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Citation: The Journal of Chemical Physics **26**, 134 (1957); doi: 10.1063/1.1743237 View online: http://dx.doi.org/10.1063/1.1743237 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/26/1?ver=pdfcov Published by the AIP Publishing

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Microwave Determination of the Structure of Fluorobenzene

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3D-, 4D-, and 2,4,6 D3-fluorobenzene have been prepared. Their microwave spectra have been recorded and analyzed. Values of their rotational constants together with known values of the rotational constants of ordinary fluorobenzene do not suffice for an unambiguous calculation of the 11 geometrical parameters of the molecule but by assistance from valence theory a small number of fairly probable models may be pointed out.

I. INTRODUCTION

HIS work was started primarily as an attempt to find out what influence the introduction of fluorine might have on the geometry of the aromatic nucleus par excellence, the benzene ring. Fluorine was chosen as the substituent, partly because the fluorine nucleus has the spin $\frac{1}{2}$ so that complications from quadrupole interaction can be excluded, partly also because most effects from substituents might be expected to be at their maximum for the highly electronegative fluorine.

The pioneering work on the present problem has been done by Erlandsson^{1,2} and McCulloh and Pollnow³ who studied ordinary fluorobenzene. Since fluorobenzene is planar, $I_c = I_a + I_b$, so that only two structural parameters resulted. The present work augments the number of experimental parameters to seven while eleven independent data would be needed for a complete determination of the geometry. The remaining four data could only be obtained by preparing isotopic fluorobenzenes with C¹³ in the benzene ring. This part of the project we have had to postpone to a later occasion. We believe, however, that the results so far obtained are sufficiently positive to justify their publication.

II. EXPERIMENTAL PART

A. Preparation of Deuterated Fluorobenzenes

Ortho-, meta-, and para-bromofluorobenzenes were prepared from the corresponding bromoanilines (50, 50, and 220 g, respectively) via the fluoroborates (52, 85, and 290 g which, by a conventional Balz-Schiemann reaction, were converted into 12.0, 23.5, and 270 g of o-, m-, and p-bromofluorobenzene boiling, respectively, at 163°, 153°, and 155°C at 760 mm Hg. The infrared absorption curves of the three samples were significantly individual. No lines from the other structural isomers could be seen in any of the spectra.

A subsequent attempt to substitute bromine by deuterium by the Grignard technique was only successful in the case of the meta- and para-compounds. decomposed by a freshly prepared solution of 6 g DCl in ether (1 hour). Precipitated MgClBr was removed by filtration, the ether and DCl was distilled off through an efficient column and 6.6 g deuterated fluorobenzene was collected at 84.0-84.5°C (p = 760 mm Hg). A trace of ether in the sample (identified by means of the infrared spectrum) was removed by a ten times repeated shaking with 5 cc conc. HCl, after which the sample was treated with anhydrous $Na_2CO_3(0.3 \text{ g})$ to remove HCl and water. A final distillation in vacuo gave 6.2 g pure sample (0.064 mole; yield 50%). Application of the same procedure for the *meta*-compound resulted in a yield of 5.9 g purified product (45%). The infrared spectra of the two deuterated species were significantly different. Contamination of the samples with ordinary fluorobenzene was very slight and they were not contaminated with each other. Somewhat unexpectedly, the Grignard procedure applied to 11.5 g o-fluorobromobenzene gave almost no yield (0.3 g) boiling in the right range but fairly large amounts of higher-boiling material (about 10 g), which decomposed when distilled at atmospheric pressure. The infrared spectrum of the 0.3 g sample showed considerable contamination with ordinary fluorobenzene but, in addition, extra lines were observed so that application of the sample for a microwave investigation was not excluded. Search for lines that could possibly be attributed to o-deuterofluorobenzene was, however, fruitless so that we decided to prepare another ortho-substituted fluorobenzene, the 2,4,6 tri-deutero fluorobenzene. 40 g 2,4,6 tribromoaniline was diazotized, giving 23 g of the fluorobrorate which, on thermal decomposition in vacuo (free flame), gave 10-11 g of a mixture of compounds boiling in the 80-145°C range at 15 mm Hg pressure. A fraction boiling fairly constant in the 143-145°C interval at 15 mm Hg was collected (5 g). By redistillation, the boiling point showed no change. Also, the melting point was constant (61-63°C). The infrared spectrum (KBr-disque) showed the lines characteristic for a brominated and fluorinated benzene derivative, but since 2,4,6 tribromofluorobenzene has never before been prepared, identification by melting point, boiling point, and spectrum is impossible.

23.5 g p-bromofluorobenzene (0.13 mole), dissolved in 50 cc anhydrous ether, reacted for two hours with

6 g Mg after which the Grignard compound was

^{*} National Science Foundation post-doctoral fellow, 1955-1956.
¹ G. Erlandsson, Arkiv Fysik 6, 477 (1953).
² G. Erlandsson, Arkiv Fysik 7, 189 (1953).
³ K. E. McCulloh and F. G. Pollnow, J. Chem. Phys. 22, 1144

⁽L) (1954).

TABLE I. Observed and o	calculated microwave	absorption frequer	icies (in MHz)	for fluorobenzene,
3D-, 4D-, ai	nd 2,4,6 D3-fluoroben	zene in the 17 500-	-28 000 MHz r	egion.

Transition :	Fluorob Observed*	enzene Calculated	Obs. — calc.	3 D-fluor Observed	obenzene Calculated	Obs. – calc.	4 D-fluor Observed	robenzene Calculated	Obs calc,	2,4,6 D3-flu Observed	iorobenzene Calculated	Obs. – calc.
$3_{0.3} \rightarrow 4_{0.4}$ $3_{1.3} \rightarrow 4_{1.4}$ $3_{1.2} \rightarrow 4_{1.3}$	16172.3 15514.1 18637.4	16172.6 15513.9 18637.3	-0.3 0.2 0.1	18271.6	18271.1	0.5	17920.4	17920.1	0.3	Nove Da Hot and Add and a second s		
$3_{2,2} \rightarrow 4_{2,3}$ $3_{2,1} \rightarrow 4_{2,2}$ $3_{3,1} \rightarrow 4_{3,2}$ $3_{3,0} \rightarrow 4_{3,1}$	17247.0 18427.2 17588.9 17676.6	17247.0 18427.4 17589.3 17676.7	$0 \\ -0.2 \\ -0.4 \\ -0.1$	18144.5 ^b	18144.4	0.1	17625.8	17625.5	0.3			
$\begin{array}{c} 4_{0.4} \rightarrow 5_{0.6} \\ 4_{1.4} \rightarrow 5_{1.5} \\ 4_{1.3} \rightarrow 5_{1.4} \\ 4_{2.3} \rightarrow 5_{2.4} \\ 4_{2.2} \rightarrow 5_{2.3} \\ 4_{3.2} \rightarrow 5_{3.3} \\ 4_{3.1} \rightarrow 5_{3.2} \\ 4_{4.1} \rightarrow 5_{4.2} \end{array}$	19678.2 19219.8 22941.0 21389.2 23393.8 22028.8 2322.1 21997.3 22006.1	19678.3 19220.0 22940.6 21389.3 23393.4 22028.9 22321.8 21996.5 22007.0	$-0.1 \\ -0.2 \\ 0.4 \\ -0.1 \\ 0.4 \\ -0.1 \\ 0.3 \\ 0.8 \\ -0.9$	19153.2 18745.2 22447.5 20931.8 23026.5 21614.6 21588.9 21601.5	19152.8 18745.3 22447.1 20932.1 23026.4 21614.5 21952.1 21588.4 21601.6	$\begin{array}{r} 0.4 \\ -0.1 \\ 0.4 \\ -0.3 \\ 0.1 \\ 0.5 \\ -0.1 \end{array}$	19103.1 18608.4 22107.4 20616.2 22378.0 21165.0 21391.0 21128.5 211134.6b	19103.3 18608.2 22106.8 20616.3 22378.1 21164.7 21390.9 21128.4 21135.7	-0.2 0.6 -0.1 -0.1 0.3 0.1 0.1 -11	18413.5 18038.6 21631.8 20175.5 22253.4 20859.0 21209.8 d	18412.9 18038.5 21631.6 20174.9 22253.8 20859.3 21210.1 20837.3 20851.6	0.6 0.1 0.2 0.6 -0.4 -0.3 -0.3
$5_{0.5} \rightarrow 6_{0.6}$ $5_{1.5} \rightarrow 6_{1.6}$ $5_{2.4} \rightarrow 6_{2.5}$ $5_{2.3} \rightarrow 6_{2.4}$ $5_{3.2} \rightarrow 6_{3.4}$ $5_{3.2} \rightarrow 6_{3.4}$ $5_{4.2} \rightarrow 6_{4.3}$ $5_{4.1} \rightarrow 6_{4.2}$ $5_{5.1} \rightarrow 6_{5.2}$	23134.6 22863.3 26960.2 25427.3 26445.2 27163.3 26483.2 26528.9 ^e 26378.8 ^e 26378.8 ^e	23134.6 22863.1 26960.1 25427.4 26445.1 27163.2 26482.9 26529.2 26378.1 26379.1	$\begin{array}{c} 0 \\ 0.2 \\ 0.1 \\ -0.1 \\ 0.1 \\ 0.3 \\ -0.3 \\ 0.7 \\ -0.3 \end{array}$	22517.0 22286.5 26316.0 24360.7 27798.1 25938.4 26754.7 25998.1 26055.9 25888.4 ^f 25888.4 ^f	22517.2 22286.8 26316.6 24861.0 27798.3 25938.5 26754.8 25998.2 26056.0 25887.8 25889.3	$\begin{array}{c} -0.2 \\ -0.3 \\ -0.6 \\ -0.3 \\ -0.2 \\ -0.1 \\ -0.1 \\ -0.1 \\ -0.1 \\ 0.6 \\ -0.9 \end{array}$	22461.6 22150.4 26055.5 24535.6 27088.5 25416.4 25980.0 25429.9 25461.1 25338.6 ⁷	22461.9 22150.5 26056.1 24535.8 27088.5 25416.6 25980.2 25429.4 25461.7 25338.4 25338.4	$\begin{array}{c} -0.3 \\ -0.1 \\ -0.6 \\ -0.2 \\ 0 \\ -0.2 \\ 0.5 \\ -0.6 \\ 0.2 \\ -0.5 \\ -0.6 \\ 0.2 \\ -0.5 \end{array}$	21648.5 21441.2 25330.1 23950.9 26847.2 25027.3 25869.5 25096.7 25159.0 24987.5 ^r 24987.5 ^r	21648.3 21441.3 25330.5 23950.8 26847.6 25027.5 25869.7 25096.7 25096.7 25096.7 25096.8 24986.8 24988.4	$\begin{array}{c} 0.2 \\ -0.1 \\ -0.4 \\ 0.1 \\ -0.2 \\ -0.2 \\ 0 \\ 0 \\ 0.7 \\ -0.9 \end{array}$
$\begin{array}{c} 6_{0.6} \rightarrow 7_{0.7} \\ 6_{1.6} \rightarrow 7_{1.7} \end{array}$	26605.3 26460.7	26605.3 26460.8	0 -0.1				25823.5 25647.9	25824.0 25648.4	$-0.5 \\ -0.5$	24905.9 24802.5	24905.9 24802.7	0 0.2
$7_{0.7} \rightarrow 7_{2.6}$ $7_{1.7} \rightarrow 7_{1.6}$	22465.2 19953.0	22464.6 19952.9	0.6 0.1				18858.0	18857.8	0.2			
$\begin{array}{c} 8_{1.8} \longrightarrow 8_{1.7} \\ 8_{1.7} \longrightarrow 8_{3.6} \end{array}$	24072.3 24300.5	24073.4 24300.5	$-1.1 \\ 0$	23141.2	23141.1	0.1	22908.8	22909.1	-0.3			
$9_{1.9} \rightarrow 9_{1.8}$ $9_{1.8} \rightarrow 9_{3.7}$ $9_{2.8} \rightarrow 9_{2.7}$	19137.0	19137.0	0	25020.2 19440.8	25020.1 19440.3	0.1 0.5	26818.2	26817.7	0.5			
$\begin{array}{c} 10_{1.9} \rightarrow 10_{3.8} \\ 10_{2.9} \rightarrow 10_{2.8} \end{array}$	23839.2	23839.5	-0.3	23984.4	23984,5	-0.1	22018.5	22018.5	0	26405.5 23386.2	26405.5 23386.4	0 -0.2
$\begin{array}{c} 11_{2.10} \rightarrow 11_{2.9} \\ 11_{3.9} \rightarrow 11_{3.8} \end{array}$							26548.8	26549.7	-0.9	17523.2	17523.5	-0.3
12 _{8.10} →12 _{3.9}				22663.2	22663.4	-0.2	19285.1	19284.2	0.9	22391.7	22392.3	-0.5

See references 1, 2, and 3.
Broad line.
Region of low klystron output.
Very weak, broad line.
Values uncertain.
f Unresolved pair.

Combustion analysis gave 21.38% C (calc. 21.64%). C₆H₂F₂Br₂ has 26.48% C. Final proof of its constitution was obtained by reducing it to 2,4,6 trideuterofluorobenzene and demonstrating that a series of microwave lines of suitable intensity, attributable to this species, could be found. The reduction was carried out by adding 4 g of 2,4,6 tribromofluorobenzene (assumed) and 16 g Zn dust to a mixture of CH₃COOD and D₂O, resulting from 7 g (CH₃CO)₂O and 25 g D₂O. After 24 hours of reflux at ca 100°C a mixture of deuterated fluorobenzene and D₂O was distilled off in vacuo. Most of the water in the distillate was separated mechanically, the rest was removed at 0°C by anhydrous Na₂CO₃ together with traces of CH₃COOD. Finally, the sample was dried over P₂O₅ and distilled in vacuo. The yield was 500 mg (40%). Qualitatively, its infrared absorption curve was consistent with its postulated formula. For example, an intense "C,F band" was seen, and two, almost equally strong, bands corresponding to the aromatic C,D and C,H vibrations were observed. From the microwave lines it is judged that the purity of the sample may be

TABLE II. Rotational constants (in MHz), asymmetry parameter (κ), and principal moments of inertia (I_a, I_b, I_c) in $amuA^2$ of fluorobenzene and three deuterated derivatives together with the quantum defect (Q.D.) for all four species.

	Fluoro- benzene	3 D-fluoro- benzene	4 <i>D</i> -fluoro- benzene	2,4,6-D3-fluo- robenzene
A	5663.54	5394.27	5663.64	5134.71
В	2570.64	2529.99	2459.72	2445.03
С	1767.94	1722.07	1714.75	1656.19
κ	0.58789	-0.55998	-0.62269	-0.54645
Ia	89.2516	93.7068	89.2500	98.4437
Īb	196.6359	199.7953	205.5031	206.7377
Ĭ.	285.9147	293.5305	294.7835	305.2065
Q.D.	0.0272	0.0284	0.0304	0.0251

anywhere between 70 and 100%. The presence of *m*and p-deutero compounds and of ordinary fluorobenzene could be excluded.

B. Spectral Measurements

Spectral measurements were made on a 50 kc square wave modulated spectrograph described previously.⁴ Transition frequencies were measured to $\pm 0.1 MHz$.

C. Measurement of Microwave Absorption Frequencies and Calculation of **Rotational Constants**

Several checks soon showed that the absorption frequencies measured by Erlandsson^{1,2} and McCulloh and Pollnow³ fit with determinations made by us. For his calculation of the rotational constants, Erlandsson used only Q lines with $J \ge 12$. In this work we shall consistently use Q lines of lowest possible J in order to reduce the effect of centrifugal stretching which is otherwise ignored. We have, therefore, measured a number of Q lines for ordinary fluorobenzene with J < 12. They are included in Table I together with the experimental material from the deuterated species and a great number of R lines for ordinary fluorobenzene, measured by the authors mentioned above. Due to the large number of closely spaced lines observed identification of lines by means of the Stark-effect was impossible.

Calculation of the rotational constants was carried out in the usual way by reading κ and (A-C)/2 from a conventional "Q-line plot." (A+C)/2 was thereafter taken as the average value best consistent with all of the observed R lines, calculated by quadratic interpolation in Turner's rigid rotor energy tables.⁵ The calculated rotational constants, moments of inertia etc. are given in Table II.

III. MOLECULAR MODEL AND DISCUSSION

As already pointed out, four experimental data are still missing for an unequivocal determination of the

TABLE III. Possible fluorobenzene models (I-IV), compatible with the microwave spectra of fluorobenzene, 3D-, 4D-, and $2,4,6D_3$ -fluorobenzene (distances in A).

	-			
Model No.	Is	11	111	1V
Distances: $C(2)$, $H(2)$	1.0841	1.0753	1.0803	1.0852
C(3), H(3)	1.0733	1.0860	1.0810	1.0760
C(4), H(4)	1.0718	1.0750 ^ь	1.0800^{b}	1.0850 ^b
C(1), C(2)	1.4018	1.3965 ^ь	1.3965 ^b	1.3965 ^b
C(2), C(3)	1.4018	1.3945 ^b	1.3945 ^b	1.3945 ^b
C(3), C(4)	1.4018	1.3955 ^ь	1.3955 ^b	1.3955 ^b
C(1), F	1.2994	1.3372	1.3315	1.3265
Angles: $C(2)-C(1)-C(6)$	120°00′ь	122°26′	121°42′	121°00′
C(1) - C(2) - C(3)	120°00′ь	117°57'	118°41′	119°23'
C(2) - C(3) - C(4)	120°00′ь	121°13′	120°29′	119°47′
C(3) - C(4) - C(5)	120°00′b	119°14'	119°58'	120°40'
C(1) - C(2) - H(2)	118°21′	119°18′	118°57'	118°37'
C(2) - C(3) - H(3)	119° 4 5′	119°01′	119°23′	119°44′
· · · · · · · · · · · · · · · · · · ·				

Benzene nucleus assumed to be a regular hexagon.
 Values assumed.

fluorobenzene structure. All calculations of the structure must, therefore, take place under certain assumptions. We have tried to answer the following questions:

1. What structure results if it is assumed that the benzene nucleus of fluorobenzene is a regular hexagon?

2. What structure results if a resonance description of the molecule is used for predicting certain of its geometrical properties?

1. Table III, model I, is the answer to the first question. It is seen that a collection of somewhat unexpected C.H distances results. For the ethylene C,H distance Gallaway and Barker⁶ found 1.071 A. Therefore, the C(3), H(3) and the C(4), H(4) distances of model I seem to be too short. Also, this model is bound to be in disagreement with a resonance description (see below) except if the C,C distances had turned out to be close to 1.395 A (the unperturbed C,C distance in benzene). Since this is not the case, we shall conclude that model I is not likely to be correct. The calculation of this model serves, however, to demonstrate that any model which fits with the microwave measurements, probably must have a C,F distance which is shortened as compared with the aliphatic C,F distance⁷ (1.390 A in CH₃F). This observation naturally leads to considering a resonance description of the molecule in which, first of all, this shortening of the C,F bond finds its explanation.

2. We must start by realizing that in the conventional resonance description of fluorobenzene (including 2 Kekulé structures, 3 Dewar structures, 2 ortho-ionic and 1 para-ionic structure (with a "+" on fluorine)) no transfer of π -electron charge (from the ring) to the C,F bond can take place except if simultaneously compensated for by a similar transfer of electronic charge from the fluorine atom to either the ortho- or

⁴ Bak, Hansen, and Rastrup-Andersen, J. Chem. Phys. 22, 2013 (1954). ⁵ Turner, Hicks, and Reitwiesner, Ballistics Research Labora-tories Report No. 878 (September, 1953).

⁶W. S. Gallaway and E. F. Barker, J. Chem. Phys. 10, 88 (1942).

⁷ Andersen, Bak, and Brodersen, J. Chem. Phys. 24, 989 (1956).

the para-carbon of the ring. This situation follows from the octet rule. It means that the π component of the total dipole moment (=1.58 D) must be directed opposite to the σ moment. Arbitrarily taking the σ moment equal to 1.80 D, its value in CH₃F, we see that roughly the π moment is 0.20 D. An estimate based on this shows that the ionic structures constitute ca 2% of the resonance picture, leaving about 76% for the Kekulé and about 22% for the Dewar structures. If the resonance description did not include the paraionic structure



the length of the C(2),C(3) and the C(3),C(4) bonds would have to be the same and about equal to the C.C bond length in benzene (1.395). Inclusion of the *para*-ionic structure means however that the C(2), C(3)bond must be expected to be slightly shorter, the C(3),C(4) bond slightly longer than 1.395 A.

All three ionic structures agree in having long C(1), C(2), resp. C(1), C(6), bonds. The charge that should have kept these bonds short has been transferred to the C.F bond at the cost of the fluorine atom transmitting an electron to the ortho and para-carbons of the ring. An estimate shows that the charge being moved around is of the order of 0.015 e which makes us expect a rather small lengthening of these bonds as compared to benzene.

As a result of our considerations we have decided to look for fluorobenzene models, having C(2), C(3)(=1.3950-0.0005),C(3), C(4) = 1.3955=1.3945(=1.3950+0.0005), and C(1),C(2)=1.3965 A. Since a fourth assumption is needed we have set C(4), H(4)=1.075, 1.080, 1.085 A, successively, which gave us the models II, II, and IV of Table III.

All three models have C,H distances of expected magnitude.

We see no way of making further distinctions between possible models. The electron-diffraction result⁸ (C,F $=1.31\pm0.03$ A) is in agreement with all four models considered here. In summarizing our results we may state that the models II, III, and IV equally well explain the microwave spectra of four isotopic fluorobenzenes. They fit semiquantitatively with the measured dipole moment and qualitatively with the wellknown chemical reactivity of fluorobenzene towards electrophilic substituents which predominantly enter the ortho- and para-positions.9

8 C. Finbak and O. Hassel, Arch. Math. Naturvidenskab 44, 3 (1941). ⁹ T. Ri and H. Eyring, J. Chem. Phys. 8, 433 (1940).

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 26, NUMBER 1 JANUARY, 1957

On the Relaxation of Vibrational Nonequilibrium Distributions. III. The Effect of Radiative Transitions on the Relaxation Behavior*

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In previous papers of this series (Parts I and II) a theoretical study has been made of the collisional relaxation of a system of harmonic oscillators (with $h\nu/kT\ll 1$) from initial vibrational nonequilibrium distributions and of the influence of the collisional transition probabilities on the relaxation behavior. This paper is concerned with the extension of this study to include the effects of concurrent radiative transitions on the relaxation behavior. It was found that concurrent radiative transitions do not change the relaxation behavior of the system of harmonic oscillators from that found previously for purely collisional transitions. The only change is in the time-scale of the relaxation in that the expressions obtained in Part I must be multiplied by a factor of the form $\exp[-t/\tau]$ where τ is the lifetime of the oscillators in their excited vibrational and electronic energy levels.

I. INTRODUCTION

N previous papers of this series¹ we have considered the collisional relaxation of a "continuum" system of harmonic oscillators contained in a constant temperature heat bath and the effect of a change of collisional transition probabilities on the relaxation behavior. In these papers we assumed that the system was at a sufficiently high pressure so that radiative transitions between the vibrational energy levels could be neglected compared to collisional ones. The relaxation behavior found in Parts I and II thus pertains to systems which approach the final equilibrium state by purely colli-

^{*} This research was supported in part by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command and by the U. S. Atomic Energy ¹Robert J. Rubin and Kurt E. Shuler, J. Chem. Phys. 24, 59,

^{68 (1956).}