The Studies of Molecular Structures by Electron Diffraction. III. The Structures of m- and p Difluorobenzene

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Introduction

The results of the recent electron diffraction studies on the carbon-fluorine distances in aromatic compounds are collected in Table I.

TABLE I

THE PREVIOUS RESULTS OF THE C–F DISTANCES OF FLUORINE-CONTAINING AROMATIC COMPOUNDS

Substance	C–F distance (Å)	Reference
C_6H_5F	1.34±0.04	1
C_6H_5F	1.31±0.03	2, 4
o-$C_6H_4F_2$	1.35±0.03	1
p-$C_6H_4F_2$	1.31±0.03	3
o-C_6H_4FCl	1.31±0.03	3
p-C_6H_4FBr	1.30±0.03	3

As shown in it, one of us[1] reported that the distance is shorter in monofluorobenzene and *o*-difluorobenzene than in aliphatic compounds, but soon later Hassel[2] reported an even shorter distance in monofluorobenzene, which seemed compatible with the recent data of chlorine-or bromine-containing compounds[3]. In these, it is difficult to determine the precise C—F distance, because the chlorine or bromine atom has much greater scattering power than fluorine. That is the reason why we feel an interest in the difluorosubstitutes, although we may find different C—F distances from the monofluorobenzene.

Experimental

The samples, *m*-difluorobenzene[5] and *p*-difluorobenzene,[6] were prepared by the Schiemann reaction. They showed the boiling points 82°C. and 88°C., respectively.

The camera length is about 9.1 cm. The electron wave length, about 0.055 Å, was calibrated with gold foil diffraction.

Interpretation

The diffraction photographs were interpreted by the usual visual method. For the calculation of the theoretical intensity curves, the formulae

$$I(q)=k\sum_i\sum_j\frac{Z_iZ_j}{r_{ij}}\exp(-a_{ij}q^2)\sin\frac{\pi}{10}qr_{ij}$$

$$q=(40/\lambda)\sin(\theta/2)\qquad a_{ij}=(\pi^2/200)l_{ij}^2$$

are used, where r_{ij} is the distance between the i-th and j-th atom, λ is the electron wave length, θ is the scattering angle, Z_i is the atomic number of i-th atom, and l_{ij} is the mean amplitude of r_{ij}. The thermal vibration terms are neglected as a first approximation, i.e., we put $l_{ij}=0$. It is assumed that the hydrogen and fluorine atoms are coplanar with the regular hexagon benzene ring, and that the distances of C—C and C—H are 1.39 Å. and 1.08 Å. respectively. All the interference terms except those of hydrogen atoms are taken into account. The five theoretical curves calculated for these molecules with C—F distances of 1.27, 1.29, 1.31, and 1.35 Å and a visual intensity curve obtained by photographs are compared in Fig. 1 and 2. The values of q of the observed and calculated maxima, and their ratios $q_{calc.}/q_{obs.}$ are given in Table II and III.

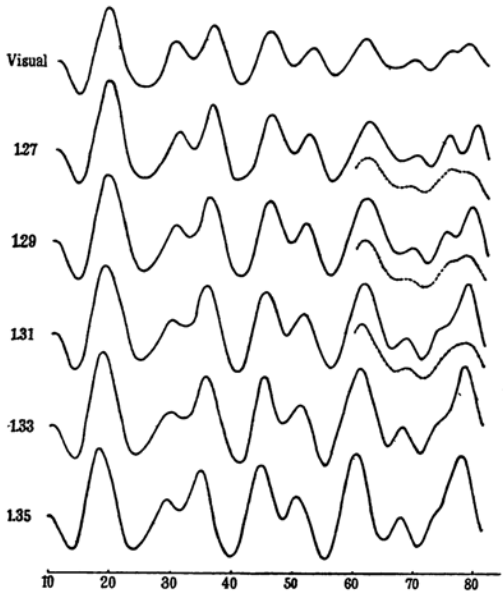

Fig. 1. The visual and theoretical curves of *m*-Difluorobenzene.

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

[2] O. Hassel and H. Viervoll, *Acta chemica Scand.*, **1**, 149 (1947).

[3] H. Oosaka and Y. Akimoto, This Bulletin, **26**, 433 (1953).

[4] T. Yuzawa and M. Yamaha, This Bulletin, **26**, 414 (1953).

[5] G. Schiemann and T. Pillarsky; *Ber*, **62**, 3039 (1929), 3035 (1929).

[6] P. Ruggli and E. Capser, *Helv. Chim. Acta*. **18**, 1414 (1435).

[7] I. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

[8] Y. Morino and Kuchizu, private communication.

TABLE II

$q_{calc.}/q_{obs.}$ OF *m*-DIFLUOROBENZENE

	C–F	1.27	1.29		1.31		1.33
Max.	$q_{obs.}$	$q_{calc.}/q_{obs.}$	$q_{calc.}/q_{obs.}$		$q_{calc.}/q_{obs.}$		$q_{calc.}/q_{obs.}$
1	18.5	1.011	1.005		1.000		0.995
2	29.6	1.024	1.020		1.017		1.014
3	35.9	0.994	0.989		0.983		0.981
4	45.2	1.011	1.007		1.002		0.998
5	52.1	0.996	0.992		0.989		0.984
6	61.0	1.012	1.008	1.005+	1.003	1.000+	1.000
7	68.8	1.016	1.006	0.999	0.999	0.991	0.994
8	74.8	1.004	1.000	1.006	0.996	1.006	0.992
9	78.5	1.013	1.006	0.996	1.000	0.993	0.996
Arithmetical mean		1.009	1.003	1.002	0.999	0.998	0.995
Mean square root deviation		±0.009	±0.009	±0.009	±0.007	±0.007	±0.009

+: These values were estimated from the dotted curves in Fig. 1, which contained the thermal vibrational terms.

Finally, as a second approximation, the thermal vibration terms l_{ij}, roughly estimated (in Table IV) in reference to the calculated aliphatic data,[7,8] are introduced into the most probable three models, for $q \geq 60$. (The values $q_{calc.}/q_{obs.}$ are given in Table II and III.)

The radial distribution function is not calculated, since the C—F distance is the only one variable.

Details and Results

(a) ***m*-Difluorobenzene** (Fig. 1 and Table II). In glancing over the intensity curves, the models for C—F=1.29, 1.31 and 1.35 Å seem right. According to the careful examination of these models on the relative intensities of the corresponding maxima, especially max. VII, the $q_{calc.}/q_{obs.}$ values, and their mean deviations, it is reasonable for the C—F distances of *m*-difluorobenzene to be 1.30±0.03 Å.

(b) ***p*-Difluorobenzene** (Fig. 2 and Table III). A procedure similar to the above, leads us to the conclusion that the C—F distance of this molecule is 1.30±0.03 Å.

They agree well with the results of the previous investigations.

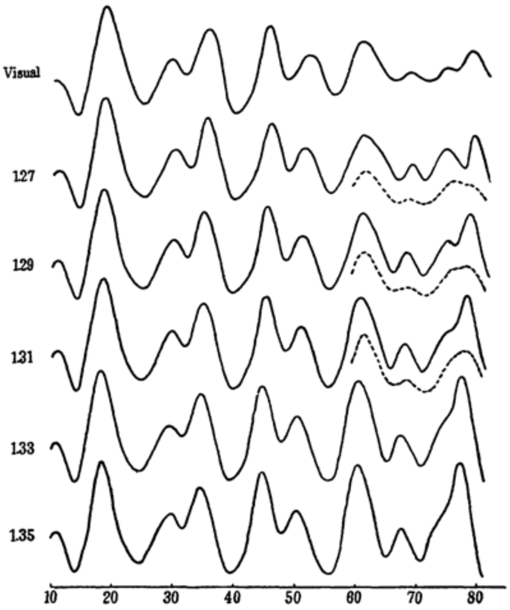

Fig. 2. The visual and theoretical curves of *p*-Difluorobenzene.

TABLE III

$q_{calc.}/q_{obs.}$ OF *p*-DIFLUOROBENZENE

	C–F	1.27	1.29		1.31		1.33
Max.	$q_{obs.}$	$q_{calc.}/q_{obs.}$	$q_{calc.}/q_{obs.}$		$q_{calc.}/q_{obs.}$		$q_{calc.}/q_{obs.}$
1	18.5	1.016	1.011		1.005		1.005
2	29.5	1.027	1.024		1.017		1.014
3	35.8	0.992	0.986		0.980		0.975
4	45.6	1.007	1.002		0.996		0.991
5	52.3	0.987	0.985		0.979		0.973
6	61.1	1.002	1.000	1.000+	0.998	1.000+	0.997
7	68.9	1.004	0.993	0.991	0.988	0.984	0.985
8	74.8	1.005	1.007	1.009	1.005	1.004	0.999
9	79.0	1.008	1.000	1.000	0.995	0.995	0.989
Arithmetical mean		1.005	1.001	1.001	0.996	0.996	0.991
Mean square root deviation		±0.011	±0.012	±0.012	±0.012	±0.011	±0.012

+: These values were estimated from the dotted curves in Fig. 2, which contained the thermal vibrational terms.

TABLE IV
THE COEFFICIENTS OF THE THERMAL VIBRATIONAL TERMS; a_{ij}

$a_{ij}=0.04935\times l_{ij}^2$

Atomic pair	a_{ij}	Atomic pair	a_{ij}
C—C	0.000049	C—F	0.000089
C···C′	0.000064	C···F′	0.000160
C···C″	0.000089	C···F″	0.000253
C—H	0.000128	C···F″′	0.000287
C···H′	0.000226	H—F	0.000130
C···H″	0.000400	$(H\cdots F)_m$	0.000240
C···H″′	0.000460	$(H\cdots F)_p$	0.000350
		$(F\cdots F)_m$	0.000260
		$(F\cdots F)_p$	0.000350

Summary

The C—F distances of *m*-difluorobenzene and *p*-difluorobenzene are investigated to be almost equal, 1.30±0.03 Å.

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