Studies of Molecular Structures by Electron Diffraction. I. The Molecular Structure of Monofluoro- and Monobromobenzenes

By Tooru YUZAWA (†) and Mashio YAMAHA

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The molecular structures of monofluoro- and *o*-difluorobenzenes with regards to the C-F distance from the resonance theory were investigated by Dr. H. Oosaka[1] using electron diffraction method. Recently a new apparatus which is capable of giving photographs of large scattering angle diffraction pattern has been constructed in our laboratory. We have reinvestigated the molecular structure of monofluorobenzene and also investigated the structure of monobromobenzene and determined the lengths of C-F, C-Br and C-C bonds using this new apparatus.

Experimental

The new apparatus is of the vertical hot cathode type, and the accelerated electron beam from the cathode is focused by an electromagnetic coil. The camera length is about 91 mm. The wave length of the electron beam is 0.062~0.054 Å, which is calibrated by the gold photographs.

Monofluorobenzene (boiling point: 85.0°C.) was synthesized[2] by the following reaction:

$$C_6H_5NH_2+HBF_4+NaNO_2 \xrightarrow[\text{ice cold}]{\text{HCl}} C_6H_5N_2BF_4 \xrightarrow{\text{heat}} C_6H_5F+N_2\uparrow+BF_3\uparrow.$$

Commercial monobromobenzene was purified by distillation. (Boiling point: 154.0°C.).

Results and Discussion

The theoretical intensity curves for several assumed molecular models have been calculated by the formula[3],

$$I=k\sum_i\sum_j Z_iZ_j/r_{ij}\cdot\exp(-b_{ij}q^2)\cdot\sin qr_{ij},$$

where $q=10s/\pi, s=(4\pi\sin\theta/2)/\lambda$, θ the scattering angle, and λ the wave length of the beam. The thermal vibration factore exp $(-b_{ij}q^2)$ is ignored here[4].

In Table 1 are shown the assumed interatomic distances of the molecular models with marks from A to H for fluorobenzene and from J to O for bromobenzene. The coplanarity of the benzene ring and the attached halogen atom is assumed for all models. The visual intensity curves of ten or more photographs of each substance are compared with the theoretical curves in Figs. 1 and 2. The q-values at the measured maxima and ratios $q/q_{obs.}$ with the deviations of the theoretical q-values from the observed are listed in Tables 2 and 3 for each substance.

Table 1

Assumed Molecular Models Corresponding Interatomic Distances (cf. Figs. 1 and 2)

	C—C	1.38	1.40	1.42 (Å)
C—F:	1.27 (Å)	A	D	
	1.31	B	E	(H)
	1.35	(C)	F	
C—Br	1.86	J	L	(N)
	1.88	K	M	O

In order to determine the consistent molecular models, we have compared the shapes and q-values of maxima of theoretical curves. and found the following characteristic features

For monofluorobenzene, 1) the 7th maximum is influenced by C—C distance variation, 2) the 4th and the 6th maxima, and the separation between the 3rd and the 4th change by C—C and C—F distances, and 3) the shape of the 9th and the 10th maxima has the characteristic feature for C—F variation, and it also depends slightly on the thermal vibration of the molecule (See Fig. 1).

For monobromobenzene, 1) generally, the q-values of intense maxima shift sligtly by the variation of C—C distance, and 2) the 6th, 8th and 11th maxima as well as the shape of the 4th maximum change with C—Br (See Fig. 2).

These considerations lead us to the conclusion that:

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[1] H. Oosaka, This Bulletin. **15**, 31 (1940). cf. C. Finbak & O. Hassel, *Arch. Math. Naturvidenskab*, **45**, No. 3,8 (1941).

[2] "Organic Synthesis" XIII. p. 46.

[3] R. Spurr and V. Schomaker, *J. Am. Chem. Soc.*, **64**, 2693 (1942). cf. L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **57**, 2684 (1935).

[4] The influence of various thermal vibrations is small as will be seen in our next report on difluorobenzenes (5).

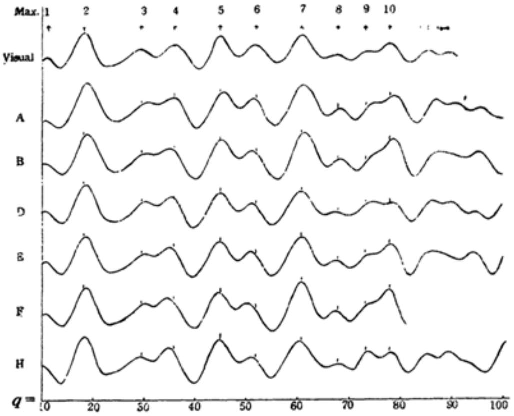

Fig. 1. Theoretical and Visual Intensity Curves for Monofluorobenzene.

The measured q-values of maxima are shown by arrows and dots on each curve. (These are the same in Fig. 2.)

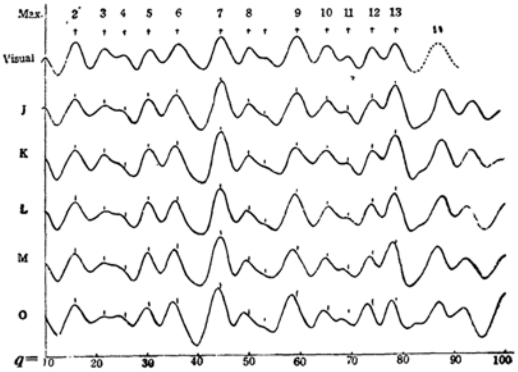

Fig. 2. Theoretical and Visual Intensity Curves for Monobromobenzene

Table 2

Observed q-values and the Comparison of Measured and Theoretical Values for Monofluorobenzene.

Models		A		B		D		E		F		
Max.	$q_{obs.}$	q/q_o	dev. (q's)	q/q_o	dev. (q's)	q/q_o	dev. (q's)	q/q_o	dev. (q's)	q/q_o	dev. (q's)	wt.
1	11.05	—	—	—	—	—	—	—	—	—	—	
2	18.05	1.042	+0.75	1.042	+0.75	1.036	+0.65	1.025	+0.45	1.019	+0.35	1
3	29.35	1.048	+0.41	1.024	+0.7	1.031	+0.9	1.028	+0.8	1.024	+0.7	1
4	35.80	0.997	−0.1	0.986	−0.5	0.989	−0.4	0.972	−1.0	0.964	−1.3	2
5	44.80	1.018	+0.8	1.011	+0.5	1.009	+0.4	0.998	−0.1	0.996	−0.2	2
6	51.90	0.990	−0.5	0.983	−0.9	0.981	−1.0	0.976	−1.2	0.970	−1.5	1
7	60.66	1.012	+0.9	1.011	+0.6	0.996	−0.2	0.996	−0.2	0.996	−0.2	2
8	67.62	1.012	+0.8	1.012	+0.7	1.004	+0.3	0.999	−0.1	0.998	−0.1	1
9	diffuse											
10	77.31	1.023	+1.4	1.017	+0.9	1.015	+0.7	1.009	+0.3	1.001	−0.3	1
*												
mean av.		1.017_8		1.010_6		1.007_5		1.000_2		0.995_2		
av. dev.		0.014_9		0.013_4		0.015_2		0.016_0		0.014_8		
wt. mean av.**		1.015_5		1.008_6		1.004_9		0.997_0		0.993_1		
mean sq.av.dev.			0.78		0.63		0.58		0.68		0.76	

* See Fig. 1. for outer halos.

** Used weights for each maximum are shown in the last column. In these average values the contribution of the C-C variation is predominant.

Table 3

Observed q-values and the Comparison of Measured and Theoretical Values for Monobromobenzene.

Models		J		K		L		M		O	
Max.	$q_{obs.}$	q/q_o	dev. (q's)	q/q_o	dev. (q's)	q/q_o	dev. (q's)	q/q_o	dev. (q's)	q/q_o	dev. (q's)
2	15.97	1.005	+0.08	0.996	−0.07	0.996	−0.07	0.989	−0.17	0.989	−0.17
3	21.56	1.020	+0.4	1.007	+0.14	1.011	+0.24	1.009	+0.19	1.011	+0.24
4	25.65	—	(−0.6)	—	—	—	—	—	(−0.8)	—	—
5	30.40	1.007	+0.2	1.005	+0.15	0.997	−0.1	0.993	−0.2	0.987	−0.4
6	35.97	0.997	−0.12	0.988	−0.42	0.990	−0.37	0.988	−0.42	0.979	−0.8
7	44.47	1.005	+0.2	1.002	+0.1	0.997	−0.12	0.996	−0.2	0.991	−
8	49.95	1.001	+0.15	0.999	−0.05	0.994	−0.3	0.989	−0.5	0.979	−0.8
	shelf										

9	59.44	1.003+0.06	0.994−0.3	0.991−0.5	0.986−0.8	0.982−1.1
10	65.30	1.006+0.4	0.997−0.2	0.999−0.05	0.992−0.5	0.989−0.8
11	69.40	0.996−0.3	0.994−0.4	0.994−0.4	0.987−0.9	0.984−1.1
*						
mean av.		1.004_4	0.997_9	0.996_6	0.992_3	0.989_0
av. dev.		0.004_7	0.004_2	0.004_0	0.004_9	0.005_6
mean sq. av. dev.		0.24	0.24	0.28	0.48	0.74

* See Fig. 2 for outer halos.

C—F = 1.30 ± 0.03 Å for monofluorobenzene, C—Br = 1.86 ± 0.02 Å for monobromobenzene, and C—C = 1.39 ± 0.02 Å for the both.

This C—F length of monofluorobenzene is shorter than the previously reported value 1.34 Å[1)], but is more accurate since the outer halos are taken into account in this case. We are investigating the carbon-halogen distances of various halogenated benzenes containing fluorine atom. For instance, the value 1.30 Å for C—F bond are obtained for *m*- and *p*-difluorobenzenes[5)].

The Pauling formula, which shows the shortening of the bond length in the molecule with resonance structures, is

$$R = R_s - (R_s - R_d)\,(3x/2x+1),$$

where x is the double bond character, R_s and R_d are the interatomic distances[6)] for a single and double bond respectively, and R is the resultant intermediate distance. The values of x estimated from our observed bond lengths are 29% for C—F of monofluorobenzene and 25% for C—Br of monobromobenzene. If we use the corrected values of R_s, 1.355 Å for C—F and 1.883 Å for C—Br, which are the length of the normal single bond proposed by Pauling and Schomaker[7)], we obtained 16.9% for C—F and 13.3% for C—Br.

Summary

The molecular structures of monofluorobenzene and monobromobenzene have been investigated by the electron diffraction method. The C—F and C—Br distances in each molecule have been determined as 1.30 ± 0.03 Å and 1.86 ± 0.02 Å respectively. These distances are shorter than the case in which the bonds have the normal single bond characters. The double bond characters for these bonds have been calculated and obtained 16.9% for C—F and 13.3% for C—Br, in which we have considered the corrected single bond lengths in both cases.

Acknowledgment

We would express our deep gratitude to the late Professor H. Oosaka for his guidance, especially for having suggested to us the study of this problem; to Mr. M. Tanaka, Director of Kichô Shindôsho Factory, for having offered to us very useful material for the construction of the apparatus; and also to Mr. S. Uchida for his kind help in its actual construction.

Department of Chemistry, Faculty of
Science, Tokyo University of
Education, Tokyo

[5)] Published shortly (we have investigated for p- and o-fluorochlorobenzenes, p-fluorobromobenzene and m- and p-difluorobenzenes).

[6)] L. Pauling, "The Nature of the Chemical Bond" p. 175 (1940).
R_S=1.41 Å, 1.91 Å for C-F, C-Br respectively, and R_d=1.21 Å, 1.81 Å for C=F, C=Br respectiveiy.

[7)] L. Pauling and V. Schomaker, *J. Am. Chem Soc.*, 63, 37 (1941).
$R_{AB}=R_A+R_B-\beta\,|x_A-x_B|$, values for C-F, C-Br bonds are as follows:
R_C=0.77 Å*, R_F=0.72 Å, R_{Br}=1.14 Å*, x_C=2.5, x_F=4.0, x_{Br}=2.8, β=0.09. C-F: 0.77+0.72—0.09(4.0—2.5)=1.355 Å, C-Br: 0.77+1.14—0.09(2.8—2.5)=1.883 Å.
* proposed by Pauling and Huggins.