Studies of Molecular Structures by Electron Diffraction. II.
The Structures of *o*-,*p*-Fluorochrolobenzene and *p*-Fluorobromobenzene

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Introduction

Recently the molecules of fluorine substituted benzene derivatives have been the subjects of several investigations. Early electron diffraction results on fluorobenzene and *o*-difluorobenzene by the visual method was reported by one of the authors.[1] The quoted bond lengths, C—F, have been 1.34± 0.04 Å and 1.35±0.03 Å respectively. A little later a discrepant result was reported by Finbak and Hassel[2] who found 1.31±0.03Å for the C—F distance in fluorobenzene by the sector method.

It was, therefore, decided to carry out the

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[1] H. Oosaka, This Bulletin, **15**, 31 (1940).

[2] C. Finbak and O. Hassel, *Arch. Math. Naturvidenskab,* XLIV (1941); O. Hassel and H. Viervoll, *Acta Chim. Scand.,* **1**, 149 (1947).

extensive measurement on the various fluorobenzene derivatives. Not long afterward, some of our collaborators have reported the result of reinvestigation of fluorobenzene.³⁾ And, in this paper, the molecular structures of *o*-, *p*-fluorochlorobenzene and *p*-fluorobromobenzene are to be reported as a second part of this series.

Materials

Each fluorobenzene derivative was prepared from corresponding nitroaniline by the successive diazotations. All steps are too familiar to describe in detail but the step, Schiemann reaction, where a fluorine atom is introduced into the aromatic nucleus.

Schiemann Reaction.⁴⁾—(The following procedures are common to the three compounds mentioned above.)

(A) **Preparations of Diazonium Fluoborates.**—To a mixture of 100 cc. of 40% fluoboric acid and 50 cc. of water is added 0.25 mole of well ground corresponding halogenated aniline. The solution (or suspension) is cooled to 5°C., and a saturated solution of 17.3 g. (0.25 mole) of sodium nitrite is added slowly, the temperature being kept under 20°C. The precipitate is washed with cold water, cold methanol and ether successively. The yields are 92% (o-$BF_4N_2ClC_6H_4$), 89% (p-$BF_4N_2ClC_6H_4$) and 93% (p-$BF_4N_2BrC_6H_4$).

Meigs⁵⁾ reported that the temperature of the reacting mixture may rise to 30°C. without ill effect during the diazotation of aniline in fluoboric acid solution. Carrying out the diazotations for several numbers of compounds,⁶⁾ we extended Meigs' conclusion over nearly all monohalogenoaniline. Table 1 serves to confirm this conclusion by showing the yields obtained under several different temperatures, in case of the diazototation of *p*-fluorochloroaniline, as an example.

Table 1
Temperature Effect for the Diazotation of *p*-chloroaniline

Sample	Temp. of bath (°C)	Max. temp. of reacting mixture (°C)	Yield (%)
1	15	30	78.5
2	7	18	88.7
3	0 (ice)	10	86.1
4	−10 (ice-NaCl)	0	84.7

All the other halogenated anilines can be treated likewise: there are no troubles up to 20°C. However, in case of nitroanilines, the reacting mixture must be kept under 7°C, because considerable decomposition occurs even at about 10°C. A more severe condition is necessary in case of tetrazotation: decomposition begins at about −8°C.

(B) **Decompositions of Diazonium Fluoborates.**—Decompositions were carried out according to the direction of Organic Reactions.⁴⁾ The yields were 68% (o-$FClC_6H_4$), 72% (p-$FClC_6H_4$), and 74% (p-$FBrC_6H_4$).

Each sample was distilled before use.

Experimental

Electron diffraction photographs of *p*-fluorochlorobenzene were taken in the apparatus of Brockway type with the camera distance of 13.4 cm. For the other two compounds a new camera, previously described,³⁾ was used.⁷⁾ About eight photographs were taken for each compound under different conditions, and were measured visually in the usual way. The electron wave length was determined to be 0.052∼0.064 Å by caribration against gold leaves.

Theoretical intensity curves were calculated by the following equation.

$$I(s)=\sum_i\sum_j Z_iZ_j\exp(-a_{ij}s^2)\frac{\sin sl_{ij}}{sl_{ij}}$$

where $s=(4\pi/\lambda)\sin\theta/_2$, l_{ij}: the distance between the i-th and j-th atoms, Z: the atomic number, a: the coefficient of thermal vibration, λ: the wave length, and θ: the scattering angle. (For *p*-fluorobromobenzene and *o*-fluorochlorobenzene, modified parameter $q(=(40/\lambda)\sin\theta/_2)$ was used in place of s.⁸⁾

For hydrogen, an effective value, 1.25, was used in order to approximate better to its low-angle scattering relative to carbon and halogen atoms.

***p*-Fluorochlorobenzene.**—In computing theoretical intensity curves, assumptions were made as below: (1) C—C=1.40 Å, (2) C—H=1.04 Å, (3) ∠H—C—C=∠Hal.—C—C=120°, (4) the molecule has a planar skeleton. The parameter values were made for fourteen models over the following ranges: C—Cl=1.66∼1.72 Å, C—F=1.27∼1.41 Å. All interactions involving hydrogen atoms were included, except H—H terms. The thermal term was neglected since the high-angle scattering region hardly contributed to the determination of parameters. Typical curves are shown in Fig. 2, and the values of the parametersin Fig. 1.

Curve C is inconsistent with the experimental data for lack of max. IV. Curves G and H can be rejected because max. III is too large. In

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3) T. Yuzawa and M. Yamaha, in press.

4) A. Roe, "Organic Reactions" Vol. V, Chap. IV. p. 193.

5) Meigs, U. S. pat. 1,916, 327 (C.A., **27**, 4539 (1933)).

6) *p*-Fluoroaniline, *o*-, *m*-, *p*-chloroaniline, *o*-, *p*-bromoaniline, *p*-iodoaniline and *o*-, *m*-, *p*-nitroaniline were diazotized for this purpose. Tetrazotations were carried out also.

7) Because of the accomplishments of a new apparatus and calculation tables in q scale in the midst of our research, such disorepances were introduced unavoidably.

8) R. Spurr and V. Schomaker, *J. Am. Chem. Soc.* **64**, 2693 (1942).

9) On account of possible majority of thermal vibration on Br···F, some additional curves were calculated with suitable values of a_{ij} for all terms, but the resulting changes were insignificant but for max. IX.

curve F, max. III is larger still compared with max. II. Curves A and B are borderline cases since max. VI is too weak as compared with max. V. Furthermore, curve B can probably be eliminated because of the disappearance of shelf II.

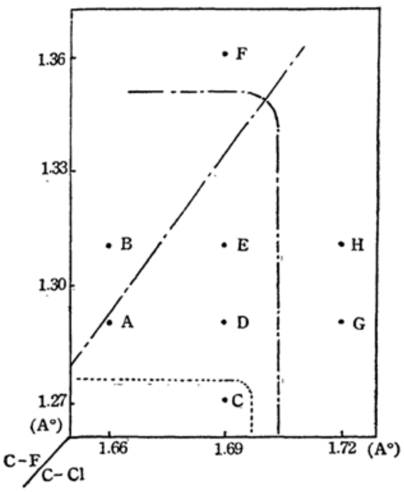

Fig. 1.—Parameter chart for *p*-fluorochlorobenzene

The position of the letters indicate the parameters of the models for which intensity curves were computed. The dashed and dotted lines indicate where particular features of the intensity curves were sufficiently different from the visual curve to make them unacceptable.

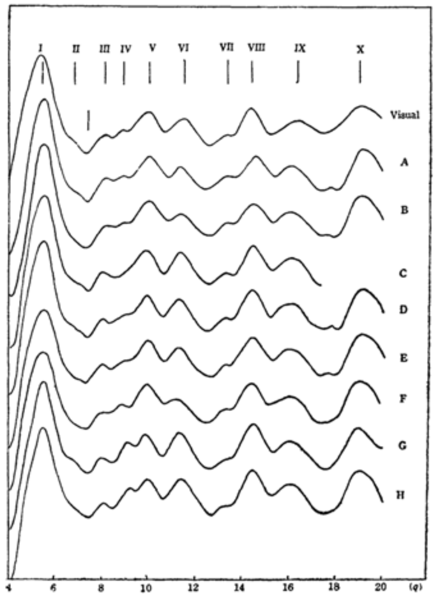

Fig. 2. Theoretical intensity curves for *p*-fluorochlorobenzene.

The best agreement with the observed pattern would be given by a model located about the midway between D and E. Finally we have C—F=1.30±0.03 Å, and C—Cl=1.68±0.02 Å. (The quantitative comparisons are in Table 2.)

Table 2

p-Fluorochlorobenzene

Max.	Min.	Obs. (s)	$s_{c.}/s_{o.}$ A	D	E
I		5.381	1.022	1.025	1.022
II		(6.778)			
	III	7.336	0.988	0.993	0.988
III		8.082	1.007	0.994	0.992
IV		8.890	1.006	1.000	0.996
V		9.935	1.006	0.997	1.000
VI		11.509	0.984	0.980	0.973
VII		(13.398)	(0.996)	(0.988)	(0.985)
VIII		14.381	1.008	1.001	1.000
IX		16.349	0.984	0.979	0.981
X		19.016	1.003	1.003	1.001
Average, 9 features			1.001	0.997	0.995
Mean deviation, Δ			0.011	0.009	0.010
Mean square root, $(\Delta^2)^{1/2}$			0.012	0.013	0.014

***p*-Fluorobromobenzene.**—Theoretical curves were calculated over the following parameter ranges: C—Br=1.84∼1.90 Å, C—F=1.27∼1.33 Å. The assumptions were made just as those of fluorochlorobenzene. Typical ones of these curves are shown in Fig. 4, and the values chosen for the parameters in Fig. 3.

In order to avoid laborious computation in a literal treatment of the thermal factors, a_{ij} was neglected over all models and a procedure was adopted wherein two curves were plotted for several models. The light curves represent only the scattering due to non hydrogen distances and the bonded C—H distances; in addition to these terms, the heavy curves include the non-bobded C···H and Hal.···H terms. The heavy curves are significant for small q and the light curves for large q.

Curve A may be excluded because of the intense max. III. Dislocation of max. V eliminated curve J and put curve I on a borderline. For the remaining curves, there are not any sufficient reasons to eliminate them qualitatively. Indeed curves F, G and H lack max. VI, and curves B, C and F show max. XI distinctly. However, they are too weak to be decisive criteria hence the thermal effects may weaken these tendencies.

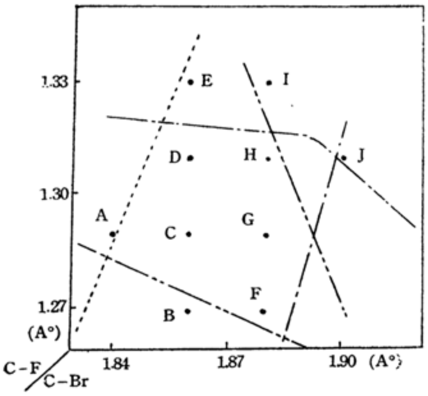

Fig. 3.—Parameter chart for p-fluorobromobenzene.

The quantitative comparisons are tabluated in Table 3. As the final result we obtain C—F = 1.30 ± 0.03 Å and C—Br = 1.87 ± 0.02 Å.

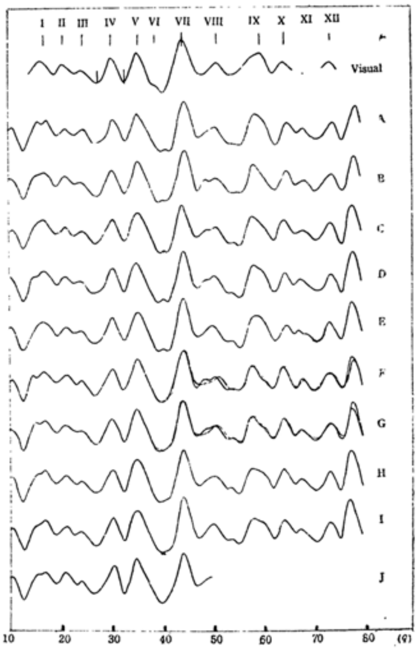

Fig. 4.—Theoretical intensity curves for p-fluorobromobenzene.

Table 3

p-Fluorobromobenzene

Max.	Min.	Obs. (q)	$q_{c.}/q_{o.}$		
			C	D	G
I		16.68	0.999	1.006	1.006
II		20.86	1.006	1.016	1.006
III		24.61	(0.980)	(0.980)	(0.976)
	IV	27.46	(0.977)	(0.970)	(0.984)
IV		30.08	1.007	1.004	1.004
	V	33.03	0.993	0.990	0.984
V		35.59	0.986	0.986	0.992
VI		(38.8)			
VII		44.42	0.999	1.008	1.000
VIII		51.35	0.993	0.985	0.993
IX		59.99	(0.958)	(0.963)	(0.953)
X		64.60	1.003	1.001	1.000
XI		73.76	1.003	1.002	1.002
Average, 9 features			0.999	1.000	0.999
			1.001	**1.002**	**1.000**
Mean deviation, Δ			0.005	0.008	0.005
Mean square root, $(\Delta^2)^{1/2}$			0.007	0.010	0.007

	B	E	F	H
Average, 9 features	1.003	1.001	0.998	0.998
	1.006	**1.002**	**1.001**	**0.999**
Δ	0.010	0.009	0.008	0.007
$(\Delta^2)^{1/2}$	0.011	0.012	0.010	0.008

Black style numerals indicate the values obtained from temperature-factored curves.

o-Fluorochlorobenzene.—In this case, we cannot always assume the coplanarity of all atoms. Using the sector method, Bastiansen and Hassel[10] concluded that the forces acting between C-halogen atoms tend to bring the halogen atoms out of the plane of the benzene ring. However, as opposed by Morino,[11] this result is inconceivable theoretically.

No matter which they may be, in computing theoretical intensity curves this problem has no significiant base of arguments; no important difference on the shapes of the curves were found between the coplanar model and non coplanar one, and hence the molecule was assumed to have a planar skelton in this case.

Parameter ranges were taken as: C—Cl=1.67~1.75 Å, C—F=1.29~1.37 Å, F—Cl=2.90~3.04 Å. The assumption and the thermal factors were treated in a way similar to the case of p-fluorobromobenzene. Fig. 5 and Table 4 show typical curves and their parameters of twenty-one models which have been tested.

Curves A, B, F, G, and H are rejected because they show considerably different shapes in the region q-=20~30. Curves C, D and E are mostly acceptable, though curve E is rather a borderline case since max. V and XII are somewhat out of step with the observed ones.

However when we examine them more strictly, they show several difficulties: max. VI is too much weaker than the observed, max. XI is too strong relative to max. X. Spreading the ∠Hal.—C—C over 120°, we can remove these difficulties, and curves K and L show the best agreement with the observations. Even curve J shows the fit better than curve C. Curves I and M are borderline cases.

Quantitative comparisons are given in Table 5. The final structure is C—F=1.30±0.03 Å, C—Cl=1.69±0.02 Å, and ∠F—C—C (adjacent of Cl)=∠Cl—C—C (adjacent of F)=121±1°.

Table 4
Parameters for o-fluorochlorobenzene

Model number	C—Cl (Å)	C—F (Å)	Cl—F (Å)	F—C—C (adj. of Cl) Cl—C—C (adj. of F)
A	1.67	1.29	2.90	120°
B	1.67	1.33	2.91	120°
C	1.70	1.29	2.92	120°
D	1.70	1.31	2.92	120°
E	1.70	1.33	2.93	120°
F	1.71	1.29	2.92	120°
G	1.73	1.31	2.94	120°
H	1.73	1.35	2.96	120°
I	1.67	1.29	2.95	121°
J	1.70	1.29	2.95	120°45′
K	1.70	1.29	2.99	121°40′
L	1.70	1.31	2.99	121°30′
M	1.71	1.31	2.99	121°20′

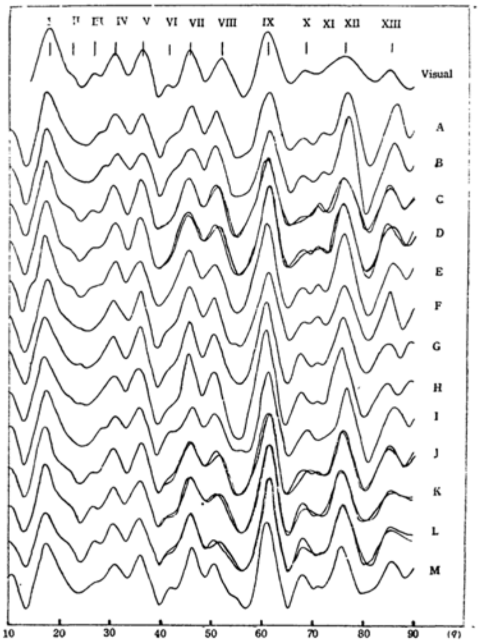

Fig. 5.—Theoretical intensity curves for o-fluorochlorobenzene.

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[10] O. Bastiansen and O. Hassel, *Acta Chim. Scand.*, **1**, 489 (1947).

[11] Y. Morino, Discussion on the Inter- and Intramolecular forces, Tokyo, June, 1952.

Table 5

o-Fluorochlorobenzene

Max.	Obs. (q)	$q_{c.}/q_{o.}$		
		C	J	K
I	17.76	(0.976)	(0.979)	(0.979)
II	(22.28)			
III	26.42	1.001	1.006	1.000
IV	30.56	1.001	1.002	1.004
V	36.29	0.992	0.989	0.989
VI	41.38	/	(1.000)	(1.000)
VII	45.62	1.000	1.001	1.003
VIII	51.98	0.978	0.981	0.981
IX	60.82	1.009	1.007	1.007
X	68.41	(0.994)	(0.996)	(0.994)
XII	76.39	1.002	0.998	0.992
XIII	85.30	0.999	0.999	1.001
Average, 8 features		0.997	0.998	0.996
		0.999	**0.999**	**0.998**
Mean deviation, Δ		0.005	0.006	0.007
Mean square root, $(\Delta^2)^{1/2}$		0.008	0.008	0.008
		D	E	L
Average, 8 features		0.998	0.995	0.997
		1.000	/	**0.998**
Δ		0,009	0.009	0.010
$(\Delta^2)^{1/2}$		0.012	0.010	0.012

Black style numerals indicate the values obtained from temperature-factured curves.

Discussion

We must confess that the value of C—F distance reported earlier by one of us is inadequate.1) In the earlier work, patterns were detectable only up to $s=15$. It is certain that the impropriety was originated from this experimental limitation.

C—Cl and C—Br distances do not contradict that of the previous works published by several authors.

In case of *o*-fluorochlorobenzene, the reason for a deviation of ∠Hal.—C—C from the value of 120° is chiefly a result of repulsion between halogen atoms. The distance to be expected in absence of such deviation must be smaller than the sum of van der Waals radii, which should be at least 3.0 Å. The slight increment of Hal.—C distance which has been found in several *o*-halogenobenzenes, were not observed. This fact may be explained as the repulsive force is not so sufficiently large as to demand the visible stretching of Hal.—C bonds in this case.

Summary

The molecular structures of *o*-, *p*-fluorochlorobenzene and *p*-fluorobromobenzene have been investigated by the electron diffraction method. The following values have been obtained by the analysis based on coplanar structures; C—F = 1.30±0.03 Å, C—Cl = 1.68±0.02 Å for *p*-fluorochlorobenzene; C—F = 1.30±0.03 Å, C—Br = 1.87±0.02 Å for *p*-fluorobromobenzene; and C—F = 1.30±0.03 Å, C—Cl = 1.69 ±0.02 Å, and $\angle \mathrm{C_1{-}C_2{-}F} = \angle \mathrm{C_2{-}C_1{-}Cl} = 121\pm1^\circ$ for fluorochlorobenzene. C—C = 1.40 Å, C—H = 1.04 Å are assumed throughout the analysis.

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