Electron Diffraction Investigation on Tropone[1]

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In recent years, considerable interest has been directed to the determination of the molecular structures of compounds having a seven-membered carbon ring by electron diffraction[2,3] as well as by X-ray crystal analysis[4-6]. However, the investigations that have hitherto been made have dealt with tropolone and its derivatives. Tropone is the simplest compound having a cycloheptatriene ring and for this reason it is most suitable for the determination of the geometric form of this carbon ring. According to the results of dipole moment measurements, this compound is characterized by special resonance stability[7], which is expected to be revealed more directly by the measurements of bond lengths. Recent advances in the experimental technique of electron diffraction by gas molecules have made it possible to obtain the values of structural parameters with high precision. In view of this situation, the present investigation was undertaken in order to determine the structure of tropone by measuring the scattered intensity using the sector-microphotometer method. In this study, it was also possible to determine the magnitudes of vibrational amplitudes of some atom pairs.

Experimental

The electron diffraction photographs of the molecule were taken using a rotating sector. The present studies were made with an r^2-sector provided with a beam trap. The trap was 20 mm. long and 2 mm. in radius[8]. The use of this trap was effective in eliminating extraneous scatterings. The apparatus used was essentially the same as that previously employed[9]. The camera distance was 12 cm. long. The electron beam passing through slits was focused onto a photographic plate, the focused spot being about 0.1 mm. in diameter. The electron wavelength was determined by calibration with a gold foil to be equal to about 0.063 Å.

The sample was kindly furnished by Professor Nozoe of Tohoku University[10]. At room temperature, tropone is a liquid having a low vapor pressure. In order to obtain vapor pressures required for taking good diffraction photographs, it was necessary to use a high-temperature nozzle. Therefore, a number of capillary tubes containing the sample were placed in the furnace. The furnace and the nozzle were maintained at about 100°C during exposures of photographic plates to diffraction beams. The vapor was led through the nozzle and was projected across the electron beam. The pressure of the sample was controlled by regulating the temperature of the reservoir.

In order to apply Karle's method[11] of density-intensity calibration, several sets of two sector photographs were taken, different exposures (about 2 : 1) being employed in each set under otherwise the same conditions. Microphotometric tracings were made on the diffraction patterns using a recording microphotometer. The conversion of the observed densities into intensity curves made after Karle's method[11].

Analysis of Data

Radial Distribution Curve.—In the first place, the structure of the molecule was studied by the radial distribution method, although the correlation method was employed later. The radial distribution curve, $f(r)$ was calculated from the experimental molecular intensity curve according to the equation[12],

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[1] A part of the results presented here has been reported at a meeting of the Chemical Society of Japan held in Sendai in October 1956. A preliminary report has been published in a short communication: K. Kimura, S. Suzuki, M. Kimura and M. Kubo, *J. Chem. Phys.*, **27**, 320 (1957).

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[8] S. Shibata, The Eighth Symposium on X-ray and Electron Diffraction, Osaka, November 1956.

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[11] I. L. Karle and J. Karle *J. Chem. Phys.*, **17**, 1052 (1949). J. Karle and I. L. Karle, ibid., **18**, 957 (1950).

[12] See, for example, P. A. Schaffer, Jr., V. Schomaker and L. Pauling, *J. Chem. Phys.* **14**, 659 (1946).

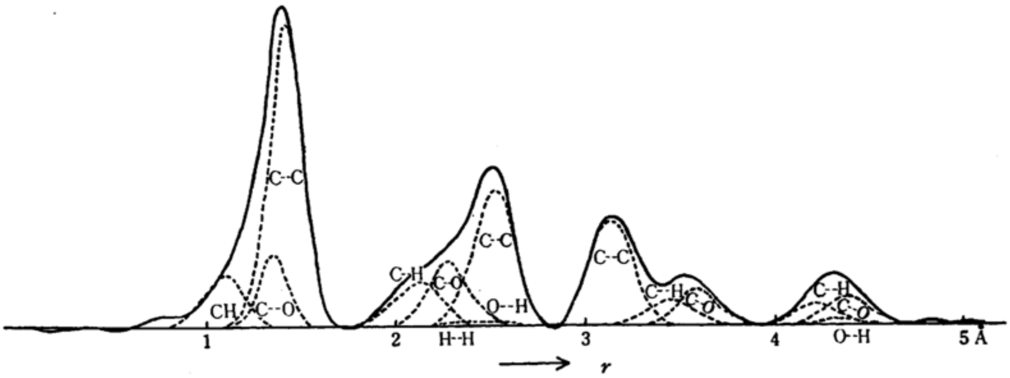

Fig. 1. Radial distribution curve for tropone.

$$f(r)=\sum_{s=0}^{s_{\max}} sM(s)\exp(-bs^2)\sin(sr)$$

where $M(s)$ is the molecular scattering intensity and other symbols have their usual significances. The experimental $M(s)$ curve was obtained by dividing the total intensity by the background intensity, corrections being made for the interference arising from non-nuclear scattering[13]. Fig. 1 shows the radial distribution curve computed with an artificial damping factor chosen so as $\exp(-bs_{\max}^2)=0.1$.

The values of distance were evaluated by fitting Gaussian peaks to the experimental curve. The first peak at about 1.4 Å is due mainly to seven bonded C-C distances (C_1-C_2, C_2-C_3, etc.) and has some contributions from bonded C=O and C—H distances (C_2—H_2, etc.) appearing on the left-hand side of the prominent peak. Here, the carbon atoms composing the ring and the hydrogen atoms attached to it are numbered as shown in Fig. 2. If it is assumed that all the bonded C—C distances are equally long and that C—H distances are also the same, the C-C peak can be located at 1.405 Å and the most probable values for the C—H and C=O distances are 1.09 and 1.26 Å, respectively. The mean amplitude of vibration has been found to be 0.050 Å for the C—C distances. Even if there is some spread in the values of C—C distances, the mean amplitude for each C—C bond will be essentially the same as the above-mentioned value derived on the assumption that all the C-C distances are equally long. However, it is not possible from this analysis to decide whether or not there are small differences among the bonded C-C distances. For example, even if the individual C-C distances were shifted by less than about ±0.01 Å, to give an average distance 1.405 Å, no appreciable change would result in either the position of the C-C peak or in the mean amplitude.

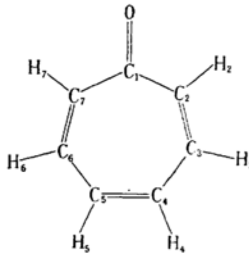

Fig. 2. The numbering of carbon and hydrogen atoms in a tropone molecule.

The second peak at about 2.5 Å can be assigned mainly to the short C···C (C_1-C_3, C_2-C_4, etc.), short C···O (C_2-O and C_7-O) and short C···H (C_1-H_2, etc.) distances. Contributions from short O···H and short H···H distances are negligibly small. The second peak was decomposed into three Gaussian peaks in the following way. The analysis of the first peak showed that even if the carbon ring is distorted from a regular heptagon form, the distortion is slight. Therefore, the short C···O and C···H distances were first assumed to be 2.26 and 2.12 Å, respectively, on the basis of the result from the first peak. Then, the corresponding peaks were subtracted from the total curve, the mean amplitudes of 0.070 and 0.100 Å being used for the C···O and C···H peaks, respectively. The subtraction yielded a peak corresponding to the short C···C distance capable of being fitted with a Gaussian peak centered at 2.52 Å. Next, the reverse procedure was followed, the C···C peak

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[13] L. S. Bartell and L. O. Brockway, ibid., **23**, 1854 (1955).

thus obtained was subtracted from the total curve and then the remaining portion was separated into two peaks, one at 2.28 Å for the $C\cdots O$ distance and the other at 2.10 Å for the $C\cdots H$ distance. The separation was made so that each of these peaks has an area proportional to the number of distances times $z_i z_j / r_{ij}$. Thus the mean amplitude turned out to be 0.066 and 0.110 Å for the $C\cdots O$ and $C\cdots H$ distances, respectively. If the seven-membered carbon ring is assumed to be undistorted from a regular heptagon form, the short nonbonded $C\cdots C$, $C\cdots O$ and $C\cdots H$ distances are calculated on the basis of the observed C—C and C—H distances to be equal to 2.53, 2.26 and 2.12 Å, respectively, in good agreement with the experimental values.

The third peak at about 3.15 Å is due almost solely to long nonbonded $C\cdots C$ (C_1-C_4, etc.) distances and a weak neighboring peak at about 3.5 Å to long $C\cdots O$ (C_3-O and C_6-O) and long $C\cdots H$ (C_1-H_3, etc.) distances. This composite peak was decomposed in the same manner as for the second peak mentioned above. In this case, the separation of the $C\cdots C$ peak was scarcely affected by the peak corresponding to the long $C\cdots O$ distances. The observed values for these three distances, 3.15, 3.58 and 3.46 Å, are in fair agreement with the respective values, 3.16, 3.60 and 3.45 Å, calculated from the model of a regular heptagon form. The mean amplitudes of the $C\cdots C$ distance is 0.079 Å. The remaining peak at 4.3 Å corresponds for the most part to longer nonbonded $C\cdots C$ (C_4-O and C_5-O) and $C\cdots H$ (C_1-C_4, etc.) distances. The distances for the Gaussian peaks resulting from the proper decomposition of the composite peak are 4.40 and 4.20 Å, while the values calculated on the assumption of the undistorted carbon ring are 4.39 and 4.23 Å, respectively.

TABLE I. COMPARISON OF THE OBSERVED DISTANCES WITH THOSE CALCULATED ON THE BASIS OF A REGULAR HEPTAGON MODEL.*

Bond type	Atom pair	Distance (Å) obs.	Distance (Å) calc.
Bonded distances	C—H	1.09	
	C=O	1.26	
	C—C	1.405	
Short nonbonded distances	$C_1\cdots H_2$	2.10	2.12
	$C_2\cdots O$	2.28	2.26
	$H_2\cdots H_3$	(2.35)	2.35
	$O\cdots H_2$	(2.43)	2.43
	$C_1\cdots C_3$	2.52	2.53
Long nonbonded distances	$C_1\cdots C_4$	3.15	3.16
	$C_1\cdots H_3$	3.46	3.45
	$C_3\cdots O$	3.58	3.60
Longer nonbonded distances	$C_1\cdots H_4$	4.20	4.23
	$O\cdots H_3$	(4.37)	4.37
	$C_4\cdots O$	4.40	4.39

* Assumed values are enclosed in parentheses.

Table I shows a comparison of the observed distances from the radial distribution curve with the calculated distances for the molecule having an undistorted regular heptagon ring. It is apparent that the observed and calculated values are in good agreement with each other. In addition, a test for the relative areas of peaks in the radial distribution curve shows an agreement within 5% between the observed and calculated values. Thus, from the analysis of the experimental curve, it was found that the curve could be interpreted adequately on the basis of a coplanar model having a regular heptagon carbon ring. It is important to note that, if the molecule is not planar, some peaks in the radial distribution curve would have appeared in shorter distances than those actually observed. Accordingly, it seems to be adequate to conclude that this molecule is definitely coplanar.

Choice of the Molecular Models.— Before the construction of theoretical curves of molecular intensity is attempted, it is necessary to define the molecular parameters required for the complete description of selected models. The parameters were chosen for the present purpose on the basis of the results obtained from the radial distribution curve. A tropone molecule is presumed to have a plane of symmetry perpendicular to the molecular plane. Consequently, the structure has C_{2v} symmetry and the geometric configuration of heavy atoms can be completely described by giving seven independent parameters, because the carbon ring of the molecule involves four nonequivalent C—C distances. The following seven parameters were chosen in order to determine the structure having the C_{2v} symmetry: C=O, C_1-C_2 (=C_1-C_7), C_2-C_3 (=C_7-C_6), C_3-C_4 (=C_6-C_5) and C_4-C_5 distances along with the x- and y-components of the $C_1\cdots C_3$ (=$C_1\cdots C_6$) distance, which determine the positions of C_3 and C_6 atoms relative to C_1 atom. The C_1-C_2 and C_3-C_4 distances will be almost equal to or longer than the C_2-C_3 and C_4-C_5 distances, since it is likely that the latter bonds have a more or less pronounced double bond character compared with the former. Therefore, two extreme cases were taken up for the C-C distances: First, all the C-C distances are equally long and secondly, C_1-C_2=C_3-C_4=1.43 Å., C_2-C_3=1.38 Å and C_4-C_5=1.37 Å. These distances give an average value that is almost the same as the observed value. As regards the position of the C_3 atom, six points were chosen on a circle of 0.04 Å in radius with its center at the position of the C_3 atom for the regular heptagon ring. The values for the C=O distance were selected at 1.21, 1.26 and 1.31 Å. Since the mean amplitude is an important factor in determining the maxima and minima of intensity curves, various values of mean amplitudes were used for C-C atom pairs as shown in Table II.

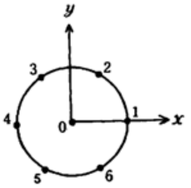

Fig. 3. Various positions of the C_3 atom for "distorted" models. The origin of rectangular coordinates coincides with the position of the C_3 atom in the regular heptagon ring.

TABLE II. VARIOUS SETS OF THE MEAN AMPLITUDES OF C-C ATOM PAIRS IN 10^{-3} Å.

Set	1	2	3	4	5	6	7	8
C—C	50	50	50	50	50	50	50	50
Short C···C	55	55	55	65	65	75	75	85
Long C···C	60	80	100	80	100	80	100	100

Comparison of Theoretical and Experimental Intensity Curves.—In calculating theoretical intensity curves, various atom pairs could be grouped into four different types: (1) C—C, short C···C and long C···C, (2) C=O, short C···O, long C···O and longer C···O, (3) C—H, short C···H, long C···H and longer C···H, and (4) nonbonded O···H and H···H. The distances belonging to types 1 and 2 determine the framework of the molecule. The contributions from the distances of type 1 dominate the greater portion of the intensity curve, i. e., 60∼80 % of the total intensity depending upon the *s* values. They practically determine the positions of maxima and minima of the intensity curve. On the other hand, the distances of type 2 affect the form of a number of shelves in the intensity curves in such a remarkable manner that the C=O distance can be evaluated with fair accuracy. The intensity curves are relatively insensitive to changes in the bond lengths and the valency angles involving hydrogen atoms, i. e., to changes in distances belonging to

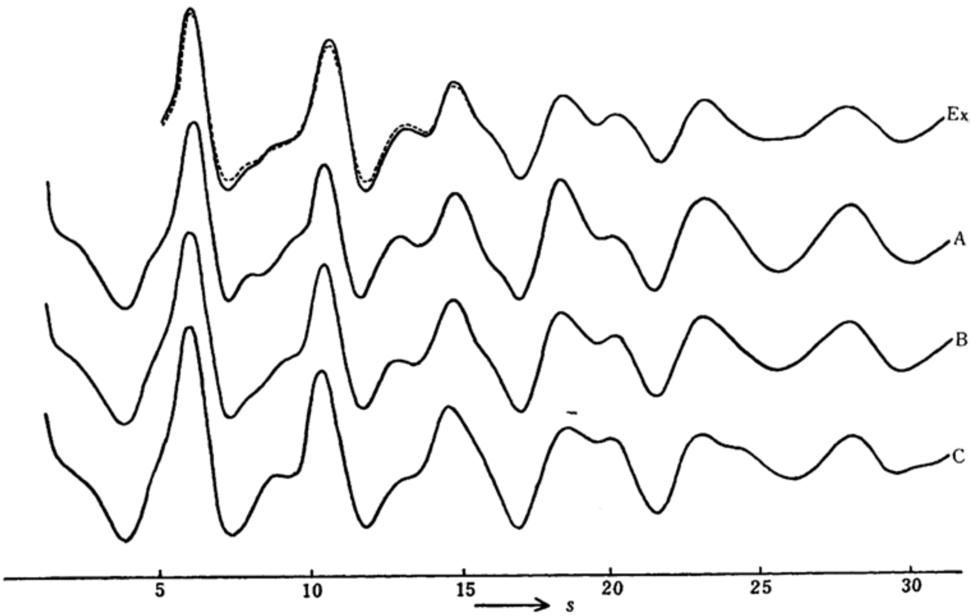

Fig. 4. Comparison between experimental and theoretical intensity curves for tropone. In the experimental curve, the full line represents the intensity curve that was corrected for the constant coefficient[13] and the broken line represents the uncorrected curve.

type 3. The changes of ±0.02 Å in the bonded C—H distances have no appreciable effect on the intensity curves. Therefore, the C—H distance, 1.09 Å, derived from the radial distribution curve was used throughout. The effect of the separations of type 4 is inappreciable. In calculating theoretical intensity curves, all terms of the function[12,13],

$$sM(s)=\sum_{ij}(Z_iZ_j/r_{ij})\exp(-b_{ij}s^2)\sin(sr_{ij})$$

were included. Theoretical curves were calculated using various values for the selected parameters mentioned in the foregoing section and were compared with the observed curve. From this comparison, it became clear that the observed curve could be adequately interpreted in terms of the heptagon model and the C=O distance of 1.26 Å determined from the radial distribution curve was also very satisfactory. An increase or decrease in this distance by 0.05 Å resulted in considerable changes in the intensity curve. Fig. 4 illustrates the experimental curve together with the theoretical curves A, B and C computed for the regular heptagon ring with C=O=1.21, 1.26 and 1.31 Å, respectively. As to the mean amplitudes of the C-C distances, set 4 in Table II was found to give the best values consistent with the experimental curve. As can be seen from Fig. 4, curves A and C show departures from the observed one: for instance, a shelf at about $s=13$ and a maximum at $s=20$ are too high in curve A and too low in curve C. The portion of the experimental curve between $s=7.5$ and 9.4 shows small humps. Curve B well reproduces this feature, whereas curves A and C do not. The value of s/s_{exp} averaged over ten maxima and minima in curve B is 1.000 with an average deviation of 0.0040.

A number of curves for various "distorted" models were also carefully compared with the experimental curve. It was shown that none of the curves for the "distorted" models reproduced the experimental curve better than the heptagon model in regard to the following points. The major points were: First the shape of shelves in the region, $s=7.0\sim9.5$ and at about 14 and 15.5, secondly the shape of the minimum at about $s=19$ and lastly the intensity relations in the region, $s=7\sim24$.

Results and Discussion

The structural results obtained for a tropone molecule are summarized in Table III. Attention should be called to the fact that the experimental radial distribution curve and various features in the experimental intensity curve can be precisely interpreted in terms of a regular heptagon model. Unlike a tropolone molecule, a tropone molecule having only one oxygen atom resonates among a single electronic structure without a formal charge on any atoms of the molecule and various electronic structures of dipolar character. Accordingly, it is likely that the C-C distances are not equally long, but have a more or less pronounced single or double bond character. Therefore, as mentioned above, various "distorted" models were tried. It was found that, provided that the average C-C distance was equal to 1.405 Å, disparities of the order of 0.04 Å in C-C bond lengths as well as of about 10° in ∠CCC valency angles did not lead to models giving theoretical intensity curves very different from that of the "undistorted" model. However, it is of particular interest that the best agreement was obtained between the observed intensity curve and the final theoretical intensity curve for the simple "undistorted" regular heptagon model.

TABLE III. STRUCTURE OF A TROPONE MOLECULE.

Essentially regular heptagon carbon ring
$C\cdots C = 1.405\pm0.005$ Å with $\langle l^2\rangle^{1/2}=0.050\pm0.005$ Å
$C=C = 1.26\pm0.02$ Å with $\langle l^2\rangle^{1/2}=0.038$ Å
$C—H = 1.09\pm0.03$ Å

It is also of interest to observe that the values determined for the C—C and C···H distances in tropone are very close to those reported for benzene[14,15]. The mean C-C distance of 1.405 Å in tropone is almost identical with that in tropolone determined as 1.40 Å[2] and 1.39 Å[3] by the electron diffraction method and with those in various crystalline modifications of tropolone derivatives studied by X-ray analysis, i. e., 1.40 Å[4] in copper(II) tropolonate (=cupric tropolone), 1.40 Å[5] in tropolone hydrochloride and 1.414 Å[6] in sodium tropolonate.

Layton, Kross and Fassel[16] showed that the stretching frequency of carbon-oxygen bonds in carbonyl compounds plotted against the bond length can be represented by a smooth curve. With the aid of this

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[14] I. L. Karle, ibid., **20**, 65 (1952).

[15] A. Almennigen and O. Bastiansen, Research Correspondence, 9 (September 1956).

[16] E. M. Layton, R. D. Kross and V. A. Fassel, ibid., **25**, 135 (1956).

relationship, it is possible to estimate the C=O bond length in a tropone molecule by interpolation from the observed vibrational frequency[17] of the C=O bond. The interpolation indicates that the C=O bond distance is about 1.27 Å, in excellent agreement with the value observed in the present work. Further, an approximate method[18] enables one to evaluate the mean amplitude from the vibrational frequency as $\langle l_{CO}^2\rangle^{1/2}=0.039$ Å, which is also in good agreement with the observed value. In Table IV, the mean amplitudes of C-C atom pairs in tropone are compared with those in benzene.

TABLE IV. COMPARISON OF THE MEAN AMPLITUDES IN Å FOR C-C ATOM PAIRS BETWEEN TROPONE AND BENZENE MOLECULES.*

Atom pair	Tropone	Benzene	
		Karle[14]	Bastiansen[19]
C—C	0.050 (1.405)	0.055 (1.393)	0.0454
Short C···C	0.066 (2.52)	0.067 (2.41)	0.054
Long C···C	0.079 (3.15)	0.075 (2.786)	0.061

* The corresponding equilibrium distances in Å are enclosed in parentheses.

Summary

The electron diffraction photographs of tropone in the gaseous state were taken with an r^2-sector. The data of the scattered intensity was analyzed by means of the radial distribution method as well as by the correlation method. The investigation of the molecule has led to the conclusion that the molecule assumes an essentially co- planar structure having a regular heptagon ring. The most probable values for the bond distances are: C—C=1.405±0.005 Å, C=O=1.26±0.02 Å and C···H=1.09±0.03 Å.

We wish to express our thanks to Professor T. Nozoe for providing us with the sample used in the present investigation, to Professor R. Uyeda for his permission to use a microphotometer and to Mr. H. Morimoto for his help in carrying out microphotometric tracings. We are also to the Ministry of Education for financial assistance.

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[17] E. Kloster-Jensen, N. Tarköy, A. Eschenmoser and E. Heilbronner, *Helv. Chim. Acta*, **39**, 786 (1956).

[18] K. Kimura and M. Kimura, *J. Chem. Phys.*, **25**, 362 (1956).

[19] O. Bastiansen and S. J. Cyvin, *Nature*, **180**, 980 (1957).