysis gave the following results: First, the length of the central C−C bond is 1.54 Å, a value generally ascribed to a normal single bond, secondly the molecule is

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9) Y. Morino, private communication.

10) I. L. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 574 (1944).

planar despite the single bond character of the C−C bond. We shall explain the above results and compare the molecular structure of oxalic acid in the gaseous state with that in the crystalline state which has hitherto been reported.

The value of 1.54 Å±0.06 Å was obtained for C−C bond length. This value is equal to C−C bond length in ethane and other saturated hydrocarbons. Therefore C−C bond in an oxalic acid molecule seems to have a small degree of double bond character. Though we cannot say definitely because of the probable errors, the double bond character seems to be less in an oxalic acid molecule than in glyoxal[14] (C−C=1.47 Å± 0.02 Å) and in oxalyl chloride.[15] The molecules of these compounds contain carboxyl groups in a conjugated system similar to that of oxalic acid, i.e. $O=C-C=O$ to which the resonating electronic structures such as $O^+-C=C-O^-$ contribute. This suggests that two carbonyl groups in the molecule are not conjugated very much with each other, presumably because the strongly electronegative hydroxyl oxygen atoms prevent an appreciable π electron conjugation across the C−C bond. Therefore the structure of the carboxyl group will be similar to that of a monobasic acid having only one carboxyl group. According to the recent data obtained by Schomaker and O'Gorman,[11] and Karle[13] shown in Table III, the structure of the carboxyl group in anhydrous oxalic acid is in good agreement with that in a formic acid monomer. The dimensions of the carboxyl group obtained have revealed a significant difference of about 0.15 Å, between the two carbon-oxygen bonds, although the difference between them is less than that expected between a pure single and a pure double bond. Accordingly it follows that the resonance form (B2) to be shown later does not contribute very much to the normal state of a carboxyl group in a gaseous oxalic acid molecule.

TABLE III

STRUCTURES OF CARBOXYL GROUP, ESPECIALLY OXALIC ACID

	C=O	C—O	C—C	material	method
Shibata and Kimura	1.22	1.37	1.54	anhydrus oxalic acid	electron diffraction
Hendricks[3]	1.22	1.29	1.57	„ (α form)	x-ray
Cox, Dougill and Jeffrey[4]	1.19	1.29	1.56	„ „	„
Hendricks[3]	1.20	1.30	1.59	„ (β form)	„
Robertson and Woodward[5]	1.24	1.30	1.43	oxalic acid dihydrate	x-ray
Brill, Herman and Peters[7]	1.21	1.28	1.55	„	„
Dunitz and Robertson[6]	1.24	1.25	1.46	„	„
Ahmed and Cruickshank[8]	1.19	1.29	1.53	„	„
Jeffrey and Parry[17]	1.23	1.25	1.56	ammonium oxalate monohydrate	„
Karle and Brockway[10]	1.24	1.42		formic acid monomer	electron diffraction
„ „	1.25	1.36		„ dimer	„
Schomaker and O'Gorman[11]	1.213	1.368		formic acid monomer	„
Karle[13]	1.23	1.36		„	„
Williams[12]	1.225	1.41		„	spectrum
Karle and Brockway[8]	1.24	1.43	1.54	acetic acid monomer	electron diffraction
„ „	1.25	1.36		acetic acid dimer	„
LuValle and Schomaker[14]	1.20		1.47	glyoxal	„
Schomaker[15]	1.20		1.50	oxalyl chloride	„

We have come to the conclusion that the molecule takes a planar configuration. To account for this fact some interpretation other than resonance interaction between carboxyl groups is necessary. According to the results obtained from Raman spectra and infrared absorption spectra, oxalyl chloride molecule in the liquid state takes a planar trans configuration rather than the *cis* configuration at room temperature and at higher

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[11] V. Schomaker and J. M. O'Gorman, *J. Am. Chem. Soc.*, **69**, 2638 (1947).

[12] V. Z. Williams, *J. Chem. Phys.*, **15**, 232 (1947).

[13] I. L. Karle and J. Karle, *J. Chem. Phys.*, **22**, 43 (1954).

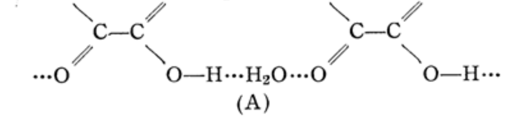
[14] J. E. LuValle and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 3520 (1939).

[15] The results by V. Schomaker cited in L. E. Sutton and P. W. Allen, *Acta Cryst.*, **3**, 46 (1950).

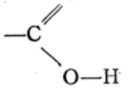
temperatures.[16] The molecular structure in the gaseous state was also confirmed to be the trans configuration by electron diffraction.[15] Moreover the molecular structure of glyoxal in the gaseous state was found to be the trans configuration, by electron diffraction experiment. The coplanarity of oxalyl chloride and glyoxal may be due to the stabilizing resonance energy associated with some double bond character of carbon-carbon bond. If molecule is planar, a consideration of electrostatic interaction and steric hindrance indicates that these molecules should take the trans rather than the *cis* configuration. On the other hand, since the double bond character which restricts rotation seems to be weak in oxalic acid, a consideration of electrostatic interaction and steric hindrance will indicate the possibility of a nonplanar form. Thus the fact that the molecule have the planar and trans configuration or the form similar to it seems to be due partly to the O—H···O intramolecular hydrogen bond similar to that in salicylic acid. This possibility may be supported by the fact that the distance 2.76 Å between the oxygen atoms (for the best model) is appropriate.

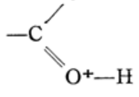
Recently Cox, Dougill and Jeffrey determined the molecular structure of anhydrous oxalic acid (α form)[4] in agreement with a work by Hendricks. Ahmed and Cruickshank carried out a refined analysis using the data obtained by Robertson and his coworkers and by Brill et al. They proposed a new molecular structure of oxalic acid dihydrate. According to these results, as shown in Table III, the C—C bond length is nearly equal to that a normal single bond, 1.54 Å, and two kinds of C—C bonds are equal to 1.29 Å and 1.19 Å respectively, and the molecule is planar.

In general the structure of oxalic acid dihydrate in the crystalline state may be represented by the following schematic formula,[6]

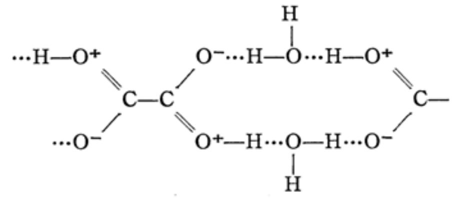

(A)

A carboxyl group may resonate between the two forms,

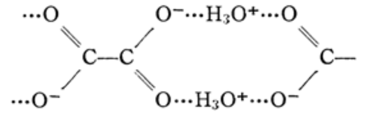

(B₁) and


(B₂)

Accordingly the resonance form,


(C)

may contribute to the normal state of oxalic acid dihydrate. If very strong hydrogen bonds are present in a crystal, the contribution of such resonance from (C) will be appreciably large. As an extreme case, a resonance form


(D)

may be considered. If H_3O^+ is separated completely from other part of oxalic acid dihydrate, two C—C bonds in an oxalate ion should be equal to each other as shown by an x-ray analysis of the crystal structure of ammonium oxalate monohydrate.[17]

Taking into account the data of themselves and of Brill et al., Dunitz and Robertson proposed a remarkable feature of results for the structure of oxalic dihydrate, i. e. the C—C bond length 1.46 Å and two C—C bonds, differing in their lengths, 1.24 Å and 1.25 Å. These results are contradictory to that of Ahmed et al. in regard to the C—C double bond character and to the equality of C—C bond length, owing to the contribution of resonance form (D) to a molecule in the crystalline state. If such is actually the case in the crystalline state, the significant discrepancies between their results and ours suggest that the molecular structure is dependent on the molecular environment.

On the otherh and, Ahmed et al. and Cox et al. concluded that the appareciable difference in two C—C bond lengths suggests the absence of H_3O^+ ion in a dihydrate and that the similarity of the molecular structure of anhydrous oxalic acid to that of its dihydrate indicate the interatomic distances unaffected by the environment of the molecule. However more remarkable difference will be found between vapor and solid than between anhydrous oxalic acid (α-form) and dihydrate.

Upon comparison of their data obtained by x-ray with our data obtained by gas electron diffraction, the following facts are found to be noteworthy: the C—C bond has a normal single bond length and two C—O bond lenghts

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[16] J. S. Ziomek, A. G. Meister, F. F. Cleveland and C. E. Decker, *J. Chem. Phys.*, **21**, 90 (1953).

[17] G. A. Jeffrey and G. S. Parry, *J. Chem. Soc.*, **1952**, 4864.

differ from each other. But the hydroxyl C—O bond is very short in crystals than in free molecules by an amount of about 0.07 Å.

The difference between the C—O and C=O bond is less in crystals than in gaseous state. If such is actually the case, this will be due to the difference between the crystalline state and the gaseous state, in other words to the difference in the environment around a molecule. Such changes of interatomic distances owing to intermolecular hydrogen bonds, have already been pointed out, for example, in the cases of acetamide[18] and hydroquinone[19] and also in the difference of the structures between the monomer and the dimer of formic acid. Therefore it seems to be probable that the structure of anhydrous oxalic acid is not exactly the same as that of its dihydrate, because the length of a hydrogen bond of 2.5 Å in a dihydrate crystal is considerably small. However the results of the molecular structure of oxalic acid dihydrate by x-ray method are not conclusive. The result obtained by Ahmed and Cruickshank seems to be more reliable than those by others, since they carried out a refined analysis using the data obtained by Robertson et al. and by Brill et al. But reinvestigation by x-ray diffraction seems to be desirable on the structure of oxalic acid dihydrate.

Summary

The molecular structure of anhydrous oxalic acid was studied by electron diffraction method. The interatomic distances and valency angles were found as follows: C=O 1.22 Å, C—O 1.37 Å, C—C 1.54 Å, ∠O=C—O 125°, and ∠O=C—C 122° with possible errors within 0.02 Å, 0.02 Å, 0.06 Å, 3° and 5° respectively. The molecule takes planar trans configuration. From these data the following conclusions were derived. The central C—C bond seems to have a small degree of double bond character with no appreciable conjugation between two carbonyl groups. The molecule takes the planar trans configuration in spite of the small degree of double bond character in the C—C bond. This fact in connection with the data of other compounds seems to suggest the possibility of the existence of intermolecular hydrogen bonds in a free oxalic acid molecule. Our data of oxalic acid in the gaseous state were compared with the data of oxalic acid in the crystalline state from x-ray diffraction. Significant differences was found between the results on molecular dimensions, especially in hydroxyl C—O bond lengths. From these fact it was inferred that the structure of a molecule (or a carboxyl group) is affected by the molecular environment such as hydrogen bond formation between molecules.

We wish to express our thanks to Prof. M. Kubo of Nagoya University for his helpful advice. Our thanks are also due to Dr. S. Seki and Dr. K. Osaki of Osaka University for their valuable suggestion regarding the x-ray diffraction data.

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Nagoya

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[18] M. Kimura and M. Aoki, This Bulletin, **26**, 429 (1953).

[19] M. Kimura and S. Shibata, Presented at the 4th annual meeting of the Chem. Soc. Japan held on April 7, 1951.