Electron Diffraction Investigation on Tribromotropolone[*]

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In a series of researches by one of the present writers and his collaborators,[1-7] measurements were made of the dipole moments of tropolone and a number of its derivatives using benzene solutions. The positions of various substituents in these tropolone derivatives were determined from a comparison of the observed moments with the theoretical moment calculated for various conceivable positions of the substituents. In this determination, an assumption was tacitly made that in analogy to ortho and para positions in benzene only carbon atoms 3 (ortho), (para) and 7 (ortho′) are to be considered for the positions of substituents such as halogen atoms or a nitrogroup. One of the present writers and his collaborator[8] calculated π-electron distribution using the molecular orbital treatment and thereby revealed that carbon atoms 3, 5 and 7 have a greater share of π-electrons than carbon atoms 4 (meta) and (meta′). This suggests that electrophilic atoms and radicals preferentially attack hydrogen atoms at ortho, ortho′ and para positions.

Although the conclusions derived from these physico-chemical considerations were found to be in conformity with the results of organic synthesis,[8] it is most desirable that this new type of ring compounds be provided with a more direct experimental proof in favor of the adequacy of the aforementioned assumption. The present investigation was undertaken in order to verify that the three bromine atoms of tribromotropolone are substituted for the hydrogen atoms of tropolone at ortho, ortho′ and para positions. This compound is comparatively complicated for an electron diffraction experiment. Fortunately two of the present writers[10] as well as Heilbronner and Hedberg[11] have already carried out an electron diffraction study on tropolone and elucidated the geometrical configuration of the molecule of this compound. It is anticipated because the atomic number of bromine is high that the positions of bromine atoms in tribromotropolone can be determined by electron diffraction method accurately enough to give a decisive conclusion.

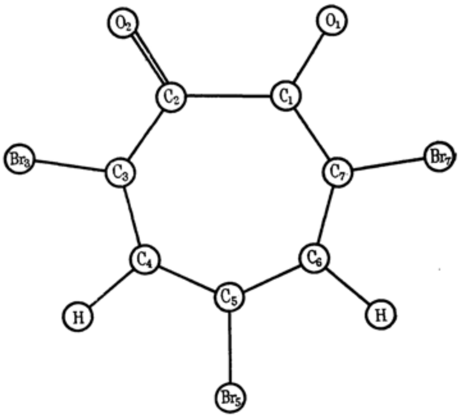

Fig. 1. o, o′, p-Tribromotropolone.

Material and Experimental Method.—A sample of tribromotropolone (m.p. 126°) was synthesized and purified in the laboratory of organic chemistry, Tohoku University. It was evaporated at a temperature 20—30° higher than its melting point and then passed through the high temperature nozzle described in a paper by one of the present writers and his collaborator.[12] The gas molecules ejected into a vacuum chamber interfered with an electron beam having a wavelength of about 0.06 Å. The wavelength was calibrated by means of gold foil. The camera length was 11 cm.

Experimental Results.—The visual intensity curve obtained is shown in Fig. 2. The q-values for the maxima and minima are given in Table I. From the visual intensity curve, a preliminary radial distribution function was calculated. The interatomic distances thus evaluated were used to obtain a preliminary theoretical intensity curve for

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

[1] M. Kubo, T. Nozoe and Y. Kurita, *Nature*, **167**, 688 (1951).

[2] Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**, 10 (1951).

[3] Y. Kurita, T. Nozoe and M. Kubo, ibid., **24**, 99 (1951).

[4] Y. Kurita, T. Mizuno, T. Mukai and M. Kubo, ibid., **26**, 192 (1953).

[5] Y. Kurita, T. Nozoe and M. Kubo, ibid., **26**, 242 (1953).

[6] Y. Kurita, S. Seto, T. Nozoe and M. Kubo, ibid., **26**, 273 (1953).

[7] Y. Kurita and M. Kubo, ibid., **27**, 364 (1954).

[8] Y. Kurita and M. Kubo, ibid., **24**, 13 (1951).

[9] See papers by T. Nozoe and his collaborators published for the most part in the *Proc. Japan Acad.* and *Science Repts. Tohoku Univ.* Series I since 1950.

[10] M. Kimura and M. Kubo, This Bulletin, **26**, 250 (1953).

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

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

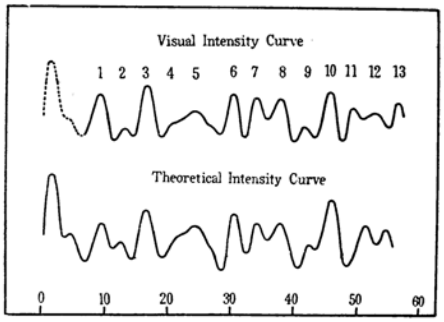

Fig. 2. The visual intensity curve and the theoretical intensity curve of tribromotropolone.

TABLE I

THE q-VALUES FOR THE MAXIMA AND MINIMA OF DIFFRACTION HALOS

Max.	Min.	q obs.	Max.	Min.	q obs.
1		9.42		8	35.64
	2	11.01	8		37.90
2		12.86		9	39.38
	3	14.45	9		41.62
3		16.36		10	43.36
	4	18.63	10		45.30
4		20.58		11	47.13
	5	22.48	11		49.20
5		24.39		12	50.88
	6	27.82	12		53.00
6		30.02		13	54.20
	7	31.61	13		56.30
7		33.73			

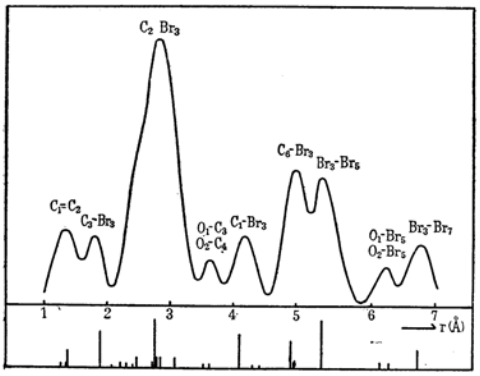

Fig. 3. The radial distribution curve of tribromotropolone.

TABLE II

INTERATOMIC DISTANCES IN TRIBROMOTROPOLONE

Atom pairs	Z_iZ_j/r_{ij}	Distances (exp.)	Distances (theor.)
Br_3–Br_5	38	5.40 A	5.40 A
Br_3–C_2	38	2.80	2.76
Br_3–C_3	28	1.82	1.88
Br_3–C_1	26	4.15	4.10
Br_3–C_6	21	4.96	4.92
Br_3–Br_7	15	6.77	6.74
C_1–C_2	13	1.36	1.36
Br_7–O_1	8	2.80	2.86
Br_3–O_2	8	2.80	2.79
C_1–C_3	8		2.47
C_1–C_4	7		3.08
Br_3–O_1	5	4.96	4.98
Br_7–O_2	5	4.96	4.92
Br_5–O_1	4	6.23	6.28
Br_5–O_2	4		6.14
O_2–C_1	4		2.22
Br_3–H_4	4	2.80	2.74
O_1–C_1	3	1.36	1.36
O_1–C_2	3		2.32
O_2–C_2	3		1.26
O_1–O_2	2		2.42
O_1–C_3	2	3.64	3.64
O_1–C_4	2		4.42
O_2–C_4	2		3.54
O_2–C_5	2		4.30
C_4–H_4	1		1.09
C_3–H_4	1		2.07

the range below $q=8$. As shown in Fig. 2, the visual intensity curve is extended to the region of small q-values by means of this theoretical intensity curve. The final radial distribution curve,

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

obtained from the visual intensity curve supplemented by the dotted curve is shown in Fig. 3. In this equation, notations have their usual significances. The constant a was chosen to give $\exp(-aq^2)=0.1$ at the maximum q-value. The atomic distance evaluated from this radial distribution curve are given in the third column of Table II. They are assigned to atom pairs given in the first column. The designation of the atom pairs is evident from Fig. 1. In the second column, the values of Z_iZ_j/r_{ij} are given in arbitrary unit. The atom pairs contributing predominantly to each peak in the radial distribution curve are also given in Fig. 3. It will be seen from Table II and Fig. 3 that the majority of peaks in the radial distribution curve are due to interatomic distance involving a bromine atom or between bromine atoms. Therefore it is possible to determine definitely the location of three bromine atoms relative to each other and also to the tropolone ring. The interatomic distances obtained from the radial distribution curve can adequately be explained if we consider that the three bromine atoms are substituted for hydrogen atoms of tropolone at otho, para and ortho′ positions. If a bromine atom were in meta or meta′ position instead of at para position, the peak at 5.40

Å would be absent and the peak at 3.00 Å should be higher than the peak attributable to C_2–Br_3 distance. If each of three bromine atoms were bonded separately to one of three carbon atoms which, in turn, are bonded together consecutively, even though a peak at 5.40 Å could appear the peak at 3.00 Å would be much higher than it is in actuality and agreement could never be attained with the observed data. Thus it is confirmed that the sample of tribromotroplone under investigation is an *o, o', p*-derivative.

The radial distribution function of tribromotropolone is not suitable for the determination of the geometrical configuration of a tropolone ring. This is because the only distance obtainable for the determination of ring structure from the radial distribution curve is C–C bond distance equal to 1.36 Å whereas a number of parameters are required for the definite detrmination of the geometrical configuration of the molecule of this compound. In addition the mean amplitudes of various normal modes of vibration will appreciably affect the form of theoretical intensity curves. Considering possible errors inherent in the visual intensity curve, it seems impossible to determine the configuration of the molecule under investigation unless some simplifications be made. Therefore we assumed as follows. (1) The cycloheptatriene ring has a plane regular heptagon form with the length of its edge equal to 1.36 Å, as already mentioned. (2) All three C–Br bonds have the same length and are directed outward from the ring along the lines bisecting the respective ∠CCC angles so that both Br(para)-Br(ortho) and Br(para)-Br(ortho′) distances are equal to 5.40 Å, as revealed by the radial distribution curve. (3) The C–H distance is equal to 1.09 Å. (4) The C–O distance is equal to 1.36 Å, while C=O istance is 1.26 Å long, as found in a tropolone molecule.[10]

A theoretical intensity based on these assumptions,

$$I(q)=\sum_{i<j}\sum\frac{Z_iZ_j}{r_{ij}}\sin\left(\frac{\pi}{10}qr_{ij}\right), \qquad (2)$$

in which a constant factor is omitted, has been calculated for a rigid model and is given in Fig. 3. The interatomic distances calculated for this model are given in the last column of Table II. The vertical bars in Fig. 3. are drawn in proportion to Z_iZ_j/r_{ij}. It will be seen that the agreement of the theoretical intensity curve with the visual intensity curve is satisfactory and that the vertical bars in Fig. 3. are in good accord with the heights of peaks in the radial distribution function.

We do not intend to assert that this theoretical intensity curve is the only possible form in agreement with experiment. For instance, the C–C distances in the ring could be a little longer or they might not be exactly equal. Despite these minor reservations, we believe that the problem of the positions of bromine atoms relative to the tropolone ring is undoubtedly settled.

Summary

Tribromotropolone of melting point 126° was investigated in gaseous state by electron diffraction method. The two Br–Br distances equal to 5.40 Å and 6.77 Å respectively were found as distinct isolated peaks in the radial distribution curve. These distances together with the known configuration of tropolone ring already studied gave decisive evidence that in this molecule three bromine atoms are substituted for hydrogen atoms of tropolone at ortho, ortho′ and para positions. This conclusion is in good agreement with the prediction of molecular orbital treatment of tropolone and proves the adequacy of the assumption made in the structural determination by dipole moment data, i.e. that electrophilic atoms and groups substiute hydrogen atoms of tropolone at ortho, ortho′ and para positions but not those at meta and meta′ positions.

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