[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Electric Moments of Some Organic Molecules in the Vapor State[1]

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The desirability of measuring the electric moments of molecules in the gas phase is well recognized although, in the case of some substances, the experimental difficulties may make such measurements impracticable. The present series of determinations were undertaken with the object of increasing the number of electric moment values established from vapor phase measurements since, with such values, a detailed inquiry may be made into the basis and extent of various intramolecular interactions such as deviations from additivity of the vector bond moments of molecules. This paper reports the results of the first of a series of such vapor phase measurements carried out in this Laboratory.

Materials and Method

The materials were Eastman Kodak Company best grade chemicals and each was fractionated in a 60-cm. Widmer column, the middle fraction being used for the measurement. The distilling temperatures and pressures (cor.) are given. The range when not indicated was of the order of 0.01°.

Fluorobenzene	84.74– 84.76°	at 760.0
Chlorobenzene	131.24–131.25°	at 745.9
o-Dichlorobenzene	179.7°	at 746.2
o-Fluorotoluene	113.1°	at 755.0
m-Fluorotoluene	115.1°	at 755.0
p-Fluorotoluene	115.5°	at 755.0

***m*-Difluorobenzene**.—This compound was prepared by Mr. Irving Waltcher in this Laboratory. The details of the preparation have been reported.[3] The n. b. p. of the fraction used was 83.05° and the f. p. −59.3°.

Diethyl Ether.—One sample of this material was Merck "pro analysi" grade and was subjected to no purification as the results of the measurements were to be compared with some values reported in the literature. The other sample was purified by refluxing over sodium and finally distilling from fresh sodium. The distillation range of the fraction used was 34.51–34.52° at 760 mm. (cor.).

Methyl Ethyl Ether.—This compound was prepared from ethyl bromide and sodium methylate by the Williamson reaction. The product was repeatedly fractionated until it was free of bromides when treated with alcoholic potassium hydroxide and was inactive toward metallic sodium. The approximate distillation temperature was 10.2° at 755 mm. (cor.).

The apparatus has been described elsewhere.[4] The method employed follows. The gas system was evacuated to < 0.05 mm. and flushed twice with the vapor to be measured. The vapor was then introduced until a usable pressure for the given temperature was obtained. After thermal equilibrium was established the gas condenser capacitance was placed in parallel with a high precision air condenser by an appropriate switching device and the pressure in the gas system slowly reduced to some lower level. After thermal equilibrium was established at the lower pressure the new setting of the high precision capacitor necessary to bring the total capacitance of the measuring circuit back to its original value was determined. Slight frequency drifts that took place during the manipulations and waiting periods were compensated for by making all readings with reference to a fixed air capacitance. The above procedure was repeated until the total pressure in the gas system was of the order of 20–30 mm.

The values of capacitance measured as above were then plotted against pressure and the resulting line extrapolated to zero pressure. The total change in capacitance caused by the gas was therefore the sum of all capacitance changes from zero pressure up to the particular pressure under consideration. The capacitance change caused by the gas was generally found to be linear with the measured values of the pressure in the pressure ranges involved, the small deviations from linearity being randomly distributed. All changes were measured in terms of a capacitance calibration unit (ΔS) which was equivalent to about 0.4 mmf. In view of the observed linearity the average value of $\Delta S/p$ was generally used for calculating the molar polarization, P, of the gas at the particular temperature. In case of a real drift of $\Delta S/p$ values with p the extrapolated value of $\Delta S/p$ at $p = 0$ was used. P was calculated from

$$P = \frac{\Delta SRT}{p3C_{g_e}}$$

Here R is the molar gas constant T the temperature in °K. and C_{g_e} is the insulator free "effective"[4] vacuum capacitance of the gas condenser. The use of this effective gas capacitance obviates the necessity of applying inductance corrections to the measured ΔS values. The average value of C_{g_e} for the temperature range involved was 2685 ΔS units and since the temperature coefficient was very small the average value of C_{g_e} was used. The values of A and B in the relation $P = A + B/T$ were obtained by least squares and the value of $\mu_{D(B)}$, in debyes was obtained from the relation

$$\mu_{D(B)} = 0.01281\sqrt{B}$$

An alternative way of calculating the moment is the method used by Wenzke,[5] Smyth[6] and others in which use is made of the relation

$$\mu_{D(R)} = 0.01281\sqrt{(P - R_D)T}$$

In the present work μ_D is calculated by both methods with R_D, the molecular refraction for the sodium lines, taken as[7]: $C_6H_6 = 26.14$, $C_6H_5CH_3$

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(1) Part of a thesis of Eunice M. Moore submitted in partial fulfillment of the requirements of the Ph.D. degree in Chemistry at Duke University, June, 1939.

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(3) I. Waltcher, M.A. Thesis, Duke University, Durham, N. C., 1939.

(4) Hobbs, Jacokes and Gross, *Rev. Sci. Instruments*, **11**, 126 (1940).

(5) Krieger and Wenzke, THIS JOURNAL, **60**, 2115 (1938).

(6) Hannay and Smyth, *ibid.*, **68**, 1005 (1946).

(7) W. Hückel, "Theoretische Grundlagen der organishen Chemie," Vol. II, 2nd Ed., Akademische Verlagsgesellschaft, Leipzig, 1935, pp. 86 and 134.

= 3.106, C = 2.418, H = 1.100, Cl = 5.967, O (ether) = 1.643 and F[8] = 1.00.

TABLE I

Substance	T	$1/T$ $\times 10^3$	ΔS $p \times 10^2$	P	$\mu_D(R)$
Fluorobenzene	350.9_5	2.849	2.607	70.62	1.60
	362.0_4	2.762	2.458	68.78	1.59
	371.9_3	2.689	2.377	68.21	1.60
	407.2_9	2.455	2.047	64.36	1.60
	423.1_9	2.363	1.914	62.47	1.59
$R_D = 26.0$; $A = 25.4$; $\mu_D(B) = 1.61$; $\mu_D(R) = 1.60$					
Chlorobenzene	353.7_2	2.827	3.038	83.30	1.74
	371.7_8	2.690	2.849	81.09	1.75
	408.2_3	2.450	2.440	77.08	1.76
	427.0_9	2.341	2.270	75.05	1.75
$R_D = 31.0$; $A = 33.9$; $\mu_D(B) = 1.70$; $\mu_D(R) = 1.75$					
m-Difluorobenzene	352.7_1	2.834	2.611	71.20	1.62
	371.9_1	2.689	2.397	68.83	1.62
	407.3_1	2.455	2.094	65.95	1.64
	423.3_0	2.363	1.931	63.10	1.61
$R_D = 25.9$; $A = 27.3$; $\mu_D(B) = 1.58$; $\mu_D(R) = 1.62$					
o-Dichlorobenzene	353.7_2	2.827	5.165	141.2	2.48
	371.9_2	2.689	4.730	136.3	2.50
	408.3_8	2.449	4.015	126.9	2.48
	424.1_0	2.341	3.708	122.2	2.45
$R_D = 35.9$; $A = 30.7$; $\mu_D(B) = 2.54$; $\mu_D(R) = 2.48$					
o-Fluorotoluene	350.7_1	2.851	2.341	63.47	1.37
	372.0_7	2.687	2.152	61.95	1.38
	407.2_3	2.456	1.873	59.00	1.37
	423.0_8	2.363	1.765	57.20	1.36
$R_D = 31.0$; $A = 31.4$; $\mu_D(B) = 1.35$; $\mu_D(R) = 1.37$					
m-Fluorotoluene	362.58	2.762	3.196	89.40	1.87
	371.7_6	2.689	3.070	88.20	1.87
	407.2_2	2.456	2.618	82.47	1.85
	423.0_9	2.363	2.456	80.41	1.85
$R_D = 31.0$; $A = 31.6$; $\mu_D(B) = 1.85$: $\mu_D(R) = 1.86$					
p-Fluorotoluene	351.0_6	2.848	3.703	100.5	2.00
	407.2_4	2.456	2.898	91.07	2.00
	423.1_5	2.363	2.719	88.78	2.00
$R_D = 31.0$; $A = 30.7$; $\mu_D(B) = 2.01$; $\mu_D(R) = 2.00$					
Diethyl ether (A)	300.0_9	3.323	2.273	52.79	1.22
Merck pro analysi	341.8_0	2.926	1.869	49.39	1.23
	372.0_1	2.688	1.649	47.44	1.24
$R_D = 22.3$: $A = 24.7$; $\mu_D(B) = 1.18$; $\mu_D(R) = 1.23$					
same (B)	302.8	3.303	2.255	51.73	1.21
(purified)	344.5	2.903	1.841	48.60	1.22
	351.7	2.843	1.770	48.10	1.22
	371.1	2.695	1.638	47.02	1.23
$R_D = 22.3$; $A = 26.0$; $\mu_D(B) = 1.14$; $\mu_D(R) = 1.22$					
Methyl ethyl ether	302.6	3.305	2.157	50.23	1.27
	340.5	2.937	1.789	46.76	1.28
	353.3	2.831	1.695	45.79	1.28
	368.8	2.711	1.583	44.86	1.29
$R_D = 17.7$; $A = 20.0$; $\mu_D(B) = 1.22$; $\mu_D(R) = 1.28$					

Results and Discussion

The data and derived values are given in Table I. The symbols in the table have their previously indicated meaning.

In Table II the essential quantities are recapitulated so as to bring the similarities and differences clearly into focus.

TABLE II

Substance	A	R_D	Δ $(A - R)$	$\mu_D(B)$	$\mu_D(R)$	$\Delta\mu(BR)$
Fluorobenzene	25.4	26.0	−0.6	1.61	1.60	+0.01
Chlorobenzene	33.9	31.0	+2.9	1.70	1.75	−0.05
m-Difluorobenzene	27.3	25.9	+1.4	1.58	1.62	−0.04
o-Dichlorobenzene	30.7	35.9	−5.2	2.54	2.48	+0.06
c-Fluorotoluene	31.4	31.0	+0.4	1.35	1.37	−0.02
m-Fluorotoluene	31.6	31.0	+0.6	1.85	1.86	−0.01
p-Fluorotoluene	30.7	31.0	−0.3	2.01	2.00	+0.01
Diethyl ether (A)	24.7	22.3	+2.4	1.18	1.23	−0.05
(B)	26.0	22.3	+3.7	1.14	1.22	−0.08
Methyl ethyl ether	20.0	17.7	+2.3	1.22	1.28	−0.06

Some of the above compounds have had their electric moment reported in the literature. Those results that were obtained from gas phase measurements are, for purposes of comparison, recorded in Table III.

TABLE III

ELECTRIC MOMENTS (DEBYES)

Substance	Present	Literature
Fluorobenzene	1.61	1.57[a]
Chlorobenzene	1.70	1.70.[a] 1.69,[b] 1.72[c]
o-Dichlorobenzene	2.54	2.51,[c] 2.16[d]
Diethyl ether	1.14	1.14,[e] 1.14,[h] 1.15,[f] 1.17[g]

[a] MacAlpine and Smyth, *J. Chem. Phys.*, **3**, 55 (1935). [b] Groves and Sugden, *J. Chem. Soc.*, 1094 (1934). [c] Hurdis and Smyth, THIS JOURNAL, **64**, 2212 (1942). [d] Groves and Sugden, *J. Chem. Soc.*, 1782 (1937). [e] H. A. Stuart, *Z. Physik*, **51**, 490 (1928). [f] R. Sanger, *Physik. Z.*, **31**, 306 (1930). [g] Groves and Sugden, *J. Chem. Soc.*, 1779 (1937). [h] O. Fuchs, *Z. Physik*, **63**, 824 (1930).

The agreement of our values with those of Smyth (Table III) are reasonably good and our value of 1.14 *D* for diethyl ether agrees with Sanger's value within the experimental error. A least-squares recalculation of Groves and Sugden's data (g) for ether gives = 1.14 *D*. In view of the low value of *A*, we feel that our value of 2.54 *D* for *o*-dichlorobenzene is probably too high. A simplified analysis of the random error for this case indicates that an error of 1.5% in μ and 2.5 cc. in *A* could be expected, therefore we suggest that the correct value of μ might be 0.04–0.05 *D* less than the reported value of 2.54 *D*. It may be remarked that all values of $\mu_D(B)$ of Table II are considered to be in error by <2% and that the error in $\mu_D(R)$ may be as much or considerably greater than the error in $\mu_D(B)$. Some of the error in $\mu_D(R)$ could be eliminated by making an allowance for atomic polarization, P_A, but such a procedure is, at best, somewhat arbitrary. In general, as the difference $(P - R_D)$ increases the influence of P_A may become less and less; however, there are certain molecules where P_A is rather

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[8] Fuchs and Wolf "Dielectrische Polarisation," Akademische Verlagsgesellschaft, Leipzig, 1935, p. 258.

large,[9] therefore moments calculated from $(P - R_D)$ should always be critically examined in light of the structure of the particular molecule.

The value of 1.18 D obtained for unpurified ether (A) indicates that some of the previous data (Fuchs and Stuart, Table III, *e* and *h*, respectively) may be based on a sample of ether that contained a significant amount of polar impurity and that the agreement of these authors values with the others recorded may be fortuitous.

The value 1.22 D for methyl ethyl ether falls between 1.14 D for diethyl and 1.30 D[10] for dimethyl ether.

A comparison of the observed moment with that calculated for vector addition for the *o*-, *m*- and *p*-halogen toluenes is given in Table IV. The bond moments used were: C_{ar}–CH_3 (vapor) = 0.37, C_{ar}–CH_3 (solution) = 0.39, C_{ar}–F(vapor) = 1.61, C_{ar}–Cl (solution) = 1.56, C_{ar}–Br (solution) = 1.53 and C_{ar}–I (solution) = 1.38. The bond moment values for solution are taken from Tiganik,[11] the vapor C_{ar}–CH_3 from Baker[12] and the 1.61 for C_{ar}–F from the present investigation.

TABLE IV

ELECTRIC MOMENTS (DEBYES)

Substance	Ortho Calcd.	Ortho Obs.	Meta Calcd.	Meta Obs.	Para Calcd.	Para Obs.
Fluorotoluene (vap.)[a]	1.46	1.35	1.82	1.85	1.98	2.01
Chlorotoluene (sol.)[b]	1.41	1.43	1.79	1.77	1.95	1.94
Bromotoluene (sol.)[b]	1.38	1.44	1.76	1.75	1.92	1.93
Iodotoluene (sol.)[c]	1.24	1.33	1.61	1.67	1.77	1.80

[a] Present investigation. [b] Reference 11. [c] H. Poltz, *Z. physik. Chem.*, **B20**, 351 (1933).

Deviation from vector additivity ~ 0.1 debye occurs only for *o*-fluoro- and *o*-iodotoluenes and these are in opposite sense to each other. Until data for the chloro-, bromo- and iodo-toluenes in the vapor phase is available it is felt that a discussion of such deviations as exist is of limited value and would necessarily be somewhat speculative.

Summary

The electric moments of several organic molecules have been determined from gas phase measurements of the dielectric constant at several temperatures and pressures. The results in debyes are: fluorobenzene—1.61, chlorobenzene—1.70, *m*-difluorobenzene—1.58, *o*-dichlorobenzene—2.54, *o*-fluorotoluene—1.35, *m*-fluorotoluene—1.85, *p*-fluorotoluene—2.01, diethyl ether—1.14 and methyl ethyl ether—1.22.

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[9] (a) Coop and Sutton, *J. Chem. Soc.*, 1269 (1938); (b) Finn, Hampson and Sutton, *ibid.*, 1254 (1938).

[10] Sanger, Steiger and Gachter, *Helv. Phys. Acta*, **5**, 200 (1932). The value 1.29 given by these authors is raised to 1.30 when the new value of N_A is used.

[11] L. Tiganik, *Z. physik. Chem.*, **B13**, 425 (1931).

[12] Baker and Groves, *J. Chem. Soc.*, 1144 (1939).

[CONTRIBUTION NO. 61 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Catalytic Hydrogenation of the Benzene Nucleus. V. The Hydrogenation of Benzene, the Cyclohexadienes and Cyclohexene

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Introduction

It is a well known fact that the benzene nucleus is hydrogenated with considerably greater difficulty than a simple unsaturated system. This is presumably due to the large resonance energy of the benzene ring system. If this is the case, one would expect the conjugated 1,3-cyclohexadiene to hydrogenate less readily than either the unconjugated 1,4-cyclohexadiene or cyclohexene. In order to test this, a study of the rates of hydrogenation of cyclohexene, the cyclohexadienes, and benzene was undertaken.

Experimental

Merck reagent thiophene-free *Benzene* was purified by fractionation in an 8-ft. Vigreux column. The fraction used for rate studies distilled at a temperature of 79.2° at 741 mm., and had a refractive index, n^{20}_D, of 1.5003.

Eastman Kodak Co. technical *cyclohexene* was first distilled through the 8-foot column and the fraction boiling between 81.8 and 82.0° collected. This was mixed with an equal volume of methanol, and azeotropic fractionation carried out in the same column. The fraction boiling at 55.8° was washed five times with cold water in order to remove the methanol, and dried with anhydrous magnesium sulfate. Fractionation of this product gave a constant boiling cut with a head temperature of 81.8° at 738 mm. pressure; n^{20}_D was 1.4458.

1,3-Cyclohexadiene and 1,4-cyclohexadiene were prepared by dehydration of quinitol according to the method of Zelinskii and co-workers.[1] Quinitol was prepared by the reduction of hydroquinone over Raney nickel at 150° and 2,000 p. s. i. hydrogen pressure. The solvent, ethanol, was removed from the hydrogenated product by distillation and the quinitol recrystallized from acetone. The quinitol was then dehydrated by heating with potassium bisulfate in a stream of carbon dioxide gas. The hydrocarbon and water were condensed in a cold-finger containing a little hydroquinone, to prevent polymerization. The hydrocarbon layer was separated, washed with sodium bicarbonate, and distilled from a simple distilling flask. The fraction boiling between 75 and 125° was again washed with sodium carbonate solution, dried over potassium carbonate, mixed with an equal volume of methanol, and fractionated in an 8-ft. Vigreux column. Three fractions were collected, washed five times with cold water, dried over anhydrous potassium carbonate, and refractionated. Two constant boiling cuts were obtained. The 1,3-cyclohexadiene distilled at 79.3° at 738 mm., and had

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[1] Zelinskii, Denisinka and Eventova, *Compt. Rend. Acad. Sci. U. S. S. R.*, **1**, 313 (1935).