Molecular Structural Studies on Compounds Containing C—O Bond[1] *by Electron Diffraction. I. Molecular Structure of Gaseous p-Benzoquinone*

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It is well-known that the quantum mechanical treatment can be applied to the problem of the π-electron distribution in a molecule to obtain the relationship between the bond order and bond length[2]. For C-C bond, such treatments have been carried out by many workers and there is much reliable information useful in the discussion of a molecular structure[1], whereas for C-O bond, the relation between the bond order and bond length has not yet been clarified in spite of its interest from the viewpoint of molecular structural theory. This is mainly due to the fact that we lack any abundant informations regarding geometrical configurations. The C-O bond length is affected sensitively by groups or atoms coexistent in the molecule. The difference between the values of the double and the single carbon-oxygen bond distances is larger than that for other heteropolar bonds, e.g. C-N and C-S. The facts mentioned above attract our interests strongly. But we must take into account the state in which the molecular configuration is determined, since the configurations of molecules containing carbonyl, carboxyl and hydroxyl groups are often affected by intermolecular interactions, such as hydrogen bond in crystals[3], in some cases even in the gaseous state. Therefore, it seems to be preferable to determine molecular structures not only by X-ray diffraction but also by gas electron diffraction. Our investigations have been undertaken in order to determine molecular structures in the gaseous state and to discuss the relationship between the bond order and bond length. The structure of methyl and ethyl alcohol[4], 1.4-dioxane[5], trioxane[5] and acetone[6] have already been investigated in our laboratory. It is desirable to choose, as material, molecules, whose physicochemical properties are well-known. The ultraviolet absorption[7] and diamagnetic anisotropy[8] of *p*-benzoquinone suggest that C=O bond is conjugated with another double bond in the molecule. It is also known that *p*-benzoquinone and hydroquinone form a molecular compound, quinhydrone. Therefore these were taken as the materials for our first investigation. The molecular structure of *p*-benzoquinone has already been studied by Robertson[9] with X-ray diffraction by crystal. Though it may be considered that the molecular structure of *p*-benzoquinone in the crystalline state is identical to that in the gaseous state, for the reason mentioned above we believe that it is necessary to determine the molecular structure of gaseous *p*-benzoquinone by the electron diffraction method and to compare the result with the value obtained by X-ray diffraction method. We could not determine the molecular structure of hydroquinone by use of the visual method with sufficient accuracy to discuss the properties of C-O bond. Therefore the result for hydroquinone will

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[1] Cf. e.g. C.A. Coulson and H.C. Longuet-Higgins, *Proc. Roy. Soc.*, A**193**, 450 (1948).

[2] Cf. e.g. C. A. Coulson, *Proc. Roy. Soc.*, A**169**, 413 (1939).

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

[4] M. Kimura, *J. Chem. Soc. Japan*, **71**, 18 (1950).

[5] M. Kimura and K. Aoki, *J. Chem. Soc. Japan*, **72**, 169 (1951).

[6] M. Kimura and Y. Kurita, *J. Chem. Soc. Japan*, **72**, 396 (1951).

[7] H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941).

[8] K. Lonsdale, *Proc. Roy. Soc.*, A**171**, 559 (1939).

[9] J. M. Robertson, *Proc. Roy. Soc.*, A**150**, 106 (1935).

be reported after reinvestigation is carried out by the electron diffraction method with a rotating sector.

TABLE I

OBSERVED VALUES OF q FOR p-BENZOQUINONE

Max.	Min.	q	Max.	Min.	q
2		18.41	8		58.17
3		24.70		8	61.48
4		29.73	9		64.25
	4	32.79		9	65.96
5		35.15	10		68.57
	5	38.31		10	71.63
6		41.77	11		74.03
	6	48.27		11	76.64
7		51.96	12		79.80
	7	55.08			

Experimental

p-Benzoquinone was prepared by the oxydation of aniline, and was purified before use: m.p. 116°C. A temperature nozzle[3] was used in order to obtain the vapor of p-benzoquinone. Seven photographs were taken using a camera length of about 11 cm.[10] and an electron wavelength of about 0.06 Å. Measurements were, as usual, carried out by the visual method[11].

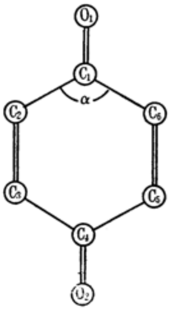

Fig. 1. p-benzoquinone.

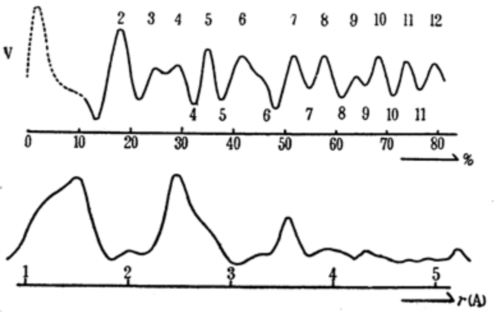

Fig. 2. Visual and radial distribution curves.

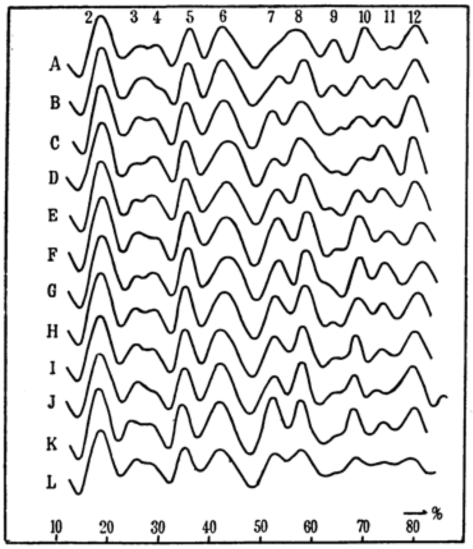

Fig. 3. Theoretical intensity curves for. p-benzoquinone.

The characteristic features of the photograph are shown in curve V of Fig. 2, and q values of maxima and minima are listed in Table I. The observed values of the second and third minima are inaccurate owing to the background. Hence these are not listed in Table I. The radial distribution curve was calculated by the use of the formula

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

where a was taken as $\exp\ (-aq^2_{\max})=0.1$. The dotted line in the visual curve was obtained by the use of the theoretical intensity curve for a model obtained from preliminary calculation of the radial distribution curve. The final radial distribution curve is shown in curve R.D. in Fig. 2. The curve has sharp maxima at 1.50 Å, 2.46 Å and 3.55 Å, corresponding to C_1—C_2, C_1—C_3, C_2—C_6 and C_3—O_1 respectively. The shelf at the left side of the peak at 1.50 Å is attributable to C_1—O_1 and C_2—C_3 (cf. Fig. 2). The peaks corresponding to the other interatomic distances could not be distinguished from ghosts since they contribute negligibly to the radial distribution curve. Though the peak at 1.50 Å might be affected slightly by the contribution of shorter interatomic distances represented as a shelf, it may be concluded that C_1—C_2 and C_2—C_3 interatomic distances are definitely different from each other and that C_1—C_2 distance is approximately equal to 1.50 Å.

The simplified theoretical intensity curves

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

were calculated for the values ranging from 106° to 103° for $\angle\alpha$, 1.48 Å to 1.54 Å for r(C—C), 1.28 Å to 1.36 Å for r(C=C), as-

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[10] M. Kimura, Chemical Research, Vol. 9, p. 53.

[11] Cf. e. g. L. O. Brockway, *Rev. Mod. Phys.*, 8, 231 (1937).

TABLE II

MODELS FOR *p*-BENZOQUINONE

	C=O (A)	C—C (A)	C=C (A)	∠α
A	1.14	1.52	1.32	116
B	1.14	1.52	1.32	112
C	1.14	1.52	1.32	110
D	1.14	1.50	1.34	110
E	1.14	1.50	1.32	110
F	1.14	1.50	1.28	116
G	1.14	1.48	1.30	110
H	1.14	1.50	1.30	110
I	1.14	1.52	1.30	110
J	1.14	1.54	1.30	110
K	1.14	1.52	1.30	108
L	modified I taking the effect of molecular vibrations into account.			

suming that r(C=O) 1.14 Å. A coplanar model was assumed with C—H distance equal to 1.09 Å. With the assumption that r(C=O)=1.14 Å, molecular forms are settled by three parameters, ∠α, r(C—C)/r(C=O) and r(C=C)/r(C=O).

Thirty-four theoretical intensity curves were drawn and the relative positions and features of maxima and minima were compared with the visual curve. Some of them are depicted in Fig. 3. The models corresponding to these curves are listed in Table II. With the increasing angle ∠α, the positions of the 8th and the following maxima shift to larger q values, and the relative intensity of the 7th and 8th maxima and that of the 9th and 10th maxima change as shown in the curves A, B and C in Fig. 3. r(C=O)/r(C=O) is related mainly to the relative intensities of the 3rd and 4th maxima, of the 7th and 8th maxima and of the 9th and 10th maxima (Curve D, E and F). r(C—C)/r(C=O) is related mainly to the relative intensity of the 9th and 10th maxima (curve G, H, I and J). From the criterion mentioned above, the models F, J and K are chosen as the models in good agreement with the visual curve in qualitative sense. The quantitative comparison with the observed values of maxima and minima was made for the calculated values of the models F, I and K.

The effect of molecular vibrations was taken into account in calculations with the following formula,

$$I(q)=\sum_{i<j}\sum\frac{z_i z_j}{r_{ij}}\exp\left(-b_{ij}q^2\right)\sin\left(\pi q r_{ij}/10\right)$$

in which the values of parameters b_{ij} for carbon-carbon and carbon-oxygen atomic pairs were estimated from the spectroscopic data for benzene and other compounds. In Fig. 3, the curve I is that of the fixed model. When the effect of vibration is taken into account we obtain the curve L. As a result it was shown that the features of intensity curves did not change, except the positions of the maxima farther apart than the 9th one, whose changes were surely within experimental errors.

The following values were obtained for the molecular structure of *p*-benzoquinone: ∠α=110°±2°, r(C—C)=1.52 Å±0.02 Å, r(C=C)=1.31 Å±0.02 Å, r(C=O)=1.15 Å±0.02Å.

Discussion

Robertson[8] determined the molecular structure of *p*-benzoquinone using X-ray diffraction method. His values are as follows: ∠α=109°, r(C−C)=1.50 Å, r(C=C)=1.32 Å, r(C=O)=1.14 Å. These values agree excellently with ours. It follows that intermolecular forces are weak in p-benzoquinone crystal and that a molecule in crystal is in an electronic state similar to a free molecule.

The value of C=O 1.15 Å is very short compared with the normal value of C=O distance in ketotype compounds, such as acetone[5]. The value of C=C distance is nearly equal to a pure double bond distance within experimental errors. In spite of the information of conjugation between C=O and C=C, the result obtained from the diffraction experiments suggests that C=O and C=C double bonds are localized to greater extent. The theoretical discussion in regard to these results will be made in our later paper.

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