Effect of Substitution on Dipole Moments of Molecules

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When hydrogen in a molecule RH is replaced by a substituent X, the polarities of the RH and RX bonds will generally differ. Therefore R in RX will be either more positive or more negative than R in RH. This polarity effect is called the inductive effect. Substituents which induce a negative charge on an adjacent atom when they replace hydrogen, are called anionoid inductive (or $-$I) substituents, and those which induce a positive charge, cationoid inductive (or $+$I) substituents. Alkyls belong to the former group, and amino, hydroxyl and halogens to the latter group. Thus, when substituents including hydrogen are arranged in the order of $+$I effect we obtain a series; halogens> hydroxyl> amino> hydrogen> alkyls. Although the inductive effect was postulated by organic chemists in order to understand various chemical properties of organic compounds (e.g. acid strength), still it should be supported by the experimental data of dipole moments. In fact, measurements of dipole moments have confirmed in many cases the existence and the sign of the electron displacement which organic chemists had postulated. For example, the dipole moments of a series of hydrogen halides and the dipole moments of a series of alkyl halides have the same tendency of variation of dipole moments from chloride to iodide; hydrogen chloride > hydrogen bromide > hydrogen iodide and methyl chloride> methyl bromide> methyl iodide. The similar tendency is observed between the two series, methyl chloride> methyl alcohol> methylamine and ethyl chloride> ethyl alcohol> ethylamine.

However, when we examine the data of dipole moments more carefully, we will find out several series of compounds which make us doubt the existence of the definite inductive effect. For example, in a series of water, methyl alcohol and dimethyl ether, the dipole moment should increase in the order water, methyl alcohol and dimethyl ether, as methyl is a $-$I substituent. The actual order is, however, quite reverse. The purpose of this paper is to find out such anomalous series of compounds which apparently seem to contradict the inductive effect and to establish a general rule which holds good in every case.

Discussion

Data of dipole moments which form the basis of discussion in the present paper are listed in Table I. First, we will consider the series of alkyl halides whose observed dipole moments suggest the existence of the definite inductive effect. From Table I it is easily seen that except in the case of fluorides, the dipole moment increases in the order hydrogen halide, methyl halide, ethyl halide, etc. and reaches fairly rapidly a definite value in all series of chlorides, bromides and iodides. This tendency can be easily explained when we consider the inductive effect. If hydrogen in methyl is replaced by another methyl, the second methyl induces a negative charge on the carbon of the original methyl and lowers its electron affinity and hence increases its −I activity. Therefore ethyl should be a more active −I group than methyl. Similarly *n*-propyl should be a more active −I group than ethyl, and *n*-butyl should be a more active −I group than *n*-propyl and so on. This second order relayed inductive effect dies away, however, down the chain. Therefore the polarity of the RX bond will be expected to increase from methyl halide to ethyl halide, from ethyl halide to propyl halide, etc. and to reach a certain definite limit. Since the polarity of alkyl itself can be neglected, the bond polarity of the RX bond corresponds directly to the observed dipole moment. Thus the data of dipole moments can be understood simply by the concept of the inductive effect.

TABLE I

DIPOLE MOMENTS* (in Debye unit)

Alcohols	
H_2O	1.85[1]
CH_3OH	1.69[2]
CH_3CH_2OH	1.67[2]
$CH_3CH_2CH_2OH$	1.657[3]
$CH_3CH_2CH_2CH_2OH$	1.63[2]

Ethers	
CH_3OCH_3	1.29[4]
$CH_3CH_2OCH_2CH_3$	1.17[4]
$CH_3CH_2CH_2OCH_2CH_2CH_3$	1.18[4]

Sulfur Compounds	
H_2S	1.1[5]
CH_3CH_2SH	1.39[5]
CH_3SCH_3	1.40[5]
$CH_3CH_2SCH_2CH_3$	1.58[5]

Fluorides	
HF	1.91[6]
CH_3F	1.808[7]
CH_3CH_2F	1.92[7]

Chlorides	
HCl	1.034[8]
CH_3Cl	1.83[9]
CH_3CH_2Cl	1.98[10]
$CH_3CH_2CH_2Cl$	2.04[9]
$CH_3CH_2CH_2CH_2Cl$	2.11[9]

Bromides	
HBr	0.79[9]
CH_3Br	1.79[11]
CH_3CH_2Br	2.01[11]
$CH_3CH_2CH_2Br$	2.15[11]
$CH_3CH_2CH_2CH_2Br$	2.15[11]

Iodides	
HI	0.38[8]
CH_3I	1.64[11]
CH_3CH_2I	1.87[11]
$CH_3CH_2CH_2I$	2.01[11]
$CH_3CH_2CH_2CH_2I$	2.08[11]

Amines	
NH_3	1.466[12]
CH_3NH_2	1.32[4]
$(CH_3)_2NH$	1.02[13]
$(CH_3)_3N$	0.65[4]
$CH_3CH_2NH_2$	0.99[13]
$(CH_3CH_2)_2NH$	0.90[13]
$(CH_3CH_2)_3N$	0.82[13]

Phosphorus Compounds	
PH_3	0.55[14]
$CH_3CH_2PH_2$	1.17[14]
$(CH_3CH_2)_2PH$	1.4[14]
$(CH_3CH_2)_3P$	1.45[14]

* Except for sulfur and phosphorus compounds, all the data were obtained for the vapor state.

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1) L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1935**, 971.

2) M. Kubo, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **27**, 65 (1935).

3) J. B. Miles, Jr., *Phys. Rev.*, **34**, 964 (1929).

4) L.G. Groves and S. Sugden, *J. Chem. Soc.*, **1937**, 1779.

5) Clark, "The Fine Structure of Matter", Vol. II, Part II, "Molecular Polarisation", John Wiley & Sons, Inc., New York, (1938), p. 405.

6) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 171 (1946).

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

8) C. T. Zahn, *Phys. Rev.*, **24**, 400 (1924).

9) P. C. Mahanti, *Phil. Mag.*, (7) **20**, 274 (1935).

10) K. Higasi, "Bunshi-kozoron no Kiso", "Table of Dipole Moments", Kawade-shobo, Tokyo, (1952), p. 172.

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

12) J. M. A. de Bruyne and C. P. Smyth, *J. Am. Chem. Soc.*, **57**, 1203 (1935).

13) P. N. Ghosh and T. P. Chatterjee, *Phys. Rev.*, **37**, 427 (1931).

14) J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds", Chap. 3, Reinhold Publishing Corporation, New York, (1956), p.129.

As the order of the inductive activities of substituents must be constant in every series of compounds, a similar situation should be expected also in the case of a series of alcohols. That is, it is expected that the dipole moment increases in the order water, methyl alcohol, ethyl alcohol, etc. But this is not the case. As is seen in Table I, the dipole moment decreases in the order water, methyl alcohol, ethyl alcohol, etc. A similar anomaly is also seen in a series of amines. The dipole moment decreases in the order ammonia, methylamine, ethylamine, etc. These two cases are related with variation of dipole moments which is caused by the second-order inductive effect. If such an anomaly is not caused by chance but comes from the definite origin, it can be expected to be seen more clearly in cases where the first-order inductive effect is related, because the first-order effect is stronger than the second-order one. Indeed this expectation is realized. As is seen in Fig. 1 the dipole moment decreases stepwise when hydrogen atoms of water and ammonia are replaced successively by alkyl groups.

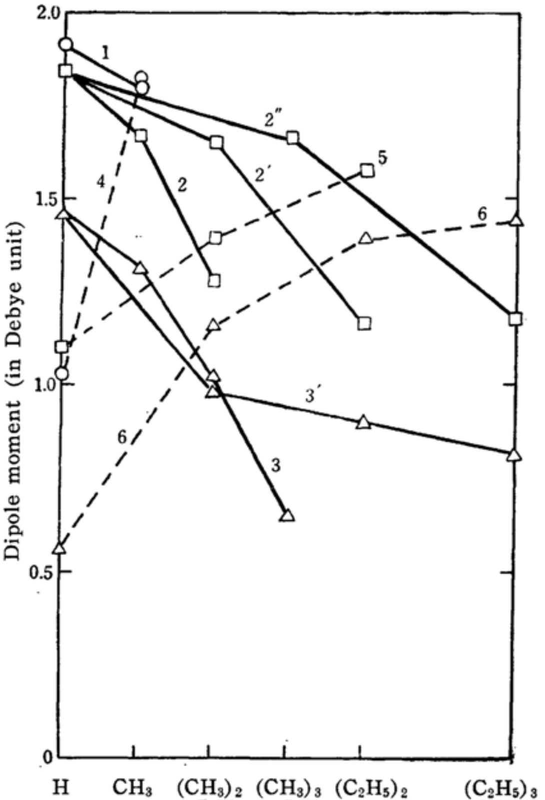

Fig. 1. Variation of dipole moments of various hydrides with successive alkyl substitution.

1 -○—○- HF and CH_3F
2 -□—□- H_2O, CH_3OH and $(CH_3)_2O$
2′ -□—□- H_2O, C_2H_5OH and $(C_2H_5)_2O$
2″ -□—□- H_2O, C_3H_7OH and $(C_3H_7)_2O$
3 -△—△- NH_3, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$
3′ -△—△- NH_3, $C_2H_5NH_2$, $(C_2H_5)_2NH$ and $(C_2H_5)_3N$
4 -○—○- HCl and CH_3Cl
5 -□—□- H_2S, C_2H_5SH and $(C_2H_5)_2S$
6 -△—△- PH_3, $C_2H_5PH_2$, $(C_2H_5)_2PH$ and $(C_2H_5)_3P$

In Fig. 1 the variations of dipole moments of a series of hydrogen sulfide, ethyl mercaptan, diethyl sulfide and of a series of phosphine, ethyl phosphine, diethyl phosphine, triethyl phosphine are also plotted. Both series indicate the existence of the normal inductive effect. In Fig. 1 the dipole moments of hydrogen fluoride, methyl fluoride and hydrogen chloride, methyl chloride are also plotted. The variation of the dipole moment from hydrogen chloride to methyl chloride is normal, while the variation of the dipole moment from hydrogen fluoride to methyl fluoride is abnormal. Here it must be noticed that such an anomaly appears only in hydrogen fluoride, water, ammonia and their alkyl derivatives. That is, the anomaly appears only in the hydrides and their alkyl derivatives of elements in the second period in the periodic table. Here it must be stated that such an anomaly was not discovered suddenly by the present author, but that its discovery was due to the works of Sidgwick[15] and of Parry[16]. Sidgwick suggested a very interesting empirical rule about the coordinating ability of various donor groups. In the series of alkyl derivatives of water and ammonia, the affinity of a donor group toward a metal ion decreases rapidly in the order water, methyl alcohol, dimethyl ether and ammonia, methylamine, dimethylamine and trimethylamine, while in a series of alkyl derivatives of hydrogen sulfide the affinity toward a metal ion increases with increasing alkyl substitution. As in his article no further discussion was given about the origin of this empirical rule, it hardly attracted the attention of other chemists at all. Recently, however, the same problem was taken up again by Parry and Keller, who noticed

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[15] N. V. Sidgwick, *J. Chem. Soc.*. **1941**, 433.

[16] J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds", Chap. 3, R. W. Parry and R. N. Keller, "The Electronic Theory of Coordination Compounds", Reinhold Publishing Corporation, New York, (1956), p. 129.

a parallel relation between the coordinating ability of a donor group and its dipole moment and showed that Sidgwick's rule could be easily understood when the increasing or decreasing order of dipole moment of donor groups was taken into consideration. At the same time they showed that alkyl substitution caused a quite reverse effect on the magnitude of dipole moment between a series of hydrides of oxygen and nitrogen and a series of hydrides of sulfur and phosphorus, and they pointed out that the coordinating ability of phosphine derivatives increases in the order phosphine, ethyl phosphine, diethyl phosphine and triethyl phosphine,

Now let us turn our attention to the origin of the anomaly. The anomaly can not be explained by the variation of the valence angles of nitrogen and oxygen. For, the valence angle of nitrogen is nearly equal to 110° in ammonia[17)], dimethylamine[19)] and trimethylamine[20)], and hence the valence angle in monomethylamine is presumed also to be nearly equal to 110°. Similarly, the valence angle of oxygen is nearly equal to 110° in water[17)] and in dimethyl ether[21)], and hence the valence angle of oxygen in alcohol is also supposed to be nearly equal to 110°. Besides, the anomaly appears also in the case of fluorides, where no valence angle can be considered. Accodingly we must consider another kind of origin. As the inductive effect is a very useful concept in understanding various chemical properties of organic compounds, the complete abandonment of this concept may only cause confusion. Far from abandonment, we must rather conclude that this anomaly has a close relation to the inductive effect, because the order of the magnitudes of dipole moments in a series is not irregular but strictly reverse to that which is expected from the consideration of the inductive effect. Therefore we take the view that the inductive effect exists in every kind of molecule. Consequently there should be the bond polarity induced by the inductive effect even in alcohols and amines, and this bond polarity should increase with successive alkyl substitution. Therefore, besides the bond polarity, we should assume another kind of component of the dipole moment which decreases reversely to the bond polarity with successive alkyl substitution. Frank[22)] and Higasi[23)] independently noticed this and attributed the variation of the dipole moment in a homologous series to the induction of alkyl groups by the primary dipole. They successfully gave the following interpretation to the systematic increase or decrease of the dipole moment in a homologous series with increasing alkyl substitution: Put the angle between the direction of the primary dipole and the line joining the center of the polarisable alkyl group and the center of the primary dipole θ. When the angle θ is below 60°, the secondary dipole is induced in the same sense as that of the primary one, and as a result the whole dipole moment increases with increasing alkyl substitution. On the contrary, when the angle θ exceeds 60°, the induced dipole has an opposite sense to the primary dipole, and hence the whole dipole moment decrease with increasing alkyl substitution. The series of alkyl chlorides, bromides and iodides belong to the former case, and the series of alcohols and amines to the latter case. This interpretation seems to be obviously reasonable. However, when we examine the data carefully, we meet several difficulties which can be by no means overcome by the theory of such a simple induction. In the first place, let us compare the data for three homologous series of alkyl chlorides, bromides and iodides. If the variation of the dipole moment in a homologous series were mainly due to the simple induction in the growing chain by the primary dipole between the carbon and halogen atoms, these three series should all show the same effect. That is, as the dipole moment of methyl halides rises in the order iodide, bromide and chloride, the dipole moment of ethyl, propyl and butyl halides should rise in the same order. The actual order is, however, iodide, chloride and bromide in these cases. In addition, as is seen in Table I, while methyl substitution in hydrogen chloride, bromide and iodide causes a marked increase in the dipole moment, the same substitution in hydrogen fluoride causes reversely the decrease in the dipole moment. The theory of induction can not give any reasonable suggestion to the

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17) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. van Nostrand Co. Inc., New York (1945), p. 439.

18) ibid., p. 489.

19) S. H. Bauer, *J. Am. Chem. Soc.*, **60**, 524 (1938).

20) L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.*, **58**, 2036 (1936).

21) H. A. Stuart, *Z. Physik.*, **59**, 13 (1929).

22) H. Frank, *Proc. Roy. Soc.*, **A152**, 171 (1935).

23) K. Higasi, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **28**, 284 (1936).

interpretation of this fact. Further, let us compare the two cases of methylamine and ethylamine series. As the secondary dipole moment induced in the ethyl group should be larger than that induced in the methyl group in every case, and as such a secondary dipole should have an opposite sense to the primary dipole in an amine molecule, all methylamines should have a larger dipole moment than the corresponding ethylamines. This expectation is fulfilled in the cases of primary and secondary amines; the dipole moments of monomethylamine and dimethylamine are both larger than those of the corresponding monoethylamine and diethylamine. However, the dipole moment of trimethyl amine is smaller than that of triethylamine. This fact can not be explained by the theory of induction.

Therefore, in order to overcome these difficulties, we must seek for a component of the dipole moment quite different from the above-mentioned induced dipole moment. Such a component should be rather predominant in an anomalous series of compounds and decrease reversely to the bond polarity with the increasing $-$I substitution. The atom dipole moment may be regarded as such a component. According to Coulson's calculation(24), the main part of the dipole moments of water and ammonia comes from "the atom dipole moment" produced by localization of electronic clouds which is caused by *s-p* hybridization of non-bonding electrons of oxygen and nitrogen, and the bond polarity contributes a little to the whole dipole moment. Thus we may assume the whole dipole moment μ_m consists of the bond polarity μ_b and the atom dipole moment μ_a;

$$\mu_m = \mu_a + \mu_b$$

Such an *s-p* hybridization of non-bonding electrons is considered to take place to a considerable extent especially in the hydrides of nitrogen, oxygen and fluorine and their derivatives. This may be presumed from the fact that the valence angle of nitrogen and oxygen is nearly equal to 110°. On the contrary, in compounds of elements below the third period in the periodic table such an *s-p* hybridization hardly ever takes place. This is presumed from the fact that the valence angles of sulfur(18) and phosphorus(25) are both near to 90°.

Now let us apply the above interpretation to methylamine and ethylamine series. Since the $-$I effect of ethyl is greater than that of methyl, the bond polarity of monoethylamine is greater than that of monomethylamine. The actual moment is, however, smaller in ethylamine than in methylamine. Further, compare the case of monoethylamine with that of dimethylamine. As the bond polarity of a secondary amine is much greater than that of a primary amine, we must assume that the atom dipole moment of primary amine is much greater than that of secondary amine, in order to explain the nearly equal dipole moments of monoethylamine and dimethylamine.

Thus we have obtained the following conclusion. *The more $-$I active a substituent is, the more the degree of s-p hybridization decreases, and hence the more the contribution of the atom dipole moment to the whole dipole moment decreases.* In addition, it must be noted that such a decrease of hybridization may have its own limit. As already stated, the dipole moment of monoethylamine is much smaller than that of monomethylamine. This suggests that the decrease of the degree of hybridization takes place to a much greater extent in the case of methyl substitution. But the introduction of the second and third ethyl groups no longer causes a great decrease of the whole dipole moment, and in this respect an ethylamine series forms a contrast to a methylamine series. This change of dipole moments in an ethylamine series may be explained as follows. In an ethylamine series, as a result of a considerably great decrease of the degree of hybridization by the introduction of the first ethyl group, the introduction of the further ethyl groups brings about the increase of the bond polarity rather than the decrease of the degree of hybridization. Consequently no marked stepwise decrease of the dipole moment which appears in a methylamine series, is observed. Similarly in the case of fluorides, the decrease of the degree of hybridization approaches to its limit at the change from hydrogen fluoride to methyl fluoride, and the further $-$I substitution brings about the increase of the bond polarity rather than the decrease of the atom dipole moment, so that the dipole moment of ethyl fluoride rises again from that of methyl fluoride. This interpretation is illustrated in Fig. 2.

Thus we have established the rule that

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24) C. A. Coulson, *Proc. Roy. Soc.*, A **207**, 63 (1951).

25) D. P. Stevenson, *J. Chem. Phys.*, **8**, 285 (1940).

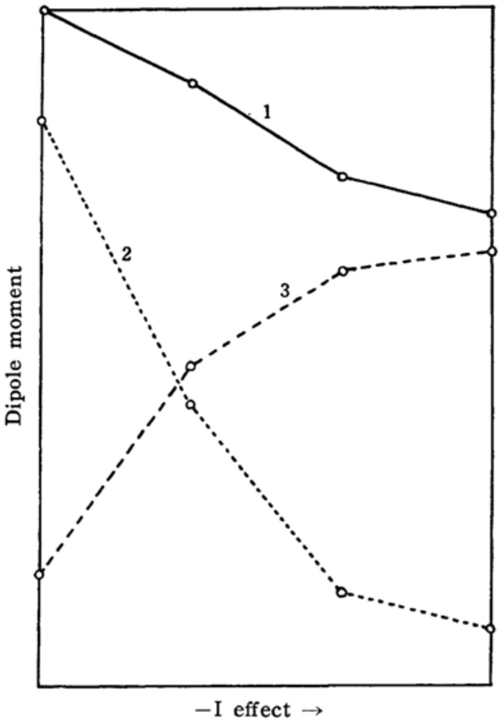

Fig. 2. Illustration of variation of the components of the dipole moment with successive −I substitution.
1 —— whole dipole moment
2 ······ atom dipole moment
3 - - - bond dipole moment

the introduction of the −I substituent prevents *s-p* hybridization of non-bonding electrons. If this rule is true, it should hold well not only for alkyl substitution, but also for any kind of substitution. Consequently, the introduction of the +I substituent should promote the *s-p* hybridization and hence increase the atom dipole moment. Therefore we can expect a large atom-dipole moment in hydrazine and hydroxylamine. But the problem is complicated in these cases. Because, these molecules consist of two parts which contribute equally or nearly equally to the whole dipole moment. These two parts make the restricted oscillation[26] near the trans positions, so that there occurs the compensation of the dipole moments of these two parts. This compensation is complete when the two parts are in the trans positions and becomes partial as they go away from the trans positions. Therefore unless the potential energy of oscillation is determined, we can not estimate the dipole moment of each part from the observed dipole moment. Therefore at present we can not prove directly the validity of the present view. With respect to the strong interaction between these molecules and metal ions, we have following evidences. Previously amine complexes of nickel(II), platinum(II) and cobalt(III) having various amines as ligands, were studied spectrochemically by the present author[27]. The result obtained shows that the affinity of amines toward these metal ions increases in the following order; ethylamine, methylamine, ethanolamine, ammonia and hydroxylamine. This series is the same as the order of the inductive effect of substituents, and the position of hydroxylamine in this series means the strong affinity toward metal ions, which indicates the large atom dipole moment of nitrogen in hydroxylamine. Further, according to Schwarzenbach's measurement[28] the consecutive formation constants of hexahydrazine nickel(II) complex are much larger than the corresponding consecutive formation constants of hexammine nickel(II) complex. This fact suggests that the atom dipole moment of nitrogen is much greater in hydrazine than in ammonia.

In addition, we can give a quite new interpretation to the unusal stability of ethylenediamine complexes. They have a great stability which can by no means be explained by the fact that they have a small probability with which a chelating agent leaves simultaneously two coordination positions. Further it must be noted that the characteristic absorption bands of ethylenediamine complexes of nickel(II), copper(II), cobalt(III), platinum(II) etc. lie in the wavelength shorter than those of the corresponding ammonia- and methylamine complexes. According to the crystal field theory[29], such characteristic absorption bands of transition metal complexes are due to the energy transitions between the split *d*-levels. As the energy intervals between the split d-levels increase with the increase of the electrostatic field set up by the ligands, it can be concluded that the stronger the field by the ligand is, the more the absorption bands of the complex appear in the shorter wavelength. Accordingly,

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[26] S. Mizushima, K. Higasi and Y. Morino, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **25**, 159 (1934); *Phys. Z.*, **35**, 905 (1934).

[27] H. Yoneda, This Bulletin, **30**, 130 (1957); **30**, 924 (1957).

[28] G. Schwarzenbach and A. Zobrist, *Helv. Chim. Acta*, **35**, 1291 (1952).

[29] For example, L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

the above-mentioned fact indicates that the electric field toward the *d*-electrons which is produced by the ligands is stronger in ethylenediamine complexes than in ammonia- and methylamine complexes, and that the atom dipole moment of ethylenediamine is greater than that of ammonia and methylamine. Such an increased atom dipole moment of ethylenediamine can be explained as being due to a result of the mutual +I effect of the two amino groups within the molecule. The difference of the coordinating abilities between mono- and poly-alcohols[30] can also be explained in the same way.

Summary

As a result of the examination of dipole moments of hydrides of various elements and their alkyl derivatives the following regularity was found. Hydrides of elements below the third period in the periodic table show the normal variation of dipole moments with successive alkyl substitution. That is, the dipole moment increases with successive alkyl substitution, which is expected from the consideration of the inductive effect of substituents. On the other hand, hydrides of elements in the second period in the periodic table show the abnormal variation of dipole moments with successive alkyl substitution, which apparently seems to contradict the existence of the inductive effect. That is, the dipole moment decreases with successive alkyl substitution. This fact was connected with the concept of *s-p* hybridization of non-bonding electrons, and the following rule was drawn. The more −I active a substituent is, the more the degree of *s-p* hybridization of non-bonding electrons decreases, and hence the more the contribution of the atom dipole moment to the whole dipole moment decreases. Some applications of this rule to the chemistry of coordination compounds were also presented.

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[30] For example, M. Kubota, *J. Chem. Soc. Japan* (*Nippon Kagaku Kaisi*), **61**, 1182 (1940).