isomers of this compound were not effectively separated.

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WEST LAFAYETTE, INDIANA RECEIVED AUGUST 11, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

The Dipole Moments of Some Fluorine-Containing Organic Compounds.[1] II

BY ALBERT L. MYERS AND THOMAS DE VRIES

A heterodyne beat frequency method was employed for the determination of dipole moments of thirty-two fluorine-containing organic compounds by the dilute solution technique. Both Hedestrand's and Guggenheim's method of calculating dipole moments were used, giving results that agree well with each other.

The purpose of this work was the determination of the dipole moments of certain fluorine-containing organic compounds. Dilute solutions of the compounds in benzene as the non-polar solvent were used and the Hedestrand equation[2] was employed to calculate the polarization of the solute at infinite dilution. During the course of the in-

TABLE I

DIPOLE MOMENTS

							Moments × 10^{18}			
	$\Delta d/f_2$	$\Delta D/f_2$	P_e	$P_{2\infty}$	E	$1/C$	Calcd.	(H.)	(G.)	Lit.
Fluorobenzene	0.112	2.893	25.92	71.87				1.50		1.47[a]
4-Fluorotoluene	.079	4.292	30.78	98.21			1.90	1.82		2.01[b]
Trifluoromethylbenzene derivatives										
2-Bromo-5-chloro	1.38	7.14	43.98	151.37	0.1277	5099	2.52	2.29	2.27	
5-Bromo-2-chloro	1.37	7.89	44.02	162.64	1.329	5439	2.56	2.41	2.42	
3-Bromo-4,5-dichloro	1.579	0.833	48.77	64.34			0.55	0.87		
5-Bromo-2,4-dichloro	1.54	3.35	50.75	102.50	.0523	6007	1.09	1.59	1.59	
2-Chloro	0.65	14.65	35.88	257.10	.3531	3832	3.75	3.29	3.31	
4-Chloro	.583	1.531	36.01	66.3			0.99	1.22		1.15[a]
3,4-Dichloro	.88	2.80	40.86	87.57	.0602	4625	1.36	1.51	1.50	
4-Ethoxy	.45	16.23	42.59	289.59	.3313	4572	3.22	3.52	3.50	
4-Methoxy	.483	14.430	37.93	257.37			3.42	3.28		
2-Isopropoxy	.46	16.10	47.23	292.29	.3191	4725	2.99	3.44	3.49	
4-Isopropoxy	.462	16.757	47.38	301.75	.3177	4897	3.22	3.53	3.55	
1,2-Bis-(trifluoromethyl)-benzene										
4,5-Dichloro	1.29	5.37	46.25	136.22	.0834	6522	1.72	2.10	2.10	
1,3-Bis-(trifluoromethyl)-benzene										
5-Butoxy	0.78	16.20	57.05	311.52	.2047	7521	3.22	3.53	3.53	
4-Chloro	1.015	4.774	41.02	123.9	.0776	6393	2.23	2.01	2.00	
5-Chloro	0.994	1.595	40.97	77.9			0.99	1.34		1.29[a]
4,5-Dichloro	1.26	2.009	46.22	87.6			1.62	1.42		1.51[a]
4,5,6-Trichloro	1.62	1.88	51.42	86.4	.0274	7504	0.56	1.31	1.29	
4-Ethoxy	0.920	23.186	47.62	400.65	.3302	6535	2.99	4.16	4.18	
5-Ethoxy	.870	20.854	48.36	367.91				3.22	3.95	
2-Methoxy	.92	18.45	42.33	326.41	.3090	5629	3.42	3.73	3.75	
4-Methoxy	.88	21.23	42.71	368.28	.3442	5793	3.14	3.99	4.02	
5-Methoxy	.864	13.428	42.73	254.20	.1933	6703	3.42	3.22	3.24	
4-Phenoxy	1.03	16.86	62.95	320.81	.2449	6445	3.09	3.55	3.58	
4-Propoxy	0.84	22.32	52.43	395.00	.3180	6637	2.99	4.09	4.13	
4-Isopropoxy	.80	20.75	52.52	373.31	.2776	7145	2.99	3.96	4.01	
1,4-Bis-(trifluoromethyl)-benzene										
2,3,5-Trichloro	1.666	1.232	51.99	75.57	.0202	7586	1.55	1.07	1.11	
2-Methoxy	0.904	3.263	43.33	103.65			1.25	1.72		
Pentafluoroethylbenzene										
3-Chloro	.84	6.24	40.82	144.73	.0995	6179	2.31	2.25	2.23	
2,5-Dichloro-4-trifluoromethyl	1.485	−0.062	51.67	67.39	.0075	9166	0.11	0.90	0.75	
1,3-Bis-(pentafluoroethyl)-benzene										
5-Chloro	1.43	1.77	51.40	101.15	.0271	10423	1.10	1.56	1.51	

[a] Frieser, Hobbs and Gross, ref. 6. [b] Moore and Hobbs, ref. 7.

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[1] Abstracted from the Doctoral Thesis of A. L. Myers whose present address is Furman University, Greenville, S. C.

[2] G. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

vestigation Guggenheim[3] published an equation for the calculation of dipole moments and this equation was also used. The Guggenheim equation is

$$\mu^2 = \frac{9kT}{4\pi N} \times \frac{3}{(D_1 + 2)(n_1^2 + 2)} \times \frac{E}{C}$$

where $E = (D - D_1) - (n^2 - n_1^2)$; D, D_1 = dielectric constant of solution and solvent, respectively; n, n_1 = refractive index of solution and solvent, respectively; m_2 = moles of solute; d = density of solution; $C = m_2d$/weight of solution; the other symbols have their usual meaning.

Experimental and Results

The apparatus and experimental methods have been described in a previous paper.[4] The compounds which were studied were prepared in this Laboratory by graduate students under the direction of Dr. E. T. McBee. They were carefully refractionated before use.

TABLE II

PHYSICAL CONSTANTS

	B.p., °C.	d^{25}_4	n^{25}_D
Fluorobenzene	85	1.0183	1.4629
4-Fluorotoluene	117	0.9918	1.4664
Trifluoromethylbenzene derivatives			
2-Bromo-5-chloro	196	1.7522	1.5058
5-Bromo-2-chloro	198	1.7486	1.5050
3-Bromo-4,5-dichloro	106[a]	1.8309	1.5196
5-Bromo-2,4-dichloro	224	1.7521	1.5170
2-Chloro	149	1.3620	1.4537
4-Chloro	136	1.3325	1.4442
3,4-Dichloro	170	1.4729	1.4719
4-Ethoxy	183	1.1837	1.4430
4-Methoxy	169	1.2339	1.4441
2-Isopropoxy	203	1.1546	1.4952
4-Isopropoxy	200	1.1440	1.4437
1,2-Bis-(trifluoromethyl)-benzene			
4,5-Dichloro	182	1.6255	1.4440
1,3-Bis-(trifluoromethyl)-benzene			
5-Butoxy	203	1.2499	1.4126
4-Chloro	148	1.5103	1.4128
5-Chloro	137	1.4835	1.4039
4,5-Dichloro	172	1.6060	1.4376
4,5,6-Trichloro	92[b]	1.7174	1.4683
4-Ethoxy	185	1.3451	1.4106
5-Ethoxy	170	1.3286	1.4121
2-Methoxy	173	1.4459	1.4157
4-Methoxy	176	1.4240	1.4125
5-Methoxy	160	1.3998	1.4048
4-Phenoxy	244	1.3665	1.4738
4-Propoxy	200	1.2976	1.4143
4-Isopropoxy	192	1.2855	1.4105
1,4-Bis-(trifluoromethyl)-benzene			
2,3,5-Trichloro	210	1.7079	1.4714
2-Methoxy	163	1.4038	1.4127
Pentafluoroethylbenzene			
3-Chloro	145	1.4265	1.4191
2,5-Dichloro-4-trifluoromethyl	181	1.6484	1.4521
1,3-Bis-(pentafluoroethyl)-benzene			
5-Chloro	153	1.5672	1.3790

[a] 20 mm, [b] 15 mm.

The dipole moment was calculated from the equation

$$\mu = 0.01281\ (P_{2\infty} - P_e)^{1/2} \times 10^{-18} \text{ e.s.u.}$$

Values of observed molar refractivities were used for the electronic polarization, P_e, of the solute. The values of $P_{2\infty}$ for the polarization of the solute at infinite dilution were obtained from Hedestrand's equation. The results for thirty-two compounds are listed in Tables I and II with the dipole moments, μ(H.), calculated with the use of Hedestrand's equation, and μ(G.) calculated with the Guggenheim equation, together with their physical constants and experimental data.

The dipole moments were also calculated by vector addition of group moments, using information and methods given in the literature.[5] The values of group moments which were used are listed in Table III.

TABLE III

GROUP MOMENTS FOR CALCULATING DIPOLE MOMENTS

Group	Moment × 10^{18}
$-F$	1.50[a]
$-Cl$	1.55[b]
$-Br$	1.52[b]
$-CH_3$	0.40[b]
$-CF_3$	2.54[c]
$-C_2F_5$	2.65[a]
$-OCH_3$	1.25[b]
$-OC_2H_5$	1.00[d]
$-OC_6H_5$	1.17[d]

[a] As reported in this paper. [b] Weissberger, ref. 5. [c] Ref. 4. [d] Sidgwick, ref. 5.

Dipole moments were given in the literature for five compounds which we studied. For fluorobenzene the observed moment, 1.50 *D*, is in good agreement with the value 1.47 *D* reported by Freiser Hobbs and Gross,[6] using a solution method. For 4-fluorotoluene the observed value 1.82 *D* is in fair agreement with 2.01 *D*, reported by Moore and Hobbs[7] using a gas method. For 4-chlorotrifluoromethylbenzene, 5-chloro-1,3-bis-(trifluoromethyl)-benzene and 4,5-dichloro-1,3-bis-(trifluoromethyl)-benzene the determined dipole moments were 1.22, 1.34 and 1.42 *D* as compared with 1.15, 1.29 and 1.51 *D*, respectively, reported by Freiser.[6]

In the case of halogen derivatives of benzene with one or two trifluoromethyl groups when the substituted groups are ortho to each other on the benzene ring, the mutual inductance between these groups leads to an observed dipole moment which is lower than that calculated by vector addition. The compounds in which this mutual inductance effect is absent have observed moments which are greater than the corresponding calculated moments. This type of behavior, in which the observed moment is greater than the calculated moment, is usually attributed to resonance in the compound.

The moment of the pentafluoroethyl group was

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[3] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

[4] P. E. Brown and T. De Vries, THIS JOURNAL, **73**, 1811 (1951).

[5] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, part II, Interscience Publishers, Inc., New York, N. Y., 1949, Chapt. XXIV; N. W. Sidgwick, *Trans. Faraday Soc.*, **30**, appendix i, (1934); Brown and De Vries, ref. 4.

[6] H. Freiser, M. E. Hobbs and P. M. Gross, THIS JOURNAL, **71**, 111 (1949).

[7] E. M. Moore and M. E. Hobbs, *ibid.*, **71**, 411 (1949).

determined from the data for the three pentafluoroethyl derivatives of benzene reported in this paper and the dipole moment of 4-pentafluoroethyl trifluoromethylbenzene reported by Brown and De Vries.[4] The group moment 2.65 *D* is 0.11 unit larger than the moment for the trifluoromethyl group on benzene.

A comparison of the dipole moments of the ether derivatives of trifluoromethylbenzene discloses some anomalous results. The moment of the trifluoromethyl group is 2.54, that of the methoxy group in anisole is 1.23, yet the moment of 4-methoxy trifluoromethylbenzene was found to be 3.28 and that of 5-methoxy-1,3-bis-(trifluoromethyl)-benzene is 3.23. A vector addition of the moments involved gives 1.31 *D*.

From the value 2.10 found for 1,3-bis-(trifluoromethyl)-benzene and 3.74 found for 2-methoxy-1,3-bis-(trifluoromethyl)-benzene, the moment of the methoxy group, when ortho to a trifluoromethyl group, seems to be 1.64. This makes the value 1.72 found for 2-methoxy-1,4-bis-(trifluoromethyl)-benzene seem reasonable. However, for 4-methoxy 1,3-bis-(trifluoromethyl)-benzene the observed value 4.01 is considerably larger than the value 1.91 calculated by vector addition from the value 1.64 for the methoxy group and 2.10 for the moment of 1,3-bis-(trifluoromethyl)-benzene.

Both the Hedestrand and Guggenheim methods of calculating dipole moments agree well with each other and appear to be applicable for moments above 1.0 *D*. Both methods are subject to relatively high percentage errors when the dipole moment is small.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Internal Rotation. VI. A Dilute Solution Method for the Spectroscopic Determination of the Energy Difference between Rotational Isomers[1]

BY J. POWLING[2] AND H. J. BERNSTEIN

A liquid phase technique for the determination of rotational isomerization energies using infrared analytical methods is presented in which the effect of solvent is adequately eliminated. The isomerization energies of some substituted ethanes have been determined and the values agree with the gas values within the experimental error.

Rotational isomerism in organic compounds was first investigated spectroscopically (Raman effect) by Kohlrausch.[3a,b] The nature of hindered rotation in symmetrical dihalogenoethanes was then extensively investigated by Mizushima[4a,4b,5] who demonstrated the existence of a solvent effect[4a] and showed that only the *trans* form existed in the solid state but the liquid and gaseous phases contained both a *trans* and a *gauche* form in thermal equilibrium.[6]

A quantitative estimation of the isomerization energy, ΔH, in liquid 1,1,2,2-tetrachloroethane was made by Langseth and Bernstein[7] assuming that the relation

$$K = \frac{\text{concn. of the less stable isomer}}{\text{concn. of the more stable isomer}} = \text{const. } e^{-\Delta H/RT} \qquad (1)$$

was valid.

The ΔH value obtained in the liquid phase was 1100 cal./mole whereas a more recent investigation[8] of this molecule in the gas phase by the variation of electric moment with temperature yielded a value of $\Delta H_{\text{gas}} = 0 \pm 200$ cal./mole. The apparent anomaly is entirely due to the environment in the condensed phase[4a] and has been observed also in the cases of 1,2-dichloroethane[3a,9,10,11] and 1,2-dibromoethane.[12] The liquid phase value for 1,2-dichloroethane was found to be ~0 cal./mole (Raman effect[11]), compared with the gas value of ~1250 cal./mole (infrared[13,14]). Recent values for liquid 1,2-dibromoethane are in good agreement but differ greatly from the gas values. Rank, *et al.*,[10] found $\Delta H_{\text{liquid}} = 740$ cal./mole using the Raman effect and Mizushima and co-workers[12] found $\Delta H_{\text{liquid}} = 760$ cal./mole (Raman effect). The latter workers using an infrared technique found $\Delta H_{\text{liquid}} = 680$ cal./mole. These liquid values are to be compared with the infrared gas phase results of Bernstein[15] and Mizushima, *et al.*,[13] which give isomerization energies of 1770 cal./mole and 1450 cal./mole, respectively.

The true energy difference can be obtained directly only from gas phase measurements and indeed the values of ΔE_0^0 may be evaluated when the dimensions and vibrational assignments of the

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[1] Presented at the Symposium on Molecular Structure held at Columbus, Ohio, June, 1950.

[2] National Research Laboratories Post-doctorate Fellow, 1949–1951.

[3] (a) K. W. F. Kohlrausch, *Z. physik. Chem.*, **B18**, 61 (1932); (b) K. W. F. Kohlrausch and F. Koppl, *ibid.*, **B26**, 209 (1934).

[4] (a) Mizushima, Morino and Higasi, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), **25**, 153 (1934); (b) Mizushima, Morino and Noziri, *ibid.*, **29**, 63, 188 (1936).

[5] Mizushima, Morino and Kubo, *ibid.*, **38**, 459 (1937).

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[7] A. Langseth and H. J. Bernstein, *J. Chem. Phys.*, **8**, 410 (1941).

[8] W. D. Gwinn and J. R. Thomas, THIS JOURNAL, **71**, 2785 (1949).

[9] H. Gerding and P. C. Meerman, *Rec. trav. chim.*, **61**, 523 (1942).

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[11] I. Watanabe, S. Mizushima and Y. Masiko, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), **40**, 425 (1943).

[12] Mizushima, Morino, Kuratani and Katayama, *J. Chem. Phys.*, **18**, 754 (1950).

[13] T. Simanouti, H. Turuter and S. Mizushima, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), **42**, 165 (1945).

[14] H. J. Bernstein, *J. Chem. Phys.*, **17**, 256 (1949).

[15] H. J. Bernstein, *J. Chem. Phys.*, **18**, 897 (1950).