[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment, Induction and Structure in Four Fluorine-substituted Molecules[1]

BY JULIAN H. GIBBS[2] AND CHARLES P. SMYTH

In order to investigate the possible effect of chain-branching in a molecule upon bond polarity and the effects of induction upon structure, the dielectric constants of four fluorine-substituted compounds are measured over a range of temperature and pressure in the vapor state and used to calculate the molecular dipole moments. The moments found are: *n*-perfluoropentane, 0; isoperfluoropentane, 0; 1,1-difluoroethane, 2.24 × 10^{-18}; trifluoroacetic acid, 2.28 × 10^{-18}. Large atomic polarizations of 8.5 cc. are found for the two perfluorocarbons. The zero moment of *n*-perfluoropentane parallels the zero moments of the saturated hydrocarbons, and that of isoperfluoropentane shows that there is no measurable difference in polarity between a carbon–fluorine bond on a tertiary carbon and one on a primary carbon. The moment of 1,1-difluoroethane agrees closely with the value calculated for the molecule by vector addition, showing that a charge shift occurs sufficient to cancel the lowering of moment by the mutual inductive effects of the two C–F dipoles. The moment value of trifluoroacetic acid is close enough to the value calculated by vector addition of group moments to indicate that the three fluorine atoms which make the acid a strong acid have little effect upon the polarity of the carboxyl group. It is shown that the carboxyl hydrogen probably oscillates well out of the plane of the carbon and oxygen atoms.

It has been shown that the replacement of a hydrogen in a saturated hydrocarbon molecule by a methyl group should not alter the electrical symmetry in the absence of secondary effects.[3] This conclusion based upon very approximate considerations of structure is borne out by the failure to observe any moment value for a saturated hydrocarbon experimentally distinguishable from zero. It has been pointed out[4] that, in view of the rough relationship between bond energy differences and dipole moments and the apparent difference between the energy of an H–C bond on a tertiary carbon and that of an H–C bond on a primary carbon, branched-chain hydrocarbons, such as isobutane, might be expected to have small dipole moments. As the approximate magnitude, 0.2 × 10^{-18}, to be expected for these moments is indistinguishable from zero by means of the usual dielectric constant measurements on liquids and hardly distinguishable from zero by means of vapor measurements, the question of these small polarities has not yet been definitely settled. The large moment associated with the carbon–fluorine bond, as evidenced by the values, 1.81 for methyl fluoride and 1.92 for ethyl fluoride,[5] has suggested the possibility of more readily detectible differences between the moments of straight and branched-chain perfluorocarbons. With this in view, dielectric constant measurements have been carried out upon the vapors of perfluoropentane and perfluoroisopentane. Measurements have also been carried out upon 1,1-difluoroethane, in order to investigate the inductive effect between two adjacent C–F bonds, and upon trifluoroacetic acid because of the abnormally high dielectric constant values recently reported[6] for it in the liquid state.

Purification of Materials

Perfluoropentanes.—The samples given us by Professor George H. Cady of the University of Washington were distilled under a dry atmosphere directly into the apparatus for measurement. The boiling points recorded by Professor Cady for these samples were 29.3° for the normal perfluoropentane and 30.1° for the isoperfluoropentane.

1,1-Difluoroethane.—Material kindly given us by the General Chemical Division of the Allied Chemical and Dye Corporation was run into the apparatus from its cylinder through large ascarite and calcium oxide towers to remove hydrogen fluoride and water vapor. It was then maintained somewhat below its boiling point in a trap by chilling while the system was pumped out in an effort to remove more volatile impurities which might have been present.

Trifluoroacetic Acid.—Material from Halogen Chemicals, Inc. was distilled under a dry atmosphere in a four-foot column, packed with helices, peaked with a Whitmore–Lux[7] type head; b.p., 72.1°.

Experimental Method

The general experimental method and apparatus have been described elsewhere.[8] However, the two oscillators of the heterodyne beat apparatus were replaced by newly constructed circuits essentially similar to those described by Jen-Yuan Chien.[9,10] The gas cell, reference condenser, precision measuring condenser, and coarse frequency setting condenser were the capacitors used in the older oscillator. The fixed frequency oscillator was constructed as nearly like the variable frequency one as possible with the exception, of course, of the grid circuit capacitance. No crystal control was used in the fixed frequency oscillator because, without it, frequency drift in the variable frequency oscillator might be expected to be at least partially compensated by a corresponding drift in the "fixed frequency" oscillator. The oscillators were operated at frequencies close to one megacycle.

The method of calibrating measuring condensers has been described previously.[8,10] Because of the accuracy required in these investigations an extensive calibration of the scale of the precision condenser was carried out, successive calibration runs being averaged by a procedure described elsewhere.[11] The "cell constant" was determined with an accuracy of 0.5% by measurements on substances of known dipole moment. The ones chosen were ammonia, which had been previously measured both in the ordinary fashion[8] and by the method of microwave spectroscopy,[12] and chlorobenzene.[13,14]

Experimental Results

For each substance in Table I, the molar polarization *P* determined by capacitance measurements over a range of

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[2] This article is based upon a thesis submitted by Julian H. Gibbs in partial fulfillment of the requirements for the degree of Ph.D. at Princeton University.

[3] C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Company (Reinhold Publ. Corp.), New York, N. Y., 1931, p. 72.

[4] C. P. Smyth, THIS JOURNAL, **63**, 57 (1941).

[5] C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **2**, 499 (1934).

[6] J. H. Simons and K. E. Lorentzen, THIS JOURNAL, **72**, 1426 (1950).

[7] F. C. Whitmore and A. R. Lux, *ibid.*, **54**, 3451 (1932).

[8] R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 352 (1941); K. B. McAlpine and C. P. Smyth, THIS JOURNAL, **55**, 453 (1933); J. M. A. de Bruyne and C. P. Smyth, *ibid.*, **57**, 1203 (1935).

[9] Jen-Yuan Chien, *J. Chem. Ed.*, **24**, 494 (1947).

[10] C. P. Smyth, "Physical Methods of Organic Chemistry," Vol. I, Part II, (A. Weissberger, Ed.), Interscience Publishers, New York, N. Y., 1949, Chap. XXIV.

[11] J. H. Gibbs, "Dielectric Studies of the Molecular Structure of Certain Vapors," Doctoral Dissertation, Princeton University, 1950.

[12] C. H. Townes, *Phys. Rev.*, **70**, 665 (1946).

[13] K. B. McAlpine and C. P. Smyth, *J. Chem. Phys.*, **3**, 55 (1935).

[14] E. C. Hurdis and C. P. Smyth, THIS JOURNAL, **64**, 2212 (1942).

pressures is given for each of several temperatures. The polarizations are calculated from the slopes of the capacitance–pressure curves by the method previously described.[8,10] Table II gives: the molar refractions, R_D, for the D sodium line; estimated values for P_E, the electronic polarization at infinite wave length; the total induced polarization, $P_E + P_A$, obtained as the value of P extrapolated to $1/T = 0$; the atomic polarization, P_A, obtained as the difference between the values in the two preceding columns; and the values of the dipole moment, μ, calculated, for the first three substances from the slopes of the P vs. $1/T$ curves and, for trifluoroacetic acid, from the difference $P - R_D$. The values of R_D for the two fluorocarbons were calculated from refractive index and density values communicated to us by Professor George H. Cady and the values for the other two substances were calculated as the sums of the bond or group refractions,[15] a C–F value, 1.83, being obtained from the values of R_D for the two fluorocarbons. In the absence of dispersion data, rough values, probably accurate to within 0.5 cc., were estimated for P_E by comparison with the differences between R_D and P_E commonly observed.

TABLE I

MOLAR POLARIZATIONS

T, °K.	P, cc.	T, °K.	P, cc.
n-Perfluoropentane		i-Perfluoropentane	
368.6	34.5	371.6	34.7
403.8	34.2	399.6	34.2
448.4	34.3	438.9	34.3
488.1	34.7	491.6	34.2
		510.4	34.4
1,1-Difluoroethane		Trifluoroacetic acid	
356.7	100.95	365.8	94.3
402.6	90.7	409.7	88.4
458.5	81.6	493.6	79.0
509.9	74.8		

TABLE II

INDUCED POLARIZATIONS AND DIPOLE MOMENTS

	R_D	P_E(est.)	$P_E + P_A$	P_A	$\mu \times 10^{18}$
n-C_5F_{12}	26.88	26.0	34.5	8.5	0
i-C_5F_{12}	26.81	26.0	34.5	8.5	0
CH_3CHF_2	11.7	11.2	14.6	3.4	2.24
CF_3COOH	13.4	13			2.28

Discussion of Results

It had been anticipated that the n-perfluoropentane, n-C_5F_{12}, would have no moment and that its total polarization could be used as an adequate approximation for the induced polarization, $P_E + P_A$, of the isoperfluoropentane, $(CF_3)_2CFC_2F_5$. Any excess of the total polarization of the latter compound over its induced polarization would then be used to calculate the moment of the branched chain molecule. However, the polarization values in Table I for the straight-chain compound over a temperature range of 120° and the values for the branched-chain compound over a range of 139° deviate from a mean value 34.5 by no more than the experimental error in the individual values. The absence of any measurable decrease of polarization with rising temperature for either compound indicates the absence of dipole moment in both molecules. The identity of the polarization of the branched-chain molecule with that of the straight-chain molecule, which would be expected to have zero moment, is a second piece of evidence to show the absence of measurable polarity in the branched-chain molecule. A moment even as small as the 0.2×10^{-18} originally anticipated as possible for the isobutane molecule appears to be excluded for isoperfluoropentane by the data in Table I.

In the analogous hydrocarbons, n-pentane has a heat of combustion 1.9 kcal./mole higher than isopentane, which, in turn, has a heat of combustion 2.8 kcal. higher than that of neopentane.[16] Insofar as an analogy may be drawn between the hydrocarbons and the fluorocarbons, one would conclude that the difference in energy is not paralleled by a difference in H–C bond polarity. Possibly, as suggested[4] some years ago, the energy differences are due to steric effects. There is certainly nothing in the present results to indicate a difference in bond polarities between the straight and branched-chain molecules.

Since it has been concluded that the moments of the two fluoropentane molecules are indistinguishable from zero, atomic polarization must be responsible for the differences between the value of their total polarizations, 34.5, and the estimated electronic polarizations in Table II. The atomic polarization, P_A, of each compound, therefore, has the unusually high value 8.5 cc., as compared with the value 0.61 for n-pentane.[17] The large atomic polarization presumably arises from the bending of the C–F dipoles, which have much larger moments than those of the C–H dipoles. It is interesting that the atomic polarizations of these two molecules, which contain twelve C–F dipoles, are almost exactly three times the value 2.86 reported,[18] for carbon tetrafluoride, which has one-third as many C–F dipoles in its completely fluorinated molecule. In 1,1-difluoroethane, where the two fluorine atoms are not surrounded by others, the atomic polarization per C–F is larger, but the probable error in the value is too large to permit the attachment of much significance to this.

The dipole moment found for 1,1-difluoroethane may be considered in comparison with the moments of other fluoroethanes and chloroethanes previously measured in the vapor state.[19-23] The observed values are given in Table III together with those calculated by vector addition for the di- and tri-substituted ethanes with the arbitrary assumption

TABLE III

DIPOLE MOMENTS OF FLUORO- AND CHLOROETHANES ($\times 10^{18}$)

	Obsd.	Calcd.		Obsd.	Calcd.
CH_3CH_2F[19]	1.92	..	CH_3CH_2Cl[20]	2.02	..
CH_3CHF_2	2.24	2.22	CH_3CHCl_2[22]	2.07	2.33
CH_3CF_3[23]	2.35	1.92	CH_3CCl_3[21,22]	1.77	2.02

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[15] Ref. 3, p. 152.

[16] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 66.

[17] R. W. Dornte and C. P. Smyth, THIS JOURNAL, **52**, 3546 (1930).

[18] I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).

[19] C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **2**, 499 (1934).

[20] R. Sänger, O. Steiger and K. Gächter, *Helv. Phys. Acta*, **5**, 200 (1932).

[21] R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

[22] A. A. Maryott, M. E. Hobbs and P. M. Gross, THIS JOURNAL, **63**, 659 (1941).

[23] C. H. Townes, R. G. Shulman and B. P. Dailey, *Phys. Rev.*, **76**, 472 (1949).

that a moment equal to that of the ethyl halide acts in the direction of each carbon–halogen bond. The angles between these bonds presumably differ little from the tetrahedral angle 110° used in the calculation.

The lowering of the moments of halogenated methanes by induction between neighboring dipoles has been discussed in a roughly quantitative fashion[24] and it has been pointed out that the apparent lowering in the chloroethanes[4,22] and the chloronitroethanes[25] is less than in the methanes. The familiar small increase in moment from the methyl to the ethyl compound,[19] attributed to inductive effect, is taken care of by using the ethyl compound moments in calculating the moments of the ethanes. The smaller decreases in the ethane moments below the calculated values as compared to those of the methane moments gives evidence of increased shifts of electronic charge in the direction of the negative ends of the molecular dipoles, shifts which have been described in terms of hyperconjugation and resonance,[25] or changing availability of the electrons of the central atoms to the attached groups.[22] In the absence of other information, the good agreement between the observed and calculated values for 1,1-difluoroethane in Table III would lead to a conclusion that there was no inductive effect between the two carbon–fluorine dipoles. However, very approximate calculations[24] have indicated that the inductive effect of one C–F dipole should lower the moment of a second C–F dipole attached to the same carbon atom by about 0.21, while one C–Cl dipole should lower the moment of another C–Cl dipole by about 0.36×10^{-18}. Evidently, the charge shift which opposes and partially cancels the effect of the inductive reduction of moment in the chloro- and chloronitroethanes is sufficient to cancel the effect of the inductive reduction in 1,1-difluoroethane and exceed it in 1,1,1-trifluoroethane, which has a moment 0.42×10^{-18} larger than the calculated value.

Polarization values were obtained at only three temperatures for trifluoroacetic acid as difficulty was encountered in maintaining constant pressures during the measurements. However, satisfactory capacitance–pressure curves were obtained at 409.7 and 493.6°K. with five points between 100 and 400 mm. pressure lying closely on each straight line. Slight curvature in the curve obtained at 365.8°K. was regarded as evidence of a small amount of molecular association at this lower temperature. Calculation of the moment at each temperature from the difference $P - R_D$ gives values which increase from 2.20 at 365.8°K. to 2.31 at 493.6°K. The mean of the two higher temperature values, which are unaffected by association, is given in Table II. Its probable error is no more than 0.1×10^{-18}. That this value corresponds to the monomer and not the dimer is shown by the linearity of the capacitance–pressure plots at the two higher temperatures and by the dissociation constant calculations of Karle and Brockway,[26] who concluded that the dimer was approximately 95% dissociated at 390°K.

The most uncertain aspect of the structure of this molecule is the location of the proton, which could not be determined from the electron diffraction studies. The moment value of 2.28 rules out the possibility of a "chelate ring in the carboxyl group"[27] in which the two oxygen atoms are made equivalent by resonance, the proton lying between them and forming a hydrogen bridge. Such a structure would yield a COOH group moment which would lie along the axis of the C–C bond as does the CF_3 moment. If this were the case, the resultant moment of trifluoroacetic acid would have to be close to the difference between the acetic acid moment,[27] 1.73, and the moment of 1,1,1-trifluoroethane,[23] 2.35. It is highly improbable that increased ionic character in this molecule should increase the moment from the small calculated difference, 0.6, to the large observed value, 2.28. The elimination of this chelate structure is in conformity with the electron diffraction results of Karle and Brockway,[26] who concluded that the two carbon–oxygen distances in acetic acid were quite different, as originally indicated by spectroscopic measurements,[28] one distance being identical with that in ketones, the other being the same as that in alcohols. The electron diffraction results do not give any direct information concerning the nature of the carboxyl group in trifluoroacetic acid because of the high scattering power of the CF_3 group, but seem to rule out the possibility of a five-membered ring containing a hydrogen bond between oxygen and fluorine insofar as they indicate that the CF_3 group is free to rotate, or, at least, oscillate at large amplitudes.

Although it has been indicated that the bond between the hydroxyl oxygen and the carboxyl carbon is essentially single, there is a remote possibility that resonance might give it sufficient double bond character to cause the hydroxyl hydrogen to lie in the OCO plane. The use of bond moments[29] to calculate extremely approximate moment values for the acetic acid molecule gives 3.2×10^{-18} for the structure in which the hydroxyl hydrogen is *trans* to the carboxyl oxygen and 1.2×10^{-18} for the structure in which it is *cis* to the carboxyl oxygen. A distribution of the acetic acid molecules between these two easily interconvertible structures could account for the observed moment. However, in view of the indications of single C–O bond character given by spectroscopic and electron diffraction measurements, it is doubtful that these structures are sufficiently stabilized to have significance. By turning the hydroxyl group so that its hydrogen is well out of the OCO plane, an intermediate moment value equal to the observed value can be obtained. By combining vectorially the group moment 1.73 for the carboxyl group acting at the calculated angle 74° with the C–C bond[10] with the moment 2.35 of 1,1,1-trifluoroethane,[23] the value 2.50 is obtained for the trifluoroacetic moment in reason-

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(26) J. Karle and L. O. Brockway, *ibid.*, **66**, 574 (1944).

(27) C. T. Zahn, *Phys. Rev.*, **35**, 1047 (1930); *ibid.*, **37**, 1516 (1931).

(28) L. G. Bonner and R. Hofstadter, *J. Chem. Phys.*, **6**, 531 (1938); M. M. Dacies and L. B. Sutherland, *ibid.*, **6**, 755 (1938).

(29) C. P. Smyth, *J. Phys. Chem.*, **41**, 209 (1951).

ably good agreement with the somewhat approximate value 2.28 reported in Table II. It would appear from this that the presence of the three fluorines, which greatly increases the acidity of the molecule, does not greatly alter the moment of the carboxyl group. In view of the evidence which has been mentioned or discussed, it appears probable that the hydroxyl hydrogen does not lie to any great extent in the plane of the rest of the carboxyl group and that the hydroxyl group is undergoing a torsional oscillation or restricted rotation with the hydrogen, on an average, well outside of this plane.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Chemistry of Persulfate. II. The Reaction of Persulfate with Mercaptans Solubilized in Solutions of Saturated Fatty Acid Soaps[1]

BY I. M. KOLTHOFF AND I. K. MILLER[2]

Mercaptans containing 8 to 12 carbon atoms solubilized in solutions of saturated fatty acid soaps are oxidized by persulfate to disulfide. Evidence is given that the first step in the persulfate oxidation of solubilized mercaptans is a reaction of persulfate with the soap forming carboxylate free radicals which oxidize the solubilized mercaptan to mercaptyl free radicals which combine to form disulfide. In the absence of mercaptan persulfate reacts with saturated fatty acid soaps removing the carboxylate group. The disappearance of persulfate in soap solutions is first order and the reaction rate is the same in the presence as in the absence of mercaptan and is independent of the soap concentration over a wide range of concentrations. The oxidation of solubilized normal mercaptans by persulfate is zero order with regard to mercaptan concentration over a wide range of concentrations. Solubilized *n*-octyl and *n*-dodecyl mercaptans are oxidized by persulfate at the same rate.

From the viewpoint of establishing the mechanism of persulfate initiation of emulsion polymerizations, it is of interest to understand the mechanism of the reaction of persulfate with water-insoluble compounds solubilized in soap solutions, especially those compounds which are used in emulsion polymerization recipes.

The oxidation of solubilized mercaptans by persulfate was found to be a satisfactory reaction for such a study because this reaction proceeds at a readily measurable rate at 50° and the disappearance of both reactants can be easily followed. Relatively high molecular weight mercaptans (C_8 to C_{14}) were used because of the small water solubilities of these mercaptans. The results of this study also contribute to an understanding of the mechanism of the action of mercaptans as chain transfer agents in emulsion polymerizations.

Preliminary investigations on the reaction of persulfate with solubilized mercaptans were first reported by Canterino and Reynolds[3] as part of a study designed to find a simple method of characterizing mercaptans with regard to their chain transfer efficiencies in emulsion polymerizations. These workers studied the rate of persulfate oxidation of mercaptans solubilized in solutions of a commercial soap mixture composed of the sodium salts of palmitic, stearic and oleic acids. Further systematic studies in this Laboratory, showed that the reaction of persulfate with mercaptans solubilized in soaps, which are partly or entirely composed of unsaturates, is not a simple oxidation of mercaptan to disulfide but involves the addition of mercaptan to the unsaturates in the soap. The work discussed in this paper was carried out using soaps prepared from saturated fatty acids.

Experimental

Materials. *n*-Dodecyl mercaptan was a product obtained from Dr. C. S. Marvel of the University of Illinois, b.p. 114–116° (6.5 mm.), n^{20}_D 1.4589. The *t*-octyl and *t*-tetradecyl mercaptans were research grade products obtained from Sharples Corp. Research grade *n*-octyl mercaptan was obtained from the U. S. Rubber Co. The saturated fatty acids used were Eastman Kodak Co. products. Merck and Co., Inc., potassium persulfate was recrystallized twice from conductivity water and dried in a vacuum desiccator at room temperature. Sodium carbonate and bicarbonate used in the buffer system were reagent grade chemicals.

Analytical Methods.—Mercaptan was determined by amperometric titration with silver nitrate in ammoniacal ethanol solution according to the method of Kolthoff and Harris.[4] Interference of persulfate with the mercaptan determination was prevented in two different ways. (1) Soap solutions containing small amounts of persulfate (0.01 *M*) were added to 90% ethanol containing ferrous ion in about fivefold excess over the persulfate present. After stirring for 15 minutes an excess of ammonia was added and the titration was performed. (2) In the presence of large amounts of persulfate (0.1 *M*) it was necessary to separate the mercaptan from the aqueous persulfate solution prior to titration of the mercaptan. This was accomplished by extraction of the fatty acid and mercaptan from an acidified sample of the soap solution into benzene. The benzene solution was added to ethanol, excess ammonia added and the mercaptan titrated by the amperometric method. Disulfide was determined by reduction to mercaptan according to the method of Kolthoff, Laitinen, *et al.*,[5] followed by amperometric titration of the mercaptan. Persulfate was determined polarographically[6] after extraction of the fatty acid and mercaptan from the acidified soap solution with benzene. To determine the total organic acids present in a soap solution, 25 ml. of the solution was acidified and shaken with 25 ml. of benzene. A 25-ml. portion of distilled absolute ethanol was added to the benzene extract and enough water to cause turbidity. The turbidity was then removed by addition of a few drops of ethanol and the solution was boiled until the odor of benzene could no longer be detected in the vapor. After dilution with 50 ml. of purified ethanol the acidity of the solution was determined by titration with

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[2] From a Ph.D. thesis submitted by I. K. Miller to the Graduate School of the University of Minnesota, 1950.

[3] P. J. Canterino and W. B. Reynolds, private communication.

[4] I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

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[6] I. M. Kolthoff, L. S. Guss, D. R. May and A. I. Medalia, *J. Polymer Sci.*, **1**, 340 (1946).