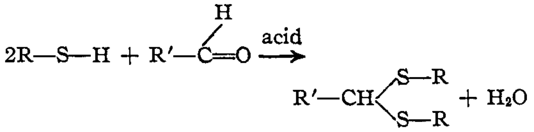
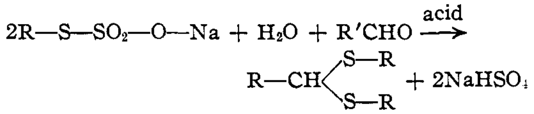
(2) 

$$2R{-}S{-}H + R'{-}\overset{H}{C}{=}O \xrightarrow{\text{acid}} R'{-}CH\begin{matrix}S{-}R\\S{-}R\end{matrix} + H_2O$$

However, there is some indication that the yields obtained by the present method are somewhat higher than those resulting from the direct action of mercaptans with aldehydes in the presence of dilute acids. Therefore it may be that some sort of a nascent state is involved or that the reaction is direct and is not in fact preceded by hydrolysis. On this account it is perhaps best, in our present state of knowledge concerning the mechanism of the process, not to assume intermediate mercaptan formation but to describe the reaction by the single equation

(3) 

$$2R{-}S{-}SO_2{-}O{-}Na + H_2O + R'CHO \xrightarrow{\text{acid}} R{-}CH\begin{matrix}S{-}R\\S{-}R\end{matrix} + 2NaHSO_4$$

Experimental

The Bunte salts were prepared in the usual way. One mol of sodium thiosulfate was dissolved in 500–600 cc. water. To this was added 1 mol of the alkyl or aralkyl halide in 500–600 cc. of alcohol. The mixture was refluxed until the solution became homogeneous or until little or no sulfur was precipitated on the addition of a mineral acid. At this point the alcohol was removed by distillation. To the resulting Bunte salt solution 0.5 mol or a little less of the aldehyde was added and, after the addition of 2 cc. of concentrated hydrochloric acid, the mixture was refluxed gently for eight to ten hours. The reaction mixture was cooled and extracted with ether, the extract dried with anhydrous magnesium sulfate and the ether removed by evaporation. The product remaining was either recrystallized from alcohol or distilled under vacuum depending on its nature. For confirmation of identity of the mercaptals some were analyzed and some were converted to the corresponding sulfones.

Formaldehyde Dibenzyl Mercaptal.—77% yield; m. p. 54–55°. *Anal.* Calcd. for $(C_7H_7S)_2CH_2$: S, 24.63. Found: S, 24.76. **Benzaldehyde Dibenzyl Mercaptal.**—72% yield; m. p. 60–61°. *Anal.* Calcd. for $(C_7H_7S)_2CH\text{-}C_2H_5$: S, 19.06. Found: S, 19.12. **Formaldehyde bis-β-Oxyethyl Mercaptal.**—The Bunte salt was prepared from ethylene chlorhydrin. The crude yield of mercaptal was 50%. *Anal.* Calcd. for $(HO\text{-}C_2H_4\text{-}S)_2CH_2$: S, 38.10. Found: S, 38.29. This compound has not been reported before. It is a pale yellow oil of b. p. 52–54° at 5 mm. **Formaldehyde Dibutyl Mercaptal.**—60% yield. The methylene bis-butyl sulfone was prepared by oxidation of the mercaptal with chromic anhydride in glacial acetic acid; m. p. in the literature is 95–96°, obsd. m. p. 95–96°. **Acetaldehyde Dibutyl Mercaptal.**—Yield 50%. Ethylidene bis-butyl sulfone was prepared by oxidation of the mercaptal; m. p. in the literature 64°, obsd. m. p. 62–64°. **Formaldehyde Diethyl Mercaptal.**—46% yield. Methylene bis-ethyl sulfone was prepared by oxidation of the mercaptal with potassium permanganate and sulfuric acid; m. p. in the literature 104°, obsd. m. p. 102–104°.

Summary

Sodium alkyl thiosulfates react with aldehydes in the presence of acid to give mercaptals, possibly by means of an acid hydrolysis to the mercaptan. This provides a new method for the preparation of these compounds as was demonstrated by the preparation of a group of representative mercaptals, including one not hitherto known.

PRINCETON, NEW JERSEY RECEIVED JULY 23, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Bond Moment Additivity and the Electric Moments of Some Halogenated Hydrocarbons

BY ARTHUR A. MARYOTT, MARCUS E. HOBBS AND PAUL M. GROSS

A problem that has received considerable attention is that of bond moment additivity and induction effects[1] between polar groups in the same molecule. A related problem is that of the magnitude and direction of the effects produced by solvents on the observed dipole moments.[2] In order to treat either of these considerations satisfactorily it is necessary to have accurate values of the net electric moment of the molecule. The determination of these values may be made with the least ambiguity through measurements in the gas phase, as there the environmental influences are completely eliminated or considerably minimized. With a view to extending the list of accurately determined values we have measured several halogen substituted compounds, namely: methylene chloride, chloroform, methyl

(1) (a) Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929); (b) Smallwood and Herzfeld, THIS JOURNAL, **52**, 1919 (1930); (c) J. W. Williams, *Chem. Rev.*, **60**, 549 (1929); (d) Smyth and McAlpine, *J. Chem. Phys.*, **1**, 190 (1933).

(2) (a) Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **28**, 284 (1936); (b) Franck, *Proc. Roy. Soc.* (London), **A152**, 171 (1935); (c) H. Mueller, *Physik. Z.*, **35**, 346 (1934).

chloroform, ethylidene chloride, 2,2-dichloropropane, *cis*-dichloroethylene, and methylene bromide. In addition we have attempted, in so far as was possible with the measured substances, to study the possible effects of resonance and induction on the observed net moment.

The apparatus and details of a measurement have been described[3] previously. One essential modification is the introduction of a trap and mercury seal "No-Lube" stopcock as shown at R and Q of Fig. 1. This arrangement furnished a means of introducing liquids of low volatility into the apparatus.

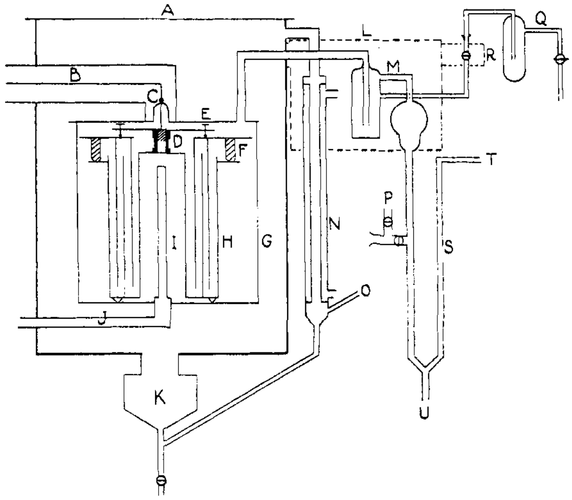


Fig. 1.—Gas System and Vapor Bath: A, vapor bath; B, lead to oscillators; C, Kovar metal to glass seal; D, three-fingered span to effect tension between E and H; E, high potential cylinders of condenser; F, quartz insulators; G, monel metal container; H, ground cylinders of condenser; I, platinum resistance thermometer; J, pipe carrying leads to Mueller bridge; K, boiler; L, trap oven; M, glass trap for vaporizing liquid during filling process; N, reflux condenser; O, outlet to pressure regulating system; P, outlet to vacuum system; Q, distilling and condensing trap; R, iron box with mercury to seal "no-lube" stopcock; S, manometer; T, outlet to McLeod gage and baromanometer; U, outlet to mercury leveling bulb.

Materials

Chloroform.—Reagent grade chloroform was washed with concentrated sulfuric acid, then dilute sodium hydroxide, and finally water. After standing overnight over solid sodium hydroxide and calcium chloride the material was fractionated in a 60-cm. Widmer still: b. p. (cor.) 61.33–61.38°, $n^{20}D$ 1.4458. Timmermans[4] gives a b. p. of 61.20°.

Methyl Chloroform.—Eastman Kodak Co. practical grade was purified in the same manner as chloroform. The fraction of b. p. 73.86–73.94° (cor.) was used, $n^{21}D$ 1.4377.

Methylene Chloride.—Eastman best grade was shaken with mercury until freshly introduced mercury was not discolored. It was then washed with sodium carbonate, water, and finally dried with calcium chloride. Two fractionations in a six-foot Dufton column gave a middle fraction of b. p. 39.93–40.12° (cor.), $n^{20}D$ 1.4249. The b. p. according to Timmermans[5] is 40.00°.

Methylene Bromide.—Eastman best grade was distilled over "Drierite" in a Widmer column. The b. p. at 746 mm. was 95.92–96.00°; Timmermans[6] found a b. p. of 96.50° at 760 mm.

***cis*-Dichloroethylene.**—Eastman material was shaken with mercury, dried over anhydrous potassium carbonate and distilled in the Dufton column over "Drierite"; b. p. 60.33–60.38° (cor.); Timmermans[7] finds 60.25°.

Ethylidene Chloride.—Eastman best grade was dried over anhydrous potassium carbonate and then distilled over "Drierite" through the Dufton still; b. p. 57.28–57.34° (cor.); Timmermans finds 57.30°.

2,2-Dichloropropane.—This compound had been purified by Gross[8] and kept in a sealed tube for about twelve years. Approximately three-fourths of the material distilled at 68.85–68.87° at 746 mm. upon refractionation in the 60-cm. Widmer still and this fraction was used.

Experimental Results

Calculation of the molar polarization was made using the general equation

$$P = \frac{\epsilon - 1}{3} \frac{RT}{p}$$

Here P is the molar polarization, ϵ the dielectric constant of the gas at the measured pressure p and temperature T. R is the molar gas constant. This equation assumes the validity of the perfect gas law. For convenience the equation was expressed as

$$P = \frac{\Delta C}{p} \frac{RT}{3C_g}$$

where ΔC is the difference between the vacuum capacity of the gas condenser, C_g, and the capacity of the condenser filled with the gas at pressure p. The capacity, C_g, was found to be somewhat dependent upon the temperature of the condenser. The relation is given by

$$C_g = 2685(1 + 2.0 \times 10^{-5} \times t°\text{C.})$$

in which the unit of capacitance is expressed in arbitrary units of approximately 0.4 mmf. The lack of ideality of the gases used was eliminated from consideration in the moment calculation by extrapolating the values of P at different pressures to zero pressure. The values of $1/T$, the pressure, and the polarization are listed in Table I.

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[3] Hobbs, Jacokes and Gross, *Rev. Sci. Instruments*, **11**, 126 (1940).

[4] Timmermans and Martin, *J. Chim. Phys.*, **23**, 747 (1926).

[5] Timmermans, *Bull. soc. chim. Belg.*, **25**, 300 (1911).

[6] Timmermans, *ibid.*, **30**, 62 (1921).

[7] Timmermans, *ibid.*, **27**, 334 (1913).

[8] P. M. Gross, *Physik. Z.*, **32**, 587 (1931).

TABLE I

$1/T \times 10^3$	p, mm.	P, cc.
Methylene Chloride		
3.317	0	69.80
	61.95	68.50
	98.1	70.21
	151.0	70.38
	205.6	70.57
2.977	0	64.92
	83.90	65.00
	123.5	64.75
	178.0	65.02
2.688	0	60.70
	32.50	60.98
	65.90	60.56
	101.9	60.70
	143.6	60.62
	183.2	60.67
2.532	0	58.11
	54.61	57.58
	99.35	58.10
	145.9	58.28
	193.2	58.29
2.342	0	55.08
	46.80	55.00
	86.59	55.12
	139.4	55.10
	187.5	54.97
Chloroform		
3.327	0	46.07
	52.22	46.13
	93.62	46.09
	141.3	46.47
	190.6	46.60
2.954	0	43.72
	34.94	43.74
	74.50	43.77
	115.8	43.90
	170.2	43.98
2.692	0	42.16
	47.92	42.23
	70.98	42.20
	122.4	42.30
	148.6	42.32
	201.8	42.42
2.532	0	41.09
	55.49	(43.02)
	119.3	41.08
	180.0	41.13
	239.7	41.10
2.342	0	39.90
	96.87	39.88
	142.8	39.92
	192.5	39.89
Methylchloroform		
3.327	0	92.15
	24.28	91.25
	74.80	92.20
	100.46	92.25
2.954	0	84.65
	24.94	84.57
	63.38	84.90
	122.8	84.75
	191.6	85.16
2.699	0	79.60
	90.85	79.80
	129.4	80.00
	173.5	80.13
2.532	0	76.70
	47.00	76.72
	93.43	76.83
	142.3	76.75
	192.1	76.90
Ethylidene Chloride		
3.316	0	107.85
	80.47	108.10
	133.3	108.20
	183.1	108.52
2.954	0	98.15
	74.52	98.20
	109.8	98.38
	144.3	98.12
2.692	0	91.75
	70.15	91.43
	102.0	92.33
	152.7	92.05
	223.1	91.80
2.532	0	87.92
	51.18	87.60
	96.63	87.95
	146.6	88.02
	195.6	87.91
2.342	0	82.20
	27.63	82.18
	68.83	82.00
	127.1	82.23
	185.3	82.17
	244.0	82.25
2,2-Dichloropropane		
3.333	49.6	
	76.4	128.0 (av.)
2.955	51.4	
	90.2	
	176.0	120.5 (av.)
2.690	57.6	
	85.8	
	116.0	
	164.4	110.8 (av.)
cis-Dichloroethylene		
3.316	0	93.13
	48.47	93.15
	95.08	93.10
	140.1	93.23
	187.7	93.43
2.989	0	85.08
	43.61	85.12
	71.45	85.23
	112.4	85.05
	161.9	85.09
2.692	0	79.57
	30.93	79.55
	104.8	79.63
	146.8	79.92
	197.8	79.67
2.476	0	74.35
	40.48	74.40
	95.14	74.30
	144.1	74.10
	194.0	74.25
2.342	0	71.42
	62.10	71.45
	123.3	71.50
	184.0	71.61
	245.8	71.64
Methylene Bromide		
2.954	0	60.35
	76.05	60.38
	106.6	60.47
	138.5	60.56
2.692	0	56.76
	66.30	56.67
	110.5	56.78
	142.2	56.75
2.688	0	57.16
	67.86	57.17
	111.5	57.11
	161.3	57.17
2.531	0	54.85
	163.7	
2.341	0	52.77
	42.33	52.86
	80.61	52.75
	120.2	52.62
	161.8	52.70

The 2,2-dichloropropane was found to decompose at temperatures as low as 100° and the points plotting P *vs.* $1/T$ fall somewhat irregularly. Its moment has therefore been calculated at each temperature by subtracting from the total polarization at each temperature the molar refraction plus 5% of the molar refraction to allow for atomic polarization. The average value of this moment is recorded in Table II.

Discussion of Results

In Table II the values of A and B in the Debye equation

$$P = A + (B/T)$$

were found by the method of least squares. The electric moment $\mu_{(\text{obsd.})}$ expressed in Debye units is calculated from the relation $\mu = 0.01281\sqrt{B}$. P_E, the electronic polarization, was calculated from the atomic refractivities for the Na D line. The electric moments calculated by the vector addition of the group moments given by Smyth[9] are compared with the values found in the present work. The group moments used are indicated below.

Tetrahedral angles have been assumed in all cases except in dichloroethylene where the Cl—C=C angle was taken as 123°.[10] For calculating the values of the methane derivatives

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[9] Smyth, *J. Phys. Chem.*, **41**, 210 (1937).

[10] Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 (1935).

TABLE II

Substance	*A*	*B*	P_E	μ(obsd.)	μ(calcd.)
Methylene chloride	19.98	15,064	16.56	1.58	2.39
Chloroform	25.28	6,251	21.43	1.02	1.86
Methylchloroform	27.00	19,400	26.05	1.79	2.03
Ethylidene chloride	21.78	25,943	21.18	2.07	2.63
2,2-Dichloropropane	...	...	25.8	2.25 (av.)	2.63
cis-Dichloroethylene	19.94	21,993	20.71	1.89	2.95
Methylene bromide	23.51	12,445	22.35	1.43	2.27

the CH_3–X group moment was used; for 2,2-dichloropropane and ethylidene chloride the C_2H_5—Cl moment was assumed; and for *cis*-dichloroethylene the C_6H_5—Cl moment was used. Obviously the calculated values are not very significant except as they indicate something of the lack of additivity of bond moments.

The observed values may well be compared with those of some previous investigations. Sanger,[11] Mahanti,[12] and Ramaswamy[13] have measured methylene chloride in the gas phase and have obtained 1.59, 1.62, and 1.53, respectively. Our moment of 1.58 is in good agreement with Sanger's value. Chloroform has been measured in the gas phase by Sanger,[11] Sircar[14] and Ramaswamy.[13] They obtain 0.95, 1.05 and 1.01, respectively. In view of our precautions with regard to the technique of measurement and purification we regard our value of 1.02 and that of Ramaswamy of 1.01 as the best values. Methylchloroform apparently has not been measured in the gas phase. Ghosh[15] reported for ethylidene chloride a moment of 2.06, which is essentially the same as our value. 2,2-Dichloropropane was found by Gross[16] to have a moment of 2.18 when measured in benzene solution. Our value of 2.25, although somewhat uncertain, probably represents a fairly accurate value for the moment of this molecule. Errera[17] found that *cis*-dichloroethylene has a moment of 1.89 in benzene solution. Sack[18] finds, in the same solvent, a value of 1.74. Our value of 1.89 can be considered in agreement with either of these values, depending on what assumption is made regarding the nature of the solvent effect. The shape of the molecule and the probable influence of the associated solvent effect might lead one to choose Sack's value as the correct solution moment. Our value for methylene bromide of 1.43 is in serious disagreement with the value of 1.91 found by Mahanti.[12] We feel that Mahanti's value is too high as our value is approximately the same as that observed in heptane solution.

Some correlations of the moments in the series CH_3Cl, CH_2Cl_2, $CHCl_3$ have been made by several earlier investigators. The observed values of 1.86, 1.58, and 1.02, respectively, are quite different from those to be expected on the basis of bond additivity. Thus one would expect a value of 1.86 for chloroform if the C–H moment has a fixed value or is zero. The observed small moment of 1.0 was at one time attributed to a distorted C–Cl valence angle but this has since been shown to be incorrect.[19] Later, efforts were made to account for the apparent discrepancy by a consideration of induction effects between the dipoles present and the neighboring polarizable atoms or groups in the molecule. Groves[20] has shown that induction may be used to explain the apparent anomaly. However, it is well known that to obtain agreement by this method one must make a very critical adjustment of the parameters, particularly with reference to the location of the centers of the dipoles and of the polarizable groups. Without doubt induction does play some role but it is probably not the important one in the present case. Eucken and Meyer have suggested that the bond moments may be smaller in $CHCl_3$ than in CH_3Cl. Stevels[21] recently suggested an explanation different from any of these. He assumed that the C–H bond moment had the negative end toward the hydrogen atom, and that the value of this moment changed with increased substitution on the carbon atom.

In an attempt to understand the trend in this series we would postulate that as additional chlorine atoms are added the availability of the electrons of the carbon atom becomes smaller and there results a net decrease of moment per bond. This essentially involves diminished bond moment values but the decrease is now to be associated with the changing availability of the carbon atom electrons. That this concept can be applied to a number of cases will be indicated below.

In particular we may consider the case of methyl chloroform. The substitution of a methyl group for an H atom may be looked on as a means of increasing the availability of the electrons and

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[11] Sanger, *Physik. Z.*, **27**, 556 (1926).

[12] Mahanti and Sen-Gupta, *J. Indian Chem. Soc.*, **5**, 673 (1928).

[13] Ramaswamy, *Proc. Indiana Acad. Sci.*, **A4**, 108 (1936).

[14] Sircar, *Indian J. Phys.*, **3**, 197 (1938).

[15] Ghosh, Mahanti and Mukherjee, *Z. Physik*, **58**, 711 (1929).

[16] P. M. Gross, *Physik. Z.*, **32**, 587 (1931).

[17] Errera, *ibid.*, **27**, 764 (1926).

[18] Sack and Müller, *ibid.*, **31**, 815 (1930).

[19] Sutton and Brockway, THIS JOURNAL, **57**, 473 (1935).

[20] Groves, *J. Chem. Soc.*, 1195 (1938).

[21] Stevels, *Rec. trav. chim.*, **57**, 108 (1938).

so results in an increase in the net observed moment. On the basis we are proposing the detailed reasons for the increase in moment are: first, the transfer of charge that takes place from the methyl carbon to the other carbon atom, and second, the transfer of some of this new charge from the chloroform carbon to the chlorine atoms. The cases of methylene chloride, ethylidene chloride, and 2,2-dichloropropane are further illustrations of the same general principle. The value of 1.58 *D* for methylene chloride shows that the availability of electrons is small since the moment per C–Cl bond is approximately 1.36 *D* (we assume the C–H moment is zero). The addition of the methyl group would increase the availability of electrons to the $-CHCl_2$ group and would thus lead to the higher observed moment for CH_3CHCl_2 of 2.07 *D*. The substitution of another $-CH_3$ for the hydrogen of the $CHCl_2$ group further increases the electrons available to the CCl_2 group but here a saturating effect is indicated since the increment in going from CH_3CHCl_2 to $(CH_3)_2CCl_2$ is smaller than that observed in going from CH_2Cl_2 to CH_3CHCl_2. If the fixed value of 1.58 *D* is assigned to the CCl_2 group and the C–H moment is taken as zero, the moment per C–C bond decreases slightly in going from CH_3CHCl_2 to $(CH_3)_2CCl_2$. In this general connection it may be noted that the increment in going from $CHCl_3$ to CH_3CCl_3 is approximately 0.8 *D* whereas the increment in going from CH_2Cl_2 to CH_3CHCl_2 is approximately 0.5 *D* and from CH_3Cl to CH_3CH_2Cl the increment is only 0.2 *D*. On the basis of any simple induction picture this sequence of increments must be regarded as very anomalous if not inexplicable. A further difficulty of the same sort is apparent when we consider the increment[22] in going from CH_3Cl to $(CH_3)_3CCl$. This is approximately 0.3 *D*. When this is compared to the increment in going from $CHCl_3$ to CH_3CCl_3 a simple dipole induction picture is practically eliminated as the explanation. On any simple induction basis the increments in these last two cases should be approximately the same.

The value for *cis*-dichloroethylene is particularly low, indicating a C–Cl bond moment contribution of approximately 1.09 *D* if the C–H moment is assumed to be zero. The moment of vinyl chloride found by Sutton[23] is 1.44 *D* and is considerably lower than that of the saturated aliphatic chlorides. If this moment is assumed for the C–Cl bonds in *cis*-dichloroethylene, the calculated moment is 2.42 *D*, a value which is still about 0.5 *D* higher than the observed. In this connection, it is interesting to note that the observed moment in *o*-dichlorobenzene is approximately 0.6 *D* lower than that calculated by simple vector addition of the bond moments. Structurally both molecules are quite similar in so far as the chlorine atoms are concerned (both contain the Cl—C=C—Cl group) and it is probable that the source of this discrepancy is the same in both cases. The simplest explanation of this lowering is that of resonance in which the C–Cl bonds assume some double bond character and a consequent ionic nature with the chlorine positive. Ketelaar[24] has been able to make some correlation between the net observed moments and the moments of structures in which resonance can occur.

Finally, it may be noted that as a logical consequence of this concept any trihalogen substituted carbon atom should exhibit a lower moment per bond relative to that observed for the monoderivative. An apparent exception is the case of fluoroform which was measured by Ramaswamy.[25] He found a value of 1.59 *D*. However, since this value depends only on one determination, we are proceeding with a remeasurement of the value for this compound in this Laboratory.

Summary

The electric moments of methylene chloride, chloroform, methylchloroform, ethylidene chloride, 2,2-dichloropropane, *cis*-dichloroethylene, and methylene bromide have been measured in the gas state and the following values obtained: CH_2Cl_2, 1.58; $CHCl_3$, 1.02; CH_3CCl_3, 1.79; CH_3CHCl_2, 2.07; $CH_3CCl_2CH_3$, 2.25; *cis*-CHClCHCl, 1.89; and CH_2Br_2, 1.43.

The trend in the moment per bond for a series in which a central atom has a repeated substitution taking place on it has been associated with the changing availability of the electrons of the central atoms to the attached groups.

The role of induction and resonance is apparently rather small except in the case of *cis*-dichloroethylene. In this case resonance is probably the controlling factor.

DURHAM, N. C. RECEIVED NOVEMBER 23, 1940

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[22] L. E. Sutton, *Proc. Roy. Soc.* (London), **A133**, 668 (1931).

[23] Hugill, Coop and Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1940).

[24] Ketelaar, *Rec. trav. chim.*, **58**, 311 (1939).

[25] Ramaswamy, *Proc. Indian Acad. Soc.*, **A2**, 364 (1935).