Molecular Structures of Fluorobenzene and *o*-Difluorobenzene by Electron Diffraction.

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The carbon-fluorine distances in molecules are in many cases shorter than expected from the Pauling and Huggins table of covalent radii.(1) Although no shortening occurs in chloromethanes, the investigation of the structures of fluoro- and fluorochloromethanes has shown the shortening of the C-F distances when the molecule contains two or more fluorine atoms.(2) For halogen-substituted benzenes, however, the shortening of the carbon-halogen bond has been found in chlorine, bromine, and iodine derivatives.(3)(4) Keeping these facts in mind the author has investigated the structures of fluorobenzene and *o*-difluorobenzene by the electron diffraction of the vapours.

Experimental. The electron diffraction apparatus of the de Laszlo type(3) was used with some modifications. The air supply to the discharge tube controlled by a Leybold valve connected to an air reservoir of the pressure about 10 cm Hg. The electron beam was focussed by a coil placed near the bottom of the discharge tube. The wave length was measured by a resistance voltmeter which was calibrated directly in terms of wave length by taking the gold photographs. All photographs

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(1) Pauling and Huggins, *Z. Krist.*, **87** (1934), 205; Pauling and Brockway, *J. Am. Chem. Soc.*, **59** (1937), 1223.

(2) Brockway, *J. Phys. Chem.*, **41** (1937), 185, 747.

(3) de Laszlo, *Proc. Roy. Soc.* (London), A, **146** (1934) 662.

(4) Brockway and Palmer, *J. Am. Chem. Soc.*, **59** (1937) 2181.

were taken on Ilford X-ray plates. The interpretation of the gas photographs was made by the usual visual method.

Fluorobenzene⁽⁵⁾ was prepared from aniline and *o*-difluorobenzene⁽⁶⁾ from anthranilic ethyl ester by using hydrofluoroboric acid.

Results. Several photographs were made for each substance, the electron wave length used being about 0.065 Å and the camera distance 29.5 cm. The observed values, s_0, of s given in Tables 1 and 2 are averages of the values found by visual measurement of ring diameters for several plates. The values for inner rings were excluded from the tables because of the strong background intensity. The quantitative comparison and results are also given in Tables 1 and 2. The theoretical scattering curves were calculated by the formula

$$I \sim \sum_{ij} Z_i Z_j (\sin sl_{ij})/sl_{ij} \ ,$$

where $s = 4\pi(\sin\theta/2)/\lambda$. In these expressions l_{ij} is the distance between the *i*th and *j*th atoms, λ the de Broglie wave length of the electrons, θ the scattering angle, and Z the atomic number. The benzene ring was taken as a regular plane hexagon and all the interference terms except those of hydrogen atoms were included, the distances C-C = 1.39 Å and C-H = 1.06 Å being assumed. The curves for several models of each substance are shown in Figs. 1 and 2, in which the observed values of the measured apparent maxima and minima are given by vertical arrows.

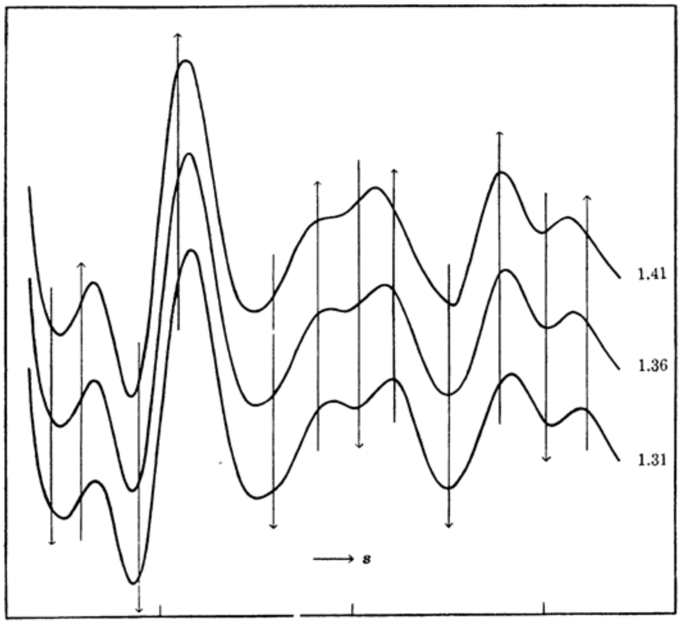

Fig. 1. Theoretical intensity curves for various models of fluorobenzene.

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(5) Carothers, "Organic Syntheses", XIII, 48, New York (1933).
(6) Bergmann, Engel and Sándor, *Z. physik. Chem.*, B, **10** (1930), 106.

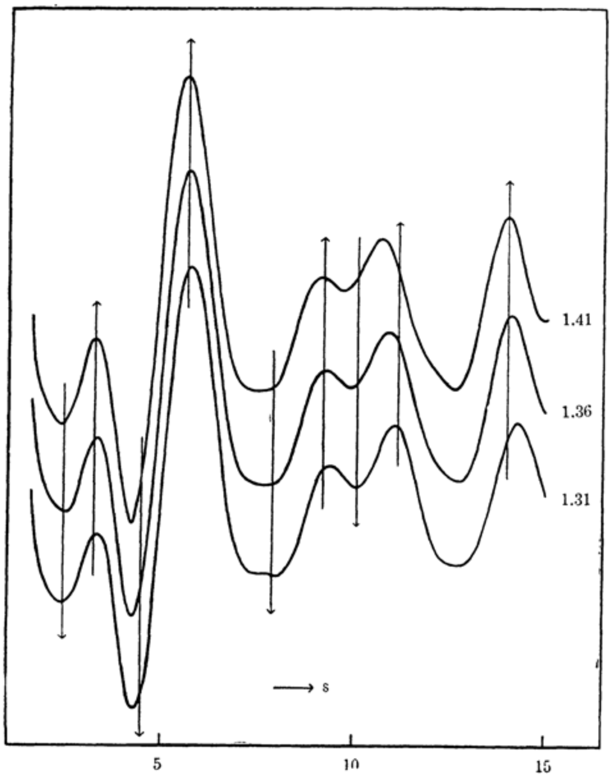

Fig. 2. Theoretical intensity curves for various models of *o* difluorobenzene.

Table 1. Fluorobenzene.

Max.	Min.	s_0	s_I	s_I/s_0	s_{II}	s_{II}/s_0	s_{III}	s_{III}/s_0
2		5.48	5.70	1.040	5.72	1.044	5.77	1.053
	3	7.96	7.50	0.942	7.50	0.942	7.50	0.942
3		9.10	9.00	0.989	9.45	1.038	9.47	1.041
	4	10.18	9.80	0.963	9.73	0.956	10.10	0.992
4		11.10	10.57	0.952	10.88	0.980	11.04	0.995
	5	12.53	12.63	1.008	12.55	1.002	12.50	0.998
5		13.85	13.92	1.005	14.05	1.014	14.15	1.022
	6	15.08	14.96	0.992	15.10	1.001	15.22	1.009
6		16.14	15.65	0.970	15.84	0.981	16.00	0.991
Average				0.985		0.995		1.005
C-F assumed				1.41		1.36		1.31
C-F observed				1.39		1.35		1.32

Final value: C-F = 1.34±0.04 Å.

Table 2. *o*-Difluorobenzene.

Max.	Min.	s_0	s_I	s_I/s_0	s_{II}	s_{II}/s_0	s_{III}	s_{III}/s_0
2		5.67	5.55	0.979	5.66	0.998	5.74	1.013
	3	7.92	7.60	0.960	7.80	0.985	8.00	1.010
3		9.09	9.12	1.003	9.28	1.021	9.40	1.034
	4	10.09	9.73	0.965	9.90	0.982	10.10	1.001
4		11.14	10.71	0.962	10.94	0.982	11.08	0.995
5		13.99	13.95	0.997	14.10	1.008	14.26	1.019
Average				0.978		0.996		1.012
C-F assumed				1.41		1.36		1.31
C-F observed				1.38		1.36		1.33
Final value: C-F = 1.35±0.03 Å.								

Fluorobenzene. The three theoretical curves calculated for fluorobenzene with carbon-fluorine distances of 1.41, 1.36, and 1.31 Å, respectively are shown in Fig. 1. Of these the curve for 1.41 Å is less satisfactory than the other with respect to the fourth minimum and maximum. The other two show qualitative agreement with the observed pattern. The final value, 1.34 ± 0.04 Å, of the C-F distance was taken as intermediate between the results from the latter two models.

***o*-Difluorobenzene.** Theoretical curves were calculated for three undistorted models of *o*-difluorobenzene with C-F distances 1.41, 1.36, and 1.31 Å, respectively. These are shown in Fig. 2. Also in this case the curve for 1.41 Å is less satisfactory for the fourth minimum and maximum. The final value is 1.35 ± 0.03 Å.

In considering the structure of this molecule the angle between the C-F bonds comes in question. In *o*-dichlorobenzene(4) the bending has been found to be less than 1°. In *o*-difluorobenzene, however, the bending of the C-F bonds would be less than the order of this amount if it existed, because the fluorine atom is smaller than the chlorine atom and the interaction between the fluorine atoms is thus expected to be less significant.

Discussion. The carbon-fluorine distances in fluorobenzene and *o*-difluorobenzene are smaller than 1.41 Å, the sum of the covalent radii of Pauling and Huggins. If we consider the various electronic structures of the molecules as shown in Figs. 3 and 4, the decrease of the C-F distance may be attributed to the contribution of electronic structures which introduce a degree of double bond character in the carbon-fluorine bonds. Although the relation of the amount of double bond character to the interatomic distance is not yet known for the C-F bond, we know the empirical relation for the C-C bond(7) and are justified to use it for

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(7) Pauling and Brockway, *J. Am. Chem. Soc.*, **59** (1937), 1223.

the C-F bond because the ratio between the interatomic distances for single and double bonds does not vary very much for different atoms. Hence the degrees of double bond character of the C-F bonds are calculated as 16% and 13% for fluorobenzene and *o*-difluorobenzene, respectively.

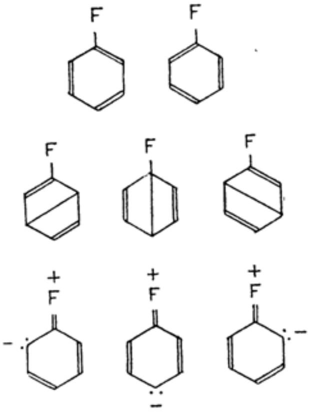

Fig. 3. Fluorobenzene.

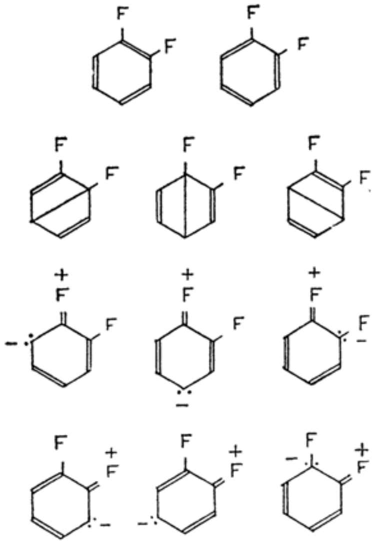

Fig. 4. *o*-Difluorobenzene.

Now the dipole moment of halogen-substituted benzenes will be considered in relation to the carbon-halogen distances. These values for monohalogen-substituted benzenes are given in Table 3 together with those of double bond character. While the moment is increasing in the order from iodobenzene to chlorobenzene, the moment of fluorobenzene is smaller than that of chlorobenzene. As the double bond character is of the same order of magnitude for chloro- and fluorobenzenes, this character seems to be unimportant as the cause of the smaller moment of fluorobenzene. The much shorter C-F bond distance might play an important rôle for the lowering of the moment, the other properties being assumed not much different from each other.

Table 3.

C_6H_5X	Dipole moment(6) (D)	Carbon-halogen distance (Å)	Double bond character (%)
F	1.45	1.34	16
Cl	1.56	1.70	16
Br	1.49	—	—
I	1.30	—	—

Generally dipole moments of ortho-substituted benezenes show the so-called ortho effect. For these molecules the moment is found to be smaller than the vector sum of the moments of substituent atoms. In the case of o-dihalogen-substituted benzenes the effect is more significant in the order from fluorine to iodine. The actual bond angles measured by electron diffraction are given in Table 4 together with interatomic distances and degrees of double bond character. The bendings of the bonds are increasing in the order from fluorine to iodine and the degrees of double bond character can be said to have the similar tendency as the accuracy of these values is not high. Both tendencies agree with the order in the markedness of the ortho effect.

Table 4.

o-$C_6H_4X_2$	Carbon-halogen distance (Å)	Double bond character (%)	Bond angle (°)
F	1.35	13	60
Cl(4)	1.71	11	61.5
I(8)	2.00	18	80

In conclusion, the author wishes to express his gratitude to Professor C. K. Ingold for his suggestion of the problem and to Mr. H. Terrey for his continued encouragement and helpful suggestions throughout the experimental work. He also wishes to thank Emeritus Professor M. Katayama for his interest in this problem and Professor S. Mizushima for discussing the result. He is indebted to the Ramsay Memorial Fellowships Trust for grants.

Summary.

The molecular structures of fluorobenzene and *o*-difluorobenezene have been investigated by the electron diffraction method. The C-F distances in these molecules have been determined as 1.34 ± 0.04 Å and 1.35 ± 0.03 Å, respectively. These distances are shorter than expected from the covalent radii of Pauling and Huggins. This shortening has been discussed in terms of resonance among several valence-bond structures. The dipole moment of halogen-substituted benzenes has been considered in relation to the carbon-halogen distances and the double bond character of the linkage.

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(8) Hendricks, Maxwell, Mosley, and Jefferson, *J. Chem. Phys.*, **1** (1933), 549.