was obtained, visceral insensitivity lasting 15–25 minutes. Procaine produced an effect lasting 35–50 minutes.

### Experimental[8]

The following procedure was used to prepare the dialkylaminoethyl alkoxybenzoate hydrochlorides reported in this paper.

**Dialkylaminoethyl Alkoxybenzoate Hydrochloride.**—Into a small round-bottomed flask was placed 0.1 mole of the alkoxybenzoic acid.[3] Four equivalents of thionyl chloride was added and the mixture was refluxed gently for one hour or until no more hydrogen chloride was evolved. After the removal of the excess thionyl chloride by distillation under reduced pressure the resulting alkoxybenzoyl chloride was vacuum distilled.

The alkoxybenzoyl chloride was dissolved in 50 cc. of dry benzene, and a benzene solution containing two equivalents of the dialkylaminoethanol was slowly added with shaking. Dialkylaminoethanol hydrochloride precipitated in the benzene solution, and the reaction was completed by refluxing the solution for one hour. The solution was chilled and then filtered, and the dialkylaminoethanol hydrochloride was discarded. Following the removal of the benzene solvent under reduced pressure the dialkylaminoethyl alkoxybenzoate, which was obtained as an oil, was dissolved in 500 cc. of absolute ether, and this ethereal solution was transferred to a 1-l. three-necked flask fitted with a stirrer. In a few cases it was necessary to add a small amount of acetone to the ethereal solution in order to obtain a homogeneous solution. Dry hydrogen chloride was passed directly into the ethereal solution with stirring until the precipitation of the dialkylaminoethyl alkoxybenzoate hydrochloride was completed. The solution was filtered and the precipitate was washed with absolute ether and dried over phosphorus pentoxide. The product was recrystallized twice from a mixture of acetone and petroleum ether (60–90°). Table I lists the dialkylaminoethyl alkoxybenzoate hydrochlorides that were prepared.

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(8) All melting points are corrected.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Dipole Moments and Molecular Structures of Some Highly Fluorinated Hydrocarbons and Ethers[1,2]

BY ARMAND DI GIACOMO[3] AND CHARLES P. SMYTH

RECEIVED SEPTEMBER 25, 1954

The dielectric constants of five halogenated methanes have been measured in the vapor state over a range of temperature and pressure and used to calculate the molecular dipole moments as follows: trifluoromethane, 1.62; trifluorochloromethane, 0.46; trifluorobromomethane, 0.65; trifluoroiodomethane, 0.92; difluorodibromomethane, 0.66. The moments are much larger than would be expected on the basis of the small differences between those of the four methyl halides and are explained in terms of the differences in induced charge shift resulting from the differences between the polarizabilities of the halogens. The charge shifts may also be interpreted qualitatively in terms of differences in electronegativity between the halogens. The moments of several tetrahalogenated methanes obtained by Dr. R. C. Miller from loss measurements at microwave frequencies are shown to be similarly explicable. Measurements upon the vapors of *n*-amyl bromide and several highly fluorinated compounds have yielded the following moment values: *n*-amyl bromide, 2.21; perfluorocyclobutane, 0; pentafluoroethane, 1.54; pentafluorochloroethane, 1.54; trifluorochloroethylene, 0.40; perfluorodimethyl ether, 0.54; perfluorodiethyl ether, 0.42. The moments of these highly fluorinated molecules are close to the values calculated geometrically from the moments of the halogenated methanes and those of the unsubstituted ethers.

The dipole moments of di- and trihalogenated methanes were found to be much lower than the values calculated on the basis of carbon–halogen moments equal to those of the methyl halides and acting at tetrahedral valence angles of 110° with each other. This was, at first, attributed to widening of the valence angle by mutual repulsion of the halogens, an hypothesis abandoned when electron diffraction showed very little widening in methylene chloride and chloroform. The lowering of moment by mutual induction between dipoles near each other in the same molecule offered a logical explanation of many differences between observed and calculated moments and explained semi-quantitatively the moments of several chlorofluoromethanes.[4] Differences in the moments of chloromethanes and chloroethanes, some of which could not be explained by mutual induction, were attributed[5] to differences in electron availability on the carbon atom to which the halogens were attached. The shifts of electronic charge were also described in terms of hyperconjugation and resonance.[6] Shortening of the carbon–halogen distance in several fluoromethanes and chlorofluoromethanes has been attributed[7] to resonance involving structures with positive double-bonded halogen and negative ionic halogen. Although this *ad hoc* hypothesis of structure has been used to explain the interatomic distances found in the trifluoromethyl halides,[8] its inadequacies have been pointed out, and changes in

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(1) This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This article is based upon a portion of a thesis submitted by A. Di Giacomo in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

(3) Procter and Gamble Fellow in Chemistry.

(4) C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **1**, 190 (1933).

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

(6) E. C. Hurdis and C. P. Smyth, *ibid.*, **64**, 2829 (1942).

(7) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 235.

(8) H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 444 (1954).

bond hybridization have been proposed as a determining factor.[9] The moment of a bond A–B may be represented according to Mulliken[10,11] as the sum of four moments: primary + overlap + hybridization + core. The hybridization moment arises from the displacement of the centers of gravity of the electronic clouds in the atomic orbitals $\psi_A$ and $\psi_B$ from the nuclei of A and B. The core moment is due to the polarization of the core $A^+B^+$ by the primary moment. The shift of electronic charge calculated as induced by a nearby dipole may be regarded as superimposed upon the core moment. There are too many variables to permit of an over-all calculation of moment, but the effect of mutual induction will be examined in the molecules of a number of halogenated compounds.

## Materials and Experimental Method

Cylinders of trifluorochloromethane, difluorodibromomethane, perfluorocyclobutane, pentafluorochloroethane and trifluorochloroethylene were given us by the Organic Chemicals Department of E. I. du Pont de Nemours and Company and cylinders of trifluoromethane, trifluorobromomethane, trifluoroiodomethane, pentafluoroethane, perfluorodimethyl ether and perfluorodiethyl ether were given us by the Minnesota Mining and Manufacturing Company. The writers wish to express their gratitude for this coöperation, which has made this research possible.

Commercially obtained *n*-amyl bromide was purified by standard methods.

The gaseous samples were admitted into the measuring apparatus through towers of ascarite and calcium chloride. The dielectric constants of the gases were measured with the heterodyne beat apparatus previously described.[12–14] The polarizations $P$ calculated from the dielectric constants of the vapors were plotted against the reciprocal of the absolute temperature and used to calculate the total induced polarizations and the dipole moments from the intercepts and slopes of the lines obtained.

## Experimental Results

The values of the total polarization $P$ obtained at each absolute temperature $T$ are given in Table I for all but three of the substances. These three substances, pentafluoroethane, perfluorodimethyl ether and perfluorodiethyl ether, were measured by Mr. A. Tulinskie, to whom the writers wish to express their gratitude.

In Table II are given values for the molar refraction, $R_D$, for the sodium-D line calculated from refractive equivalents,[15] the value of 1.83 cc. being used for each C–F group; values for $P_E$, the electronic polarization at infinite wave length estimated by comparison with the differences between $R_D$ and $P_E$ commonly observed; the total induced polarization, $P_E + P_A$; the atomic polarization, $P_A$, as the difference between the two preceding columns; and the dipole moments calculated from the slope of $P$ vs. $1/T$ curves.

TABLE I

MOLAR POLARIZATIONS

| $T$, °K. | $P$, cc. | $T$, °K. | $P$, cc. | $T$, °K. | $P$, cc. |
|---|---|---|---|---|---|
| $CHF_3$ | | $CF_3Cl$ | | $CF_3Br$ | |
| 307 | 62.7 | 304 | 19.4 | 307 | 26.1 |
| 349 | 56.1 | 306 | 19.4 | 350 | 24.7 |
| 398 | 49.4 | 352 | 19.3 | 398 | 24.4 |
| 450 | 46.2 | 354 | 19.3 | 450 | 23.3 |
| 507 | 41.8 | 412 | 18.8 | 507 | 22.5 |
| | | 493 | 18.1 | | |
| | | 517 | 17.7 | | |
| $CF_3I$ | | $CF_2Br_2$ | | $n$-$C_5H_{11}Br$ | |
| 307 | 42.0 | 303.8 | 33.2 | 384.1 | 110.3 |
| 351 | 40.3 | 306.3 | 32.8 | 392.2 | 108.1 |
| 398 | 38.2 | 351.5 | 32.3 | | |
| 450 | 36.7 | 412 | 31.2 | | |
| 508 | 35.2 | 493 | 29.8 | | |
| | | 517 | 29.2 | | |
| Cyclic $C_4F_8$ | | $CF_2{=}CFCl$ | | $C_2F_5Cl$ | |
| 305 | 24.8 | 305 | 22.6 | 305 | 27.4 |
| 340 | 24.7 | 340 | 22.1 | 340 | 26.8 |
| 386 | 24.7 | 386 | 21.8 | 388 | 26.5 |
| 432 | 25.1 | 432 | 22.3 | 432 | 26.0 |
| 513 | 24.8 | 504 | 21.4 | | |
| | | 519 | 20.8 | | |

TABLE II

INDUCED POLARIZATIONS AND DIPOLE MOMENTS

| | $R_D$ | $P_E$ (est.) | $P_E + P_A$ | $P_A$ | $\mu \times 10^{18}$ |
|---|---|---|---|---|---|
| $CHF_3$ | 7.2 | 6.8 | 10.0 | 3.2 | 1.62 |
| $CF_3Cl$ | 12.0 | 11.6 | 15.8 | 4.2 | 0.46 |
| $CF_3Br$ | 15.0 | 14.5 | 17.4 | 2.9 | .65 |
| $CF_3I$ | 20.0 | 19.5 | 25.1 | 5.6 | .92 |
| $CF_2Br_2$ | 23.5 | 22.7 | 24.6 | 1.9 | .66 |
| $n$-$C_5H_{11}Br$ | 32.2 | | | | 2.21 |
| Cyclic-$C_4F_8$ | 19.2 | 18.5 | 24.8 | 6.3 | 0 |
| $C_2F_5H$ | 12.1 | 11.6 | 16.0 | 4.4 | 1.54 |
| $C_2F_5Cl$ | 16.9 | 16.3 | 22.1 | 5.8 | 0.52 |
| $CF_2{=}CFCl$ | 16.2 | 15.6 | 19.4 | 3.8 | .40 |
| $(CF_3)_2O$ | 13.9 | 13.4 | 18.2 | 4.8 | .54 |
| $(C_2F_5)_2O$ | 23.7 | 22.9 | 31.1 | 8.2 | .42 |

## Discussion of Results

The moment found for fluoroform, $1.62 \times 10^{-18}$, is in good agreement with the value 1.645 recently obtained by microwave measurements.[16] The F–C–F angle in fluoroform[16] is 109° so that, if it were merely a matter of vector addition, the moment of fluoroform should be equal to that of methyl fluoride,[16,17] 1.81. As has been previously observed,[4] however, when two or more halogens are attached to the same carbon, there is a lowering of each carbon–halogen bond moment by the inductive effect of the others. The electrostatic inductive lowering of one C–F moment by another attached to the same carbon has been estimated[4] as 0.21. This quantity may now be obtained directly from the known moment of methylene fluoride,[18] 1.96. The resultant, $\mu$, of two equal vectors, $m$, making a tetrahedral angle with each other

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[9] J. Duchesne, *Trans. Faraday Soc.*, **46**, 187 (1950).

[10] R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949); THIS JOURNAL, **72**, 4493 (1950).

[11] W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953.

[12] K. B. McAlpine and C. P. Smyth, THIS JOURNAL, **55**, 453 (1933).

[13] R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 352 (1942).

[14] J. H. Gibbs and C. P. Smyth, THIS JOURNAL, **73**, 5115 (1951).

[15] C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Company, New York, N. Y., 1931, p. 152.

[16] S. N. Ghosh, R. Trambarulo and W. Gordy, *Phys. Rev.*, **87**, 172 (1952).

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

[18] D. R. Lide, Jr., THIS JOURNAL, **74**, 3548 (1952).

is $\mu = 1.15\ m$. Substitution of the quantity 1.96–1.15 $\mu$ (C–H) for the resultant of the two C–F moments gives a value of 1.70 $\mu$ (C–H) for the C–F moment, a value 0.11 lower than that for methyl fluoride. As an approximation, we may assume that 2 C–F dipoles will produce a lowering of 0.22 in a third C–F moment, which should result in a moment of 1.59 for $CHF_3$, in good agreement with the observed value 1.62.

As a rough approximation, the moments of the $CF_3X$ molecules might be treated as equal to the differences between the $CH_3X$ moment and the $CHF_3$ moment, that is

$$\mu\,(CF_3Cl) = 1.87 - 1.62 = 0.25$$
$$\mu\,(CF_3Br) = 1.80 - 1.62 = 0.18$$
$$\mu\,(CF_3I) = 1.64 - 1.62 = 0.02$$

These values are much smaller than the observed and change in the wrong direction from chloride to bromide to iodide. The approximate calculations[4] of electrostatic induction which gave the lowering of a C–F moment by an adjacent C–F dipole as 0.21 gave the lowering of a C–Cl moment by a C–F dipole as 0.56 and the lowering of the C–F moment by the C–Cl dipole as only 0.11. Although it has just been shown that the lowering of moment in $CH_2F_2$ and $CHF_3$ is less than the calculated, it would appear that the lowering should be quite sufficient to reduce the C–Cl moment to a value 0.46 lower than the $CF_3$ moment as required to give the observed value. The increase in polarizability from chlorine to bromine to iodine would increase the inductive lowering of the C–X moment by the three C–F dipoles, thereby increasing the difference in moment between the $CF_3$ and CX, as observed, the positive end of the resultant molecular dipole being toward the chlorine, bromine or iodine. The ratio of the three fields calculated as necessary to produce the observed moments by induction in the chloride, bromide or iodide is found[19] to be very close to the ratio of the intensities of the $CF_3$ field acting at the center of the chloride, bromide and iodide, showing that the inductive explanation has, at least, a semi-quantitative validity.

The charge shift, which gives rise to most of the molecular moment, may also be qualitatively treated in terms of the relative electronegativities of the halogens. The less electronegative halogen X is, the more readily the three highly electronegative fluorines will draw electronic charge away from it to increase the molecular moment. This may also be described in terms of resonating structures.[8]

The moment of $CF_2Br_2$ might be treated as the difference between the moments of $CH_2F_2$,[20] 1.96, and $CH_2Br_2$,[21] 1.43, that is, 0.53, or because of the tetrahedral angle it might be calculated as 1.15 ($CH_3F$–$CH_3Br$) = 0.01, or 1.15 ($CF_3Br$) = 0.75, or 1.15 ($CFBr_3$) = 0.67. The observed value 0.66 is much larger than the negligible value 0.01 for the same reasons that the moment of $CF_3Br$ is much larger than 0.18, but is close to the other two calculated values.

Similar relationships are shown by the moment values obtained by Dr. Robert C. Miller in this Laboratory from the losses of pure liquids at microwave frequencies. The value 0.68 thus obtained for $CF_2Br_2$ agrees well with the 0.66 found in the present work for the vapor. As just shown, it is almost exactly 15% higher than the moment 0.58 found by Dr. Miller for $CFBr_3$. The moment values, 0.21 for $CCl_3Br$ and 0.25 for $CCl_2Br_2$ are much smaller because the difference between the polarizability of chlorine and that of bromine is smaller than that between the polarizability of fluorine and that of bromine. Again, the dibromo compound moment is close to 15% higher.

Measurements on *n*-amyl bromide could not be carried out over a wide temperature range because of possible decomposition at temperatures much above the boiling point. The dipole moment, therefore, was computed from the polarization at a single temperature and the molar refraction, which was calculated from literature values for density and refractive index without further allowance for the atomic polarization. The moment thus calculated for this compound, 2.21, is consistent with the values reported for normal alkyl halide vapors by Groves and Sugden,[22] who subtracted an additional 5% of $R_D$ to allow for atomic polarization, and obtained values which increased from 1.79 for $CH_3Br$ to 2.15 for *n*-butyl bromide. With the use of a similar correction, the moment of *n*-amyl bromide comes out to be 2.19, which is still slightly higher than the moment of *n*-butyl bromide. It would seem, therefore, that the inductive effect of the C–Br moment may still be felt at the end of a five carbon chain, although, it should be noted, the difference of 0.04 between the moments of these two bromides lies just within the sum of the probable errors in the two determinations.

It has been previously noted[23] that the atomic polarizations, 8.5, of perfluoropentane and isoperfluoropentane, which contain twelve C–F dipoles per molecule, are three times as large as that of carbon tetrafluoride, which contains four C–F dipoles. A similar rough proportionality between the atomic polarization and the number of C–F dipoles is evident in the highly fluorinated molecules in Table II. The accumulation of experimental errors in the values of $P_A$ makes them somewhat approximate, but it appears that the atomic polarization in these molecules arises largely from the bending of the polar C–F bonds. The atomic polarization of perfluorodiethyl ether, which contains ten C–F dipoles, is close to that of the perfluoropentanes. The value for perfluorocyclobutane, which contains eight C–F dipoles, is somewhat lower, the values for the three molecules containing five or six C–F dipoles are about 5, and those for the two molecules containing three C–F and a C–Cl dipole are close to 4. For the four remaining substances in Table II, three have the moderate $P_A$ values to be expected, but trifluoroiodomethane has a somewhat high value, perhaps, because of an accumulation of unusually large errors. An apparently satisfactory set of measurements which gave a dipole moment value of 0.46 for perfluoropropylene is not repro-

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(19) A. Di Giacomo, Ph.D. Thesis, Princeton University, 1953.

(20) D. R. Lide, Jr., THIS JOURNAL, **74**, 3548 (1952).

(21) A. A. Maryott, M. E. Hobbs and P. M. Gross, *ibid.*, **63**, 659 (1941).

(22) L. G. Groves and S. Sugden, *J. Chem. Soc.*, 158 (1937).

(23) J. H. Gibbs and C. P. Smyth, THIS JOURNAL, **73**, 5115 (1951).

duced because of the improbably high atomic polarization value 14.4, which they gave.

Electron diffraction measurements[24] on perfluorocyclobutane have shown the four-membered ring to be non-planar, with a carbon–carbon distance of 1.60 Å., distinctly larger than the normal carbon–carbon distance, 1.54 Å. This structure seems to be determined by the repulsion between the fluorine atoms, since the distance of closest approach between fluorine atoms attached to adjacent carbon atoms is 2.73 Å., or twice the van der Waals radius of fluorine.[24] No moment was found for this compound, showing that its structure contains no net electrical dissymmetry, which is not inconsistent with the puckered ring structure proposed by Lemaire and Livingston.

From a purely geometrical point of view, the moment of pentafluoroethane should be the same as that of trifluoromethane, 1.62, since the resultant moment of three C–F dipoles making an angle of 110° with one another should be equal to that of one C–F dipole, and the moment of pentafluorochloroethane should be the same as that of trifluorochloromethane, 0.46. In view of the possible differences in the various factors determining the molecular moments, the observed values, 1.54 and 0.52, may be regarded as surprisingly close to the geometrically calculated values. In the analogous case of pentachloroethane and chloroform, the moment of the former, 0.92, is 0.10 lower than that of the latter, a difference indistinguishable from that between pentafluoroethane and trifluoromethane.

The moment of trifluorochloroethylene, 0.20, is slightly lower than those of $CF_3Cl$ and $C_2F_5Cl$, which, to some extent, might be expected from the presumably smaller inductive lowering of the C–Cl moment by the C–F dipoles on the other carbon. However, the difference between the interactions of the chlorine and the fluorines with the double bond should also affect the moment.

The moment of dimethyl ether, 1.29, may be treated as the resultant, $2m \cos 111°$, of two moments, $m = 1.12$, acting in the directions of the C–O bonds. As an approximation, the molecule of perfluorodimethyl ether may be treated as containing two moments equal to that of trifluoromethane, 1.62, acting in opposite directions to the two moments, 1.12, and, therefore, giving a resultant moment, $2(1.62 - 1.12) \cos 111° = 0.58$, in good agreement with the observed value, 0.54. The moment of perfluorodiethyl ether is lower than that of perfluorodimethyl ether by almost the same amount, 0.13, as the difference between diethyl and dimethyl ethers.

It is evident that electrostatic inductive effects play an important part in determining the moments of the twelve molecules which have been discussed. The fact that they are sufficient to account in a semi-quantitative fashion for many of the observed moments and the differences between them does not, however, mean that the incalculable factors determining the bond moments are not altered somewhat by their environment. The net effect of these alterations on the moment would evidently be a change that is small or in the same direction as the effect of electrostatic induction.

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[24] H. P. Lemaire and R. L. Livingston, THIS JOURNAL, **74**, 5732 (1952).

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[CONTRIBUTION FROM THE DEPARTAMENTO DE FÍSICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO]

# Studies on the Coördinate Bond. III. Absorption Spectra of Mono-α,α'-dipyridyl and Mono-*o*-phenanthroline Complexes[1]

BY KÔZÔ SONE,[2] P. KRUMHOLZ AND H. STAMMREICH

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The ultraviolet absorption spectra of mono-α,α'-dipyridyl and mono-*o*-phenanthroline complexes of cadmium, calcium, cobalt, copper, lead, magnesium, manganese, nickel, silver and zinc will be reported in this paper. The long wave length band of the mono-α,α'-dipyridyl complexes of the bivalent metal ions shows a characteristic splitting, the relative height of the two peaks depending on the stability of the complexes. A similar but less distinct splitting is observed in the short wave length band of the corresponding *o*-phenanthroline complexes. Approximate stability constants are reported for some of the complexes. The bathochromic shift of the absorption bands of the bases caused by complex formation is related to the difference between the stabilities of the complexes in the ground state and in their excited states.

The absorption spectra of complexes of metal ions generally show three more or less distinct groups of absorption bands.[3]

The first two groups may be attributed to the electronic excitation of (a) the metal atom (or ion) and (b) of the coördinated molecules (or ions), the energy levels involved being more or less perturbed by the formation of the complex. The last group may be attributed to electronic transitions involving those electrons, that participate directly in the coördinate bond.

It was thought that a detailed study of the absorption bands of the coördinated molecules could supply some useful information on the nature of the perturbation of their electonic levels due to the coördinate bond and possibly on the nature of the bond itself. α,α'-Dipyridyl and *o*-phenanthroline were selected as coördinated molecules, and the in-

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[1] Paper II, THIS JOURNAL, **75**, 2163 (1953).

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[3] See for instance, K. Yamasaki, *Bull. Chem. Soc. Japan*, **12**, 390 (1937); R. Tsuchida, *ibid.*, **13**, 388, 436, 471 (1938); A. v. Kiss and D. V. Czegledy, *Z. anorg. Chem.*, **233**, 407 (1938); M. Linhardt and M. Weigel, *ibid.*, **266**, 49 (1951), and earlier papers; K. Sone, THIS JOURNAL, **75**, 5207 (1953). See also R. S. Mulliken, *ibid.*, **74**, 811 (1952).