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Microwave Spectrum of *o*-Difluorobenzene[*1]

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The microwave spectrum of *o*-difluorobenzene has been studied in the 7.8- to 28-Gc/sec region, R- and Q-branch transitions of the a-type being assigned for the lowest vibrational state. The rotational constants obtained are $A=3263.55$ Mc/sec, $B=2227.91$ Mc/sec, and $C=1323.87$ Mc/sec. Four possible sets of structural parameters were obtained. It seems probable that the angle made by two C–F bonds is larger than 60°. The value of the dipole moment obtained is 2.46 ± 0.03 D.

An electron diffraction investigation[1] has established that the molecule of *o*-dibromobenzene is planar or nearly planar, that the angle made by two C–Br bonds is larger than 60°, and that the opening of this angle may be due to the repulsive force between the bromine atoms. However, no such opening of the angle has been reported in the study of the microwave spectrum of *o*-fluorochlorobenzene.[2]

The present study was undertaken in the hope of determining the structure of *o*-difluorobenzene in detail, especially the angle made by two C–F bonds.[*2]

Experimental

The spectrum was measured over the frequency range from 7800 to 22600 Mc/sec with a conventional Stark-modulation microwave spectrometer, employing 110-kc/sec square-wave modulation. All measurements were made at room temperature. The frequencies were measured by comparison with a frequency standard which was monitored against the standard signals from Station JJY. The spectrum was displayed on an oscilloscope and, for weak absorptions, on a recorder.

o-Difluorobenzene was prepared from commercial *o*-fluoroaniline by the method of Schiemann and Pillarsky.[3]

Results and Discussion

Assignments of the spectrum were difficult because of the richness of the spectrum. Qualitative Stark patterns of the observed transitions were very helpful in identification. Since the C_2 axis coincides with the a-axis, only a-type transitions were observed.

The B and C rotational constants were calculated from the $1_{10}\rightarrow2_{11}$ and the $2_{21}\rightarrow3_{22}$ transitions, which occur at frequencies of $(3B+C)$ and $(3B+3C)$ respectively. The A constant was calculated from the observed Q-branch transitions. It is estimated that the A, B, and C rotational constants are accurate to ±0.015 Mc/sec. The rotational constants thus obtained agree with those of Nygaard *et al.* Since we used lower J-transitions in our determination than they did, the effect due to centrifugal distortion will be disregarded.

The measured frequencies and the assignments in the ground state are listed in Table 1, together with deviations between the measured frequencies and those calculated by the use of the rigid-rotor rotational constants given in Table 2. The agreement shown in Table 1 is such that it can be said that centrifugal distortion is not an important effect in the transitions studied. The transition frequencies and the rotational constants in terms of the geometrical parameters of the molecule were all calculated on a FACOM 222 digital computer.

The principal moments of inertia derived from the rotational constants are listed in Table 2. As is shown in Table 2, the inertia defect is 0.049 amu. Å^2 The small value of the inertia defect is strongly indicative of the planar configuration.

Since the molecule is planar, only two of these moments of inertia are independent. Therefore, a number of assumptions or approximations are required in order to extract any structural information. First of all, it may safely be assumed that the symmetry of the molecule is C_{2v}. Even if we assume that all the C–C bonds and all the C–H bonds are of equal length, and that the C–F bonds and the C–H bonds are located along the C–C–C angle bisectors,

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[*1] Presented in part at the symposium on structural chemistry held by the Chemical Society of Japan, Osaka, Oct., 1966.

1) T. G. Strand, *J. Chem. Phys.*, **44**, 1611 (1966).

2) P. Kökeritz and H. Selén, *Arkiv Fysik*, **30**, 193 (1965).

[*2] While we were preparing this manuscript, we read a pre-publication copy of an article on the same topic written by L. Nygaard, E. R. Hansen, R. L. Hansen, J. Rastrup-Andersen, and G. O. Sφrensen, an article which was kindly sent us by Professor Yonezo Morino of the University of Tokyo. The transitions measured were different from each other, and the lower J-transitions were obtained by us. For some of the R-branch transitions, those of our observed frequencies and assignments which agree with theirs are omitted in Table 1.

Note added in proof–Their article appeared in *Spectrochim. Acta*, **23**, 2813 (1967).

3) G. Schiemann and R. Pillarsky, *Ber.*, **62**, 3035 (1927).

TABLE 1. ASSIGNED GROUND-STATE TRANSITIONS OF *o*-DIFLUOROBENZENE

Transition	Observed* in Mc/sec	$\nu_{obs}-\nu_{calc}$	Transition	Observed* in Mc/sec	$\nu_{obs}-\nu_{calc}$
$1_{10} \to 2_{11}$	8007.7	+0.1	$6_{15} \to 7_{16}$	22585.5	−0.3
$2_{12} \to 3_{13}$	9092.7	+0.2	$7_{17} \to 8_{18}$	22507.2	+0.1
$2_{02} \to 3_{03}$	9422.8	0.0	$7_{35} \to 7_{34}$	8063.5	+0.2
$2_{21} \to 3_{22}$	10655.3	0.0	$4_{14} \to 4_{13}$	8333.5	0.0
$2_{11} \to 3_{12}$	11689.2	0.0	$9_{46} \to 9_{45}$	9206.6	−0.1
$2_{20} \to 3_{21}$	11887.8	−0.1	$4_{04} \to 4_{23}$	9474.0	0.0
$3_{13} \to 4_{14}$	11856.1	−0.1	$4_{13} \to 4_{32}$	9587.2	−0.1
$3_{03} \to 4_{04}$	11988.3	0.0	$6_{25} \to 6_{24}$	10118.4	0.0
$4_{32} \to 5_{33}$	18317.7	0.0	$5_{14} \to 5_{33}$	10348.1	+0.1
$4_{41} \to 5_{42}$	18604.7	+0.1	$5_{15} \to 5_{14}$	11343.3	−0.1
$4_{40} \to 5_{41}$	18809.0	+0.1	$8_{36} \to 8_{35}$	11735.5	0.0
$4_{31} \to 5_{32}$	19821.7	−0.1	$5_{05} \to 5_{24}$	11798.9	−0.2
$4_{22} \to 5_{23}$	19880.0	+0.3	$7_{25} \to 7_{44}$	13032.3	−0.1
$5_{24} \to 6_{25}$	19754.2	+0.3	$7_{26} \to 7_{25}$	13373.7	+0.2
$5_{14} \to 6_{15}$	20045.8	0.0	$6_{16} \to 6_{15}$	14181.2	−0.2
$5_{33} \to 6_{34}$	21669.0	0.0	$6_{06} \to 6_{25}$	14334.0	+0.1
$6_{25} \to 7_{26}$	22481.6	−0.1	$9_{36} \to 9_{55}$	15663.5	−0.3

* Maximum experimental uncertainty in the frequency measurements is ±0.2 Mc/sec

TABLE 2. ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA

Rotational constant Mc/sec		Moments of inertia* amu·Å²	
A	3263.55	I_a	154.854
B	2227.91	I_b	226.838
C	1323.87	I_c	381.741
Asymmetry parameter $\kappa=-0.06785$		Inertia defect $\Delta=0.049$ amu·Å²	

* Conversion factor: 5.05375×10⁵, corresponding to $^{12}C=12$ atomic weight scale.

TABLE 3. STRUCTURAL PARAMETERS OF *o*-$C_6H_4F_2$

	Set I	Set II	Set III	Set IV
r_{C-C}	1.397*	1.395*	1.397*	1.402*Å
r_{C-H}	1.084*	1.084*	1.084*	1.084*Å
r_{C-F}	1.310*	1.313	1.308	1.294 Å
α	119°26′	119°20′	119°16′	119°7′
θ	60°22′	60°40′**	60°44′**	60°53′**

α: The valency angle of the carbon, ∠C–C–C, to which the F atom attaches.

θ: The angle made by two C–F bonds.

* Assumed by taking into account the data reported in Refs. 2, 4, 5, and 6.

** For these cases the C–F bonds are assumed to be along the bisectors of α.

we find that there are still four undetermined structural parameters. In addition, if we assume that the valency angle of carbon, ∠C–C–C, is 120°, three structural parameters, *i.e.*, the C–C distance, r_{C-C}, the C–H distance, r_{C-H}, and the C–F distance, r_{C-F}, remain to be determined. On these assumptions, however, we could not obtain any set of reasonable parameters to fit the observed moments of inertia.

Therefore, by assuming the values of the three bond lengths to be those reported by Kökeritz and Selén,[2] the valency angle α, ∠C–C–C, of the carbon atom to which the fluorine atom attaches and the angle, θ, made by two C–F bonds were determined. The parameters thus obtained are shown in Table 3 as set I. For the II, III, and IV sets, the values of r_{C-F} and α were determined by assuming that the C–F bond is located along the bisector of α, that the value of r_{C-C} is one of those reported previously,[2,4-6] and that the value of r_{C-H} is 1.084 Å. The parameters obtained are shown in Table 3 as the II, III, and IV sets.

The evaluation of $\partial R_j/\partial X_j$ was very useful in estimating the structural parameters, where R_j represents the jth rotational constant of the assumed structure and X_i is the ith structural parameter. All of the sets of the structural parameters were determined so as to get agreement between the calculated and observed values for the moments of inertia of I_a and I_b.

TABLE 4. STARK COEFFICIENTS AND DIPOLE MOMENT OF *o*-$C_6H_4F_2$

Transition		$\Delta\nu/E^2$(Mc/sec)/(V/cm)²×10⁵ observed	calculated
$1_{10} \to 2_{11}$	$M=0$	4.7±0.1	4.7
	$M=1$	−37.7±0.8	−38.0

$\mu=2.46\pm0.03$D

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[4] B. Bak, D. Christensen, L. Hansen-Nygaard and E. Tannenbaum, *J. Chem. Phys.*, **26**, 134 (1957); R. L. Poynter, *ibid.*, **39**, 1962 (1963).

[5] E. Rosenthal and B. P. Dailey, *ibid.*, **43**, 2093 (1965).

[6] H. Forest and B. P. Dailey, *ibid.*, **45**, 1736 (1966).

It is probable that the angle made by two C–F bonds is larger than 60°, inasmuch as the values of r_{C-C}, r_{C-F}, and r_{C-H} are not very different from those previously reported.

Stark effect coefficients were measured for the $M=0$ and 1 components of the $1_{10} \rightarrow 2_{11}$ transition. The data are shown in Table 4. The cell was calibrated using the $J=0 \rightarrow 1$ transition of OCS, taking the dipole moment of OCS to be 0.7124 D.[7] The value of the dipole moment obtained is 2.46±0.03 D. This value is in agreement with that of 2.38 D obtained by a solution method,[8] and slightly different from that of 2.59±0.02 D obtained by Nygaard *et al.*

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[7] S. A. Marshall and J. Weber, *Phys. Rev.*, **105**, 1502 (1957).

[8] E. Bergmann, L. Engel and S. Sándor, *Z. physik. Chem.*, **10B**, 106 (1930).