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The Electric Moments of Some Aliphatic Fluorides, Cyanides and Amines

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A comparison of the electric moments of the aliphatic chlorides, bromides and iodides shows that there is a small increase in moment with increase in length of the hydrocarbon chain, and a further increase with chain branching in the secondary and tertiary compounds. Measurements for most other series are not extensive enough to reveal definite trends and, since the values might give some information concerning hyperconjugation in these molecules, data have been obtained for the aliphatic fluorides, cyanides, and amines.

Few measurements of aliphatic monofluorides have been made but the values reported for *n*-amyl and *t*-amyl fluorides in carbon tetrachloride solution[1] are low compared with the presumably more reliable vapor measurements on methyl and ethyl fluorides[2] and would indicate that the trend here was in the opposite direction from that in the other halide series. Although the fluorides might be expected to show unusual behavior, it seemed desirable to confirm these values and therefore *n*-amyl, *t*-amyl, and benzyl fluorides have been studied in benzene solution.

Evidence from measurements in the vapor state indicates that all aliphatic nitro compounds beyond nitroethane have the same moment, and it would appear from available data[3,4] that the same would be true for the cyanides although no values are available for secondary, tertiary, or long-chain primary aliphatic cyanides. Measurements of *i*-amyl, *i*-propyl and *t*-butyl cyanides have therefore been made along with normal, secondary and tertiary butylamines to determine the effect of chain branching in these series; none of the cyanides or amines has been reported previously.

Experimental

Preparation of Materials.—Benzene was purified as in previous work,[5] d^{25}_{4} 0.87345.

***n*-Amyl Fluoride.**—*n*-Amyl iodide (prepared from *n*-amyl alcohol and phosphorus triiodide and fractionated before use) was dropped slowly on a mixture of anhydrous silver fluoride and sand. The products were swept by a stream of dry nitrogen into a Dry Ice-cooled receiver. The mixture of amylene and amyl fluorides was washed with sodium bicarbonate solution, water, dried over calcium chloride and fractionated through an efficient packed column, b. p. 62.0–62.5° (751 mm.), d^{25}_{4} 0.7849, n^{25}_{D} 1.3573. Swarts[6] reports d^{20}_{4} 0.7880, n^{20}_{D} 1.3550 (by interpolation). The secondary fluoride (b. p. 55°) formed by readdition of hydrogen fluoride to pentene-1, is difficult to remove completely.

***t*-Amyl Fluoride.**—Trimethylethylene obtained from the dehydration of *t*-amyl alcohol was fractionated through a packed column and a fraction boiling at 38°, n^{25}_{D} 1.3842, d^{25}_{4} 0.6564 was obtained. This was added dropwise with stirring to an excess of anhydrous liquid hydrogen fluoride contained in a copper vessel held at −75°. After three hours the product was poured onto ice in a monel beaker and the excess acid neutralized with potassium hydroxide solution. The upper layer was separated, washed with sodium bicarbonate solution, water and dried over anhydrous sodium sulfate. The product was fractionated through a packed column, b. p. 45° (752 mm.), n^{25}_{D} 1.3462. After about 2 g. had distilled at 45° decomposition started and samples collected thereafter fumed strongly, etched the containing vials and became cloudy. The sample used for measurement kept well and showed no evidence of decomposition even after a day in benzene solution. A second preparation gave a high yield of crude fluoride but repeated attempts at fractionation all resulted in partial decomposition. The moment reported is, therefore, based on only one reliable measurement.

The method of preparation is that of Grosse and Linn[7] who, however, gave no experimental details. They report n^{25}_{D} 1.3477, MR_{D} 24.36. The addition of anhydrous hydrogen fluoride to a double bond at low temperature is the most satisfactory method for preparing pure secondary and tertiary fluorides.

Benzyl Fluoride.—Benzyl fluoride was prepared by the pyrolysis of benzyl trimethylammonium fluoride,[8] the product was fractionated through an efficient packed column and the fraction used boiled at 62° (67 mm.), n^{25}_{D} 1.4908. About 1 g. of pure material was obtained after which rapid autocatalytic decomposition destroyed the remainder of the material. The solutions used for measurement showed no evidence of decomposition.

***i*-Amyl Cyanide.**—*i*-Amyl cyanide was prepared from *i*-amyl bromide and potassium cyanide, dried over calcium chloride and fractionated, b. p. 65.2° (35 mm.), n^{25}_{D} 1.4040, d^{25}_{4} 0.80271.

***i*-Propyl Cyanide.**—*i*-Propyl cyanide was prepared by the dehydration of isobutyramide with phosphorus pentoxide. The crude product was fractionated at 202 mm. and the fraction boiling at 63.1° used, n^{25}_{D} 1.3712, d^{25}_{4} 0.76572.

***t*-Butyl Cyanide.**—Trimethylacetamide was dehydrated by heating with phosphorus pentoxide. The crude nitrile which distilled over was fractionated, b. p. 58.9°, n^{25}_{D} 1.3751, d^{25}_{4} 0.75857.

***t*-Butylamine.**—*t*-Butylamine was prepared from trimethylacetamide by the Hofmann reaction, dried over barium oxide and fractionally distilled, b. p. 44.5° (752 mm.), n^{25}_{D} 1.3769.

***n*- and *s*-Butylamines.**—Eastman Kodak Co. White Label materials were fractionally distilled from barium oxide: *n*-butylamine, b. p. 76.2° (752 mm.), d^{25}_{4} 0.7364, n^{25}_{D} 1.3992; *s*-butylamine, b. p. 62.0° (752 mm.), n^{25}_{D} 1.3900.

Acetone Cyanohydrin.—Material supplied by Dr. Tod Campbell was fractionated at 40 mm., b. p. 95°, d^{25}_{4} 0.9267, n^{25}_{D} 1.3980.

Chloroacetonitrile.—Eastman White Label material was dried and fractionated at 100 mm., b. p. 60.5–61.0°, d^{25}_{4} 1.1893, n^{25}_{D} 1.4202.

Measurements and Calculations.—The electric moments were measured in dilute benzene solution at 25°. Dielectric constants were measured with a heterodyne-beat apparatus described elsewhere,[5] and densities were measured with a modified Ostwald pycnometer.[9] Chloro-

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[1] A. Audsley and F. Goss, *J. Chem. Soc.*, 497 (1942).

[2] Smyth and McAlpine, *J. Chem. Phys.*, **2**, 499 (1934).

[3] C. P. Smyth, THIS JOURNAL, **63**, 57 (1941); Groves and Sugden, *J. Chem. Soc.*, 158 (1937).

[4] Cowley and Partington, *J. Chem. Soc.*, 604 (1935).

[5] M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946).

[6] Swarts, *Bull. Soc. Chim. Belg.*, **30**, 302 (1921).

[7] Grosse, Wackher and Linn, *J. Phys. Chem.*, **44**, 275 (1940).

[8] C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2249 (1928).

[9] G. R. Robertson, *Ind. Eng. Chem.*, **11**, 464 (1939).

acetonitrile was measured using a new low drift heterodyne-beat apparatus.

The dipole moments were calculated from the measured dielectric constants ϵ and densities d of solutions of solute mole fraction f_2 with the usual equations.[10]

The experimental data are shown in Table I and Table II lists the values of P_∞, MR_D and μ for each compound. The values of P_2 for the most reliable samples of benzyl and t-amyl fluoride were taken equal to P_∞. This increases the probable error in the moment somewhat but, since the values of P_2 for fluorides change only slowly with concentration in dilute solution, the moments are probably accurate to about 0.05 debye. Values of MR_D are from experimental values of n and d.

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND MOLAR POLARIZATIONS OF BENZENE SOLUTIONS AT 25°

f_2	ϵ	d	P_2
n-Amyl fluoride			
0.00000	(2.2725)	0.87345	$P_1 = 26.636$
.00723	2.302	.87255	94.0
.00751	2.305	.87266	97.0
.01552	2.337	.87164	94.2
.01820	2.349	.87144	95.3
.02123	2.360	.87091	93.9
t-Amyl fluoride			
0.00745	2.306	0.87260	99.9
Benzyl fluoride			
0.01886	2.354	0.87640	95.4
i-Amyl cyanide			
0.00218	2.309	0.87334	279.4
.00441	2.347	.87317	280.2
.00729	2.396	.87292	277.7
.00896	2.424	.87260	276.0
.01200	2.474	.87233	273.0
.02033	2.615	.87156	266.6
t-Butyl cyanide			
0.00454	2.355	0.87293	293.3
.00567	2.374	.87274	290.0
.00683	2.392	.87252	283.3
.00795	2.417	.87244	290.0
.01265	2.504	.87167	287.8
.02097	2.648	.87062	275.3
i-Propyl cyanide			
0.00301	2.326	0.87326	281.5
.00523	2.366	.87301	282.6
.00956	2.442	.87260	277.2
.01301	2.502	.87226	272.6
.01834	2.598	.87121	268.9
.02517	2.718	.87108	261.8
n-Butylamine			
0.00822	2.293	0.87230	65.4
.00979	2.295	.87178	63.8
.01409	2.305	.87116	64.0
.02079	2.321	.87002	64.1
.04011	2.367	.86697	64.0
.06068	2.418	.86346	64.4
s-Butylamine			
0.01144	2.293	0.87131	57.2
.01885	2.309	.87011	58.6
.03273	2.335	.86755	58.3
.04222	2.354	.86565	58.7
.005545	2.379	.86326	58.4
.06386	2.395	.86173	58.2
t-Butylamine			
0.00891	2.291	0.87183	60.7
.01336	2.297	.87085	57.5
.02444	2.318	.86840	58.3
.03718	2.341	.86557	58.3
.02005	2.309	.86930	58.1
.03304	2.336	.86647	59.4
Acetone cyanohydrin			
0.00324	2.316	0.87360	223.2
.00435	2.330	.87359	221.4
.00620	2.356	.87375	222.1
.00903	2.392	.87383	217.5
.01186	2.428	.87399	213.7
.01601	2.479	.87424	208.4
Chloroacetonitrile			
0.01271	2.434	0.86722	198.0
.01576	2.474	.87693	197.7
.01947	2.522	.87774	196.0

TABLE II

POLARIZATIONS, MOLE REFRACTIONS AND DIPOLE MOMENTS

Substance	MR_D	P_∞ (25°)	μ (Debye)
n-Amyl fluoride	25.16	94.9	1.85
t-Amyl fluoride	24.36	100.0	1.92
Benzyl fluoride	31.09	95.4	1.77
i-Amyl cyanide	29.60	284.0	3.53
i-Propyl cyanide	20.47	287.0	3.61
t-Butyl cyanide	25.09	298.0	3.65
n-Butylamine	24.06	64.0	1.40
s-Butylamine	24.34	58.0	1.28
t-Butylamine	24.44	58.5	1.29
Acetone cyanohydrin	22.16	228.0	3.17
Chloroacetonitrile	16.07	200.0	3.00

Discussion of Results

The values reported here are listed in Table III along with all available values of aliphatic fluorides, cyanides and amines; solution values of certain chlorides and bromides are included for comparison and all moments listed therefore refer to benzene solution at 25°, unless otherwise indicated. Although the effects observed in these series are small, and in some cases scarcely larger than solvent effects and experimental error, the trends observed seem to be definite and significant, especially for comparisons of compounds measured under the same conditions.

The electric moments reported here for *n*-amyl fluoride and *t*-amyl fluoride are somewhat larger than the values 1.48 and 1.77 calculated from the P_∞ values reported by Audsley and Goss[1] for these compounds in carbon tetrachloride solution. Their reported boiling point for *t*-amyl

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(10) Smyth, "Dielectric Constants and Molecular Structure," Chemical Catalog Co., Reinhold Publishing Corp., New York, N. Y., 1931, chap. I.

TABLE III

DIPOLE MOMENTS IN BENZENE SOLUTION[a]

	F	Cl	Br	CN	NH_2
Methyl	(1.60)[d]	1.65	(1.45)[d]	3.44[4]	1.23 (gas)
Ethyl	(1.70)[d]	..	1.85[b]	3.57[4]	1.31 (gas)
n-Propyl	..	1.94	1.94	3.57[4]	1.39 (gas)
i-Amyl	..	1.92	1.93	3.53	
Benzyl	1.77	1.85	1.85	3.48	
n-Amyl	1.85	..	1.95	..	1.40 (*n*-butyl)
i-Propyl	..	2.04	2.04[b]	3.61	1.28 (*s*-butyl)
Cyclopentyl	1.87[5]	2.09[5]	2.22	3.72[5]	1.29 (cyclohexyl[c])
t-Butyl	..	2.15	2.21	3.65	1.32
t-Amyl	1.95	2.14	2.25		

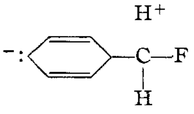
[a] Values other than those for which a reference is given or those reported in this paper, are taken from the compilation in the Appendix on Dipole Moments, *Trans. Faraday Soc.*, **30** (1934). [b] Cowley and Partington, *J. Chem. Soc.*, 977 (1938). [c] Lewis and Smyth, THIS JOURNAL, **61**, 3063 (1939). [d] The values in parentheses are estimates of the solution value obtained by subtracting 0.2*D* from the observed vapor measurement.

fluoride (38°/458 mm.) is about 5° higher than recorded by Grosse, Wackher and Linn[7] and confirmed here; their value of refractive index is likewise high. The reaction of *t*-butyl alcohol with aqueous hydrogen fluoride would probably give a mixture of isomers difficult to separate.

These data for the electric moments of the aliphatic fluorides indicate that they behave similarly to other halide series, the carbon–fluorine bond moment being about 0.2*D* less than the carbon–chlorine moment.[11] The increase from methyl to *n*-amyl fluoride is about 0.25*D*, equal within experimental error to that for the chlorides, while the increase of 0.1*D* from *n*- to *t*-amyl is somewhat less than the 0.2–0.3 differences observed in the other halide series.

The increase (0.2*D*) in going from methyl to *t*-butyl cyanide is smaller than the corresponding increases in the halide series (0.6*D*) and, indeed, may be principally a solvent effect since the increments observed in the vapor measurements on the chloride series were smaller than solution measurements had indicated.[3] It is not unlikely then that the cyanides are similar to the corresponding nitro compounds which show, in the vapor, no increases beyond nitroethane. If these increments are attributed to hyperconjugation, then this effect must either be quite small in these series , or else be but little altered by the substitution of methyl groups for hydrogen atoms.

i-Amyl cyanide has a moment nearly equal to *n*-butyl cyanide as would be expected. The moment of benzyl fluoride is slightly lower (0.1*D*) than that of *n*-amyl fluoride–benzyl halides in general being lower than expected from the size and polarizability of the phenyl group. This may result from hyperconjugation, with structures such as I contributing a small moment opposed to the original dipole. No vapor measurements are available on benzyl derivatives to confirm this behavior and show whether this tendency is truly independent of solvent, however.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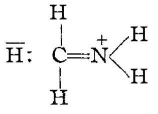
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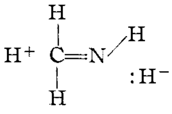
III

The moments of the secondary and tertiary butylamines are 0.1*D* less than that of *n*-butylamine; a like decrease with chain branching has been observed for the alcohols.[3] The interpretation here is complicated by the non-axial character of the —NH_2 (and —OH) moments, combined with the uncertainty in bond angles in these compounds. An increase in the C—N—H bond angle in going from methyl to *t*-butylamine would account for the small decrease in moment or the decrease might result from the nature of hyperconjugation in the amines. Thus structures such as II would be expected to be more stable than III and, since carbon has a higher electron affinity than hydrogen, structures II would be favored in the more branched amines; the effect of chain branching would then be to lower the moment. It must be borne in mind that solvent effects may also enter here.

The dipole moment of chloroacetonitrile is, within experimental error, that predicted from additivity of bond moments. A reduction in moment due to interaction between the dipoles is not observed. The moment of acetone cyanohydrin is about 0.25*D* less than calculated from bond moments, assuming free rotation. This may be an indication that the *cis* position of the hydrogen atom is somewhat favored; the difference is, however, hardly greater than the experimental error and the uncertainty in the calculation.

Combining the values of tertiary aliphatic derivatives reported here with solution values of phenyl compounds, we may calculate mesomeric moments[12] of −0.50, −0.19 and 0.24 for fluoride, amino and cyanide groups, respectively. These are close to those calculated using the primary aliphatic derivatives for comparison with the phenyl compounds.

Summary

The dipole moments of certain primary, secondary and tertiary aliphatic fluorides, cyanides and amines have been measured in benzene solution. The fluorides and cyanides show small increases in moment with increased chain branching while the amines show a decrease and these effects have been briefly discussed.

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[11] For the usual interpretation of bond moment, see, for example, Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933.

[12] L. E. Sutton, *Proc. Roy. Soc.* (London), **A133**, 168 (1931).

[13] Original manuscript, except for data on acetone cyanohydrin and chloroacetonitrile, received on January 28, 1946.