TABLE I

EMPIRICAL CONSTANTS AND MOLAR POLARIZATIONS IN BENZENE SOLUTION AT 25°, MOLAR REFRACTIONS AND DIPOLE MOMENTS

	ϵ_1	a	v_1	b	P_2	MR_D, obs.	Obsd.	Calcd.
3-Bromopropyne-1 (propargyl bromide)	2.2718	3.08	1.14500	−0.778	67.74	22.14	1.49	1.57
3-Iodopropyne-1 (propargyl iodide)	2.2720	2.20	1.14460	−1.335	57.86	27.76	1.21	1.23
2-Bromobutyne-3	2.2730	4.21	1.14450	−0.700	90.97	27.18	1.76	1.71
2-Methyl-2-bromobutyne-3	2.2724	5.02	1.14440	− .640	109.0	32.00	1.94	1.84
1-Chlorooöctyne-4	2.2730	4.85	1.14480	− .140	117.3	42.08	1.92	1.85
2-Propyne-1-ol (propargyl alcohol)	2.2725	4.25	1.14440	− .043	80.54	15.35	1.78	1.77
3-Butyne-1-ol	2.2700	3.91	1.14450	+ .007	81.30	20.02	1.73	1.82
3-Butyne-2-ol	2.2720	3.66	1.14490	+ .020	78.20	20.11	1.69	1.77
2-Methyl-3-butyne-2-ol	2.2722	3.13	1.14490	+ .090	76.78	25.05	1.59	1.77
3-Octyne-1-ol	2.2720	4.12	1.14480	+ .010	103.8	39.00	1.78	1.66
Propargyl ethyl ether	2.2725	2.54	1.14480	+ .080	67.87	24.45	1.46	1.28
1-Diethylaminopropyne-2	2.2725	0.50	1.14490	+ .170	49.21	36.07	0.80	1.10

A hyperconjugation moment of 0.8, and $\overset{-}{C}$–$\overset{+}{X}$ moment of 0.3 have been added vectorially to the moment of the corresponding saturated derivative in benzene solution. By using the moment of the corresponding saturated derivative as the basis of each calculation ordinary inductive effects are to a large extent allowed for.

pyridine. The reaction mixture was washed with water, the organic layer removed, dried with calcium chloride, and fractionated; d^{25}_4 1.3815, n^{25}_D 1.4766. No product was obtained when thionyl bromide replaced the phosphorus tribromide.

2-Methyl-2-bromobutyne-3.—Dry hydrogen bromide was passed through[11] pure 2-methyl-3-butyne-2-ol at 0° as long as it was absorbed. The organic layer was washed with water, neutralized and dried over potassium carbonate (all at 0°). The crude product was fractionated under reduced pressure; n^{25}_D 1.4631, d^{25}_4 1.2657.

Method

The dielectric constants and densities of six benzene solutions of each compound, ranging from 0.001 to 0.020 mole fraction solute, were determined at 25°. The apparatus, technique and method of calculation have been described in a previous publication[12] and the symbols used there have been retained. The electric moments were calculated from the observed molar refractions, and from the molar polarizations of the solutes derived by the method of Halverstadt and Kumler.[13] The constants ϵ_1, v_1, a and b of their equation and the values of the molar polarization of the solute at infinite dilution P_2 for each compound are shown in Table I along with the observed molar refractions MR_D and the calculated dipole moments μ. The probable error in the dipole moment is about ±0.05 D.

Acknowledgment.—The authors are indebted to Professor Thomas L. Jacobs for the gift of a sample of pure propargyl bromide and to Mr. M. Patapoff for preliminary work on this problem.

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[11] K. N. Campbell and J. T. Ely, THIS JOURNAL, **62**, 1798 (1940).

[12] M. T. Rogers, *ibid.*, **77**, 3681 (1955).

[13] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Fluorocarbon Derivatives

BY MAX T. ROGERS AND RICHARD D. PRUETT

RECEIVED FEBRUARY 15, 1955

The electric moments of perfluoroethyl ether, perfluorotetramethylene oxide, chlorotrifluoroethylene and 1,1,2,2,3,3,3-heptafluoropropane have been determined from measurements of the dielectric constants of the gases at several temperatures. The electric moments of perfluorotriethylamine and ethyl perfluorobutyrate were measured in benzene solution at 25°. The observed moments of the ethers are close to the values calculated by use of bond moments but the amine and ester have larger moments than calculated. The values have been discussed and compared with moments calculated on the basis of reasonable models for the molecules.

The physical properties of completely fluorinated ethers and amines suggest that these compounds are less polar than the normal amines and ethers and that the lone-pair electrons are less available for coördination with an acid.[1] Since the electric moments of these compounds should provide information concerning their electronic structures, we have measured the moments of two perfluoroethers and a perfluoroamine and have compared the results with the corresponding hydrogen compounds. To obtain a value for the difference between the C–H and C–F bond moments for use in the calculations, a measurement of the moment of 1,1,2,2,3,3,3-heptafluoropropane was made.

Results

The electric moment of 1,1,2,2,3,3,3-heptafluoropropane, 1.62, is somewhat lower than that of *n*-amyl fluoride (1.85).[2] The decrease is analogous to that observed in going from methyl fluoride (μ = 1.808) to fluoroform[3] (μ = 1.645) and may be attributed to larger inductive effects in the compounds with many fluorine atoms. If the C–H moment is taken to be 0.4 D, with hydrogen positive, then the C_3F_7 group moment is 1.22 D.

A moment may then be calculated for perfluorodiethyl ether or perfluorotetramethylene oxide by replacing the C_2H_5 group moment (0.4) by the

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[1] J. H. Simons, Ed., "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, Chap. 14.

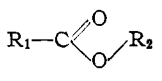
[2] M. T. Rogers, THIS JOURNAL, **69**, 457 (1947).

[3] "Tables of Electric Dipole Moments of Substances in the Gaseous State," Bureau of Standards Circular 537, Washington, D. C., 1953.

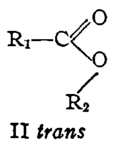
C_3F_7 group moment (1.22), using the C–O bond moment (0.7) derived from ethers, and assuming a value for the C–O–C angle (110°). The value 0.62 *D* obtained in this way agrees within experimental error with the values observed for perfluorodiethyl ether (0.51) and perfluorotetramethylene oxide (0.56). If the bond angle C–O–C in the perfluoroethers is taken to be 125° the moment calculated for both ethers is 0.49 *D*.

A similar calculation for perfluorotriethylamine using the assumed C–N–C bond angle of 110° and the C–N bond moment of 0.4 from trialkylamines, leads to a predicted moment of 0.82 directed away from the nitrogen atom. The observed moment (1.36) is much larger than this; one might have expected a lower value by analogy with nitrogen trifluoride since in both compounds the moment of the lone-pair electrons[4] subtracts from the principal moment. Although the moment might be somewhat smaller if the atomic polarization in this compound were unusually large,[5] it is unlikely that this would reduce the experimental value below about 1.25 *D*. It is possible that the bond angles C–N–C in this amine are larger than in the trialkylamines; this would indicate a tendency toward sp^2 hybridization and would reduce the contribution of the lone-pair electrons to the total moment.

Most esters of aliphatic carboxylic acids (R_1CO-OR_2) have electric moments about 1.7–1.8 *D*. Since the addition of bond moments leads to a value about 1.6 *D* for configuration I (*cis*) and 3.5 for configuration II (*trans*) it is concluded that the actual molecule is nearly in the *cis* configuration or that in the equilibrium mixture most molecules are *cis*. Substitution of the C_3F_7 group for R_1 in an ester should decrease the moments expected for configurations I and II to about 1.5 and 2.4. The observed value 3.09 is then larger than calculated even for the *trans* configuration and it seems difficult to account for the observed value without assuming that the *trans* configuration is highly favored. If an internal C–H...F hydrogen bond is responsible for one configuration predominating then this assumption would be plausible. The electric moment of ethyl trichloroacetate[6] (2.53) also is better accounted for by the *trans* configuration II (2.52 *D* calcd.) than by the *cis* configuration I (1.52 *D* calcd.).

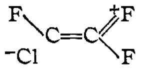


I *cis*

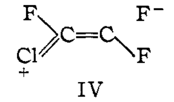


II *trans*

The electric moments of fluorobenzene and chlorobenzene are[3] 1.60 and 1.70, respectively. The moment of chlorotrifluoroethylene might be expected to be close to the difference between these, or 0.1 *D*. The observed value, 0.38 indicates that the contribution from structures such as III are favored over those of type IV to the extent of contributing 0.3 *D* to the moment. The sign of the electric moment is not known but the shortening of the CF distances observed in various chlorofluorides[7] supports this interpretation rather than the reverse one (IV more important than III). Moments of the same order of magnitude have been observed[3] in trichlorofluoromethane (0.45) and dichlorodifluoromethane (0.505) and chlorotrifluoromethane (0.39).



III



IV

Experimental

Materials

Chlorotrifluoroethylene.—A sample obtained from the Oak Ridge National Laboratory was distilled three times, the center cut of each distillation being carried to the next stage.

Ethyl Perfluorobutyrate.—Material from the Columbia Chemicals Co. was used directly; $n^{25}{}_D$ 1.3005, $d^{25}{}_4$ 1.3936.

Perfluorodiethyl Ether, Perfluorotetramethylene Oxide, Perfluorotriethylamine and 1,1,2,2,3,3,3-Heptafluoropropane.—Purified samples of these compounds were the gift of the Minnesota Mining and Manufacturing Co. and were used after three simple trap-to-trap distillations in which the middle fraction was retained each time.

Ammonia.—Ammonia from a cylinder (Ohio Chemical Co.) was dried and purified by three distillations. The final middle fraction was used for calibrating the cell.

Apparatus and Method

Measurements in the Vapor State.—The apparatus, technique and method of calculation are similar to those described in another article.[8] However, in this work a cell with a glass envelope was used. It contained five concentric nickel-plated brass cylinders insulated from one another by Teflon spacers; alternate cylinders were grounded and the ungrounded inner cylinders which were shorter were connected to the oscillator. The cell had a replaceable capacitance of about 350 micro-microfarads and its volume was about 500 ml. The cell was calibrated with ammonia, the dielectric constant of which is known[9] as a function of temperature at one atmosphere pressure. Pressures were measured with a mercury manometer and the temperature of the cell was controlled by a constant-temperature bath which was regulated at each temperature.

The capacitance of the cell at a given temperature was plotted as a function of pressure and the capacitance change ΔC from vacuum to one atmosphere obtained from the graph. This method provides some correction for deviations from the ideal gas law. From ΔC and the known replaceable capacitance of the cell the dielectric constant ϵ of the gas at one atmosphere pressure was calculated at each temperature. The results are shown in Table I, for each compound. The molar polarization was then computed from the Debye equation using the ideal gas law. The molar polarizations for each compound were plotted *versus* the reciprocal of the absolute temperature and the slope *B* and intercept *A* (at $1/T = 0$) found; these values were checked by the method of least squares. The intercept gives the distortion polarization P_D and the dipole moment is found by use of the equation

$$\mu = 0.0128\sqrt{B} \quad \text{Debye}$$

Values of P_D and μ are included in Table I along with the estimated probable errors.

Measurements in Solution.—Measurements were made in benzene solution at 25°. The apparatus, technique and method of calculation have been described in a previous

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[4] See, for example, Coulson, "Valence," Oxford University Press, 1952.

[5] In the perfluoropentanes it is about 8.5 cc.; C. P. Smyth, THIS JOURNAL, **73**, 5115 (1951).

[6] M. A. Luferova and Y. K. Syrkin, *Doklady Akad. Nauk U.S.S.R.*, **59**, 79 (1948).

[7] L. Pauling, "Nature of the Chemical Bond," Second Edition, Cornell University Press, Ithaca, N. Y., 1940.

[8] M. T. Rogers, R. D. Pruett and J. L. Speirs, to be published.

[9] A. van Itterbeek and K. de Clippeleier, *Physica*, **14**, 349 (1948).

TABLE I

DIELECTRIC CONSTANTS AND MOLAR POLARIZATIONS AT VARIOUS TEMPERATURES FOR SOME FLUOROCARBON DERIVATIVES IN THE VAPOR STATE

T, °K.	$(\epsilon - 1) \times 10^6$	P_M, cc./mole
1,1,2,2,3,3,3-Heptafluoropropane		
299.8	8104	66.3
307.3	7778	65.2
314.1	7481	64.1
321.5	7084	62.2
334.2	6699	61.1
342.5	6387	59.7
352.5	6053	58.3
362.3	5758	57.0
372.9	5497	56.0
382.1	5271	55.0
$\mu = 1.62 \pm 0.12$ *D*		$P_D = 13.0 \pm 1.0$ cc./mole
Perfluoromethylene Oxide		
299.2	4039	33.0
310.1	3894	32.9
317.2	3753	32.5
329.1	3588	32.3
339.8	3485	32.4
347.7	3385	32.2
356.1	3273	31.9
366.3	3167	31.8
375.4	3110	31.9
384.2	3016	31.6
$\mu = 0.56 \pm 0.12$		$P_D = 26.5 \pm 1.0$
Perfluoroethyl Ether		
299.3	4004	32.7
307.9	3893	32.8
314.0	3811	32.7
320.1	3658	32.0
328.1	3587	32.2
335.4	3519	32.2
345.8	3375	31.9
355.3	3284	31.9
364.9	3182	31.7
373.7	3108	31.7
$\mu = 0.51 \pm 0.12$		$P_D = 27.2 \pm 1.0$
Chlorotrifluoroethylene		
301.3	2729	22.5
307.8	2712	22.8
317.6	2616	22.7
327.5	2508	22.5
336.7	2495	22.9
349.6	2314	22.1
357.5	2264	22.1
365.7	2367	22.3
377.3	2140	22.0
$\mu = 0.38 \pm 0.12$		$P_D = 20.2 \pm 1.0$

publication[10]; the symbols used there have been retained. The observed dielectric constants ϵ_{12} and specific volumes v_{12} of six solutions, varying from 0.001 to 0.01 mole fraction solute, were plotted graphically *versus* mole fraction solute. The slopes, a and b, and intercepts at zero mole fraction solute, ϵ_1 and v_1, are shown in Table II along with the molar polarizations of the solutes at infinite dilution P_2 and the dipole moments μ calculated by the method of Halverstadt and Kumler.[11] The observed molar refractions are shown in the table; the value for the perfluorotriethylamine is from gas measurements.[12] A correction of 0.15 MR_D for atom polarization has been included since the atom polarizations of fluorocarbons appear to be unusually large.[5]

TABLE II

EMPIRICAL CONSTANTS[11] AND MOLAR POLARIZATIONS AT 25° IN BENZENE SOLUTION, MOLAR REFRACTIONS AND DIPOLE MOMENTS

ϵ_1	a	v_1	b	P_2	MR_D	μ
Perfluorotriethylamine						
2.2728	−0.586	1.14380	−1.735	77.4	34.96	1.36
Ethyl Perfluorobutyrate						
2.2718	12.113	1.14470	−1.193	232.81	32.53	3.09

Acknowledgment.—We are indebted to Dr. W. H. Pearlson, and to the Minnesota Mining and Manufacturing Co., for the gift of purified samples of four fluorocarbon derivatives. This work was supported by the Atomic Energy Commission through contract AT(11-1)-151.

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[10] M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

[11] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

[12] M. T. Rogers and J. G. Malik, unpublished results.