[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Vapor Dipole Moments of Some Organic Molecules Containing the Trifluoromethyl Group[1]

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The vapor dipole moments of benzotrifluoride, *o*- and *p*-chlorobenzotrifluoride, 1,1,2-trichloro-3,3,3-trifluoropropene, 3,3,3-trifluoropropene, *o*- and *p*-chlorotoluenes have been determined. Deviation of the measured dipole moment from the vector additivity of bond moments is discussed on the basis of intramolecular interactions.

The effects of resonance and induction on the dipole moment of a molecule containing one or more polar groups are well recognized. Because of the unusual and unique properties of organic compounds containing the trifluoromethyl group, we have determined the dipole moments of a series of such compounds as gases and have attempted to interpret any deviation of the measured dipole moment from the additivity of the vector bond moments on the basis of the above mentioned intramolecular interactions.

In addition we have made similar measurements on the *o*- and *p*-chlorotoluenes in order to observe the effect on dipole moment when the simple unsubstituted methyl group takes the place of the trifluoromethyl group.

Experimental

Benzotrifluoride was purified by repeatedly treating with boiling sodium carbonate solution until no tests for chloride ion were obtained in the solution, drying over anhydrous potassium carbonate and then over phosphorus pentoxide, followed by fractional distillation. With the exception of 3,3,3-trifluoropropene, all the compounds used in this investigation were purchased from Halogen Chemicals Inc. or Eastman Kodak Co., and were purified by fractional distillation in a column of thirty theoretical plates. The middle fraction, with a boiling range of 0.2°, was taken in each case, except for *o*-chlorobenzotrifluoride, boiling range 0.8°, and for 1,1,2-trichloro-3,3,3-trifluoropropene, boiling range 0.5°. A summary of the physical properties of the compounds is given in Table I[4]; the last column in this table lists the molar refractions, R_D, calculated from bond refractivities given by Denbigh.[4a]

TABLE I

SUMMARY OF PHYSICAL PROPERTIES OF COMPOUNDS

Compound	B.p., °C. (cor.)	d^{30}_4	n^{30}_D	R_D	R_D, calcd.
Chlorobenzene	132.0	1.0930	1.5197	31.2	31.2
Benzotrifluoride	102.5	1.1739	1.4100	30.8	31.0
o-Chlorobenzotrifluoride	152.1	1.3540	1.4513	35.9	35.8
p-Chlorobenzotrifluoride	139.3	1.3268	1.4431	36.0	35.8
o-Chlorotoluene	159.6	1.0723	1.5203	35.8	35.8
p-Chlorotoluene	162.4	1.0583	1.5152	36.1	35.8
1,1,2-Trichloro-3,3,3-trifluoropropene	88.5	1.5965	1.4051	30.5	30.0

3,3,3-Trifluoropropene, $CF_3CH{=}CH_2$, was prepared[5] by treating with alkali a sample of $CF_3CH_2CH_2Cl$ dissolved in CH_2Cl_2, which was kindly given us by Professor A. L. Henne of Ohio State University and Dr. Milton Orchin of the United States Bureau of Mines. A determination of the vapor tension of the olefin between −84 and −30° gave a smooth log *p* *vs.* 1/*T* curve, the slope of which permitted a calculation of the latent heat of vaporization as 5490 ± 70 cal./mole. The normal boiling point was estimated to be −25° and the Trouton constant calculated to be 22 cal./deg. mole. From this, and from the molecular weight (96.5) calculated from vapor density measurements at 24°, we conclude that the olefin exists as a monomer.

A schematic diagram of the dielectric constant apparatus is shown in Fig. 1. The details of the construction of the several components, such as the gas capacitor and the vernier capacitor, are described elsewhere.[6] The variable-fixed oscillator may be considered to consist of two oscillators, the variable oscillator functioning when the capacitor branch consisting of C_V, C_G and the associated C_T and C_t are connected across L_R, and the fixed oscillator functioning when the capacitor branch consisting of C_F and the associated C_T and C_t are connected across L_R. These two oscillators have the same frequency when the total capacity of their respective capacitor branches are the same, since all other circuit components are identical for the two oscillators. Comparing and matching the frequencies of the variable and fixed oscillators is accomplished by comparing the fixed and variable oscillator frequencies in turn with the frequency of a third oscillator, the crystal oscillator. This is accomplished by feeding the output from the variable-fixed oscillator into the vertical deflecting plates and that of the crystal oscillator into the horizontal deflecting plates of a cathode ray oscilloscope. A stationary Lissajou figure indicates an integral ratio between the two frequencies. In the design of the variable-fixed oscillator it was intended to cancel out as much as possible the effect that variations in supply voltages to the electron tube have on the frequency and consequently on the precision of the measurements. In this circuit, so long as the variable and fixed oscillators are electrically identical, changes in tube characteristics or supply voltages affect their frequencies identically and so do not result in an error due to frequency drift.

The dielectric constant apparatus was calibrated with nitrogen[7] at four temperatures covering approximately the usable temperature range. The values of the ratio, *F*, of the change in the vernier capacitor setting, measured in inches, to the corresponding change in the pressure in the gas capacitor, measured in cm., were plotted against the reciprocal of the corresponding absolute temperatures. The best straight line was drawn through these points to give a calibration curve.

Calculation of the molar polarization, *P*, was made using the general equation

$$P = \frac{E-1}{3} \times \frac{RT}{p} \qquad (1)$$

Here *E* is the dielectric constant of the gas at the measured

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[1] Paper X in a series on dielectric studies. For paper IX, see N. C. Li and T. D. Terry, THIS JOURNAL, **70**, 344 (1948).

[2] This paper is based largely on a thesis presented by Joseph J. Conradi for partial fulfillment of the requirements for the Ph.D. degree, St. Louis University, 1951.

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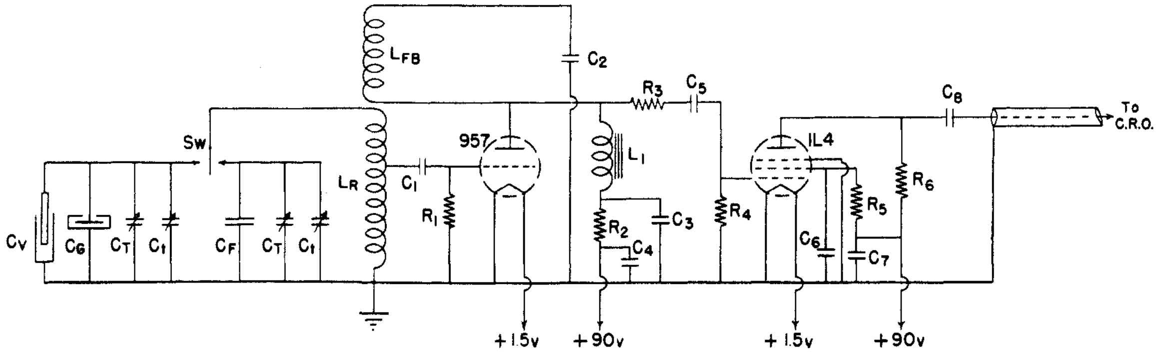
[4] We wish to thank Mr. Leon Fennoy who carried out the purification of the compounds.

[4a] K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

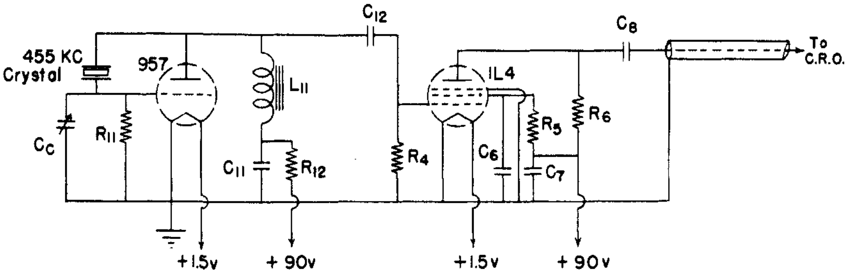
[5] We wish to thank Messrs. L. Basile and H. Uchida, working in Professor G. W. Schaeffer's Laboratory at this University for carrying out the preparation, purification and determination of the properties of this compound in a high vacuum apparatus.

[6] J. J. Conradi, "Electric Moments in the Vapor State and Resonance Effects in Some Organic Molecules Containing the Trifluoromethyl Group," Doctoral Dissertation, St. Louis University, 1951.

[7] Nitrogen of 99.6% in which the principal impurity is oxygen, was dried by passing through a five foot length of copper tubing immersed in liquid nitrogen.



SCHEMATIC CIRCUIT DIAGRAM of the VARIABLE—FIXED OSCILLATOR.



SCHEMATIC CIRCUIT DIAGRAM of the CRYSTAL OSCILLATOR.

Fig. 1.—R_1, R_2, R_3, 0.5 megohms; R_4, 4.0 megohms; R_5, R_6, 50,000 ohms; R_{11}, 2.0 megohms; R_{12}, 1.0 megohm; C_1, C_3, C_4, C_6, C_7, 0.01 μf.; C_2, 1.0 μf.; C_8, 200 μμf.; C_5, C_{12}, 100 μμf.; L_1, L_{11}, 10 mh. choke.

C_G is the gas capacitor. It consists of three concentric stainless steel cylinders and has a capacity of approximately 1700 μμf. C_v is the vernier capacitor. Essentially it is a variable coaxial capacitor having a variable capacity of approximately 2 μμf., which is divided into 13,000 units by means of a scale and vernier. C_T and C_t are small (50 and 11 μμf. maximum capacity, respectively) variable capacitors used to make fine adjustments of the frequencies of the associated oscillator circuits. L_R is the inductor in the resonant circuit of the variable-fixed oscillator. It consists of $^1/_8$ inch Invar wire heavily silver plated and wound on a Pyrex cylinder of six inches diameter. The inductor has nine spaced turns and an inductance of approximately 18 μh. $L_{F.B.}$ is the feed-back inductor. It consists of five turns of copper wire wound on the inside surface of the aforementioned Pyrex cylinder. C_F is the fixed capacitor. It consists of a bank of six variable air condensers arranged in parallel and adjusted to have nearly the same capacity as that of the gas capacitor. S_w is the switch used to connect either the gas capacitor or the fixed capacitor across the resonant inductor. C_c is a small variable capacitor used to make fine adjustments in the frequency of the crystal oscillator.

pressure p and temperature T, and R is the molar gas constant. For convenience we expressed the equation as

$$P = 4.33\ F/F_{N_2} \qquad (2)$$

where F_{N_2} is the value of F interpolated from the nitrogen calibration curve at the temperature at which the vapor dipole moment of the compound was being made.

The experimental data and derived values are given in Table II. A polarization value, P, was obtained at a temperature T by measurements over a range of pressures and from the average polarization, a corresponding value of the dipole moment in debyes was calculated by means of the equation

$$\mu = 0.0128\,((P - R_D)T)^{1/2} \qquad (3)$$

It is to be emphasized here that all of the vapor dipole moments reported in this paper were calculated by means of equation (3), and not by means of the dependence of the molar polarization on temperature. The molar refractions are the measured values given in Table I.

The measurements on chlorobenzene were run as a check on the accuracy of the determination. The average moment of this compound, 1.76, is in good agreement with the values 1.75[8a] and 1.72[8b] reported in the literature. With the exception of chlorobenzene, the vapor dipole moments listed in Table II have not been reported in the literature.

Discussion

The average of the vapor dipole moments are summarized in Table III. A comparison of the observed moment, μ_m, with that calculated by vector addition, μ_c, is also given in this table. In the vector addition, the bond moments used were: C_{ar}–Cl (vapor) = 1.76, C_{ar}–CF_3 (vapor) = 2.86, C_{ar}–CH_3 (vapor) = 0.42 *D*. The bond moment of C_{ar}–CH_3 (vapor) was calculated from the average of the molar polarization values for toluene determined by McAlpine and Smyth[9] and Baker and Groves.[10] The other bond values were from the present investigation.

The effect of resonance on the moment of benzotrifluoride which involves the trifluoromethyl group is indicated by comparing the dipole moment of benzotrifluoride, 2.86, with that of 1,1,1-trifluoroethane, 2.34,[11] in which resonance is considered not to occur.[12] The high moment of benzo-

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(8) (a) E. M. Moore and E. Hobbs, THIS JOURNAL, **71**, 412 (1949); (b) E. C. Hurdis and C. P. Smyth, *ibid.*, **64**, 2213 (1942).

(9) K. B. McAlpine and C. P. Smyth, *ibid.*, **55**, 458 (1933).

(10) J. W. Baker and L. G. Groves, *J. Chem. Soc.*, 1149 (1939).

(11) R. M. Fuoss, THIS JOURNAL, **60**, 1633 (1938), reported the moment of this compound as 2.27. Since the vapor dipole moments of this paper were calculated by means of equation 3 only, this value has been recalculated to be 2.34, using the bond refractivities given in ref. 4.

(12) When comparing the moments of alkyl and aryl compounds to evaluate the resonance effect on the latter, one should make the comparison for alkyl and aryl radicals which have the same polarizability. We are limited, however, to the alkyl compounds whose moments are available in the literature.

TABLE II

MOLAR POLARIZATIONS AND DIPOLE MOMENTS

T, °K.	Pav.	μ
	Chlorobenzene	
364.2	83.1	1.76
382.8	80.6	1.76
408.2	77.9	1.77
430.2	75.2	1.76
	Benzotrifluoride	
353.5	173.7	2.88
374.7	164.0	2.86
394.3	154.8	2.84
	o-Chlorobenzotrifluoride	
394.8	219.5	3.45
415.7	213.0	3.47
	p-Chlorobenzotrifluoride	
375.3	71.8	1.61
400.6	67.1	1.57
416.5	66.1	1.57
	p-Chlorotoluene	
401.3	110.8	2.22
435.0	103.2	2.19
	o-Chlorotoluene	
412.0	71.8	1.56
432.9	69.8	1.55
	1,1,2-Trichloro-3,3,3-trifluoropropene	
370.9	57.8	1.29
394.8	55.5	1.27
	3,3,3-Trifluoropropene[a]	
329.5	128.0	2.46
376.8	111.7	2.43

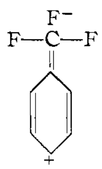
[a] For this compound the calculated value, 15.6, is used for R_D.

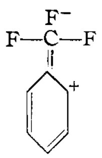
TABLE III

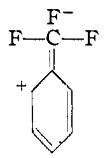
DIPOLE MOMENTS (DEBYES)

Compound	Vapor dipole moments	$\mu_m - \mu_c$
Chlorobenzene	1.76	
Benzotrifluoride	2.86	
o-Chlorobenzotrifluoride	3.46	−0.58
p-Chlorobenzotrifluoride	1.58	.48
o-Chlorotoluene	1.56	− .03
p-Chlorotoluene	2.21	.03
1,1,2-Trichloro-3,3,3-trifluoropropene	1.28	
3,3,3-Trifluoropropene	2.45	

trifluoride may be accounted for by considering the following resonance structures of the molecule

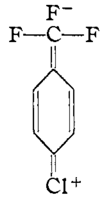






These structures would have large moments acting more or less in the same direction as the normal C–CF_3 bond, and hence small contributions from them could be responsible for the elevation of the moment of benzotrifluoride over that of 1,1,1-trifluoroethane. Essentially the same argument has been advanced by Smyth[13] to account for the elevation of the moment of nitrobenzene over that of 2-nitro-2-methylpropane, except that in the case of the nitro compound, first order conjugation rather than hyperconjugation is assumed to exist.

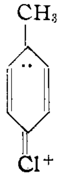
The calculated moment of *p*-chlorobenzotrifluoride is appreciably lower than the observed value. The reason is probably that in vector addition no consideration is given to contributions from highly polar structures such as



In this structure it is assumed that reinforcement of resonance occurs, so that the double bond character of both the C–Cl and the C–CF_3 bonds is increased, thereby further lowering the C–Cl bond moment and increasing the C–CF_3 bond moment. A similar effect is observed and accounted for by Hurdis and Smyth[8b] for *p*-chloronitrobenzene, although the difference between the observed and calculated moments in this case is only 0.25.

In the case of *o*-chlorobenzotrifluoride, we presume that the mutual inductive effects of the chloro and trifluoromethyl group, and to some extent the distortion of the bond angles, is responsible for the decrease, 0.58, in the measured vapor dipole moment below the calculated moment. This "ortho" effect is typical of what happens when two dipoles are in close proximity.[13] Thus, the observed vapor dipole moment of *o*-dichlorobenzene, 2.51,[8b] is 0.52 below the calculated value.

The measured moment of *p*-chlorotoluene agrees with the calculated moment within 0.03. For this compound two of the contributing polar structures may be written



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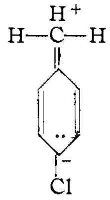

II

In (I) resonance involves the chloro and not the methyl group; while in (II) resonance involves the methyl group only. Since resonance involving both chloro and methyl group cannot occur in the molecule simultaneously, it is reasonable to suppose that no resonance reinforcement, as in the case of *p*-chlorobenzotrifluoride, can occur. In the absence of intramolecular interaction, then, the moment of *p*-chlorotoluene should equal the sum of the values for chlorobenzene and toluene, and actually the deviation from additivity is very small.

The close agreement between the measured and

(13) C. P. Smyth, in "Frontiers in Chemistry," Vol. V, Interscience Publishers, Inc., New York, N. Y., 1948, p. 23.

calculated moments, of *o*-chlorotoluene indicates that the "ortho" effect, which is usually ascribed to mutual induction, is absent or at least too small to be detected by dipole moment measurements in this compound.

The dipole moment of 3,3,3-trifluoropropene, 2.45, is intermediate in value between the vapor moment of benzotrifluoride, 2.86, and the moment, 2.36, of trifluoromethylacetylene,[14] determined from microwave spectra. It is interesting to note that the moment of the acetylenic compound containing the trifluoromethyl group is close to the vapor dipole moment, 2.34, of 1,1,1-trifluoroethane.

[14] J. N. Shoolery, R. G. Shulman, W. F. Sheehan, Jr., V. Schomaker and D. M. Yost, *J. Chem. Phys.*, **19**, 1364 (1951).

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[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

An Assignment of Frequencies for the Methyl Halomethanes and Silanes $(CH_3)XY_3$, $(CH_3)_2XY_2$ and $(CH_3)_3XY$

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Complete assignments of frequencies based on spectroscopic data found in the literature are given for thirteen methyl halomethanes and silanes of the types $(CH_3)XY_3$, $(CH_3)_2XY_2$ and $(CH_3)_3XY$. It is pointed out that in these compounds there is relatively little interaction between methyl and skeletal frequencies.

In spite of the numerous difficulties involved, it has occasionally proved possible to make assignments of frequencies for large molecules, especially when relatively high symmetry is present. This has been done, for example, by Young, Koehler and McKinney[1] for the group IV tetramethyl compounds. A modification of their assignment, based on new experimental data, has been used by Lippincott and Tobin[2] to calculate the thermodynamic functions of lead, tin and germanium tetramethyls.

In this paper, assignments of fundamental frequencies are given for those methyl chloro-, bromo- and iodomethanes and silanes for which spectroscopic data have been published, considering the molecules to have C_{2v} or C_{3v} symmetry. Following Young, Koehler and McKinney, internal vibrations of the methyl groups are assumed to lie above 1200 cm.$^{-1}$. For the methanes, the CH_3 rocking frequencies lie roughly in the region 1000–1200 cm.$^{-1}$, skeletal frequencies below 1000 cm.$^{-1}$. For the silanes, the CH_3 rocking frequencies lie roughly in the region 800–900 cm.$^{-1}$, skeletal frequencies below about 800 cm.$^{-1}$.

Within any one of these regions, it is assumed that: (1) Frequencies corresponding to similar normal modes, such as symmetric C–H stretching, fall in the same region of the spectrum, regardless of symmetry species. (2) For a given type of vibration within a given symmetry species, symmetric modes lie below asymmetric modes. (3) Angle bending frequencies lie below bond stretching frequencies. (4) Characteristic bond frequencies do not change much in going along the series $X(CH_3)_4 \rightarrow XY_4$.

The Classification of the Normal Modes for the types of molecules considered in this paper is given in Table I. The notation follows that of Herzberg.[3]

TABLE I

NORMAL MODE CLASSIFICATIONS

$(CH_3)XY_3$

	A_1	A_2	E
CH_3 asym. stretching			ν_7
CH_3 sym. stretching	ν_1		
CH_3 asym. bending			ν_8
CH_3 sym. bending	ν_2		
CH_3 rocking			ν_9
C–X stretching	ν_3		
X–Y stretching	ν_4		ν_{10}
XY_3 rocking			ν_{11}
XY_3 bending	ν_5		ν_{12}
CH_3 torsion		ν_6	
Activity	R. pol., I.	Inactive	R., I.

$(CH_3)_2XY_2$

	A_1	A_2	B_1	B_2
CH_3 asym. stretching	ν_1	ν_{10}	ν_{15}	ν_{22}
CH_3 sym. stretching	ν_2		ν_{16}	
CH_3 asym. bending	ν_3	ν_{11}	ν_{17}	ν_{23}
CH_3 sym. bending	ν_4		ν_{18}	
CH_3 rocking	ν_5	ν_{12}	ν_{19}	ν_{24}
C–X stretching	ν_6		ν_{20}	
X–Y stretching	ν_7			ν_{25}
XC_2 bending	ν_8			
XY_2 bending	ν_9			
Skeletal twisting		ν_{13}		
Skeletal rocking			ν_{21}	ν_{26}
CH_3 torsion		ν_{14}		ν_{27}
Activity	R. pol., I.	R.	R., I.	R., I.

$(CH_3)_3XY$

	A_1	A_2	E
CH_3 asym. stretching	ν_1	ν_9	ν_{13}, ν_{14}
CH_3 sym. stretching	ν_2		ν_{15}
CH_3 asym. bending	ν_3	ν_{10}	ν_{16}, ν_{17}
CH_3 sym. bending	ν_4		ν_{18}
CH_3 rocking	ν_5	ν_{11}	ν_{19}, ν_{20}
C–X stretching	ν_6		ν_{21}
X–Y stretching	ν_7		
XC_3 bending	ν_8		ν_{22}
Skeletal rocking			ν_{23}
CH_3 torsion		ν_{12}	ν_{24}
Activity	R. pol., I.	Inactive	R., I.

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[1] C. Young, J. Koehler and D. McKinney, THIS JOURNAL, **69**, 1410 (1947).

[2] E. R. Lippincott and M. C. Tobin, "The Thermodynamic Functions of Lead Tetramethyl," "The Thermodynamic Functions of Tin Tetramethyl and Germanium Tetramethyl," ONR Reports No. 1 and 2, University of Connecticut, 1951.

[3] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.