

# DIELECTRIC PROPERTIES OF 2, 4-DINITROFLUOROBENZENE

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**ABSTRACT.** The dipole moment of 2, 4-dinitrofluorobenzene is determined in solution in benzene at 30°C. and the value obtained 3.56D is found to be in exact agreement with that calculated using the general method given by the author previously. The absorption of the molecule at 3 cm., is also studied in the same solvent and a value of 3.30 D for the dipole moment and  $5.3 \times 10^{-11}$  sec., for the relaxation time are obtained. It is expected from the value of the relaxation time that the molecule will show maximum absorption near about 10 cm.

## INTRODUCTION

A general method for the calculation of the dipole moments of 1:2:4 tri-substituted benzenes was given by the author (1955a) previously. The method was applied in the first instance to a few compounds for which data on the dipole moments were available. It is noticed that the discrepancy between the calculated and the observed values increases in the group of molecules — 2:4 dinitro-chlorobenzene, 2:4 dinitro-bromobenzene and 2:4 dinitro-iodobenzene—the deviation increasing as we pass from chloro to bromo to the iodo compound (cf. Table I below).

TABLE I

Compound	$\mu$ (calculated)	$\mu$ (observed)
2, 4-Dinitro-fluoro* benzene	3.56D	3.56
2, 4-Dinitro-chloro benzene	3.10	3.0 $\pm$ .1 3.20
2, 4-Dinitro-bromo benzene	3.54	3.1 $\pm$ .1
2, 4-Dinitro-iodo benzene	4.20	3.4 $\pm$ .1

Hence we may expect a fair agreement in the case of the fluoro compound. A reference to the existing literature indicates that there is no published record of the dipole moment of this molecule. It is thought worthwhile to calculate the

\* Present investigation, briefly reported in *Curr. Sci.*, 1955, 24, 407.

moment of the compound using the general equation and also to carry out an experimental investigation on the molecule.

Further, it may be of interest to study the microwave absorption of the molecule which also gives the value of the dipole moment. The monosubstituted benzenes—fluoro and nitro-benzenes—have wavelengths of maximum absorption near about 3 cm. In the case of this molecule the region of maximum absorption may shift to longer wavelengths due to the increased size as a result of the three substituted radicals.

#### CALCULATION

The moments of the monosubstituted compounds are assumed as  $m_{e1} = 1.45$  and  $m_{e2} = m_{e3} = 3.90$ . The polarizability of the  $\text{NO}_2$  group is the same as used previously and that of  $-\text{F}$  is taken as  $0.57 \times 10^{-24}$  obtained from the value of the refraction of HF (Syrkin and Dyatkina 1950). As a result of the application of Equation (5) of the previous article (1955a) the moment turns out to be 3.64 D. When the correction for the dielectric constant of the internuclear space is also effected, this reduces to 3.56 D. It is easily seen that the simple vectorial addition gives a value of 3.42D for the moment of the molecule.

#### EXPERIMENTAL RESULTS

The method of measurement of the dipole moment in dilute solution was described in a previous communication (1955b). For the measurement of the dielectric constant an improved set up is used. This is a Franklin-oscillator wavemeter combination operated at a fixed frequency of 1 Mc/s similar to the one described by Le Fevre *et al* (1950). The results are given in Table II, in which the symbols have the usual significance (author, 1955b).

TABLE II

Temperature = 30°C.							
Density of benzene = 0.8704 gm/c.c.							
$w$	$\epsilon_{12}$	$\Delta\epsilon$	$\Delta\epsilon/w$	$n_{12}$	$n^2_{12}$	$\Delta n^2$	$\Delta n^2/w$
	2.2640	—	—	1.49354	2.23065	—	—
0.01901	2.4065	0.1425	7.498	1.49522	2.23569	0.00504	0.265
0.03162	2.4922	0.2282	7.216	1.49575	2.23727	0.00662	0.209
0.05017	2.6158	0.3518	7.013	1.49636	2.23909	0.00844	0.168
0.07084	2.7583	0.4943	6.977	1.49757	2.24273	0.01208	0.171
0.10240	2.9651	0.7011	6.844	1.49783	2.24350	0.12855	0.125
0.14952	3.1083	0.8443	7.0687	1.49797	2.24391	0.01326	0.111
$(\Delta\epsilon/w)_{w \rightarrow 0} = 7.470$		$(\Delta n^2/w)_{w \rightarrow 0} = 0.256$		$(\Delta/w)_{w \rightarrow 0} = 7.214$			
$P_d = 254.1 \text{ c.c.}$		$\mu = 3.55 \text{ D.}$		(graphical)			

Details of the microwave measurements at 3 cm. are described elsewhere (1955c). The values of the orientation polarisation ( $P_d$ ) and the relaxation time ( $\tau$ ) are calculated using the equations

$$P_d = \frac{P_i^2 + (P_0 - P_r)^2}{P_0 - P_r} \text{ and } \tau = I' \omega \cdot \frac{P_0 - P_r}{P_i}$$

since in this case  $\omega\tau > 1$ . The value of the total polarisation ( $P_0$ ) at infinite dilution obtained from the r.f. measurements described above by adding the molecular refraction (obtained from bond refractions) to the value of  $P_d$ . Benzene is used as the solvent in both cases. The results are tabulated below.

TABLE III  
Frequency 9515 Mc/s.  
Temperature 30°C.

$w$	$\epsilon'$	$\epsilon''$	$D$	$p_r$	$p_i$
0.02810	2.36	0.0623	0.8884	0.3514	0.01106
0.04076	2.40	0.1029	0.8932	0.3567	0.01785
0.05927	2.45	0.1301	0.8978	0.3625	0.02197
0.07767	2.48	0.1572	0.9086	0.3640	0.02587
0.09018	2.49	0.1851	0.9122	0.3652	0.03013
0.10212	2.51	0.2053	0.9152	0.3668	0.03308

Extrapolated values  $P_r = 95.0$  c.c.  $P_i = 62.5$  c.c.  
 $P_0 = 293.0$  c.c. ( $P_d = 254.1 + R_D = 38.9$ —r.f.measurements)  
 $\mu = 3.30$  D.  $\tau = 5.3 \times 10^{-11}$  sec.

It will be seen from the value of the moment of the molecule obtained by the simple vector addition of the group moments and that derived using the detailed calculation of the general method that the induced contribution to the value of the moment is not considerable, whereas in the case of the similar iodo compound it is appreciable. This may be attributed to the difference in the polarizability values of the two radicals. Thus for fluorine with the least value of the polarizability the correction term is least. The observed value of the moment 3.55D is in good agreement with the calculated value of 3.56D. When the small correction term of Palit (1952) to the Guggenheim equation used in deriving the value of the moment from the observed data is also considered, the moment turns out to be 3.56D in exact agreement with the calculated value.

The absorption measurements at 3cm. give a value of 3.30D for the dipole moment of the molecule which agrees within about 8% with the r.f. measurements. The relaxation time obtained is fairly higher than that of the mono substituted benzenes; this may be due to the increased size of the molecule. From the value of the relaxation time obtained in this investigation, the wavelength of maximum absorption is expected at about 10 cm. It would be of interest if the absorption in this region is examined for this molecule.

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# *Letter to the Editor*

## STRUCTURE OF THE SPECTRUM OF SINGLY IONISED BROMINE

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The line spectrum of singly ionised bromine (Br II) was investigated by Bloch and Lacroute (1934), Lacroute (1935), and Rao and Ramanadham (1944); the term values known till now are collected by Moore (1952). Still several strong lines in the spectrum remain unclassified, and the analysis is far from complete. An extensive study of the spectrum has been made over the range from  $\lambda$  9000Å to  $\lambda$  400Å with spectrographs of small and large dispersion. Several levels have been newly determined by which about 250 additional lines are classified. The new levels with their designations and  $J$  values are given in table below in ascending order of magnitude calculated with respect to the ground level  $4p^4 \ ^3P_2$  as zero; the notation is that adopted by Moore.

Details of the analysis will be published shortly.

TABLE I

Designation	$J$	Level	Designation	$J$	Level	Designation	$J$	Level
$4p^4 \ ^1D$	2	12098	$5p^4 \ ^3P_2$	1	142839.9	$5d' \ ^1G^\circ$	4	156963.8
$4p^4 \ ^1S$	0	27876	$5p^4 \ ^3P_1$	0	143148.1	$5d' \ ^1G^\circ$	3	157226.9
				1	145601.6			
$4p^5 \ ^3P^\circ$	2	96439.4*		2	145921.5	$5d' \ ^3D^\circ$	1	157369.7
	1	98807.3*					2	157632.8
	0	100242.2	$5p^4 \ ^1P_1$	0	143486.4		3	157808.8
$4d \ ^5D^\circ$	4	104097.9	$5p^4 \ ^1P_1$	1	144517.7	$5d' \ ^1G^\circ$	2	158327.4
	3	104044.6						
	2	104087.2	$5p^4 \ ^1D_2$	2	145370.0	$5d' \ ^1F^\circ$	3	158414.5
	1	104152.3	$4f \ ^5F$	5	145931.6	$5d' \ ^3P^\circ$	0	
	0	104206.6		4	145929.9		1	159778.4
				3	145934.0		2	159910.8
$4p^5 \ ^1P^\circ$	1	113342.8		2	145937.9			
$4d' \ ^3F^\circ$	2	117744.6		1	145941.6	$5d' \ ^1G^\circ$	2	160449.7

TABLE I (Contd.)

Designation	<i>J</i>	Level	Designation	<i>J</i>	Level	Designation	<i>J</i>	Level	
4d' 3P	3	118509.1	4f' 3F	2	146087.5	4f' 3G	3	160884.4	
	4	119432.1		3	146081.3		4		
				4	146095.6		5		
4d' 1G	4	122191.9							
4d' 1P	3	122720.7	6s' 3D°	1	151357.8	5d' 1D°	2	160887.7	
				2	151502.3	4f' a	2	161132.8	
5s" 1P°	1	125058.7		3	152380.6	4f' 1H	5	161289.7	
4d' 3P°	1	126788.2	6s' 1D°	2	152832.3	4f' 1D	4	161526.4	
	2	127687.7		5d' 1P°	1	155148.0	4f' 1G	2	161896.2
	3	127940.6		5d' 3G°	3	156116.1*	4f' 3F	4	162210.2
4d' 1P°	2	128890.5		4	156152.3*		3	162255.9	
5p" 3D	1	142095.3		5	156756.6		2	162313.9	
	2	142854.1							
	3	143704.8	5d' 3G°	1	156512.2				
4f' 3D	3	162344.0	6s" a°	2	166487.2	5d" c°	2	169676.2	
	2	161169.1							
	1	162395.7	6s" 1P°	1	167439.0	5d" d°	2	169768.9	
					or	3			
4f' 1F	3	162364.6	5d" a°	2	169127.6	5d" 1D°	2	170703.1	
			or	3					
6s" 3P°	0		5d" b°	2	169368.1	5d" 1P°	1	170827.4	
	1	165329.3		or		3			
	2								

\*Identified in previous investigations.

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