in the presence of $NaHC^{14}O_3$ containing 1.25 µc. of radioactivity. Of the total activity (69.0%), recovered, 26.2% was present in the methane.

It is evident that the results obtained from the fermentation of α-, β- and carboxyl-labeled propionic acid must, therefore, be interpreted keeping in mind the fact that carbon dioxide is reduced to methane. The extent of this reduction depends upon the duration of the fermentation.

URBANA, ILL. RECEIVED SEPTEMBER 23, 1950

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

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

BY PAUL E. BROWN AND THOMAS DE VRIES

A heterodyne beat frequency method was employed for the determination of dipole moments of fifteen fluorine-containing organic compounds by the dilute solution technique. Hedestrand's equation was used to calculate the polarization of the solute at infinite dilution.

The purpose of this work was the determination of the dipole moments of certain fluorine-containing compounds. A solution technique permitting the use of Hedestrand's equation was employed.[2]

Experimental

Materials.—Barrett thiophene-free benzene was purified by recommended procedures. After the final distillation it was stored over sodium.[3] The refractive index and density were checked and were found to agree very well with the values listed by Rossini.[4]

Paragon cyclohexane was rectified and a fraction boiling within a 0.1° boiling range was collected, refluxed and stored over sodium.[3] The density at 25° was 0.7713 as compared with 0.77389 reported by Rossini.[4]

The physical constants and sources of the other materials employed are given in Table II.

Apparatus.—The dielectric constant measuring cell had a cylindrical plate assembly consisting of three concentric nickel cylinders.[5] Its air capacity was about 188 mmf., its volume 30 ml. The cell and a solution mixing chamber attached to it were encased in a metal can extending to the bottom of the mixing chamber which was external to this can. Water from a temperature-controlled bath (25 ± 0.02°) was circulated through the can by means of a rotary pump.

A heterodyne beat frequency oscillator was employed for the measurements. The stable oscillator was frequency controlled at 100 kc. with a crystal. The variable oscillator was a modified Hartley circuit. Its frequency was determined by the cell and a variable capacitor in parallel. The output from a mixer stage and amplifier was compared with the 60-cycle, 110-volt a.c., current from the Public Service Co. lines. A Lissajou pattern obtained on an oscilloscope facilitated the tuning of the variable oscillator to exactly 99,940 cycles per second. A comparison capacitor (General Radio 722-D) could be switched into the cell circuit parallel to the variable capacitor in place of the measuring cell. This capacitor was used to correct for oscillator drift. If the comparison capacitor was set at some fixed value and the oscillator did not drift, then a given setting of the variable (measuring) capacitor should be found to always produce the same frequency in the heterodyne beat frequency oscillator output. If the oscillator drifted, the setting of the variable capacitor would also vary and this correction could be noted. The variable capacitor was a General Radio 722-M capacitor calibrated in capacitance removed up to 1,000 mmf. A vernier scale permitted the setting to be read to the nearest 0.02 mmf.

A Sprengel–Ostwald pycnometer was used for determining densities of liquid. A Pulfrich refractometer was used for determining refractive indices.

Procedure.—With dry air in the cell two readings of the variable capacitor were recorded, one with the measuring cell in the circuit and the other with the comparison capacitor in the circuit. The solvent to be employed (benzene or cyclohexane) was transferred from the storage bottle to the mixing chamber by means of a 30-ml. hypodermic syringe. The solvent was forced into the measuring cell up to a marked level above the top of the plates. After a sufficient time interval to permit temperature equilibrum to be established, two more variable capacitor readings were taken as previously described.

A small quantity of the sample being investigated (0.2 g.) was added to the mixing chamber and mixed with the solvent by forcing the liquid back and forth between the cell and the mixing chamber. When the sample was considered sufficiently dispersed, another set of variable capacitor readings were taken. This was continued until the readings for five or six different concentrations of the solution were obtained.

Since the mole fraction of the solute was never more than 0.02, the change in density with mole fraction was assumed linear. The change in dielectric constant with mole fraction (linear in dilute solution) was determined by the method of least squares. This datum and the change in density with mole fraction were substituted in the Hedestrand equation

$$P_{2\infty} = P_1 \frac{M_2}{M_1} - \frac{P_1 \Delta \mathrm{d}}{d_1 f_2} + \frac{3P_1}{(D_1 - 1)(D_1 + 2)} \frac{\Delta D}{f_2}$$

$P_{2\infty}$ = polarization of solute at infinite dilution
P_1 = polarization of solvent
d_1 = density of solvent
M_2 = molecular weight of solute
M_1 = molecular weight of solvent
Δd = density of solution minus density of solvent
f_2 = mole fraction of solute
D_1 = dielectric constant of solvent
ΔD = dielectric constant of solution minus dielectric constant of solvent

The dipole moment of the solute was calculated from the equation

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

The electronic polarization of the solute, P_e, and the polarization of the solvent, P_1, were considered equal to the molar refractivity. These were calculated with the Lorentz–Lorenz equation except in the case of the perfluorocyclohexanes. For these the refractive indices were too low to be determined with the instruments available, hence, the molar refractivities were calculated from atomic refractivities.

Results

The results of the determination of the dipole moments of seventeen compounds are listed in

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(1) Abstracted from the Doctoral Thesis of Paul E. Brown, whose present address is Westinghouse Electric Corporation, Pittsburgh, Pa.

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

(3) W. T. Richards and J. H. Wallace, THIS JOURNAL, **54**, 2705 (1932); A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Press, New York, N. Y., 1935.

(4) F. D. Rossini, *J. Research, Natl. Bur. Standards*, **36**, 129 (1946).

(5) L. J. Berberich, *Ind. Eng. Chem., Anal. Ed.*, **17**, 582 (1945).

TABLE I

DIPOLE MOMENTS

Compd.[a]	$\Delta d/f_2$	$\Delta D/f_2$	P_e	$P_{2\infty}$	μ	Solvent	μ(lit.)
1 Bromobenzene	0.7252	3.528	33.93	83.25	1.55	Benzene	1.35–1.70[b]
2 Chlorobenzene	.2711	3.656	31.16	83.82	1.60	Benzene	1.52–1.64[b]
3 Trifluoromethylbenzene	.3799	8.470	30.74	162.68	2.54	Benzene	
	.5150	6.783	30.74	166.73	2.58	Cyclohexane	2.56[c]
4 3-Chlorotrifluoromethylbenzene	.6312	5.930	36.02	129.45	2.14	Benzene	2.22[c]
5 2-Ethoxytrifluoromethylbenzene	.6342	12.642	42.52	300.16	3.54	Cyclohexane	
6 2-Methoxytrifluoromethylbenzene	.6263	12.853	37.70	295.28	3.54	Cyclohexane	
7 4-Pentafluoroethyl trifluoromethylbenzene	1.050	−0.5132	40.75	50.50	0.69	Benzene	
8 1,2-Bis-(trifluoromethyl)-benzene	0.9163	16.83	35.61	377.60	4.09	Cyclohexane	
9 1,3-Bis-(trifluoromethyl)-benzene	.7911	5.233	35.76	125.77	2.10	Benzene	2.43[c]
10 1,4-Bis-(trifluoromethyl)-benzene	.7992	−0.3168	35.69	43.98	0.64	Benzene	
11 2,5-Bis-(trifluoromethyl)-bromobenzene	1.470	1.556	45.04	77.97	1.27	Benzene	
12 2,5-Bis-(trifluoromethyl)-chlorobenzene	1.071	2.128	41.02	82.95	1.44	Benzene	1.14[c]
13 3,5-Bis-(trifluoromethyl)-bromobenzene	1.460	2.085	44.02	86.04	1.43	Benzene	
14 1,3-Bis-(trifluoromethyl)-4-trifluoromethoxybenzene	1.315	4.071	42.65	134.61	2.12	Cyclohexane	
15 Perfluoro-(ethylcyclohexane)	2.050	−0.5977	35.34	46.71	0.73	Cyclohexane	
16 Perfluoro-(1,3-dimethylcyclohexane)	1.998	− .8541	35.34	42.87	.61	Cyclohexane	
17 Perfluoro-(1,4-dimethylcyclohexane)	1.982	− .5610	35.34	49.37	.83	Cyclohexane	

[a] All the compounds except the first three were prepared in this Laboratory by graduate students under the direction of Dr. E. T. McBee. [b] Sidgwick, *Trans. Faraday Soc.*, **30**, appendix i, (1934.) [c] Freiser, Hobbs and Gross, THIS JOURNAL, **71**, 111 (1940).

Table I. Literature values for the dipole moments of these compounds are included if such are available.

TABLE II

PHYSICAL CONSTANTS

Compd.	B.p., °C.	d^{25}_4	$n^{25}D$
1	156.1	1.4897	1.5570
2	132.0	1.1011	1.5215
3	102.6	1.1822	1.4119
4	137.3	1.3311	1.4438
5	185.3	1.1897	1.4447
6	173.1	1.2553	1.4499
7	129.0	1.4537	1.3665
8	141.2	1.4304	1.3916
9	116.3	1.3790	1.3775
10	117.1	1.3808	1.3767
11	158.3	1.6584	1.4236
12	148.4	1.5039	1.4109
13	153.9	1.6989	1.4241
14	135.7	1.5392	1.3592
15	102.2		
16	101.2		
17	102.0		

Determinations of the dipole moments of trifluoromethylbenzene, chlorobenzene and bromobenzene were made to indicate the accuracy of the equipment and method. In the case of bromobenzene the literature values range from 1.35 to 1.70 *D* but most of the values are between 1.50 and 1.55 *D*.

The dipole moment found for trifluoromethylbenzene is 2.54 *D* and for 2-methoxytrifluoromethylbenzene 3.54 *D*. For the methoxy group the value 1.23 is given.[6] The resultant moment, when both groups rotate freely on the bond to the ring, is calculated to be 3.35 assuming a 60° angle between the bonds to the ring. If resonance gives enough double bond character to the bond of the methoxy group, the methyl group may be coplanar with the ring. By using the equation $\mu^2 = m_1^2 + m_2^2 + 2m_1m_2 \cos \theta$, and 2.14 *D* for the directed moment of the methoxy group which is normally at 55° to the bond on which it rotates, a value of 83° is calculated for the angle θ. It seems reasonable that the methyl group has been forced away from the trifluoromethyl group by steric repulsion.

The dipole moment found for 2-ethoxytrifluoromethylbenzene is 3.54 *D*. The moment for ethoxybenzene is given by Wesson as 1.00 to 1.40.[6] A value of 1.4 gives a calculated moment of 3.48, assuming a 60° angle between the bonds to the ring.

The dipole moment found for 2.5-bis-(trifluoromethyl)-chlorobenzene is 1.44 *D*. Assuming no interaction, the moments of the two trifluoromethyl groups might be expected to cancel each other and the molecule might be expected to have a dipole moment about the same as chlorobenzene (1.60 *D*). Similarly, the value 1.27 *D* found for 2,5-bis-(trifluoromethyl)-bromobenzene is lower than the expected value 1.55 *D*. Again, the moment 2.14 *D* found for 3-chlorotrifluoromethylbenzene is lower than 2.24 *D* calculated from 1.60, the moment for chlorobenzene and 2.54, the moment for trifluoromethylbenzene. Such decreases can be expected due to a mutual interaction between two electron attracting groups.

For 1,2-bis-(trifluoromethyl)-benzene the observed moment is 4.09 *D*, which makes the moment of each trifluoromethyl group now 2.36 instead of 2.54 when alone on the ring. The moment found for 1,3-bis-(trifluoromethyl)-benzene, 2.10 *D*, is much lower than the expected value 2.56. For 1,4-bis-(trifluoromethyl)-benzene the moment found is 0.64 *D*, much higher than the zero moment expected. It is believed that the meta and para

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(6) A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, Vol. I, part II, p. 1614; L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1950, p. 36.

isomers of this compound were not effectively separated.

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[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).