Electron Diffraction Investigation on Tropolone*

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We have already measured the dipole moments of tropolone and some of its derivatives in benzene solution.(1) The high moments of tropolone were explained adequately by taking into account the contribution of various resonance structures with a formal positive charge at the ring carbon atoms. The resonance was supposed to give a certain amount of double bond character to each bond in the ring, resulting in a coplanar heptagon configuration. The supposition was still too indirect to allow a definite conclusion and hence we undertook an electron diffraction experiment on tropolone to get more direct evidence in support of a regular heptagon ring. After the experiment was complete, an experiment similar to ours was published by Heilbronner and Hedberg(2) and X-ray study by Robertson(3) on the copper complex of tropolone. Though our results were essentially the same as those of Heilbronner and Hedberg, we think it worthwhile to report them in detail, because we could explain the appearance of a peak in the radial distribution function which they failed to assign to any possible distance, and in addition we could deal with the two C-O distances in more extensive manner, the results of which will be of much interest concerning the possible symmetry of this molecule.

Material and Experimental Method.—The tropolone sample (m. p. 50∼51°) was synthesized and purified at the laboratory of organic chemistry, Tohoku University.(4) It was evaporated at a temperature several degrees higher than its melting point, and was led through a high temperature nozzle into a vacuum chamber to interfere with an electron beam of 0.05∼6 A. wavelength calibrated with a gold foil. The diffraction photographs were prepared in the usual way.(5) The camera distance was 11 cm.

Experimental Results.—The visual intensity curve obtained is shown in Fig. 1 (V_1).* The q $(=10s/\pi)$ values for the maxima and minima of diffraction halos are given in Table 1.

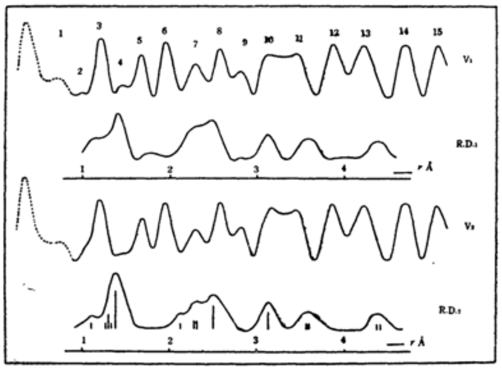

Fig. 1.—Visual curve and the radial distribution function of tropolone

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* Read before the scientific meeting of the Chemical Society of Japan held on April 4, 1952.

(1) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin **24**, 10, 99 (1951).

(2) E. Heilbronner and K. Hedberg, *J. Am. Chem. Soc.* **73**, 1386 (1951).

(3) J. M. Robertson, *J. Chem. Soc.*, **1951**. 1222.

(4) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**, (7) 38 (1950).

(5) M. Kimura, *Chemical Researches*, **9**, 53 (1951).

* The dotted portion was obtained from the theoretical intensity curve calculated for the molecular structure inferred from the preliminary radial distribution function, which was derived from the full line part of the visual intensity curve.

Table 1

The q values for the maxima and minima of diffraction halos

Max.	Min.	q	Max.	Min.	q
1		10.06		9	49.04
	2	12.10	9		51.59
2		14.68		10	54.23
	3	16.62	10		58.74
3		19.10		11	62.61
	4	21.78	11		65.18
4		24.10		12	68.20
	5	26.13	12		72.32
5		28.43		13	75.89
	6	31.04	13		79.60
6		33.91		14	85.00
	7	37.39	14		89.03
7		40.89		15	92.99
	8	43.70	15		96.51
8		46.47			

Table 2

Interatomic distances in tropolone

Bond	Ratio of Z_iZ_j/r_{ij}	Interatomic distance, A.		
		calc.	obs. RD_1	obs. RD_2
C_1-C_2	18	1.39	1.39	1.39
C_1-C_3	11	2.51	2.48	2.51
C_1-C_4	8	3.12	3.13	3.13
O_1-C_2	8	2.28	2.30	2.32
C_1-O_1	7	1.30	—	—
O_1-C_3	5	3.61	3.59	3.60
O_1-C_4	4	4.40	4.38	4.39
O_1-O_2	3	2.52	—	—
C-H	3	1.10	1.10	1.10
C···H	3	2.13	—	2.13

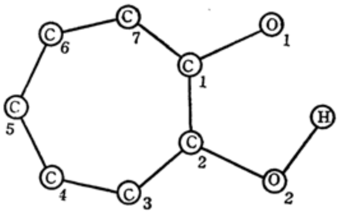

Fig. 2.

The radial distribution function,

$$rD(r)=\sum_{q=1}^{\max} I_q \exp(-aq^2)\sin\left(\frac{\pi}{10}\,qr\right)$$

calculated from the visual intensity curve V_1 is shown in Fig. 1 (RD_1). Here notations have their usual significances and the constant a was chosen so that $\exp(-aq^2)=0.1$ at $q_{\max}$. The peaks at 1.39 and 3.13 A. are sharp and hence the values are accurate. Those at 3.59 and 4.38 A. are distinct but broad, presumably due to the close proximity of two different distances.* The humps at 1.10, 2.30 and 2.48 A. are less distinct and are not suitable for obtaining accurate values for the distance. Of the three weak maxima at 1.75, 2.80 and 4.02 A., the latter two seem to be insignificant, while the first one corresponds evidently to the fairly conspicuous peak at 1.73 A. of Heilbronner and Hedberg. These peaks and humps can be explained properly except the three weak maxima as shown in Table 2 (3rd and 4th columns) with the following two assumptions. (1) The tropolone ring has a plane regular heptagon form shown in Fig. 2 with edges 1.39 A. long. (2) Each of the C-O bonds of 1.30 A. in length lie along a line bisecting the respective ∠CCC angle.

The C-O distance of 1.30 A., O-O distance of 2.52 A. and C-H distance of 2.13 A. will be masked respectively by peaks at 1.39, 2.51 and 2.28 A. The flat peak at 1.75 A. less obvious than that of Heilbronner and Hedberg does not correspond to any possible distance. We suspected that the appearance of this peak might be due to the inaccuracy of intensity estimation by visual method on the 1st, 2nd, 4th, 7th and 9th maxima. We therefore tried to modify the visual curve V_1 in such a way that the ghost disappears. The resulting curve and the radial distribution function obtained from it are shown in Fig. 1 (V_2 and RD_2). The three ghosts in question disappear in the radial distribution function. The curve V_2 is in conformity with the visual estimation except that here the 2nd and 4th weak maxima in V_1 appear as inflection points. It is very hard to determine accurately the intensity of such maxima by visual method. In fact it is known that a weak maximum observed by naked eyes, if examined by microphotometry on a diffraction photograph taken with a sector, turns out to be an inflection point of the curve. Hence we believe that V_2 rather than V_1 is nearer the truth and wish to point out that in view of the fact that the whole visual curve affects the radial distribution function, it is possible that small errors in visual curve may give rise to fortuitous maxima in radial distribution function. The interatomic distances from the modified radial distribution function RD_2 are given in the last column of Table 2. The agreement with the calculated values is excellent.*

In order to determine C-O distance which was masked by a very strong peak at 1.39 A. in the radial distribution function, we calculated the theoretical intensity curve

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* Another explanation that this is due to the vibrational motion of atoms is less likely, because we should then expect similar broadening for the peak at 3.13 A as will be clear in later paragraphs.

* Vertical bars in Fig 1 (RD_2) indicate distances calculated for the best model. The heights of the bar are drawn proportional to Z_iZ_j/r_{ij}.

$$I(q) = \sum_{i<j}\sum \frac{Z_i Z_j}{r_{ij}} \sin\left(\frac{\pi}{10}\, q r_{ij}\right)^*$$

for various values of C_1-O_1 and C_2-O_2 distances ranging from 1.18 to 1.38 A. Here Z_i and Z_j denote the atomic numbers of i- and j-atoms respectively and r_{ij} the distance between them. The ring was assumed to have a regular heptagon form with C-C distance equal to 1.39 A. The line along the C-O bond was assumed to bisect ∠CCC angle. The effect of hydrogen atom could be neglected. A part of the results are summarized in Table 3 and Fig. 3.

Table 3

Various models for the theoretical intensity curves

Model	C_1-O_1 distance, A.	C_2-O_2 distance. A.
1	1.26	1.26
2	1.30	1.30
3	1.34	1.34
4	1.22	1.30
5	1.22	1.38
6	1.26	1.34
7	1.30	1.38

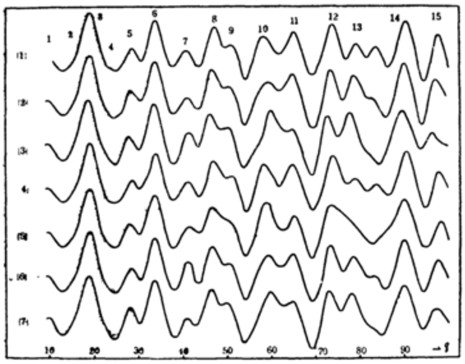

Fig. 3—Theoretical intensity curve

The following experimental facts will serve as a criterion to discard some of the presumed values of C-O distance. (1) The 10th and 11th maxima in the visual intensity curve with nearly equal intensity are broad. (2) The 12th and 13th maxima have nearly equal strength and are sharp. It was found that if the two C-O distances were assumed to have equal length (Cf. models 1∼3), a distance of 1.26 as well as 1.34 A. does not fit the experiment. If the two C-O distances are different, we have naturally a variety of choice, though a distance less than 1.22 A. or greater than 1.40 A. (Cf. models 4 and 5) for one of the two C-O bonds does not give any theoretical intensity curve in agreement with the experiment. If we take vibrational motion into account, the theoretical intensity curve changes in such a way that both the 10th and the 11th maxima become a little flatter, the degree of change being greater for the former than for the latter and that the shelf at the lower right foot of the 13th maximum becomes less obvious. These changes, however, do not alter the conclusions derived for the fixed model. After closer examination,** we found that the best fit with experiment could be obtained for the model 6. The agreement of this model with experiment and the broad peak at 3.60 and 4.39 A. in the radial distribution function seem to imply that tropolone is a mobile tautomeric system of unsymmetrical molecules with the hydrogen atom not occupying a position midway between the two oxygen atoms. The unsymmetrical structure was also favored by Dewar,(6) Cook(7) and others(8) and by Nozoe.(9)

Summary

The molecular structure of tropolone was studied by the electron diffraction method. The most plausible model was found to be a plane regular heptagon form with C-C distance 1.39 A. long and C-H distance 1.10 A., having two slightly different C-O distances, i.e., C-O =1.34 A. and C=O=1.26 A.

We wish to express our thanks to Prof. Nozoe of Tohoku University for providing us with the material prepared for use in the present investigation and to Prof. Morino of Tokyo University for valuable discussions. Our thanks are also due to the Ministry of Education for grants in aid of this research.

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* The effect of vibration of atoms in the molecule, which is not taken into account in this equation, did not affect appreciably the position of maxima and minima and also the relative intensity of maxima lying close together. This will be explained in detail later.

** It was found that a deviation less than 5° of C-O directions in or out of the ring plane does not affect appreciably the theoretical intensity curve. The deviation of this direction greater than about 5° is unlikely, though it may afford another possibility of explanation for the broadness of peaks at 3.60 and 4.39 A.

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(8) H. P. Koch, ibid., **1951**, 512; G. P. Scott and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 240 (1950).

(9) T. Nozoe, T. Mukai and J. Minegishi, *Proc. Japan Acad.*, **27**, 419 (1951); N. Yui and T. Nozoe, *Sci. Reports Tohoku Univ.*, **35**, 83 (1951).