

Molecular Constants and Chemical Theories III. Bond Moments of Higher Valence States

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Molecular Constants and Chemical Theories

III. Bond Moments of Higher Valence States

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In continuation of Part I and Part II of this paper, bond moments are calculated for such molecules as are formed by a marked central atom in a higher state of valency. Again the classical structures are taken as a basis. The bond moments are additive in the same molecule and unchanged from molecule to molecule as long as the multiplicity of the bond and the state of valency of either atom remain the same. This treatment on the basis of classical formulae makes possible the simple and straightforward calculation of the total moments of a considerable number of molecules formed by pentavalent nitrogen (azoxybenzenes, *N*-ethers of nitrobenzophenoneoximes), for which no other such calculation has been possible so far. Observable facts of dipole measurements, therefore, are at least as well represented by the classical structures and their underlying concepts, as by any other theory of the covalent bond. Hence, dipole moments do not provide any evidence of the existence of such linkages as a semipolar double bond or its wave-mechanical equivalent, i.e., enhanced resonance with ionic parent structures.

INTRODUCTION

IT has been shown¹ that additive molecular constants are unable to distinguish between different types of covalent linkage. In this paper a more complete system of bond moments will be developed. It will be seen that the electric moments of molecules may be separated into bond moments, which remain strictly additive as long as the atoms retain their state of valency. The classical structures are taken as the basis of calculation, their validity having been discussed previously.¹ It follows that dipole moments do not provide any criterion which could distinguish between these classical structures and others which use the concept of the coordinate (semipolar) link or enhanced resonance with ionic parent structures. Again this refers not to molecules with aromatic structures but to those of Werner's first order which are formed by a marked central atom. It has been shown that for them the energy difference between different resonance forms is very great, if compared with their bond energies.

The new bond moments depict the course of polarity in the periodic table in a very reasonable way, and permit the drawing of some conclusions on the change of polarity in the transition of an atom from one valence state to another. Furthermore, these bond moments are then applied to a

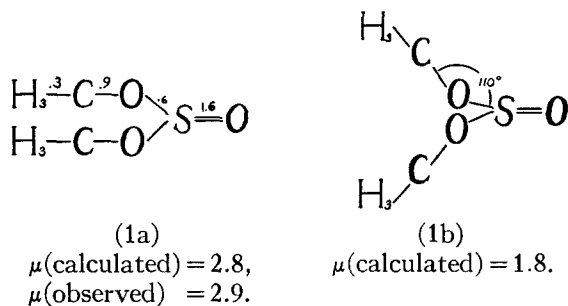
considerable number of molecules, whose total moments have up to now remained unexplained. Typical are the azoxybenzenes and certain oximes, formed by imino-nitrogen. All attempts to account for these moments on the basis of constant bond moments of tetravalent nitrogen have failed, but the new bond moments ascribed to pentavalent nitrogen permit their reconstruction with the same ease as those of any other molecule.

CALCULATIONS OF BOND MOMENTS

According to the underlying concepts of the classical structures, it has to be assumed that the polarity of a certain bond changes with the valency of the central atom. The moment of the S—Cl bond, for instance, cannot be the same in SCl_2 , SOCl_2 , and SO_2Cl_2 , as the field of the core of S^{6+} is screened by two *s* and two *p* electrons in SCl_2 , by two *s* electrons in SOCl_2 , and by none in SO_2Cl_2 . It is, therefore, not possible to establish the value of $\mu(\text{S}=\text{O})$ in $\text{S}^{\text{IV}}\text{OCl}_2$ by subtracting $\mu(\text{S}^{\text{II}}\text{Cl}_2)$ from $\mu(\text{S}^{\text{IV}}\text{OCl}_2)$. In such calculations naturally a great variety of quite irregular values for the S=O bond is obtained. Following the other course, it is expected to obtain three values each for the S—Cl and the S=O bond, each of them definitely associated with one of the three valence states of sulphur, and constant in any molecule formed by this atom in this particular valency.

¹ R. Samuel, *J. Chem. Phys.* **12**, 167, 180 (1944).

From the purely arithmetical point of view, this concept immediately increases the number of unknowns. In some cases, like tetravalent sulphur, sufficient moments have been measured to permit an unambiguous solution of all equations. In others, e.g., tetravalent selenium, this is not so, and an additional equation has to be supplied by extrapolation. In this instance, it is assumed that the ratio of $\mu(\text{Se}^{\text{IV}}=\text{O}) : \mu(\text{Se}^{\text{IV}}-\text{Cl})$ is the same as that of $\mu(\text{S}^{\text{IV}}=\text{O}) : \mu(\text{S}^{\text{IV}}-\text{Cl})$. It will be seen that some care has been taken to reduce such extrapolations to a minimum and to compare the unknown strength of a bond only with another one of very similar nature. The electric moments of a number of more complex molecules are then calculated and agree with the observed value. As each calculation represents an independent equation these extrapolations may be taken as justified. It should be borne in mind that bond moments cannot be expected to behave rigorously additively, on account of the effects of the solvent and of the induction of one moment upon another. The table of bond moments by necessity comprises only rough values, which, however, are entirely sufficient to throw some light upon the nature of polarity, when related to the position of the atom in the periodic table. But, for this reason small errors introduced by such an extrapolation do not matter much, as is also the case with small variations of valence angles. The moments calculated by Smyth² are again taken as a starting point, particularly for molecules formed by atoms in their lowest valence state.*



² C. P. Smyth, J. Am. Chem. Soc. **60**, 183 (1938) and earlier.

* All moments not otherwise mentioned are taken from the compilation in Trans. Faraday Soc. **30** (1934) or the article of E. Bergmann and A. Weizmann, Chem. Rev. **29**, 553 (1941). In addition, C. P. Smyth, G. L. Lewis, A. J. Grossman, and F. B. Jennings, III, J. Am. Chem. Soc. **62**, 1219 (1940); I. E. Coop and L. E. Sutton, Trans. Faraday Soc. **35**, 505 (1939). Electron diffraction data from L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).

As most of the moments are measured in solution, these values have been taken as a basis rather than the slightly different ones for the gaseous state. Although these represent the true values, too few are known to make an extensive comparison possible at this time.

BOND MOMENTS OF TETRAVALENT SULPHUR, SELENIUM, AND TELLURIUM

For sulphur dioxide the moment is 1.61D and the valence angle has been determined³ as $121^\circ \pm 5^\circ$; the moment of $\text{S}^{\text{IV}}=\text{O}$, therefore, is 1.6D. For SOCl_2 ($\mu = 1.44$) the angle (ClSCl) is 114° , that of (OSCl) $= 106^\circ \pm 1.4$. This gives an angle of about 120° for the $\text{S}=\text{O}$ bond against the bisecting line of the angle (ClSCl), and with the above value of $\mu(\text{S}^{\text{IV}}=\text{O})$, $\mu(\text{S}^{\text{IV}}-\text{Cl})$ is calculated to be 1.1.

In exactly the same way but assuming the ratio of $\mu(\text{Se}^{\text{IV}}=\text{O}) : \mu(\text{Se}^{\text{IV}}-\text{Cl})$ to be the same as that of $\mu(\text{S}^{\text{IV}}=\text{O}) : \mu(\text{S}^{\text{IV}}-\text{Cl})$ we obtain from SeOCl_2 ($\mu = 2.6$) the values of $\mu(\text{Se}^{\text{IV}}=\text{O}) = 2.1$ and $\mu(\text{Se}^{\text{IV}}-\text{Cl}) = 1.4$. The angle (ClSeCl) is taken as 110° , that of its bisector against $\text{Se}=\text{O}$ as 115° . Both are slightly smaller than the corresponding angles in SOCl_2 , because the longer distances should reduce the repulsive forces.

In order to justify these values and to show their additivity, they may be applied to some other molecules. Dimethyl sulphite may serve as a first example. The value of the ($\text{S}^{\text{IV}}-\text{O}$) single bond may be obtained by extrapolation. Assuming the ratio $\mu(\text{S}^{\text{IV}}-\text{O}) : \mu(\text{S}^{\text{IV}}-\text{Cl})$ to be the same as that of $\mu(\text{C}^{\text{IV}}-\text{O}) : \mu(\text{C}^{\text{IV}}-\text{Cl})$, a value of 0.6D obtains, while $\mu(\text{S}^{\text{IV}}-\text{O}) : \mu(\text{S}^{\text{IV}}=\text{O}) = \mu(\text{C}^{\text{IV}}-\text{O}) : \mu(\text{C}^{\text{IV}}=\text{O})$ results in the value of 0.5D.

As the sulphite ion exhibits tetrahedral angles, we take 110° for the angle ($\text{O}-\text{S}-\text{O}$) and 125° for its bisecting line against $\text{S}=\text{O}$, and again 110° for (COS). Then with the above values of the individual moments that of the molecule is calculated to be 2.8 in position (1a), the observed value in 2.9. A rotation of the $\text{H}-\text{C}-\text{O}$ moment by 180° about the $\text{S}-\text{O}$ axis would reduce the moment to 1.8, showing position (1a) as the preferred one. The same valence angles as in diphenyl sulphite

³ V. Schomaker and D. P. Stevenson, cf. L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1944).

⁴ K. J. Palmer, J. Am. Chem. Soc. **60**, 2360 (1939).

should persist in diphenyl sulfoxide as the resolution into optically active isomeric forms of very similar compounds shows the S^{IV} atom on the apex of a pyramidal structure. The dipole moment of Ph_2SO of 4.1D then permits us to calculate the moment of the carbon-sulphur bond. The moment of *p, p'*-dichloro diphenyl sulfoxide of 2.7 is much too small to be explained by a slight change of valence angles. The difference of these two moments is of the correct order for $\mu(H \rightarrow C) - \mu(C \rightarrow Cl)$. Hence, in the sulfoxides the bond moment $S^{IV} \leftarrow C$ is pointing towards the sulphur atom. The direction can immediately be verified, but is nevertheless unexpected. Its implication will be discussed below.

With $\mu(S^{IV} \rightarrow O) = 1.6$, and with angles of 110° and 125° , the moment $\mu(S^{IV} \leftarrow Ph)$ in diphenyl sulfoxide comes to 2.6D, leaving about 2.2D for $\mu(S^{IV} \leftarrow C_{AR})$. For the aliphatic carbon atom the slightly smaller value of 2.1D is derived from diisobutyl sulfoxide ($\mu = 3.9$). The value of 2.2, now used for the substituted molecules, leads to *p*-chloro diphenyl sulfoxide:

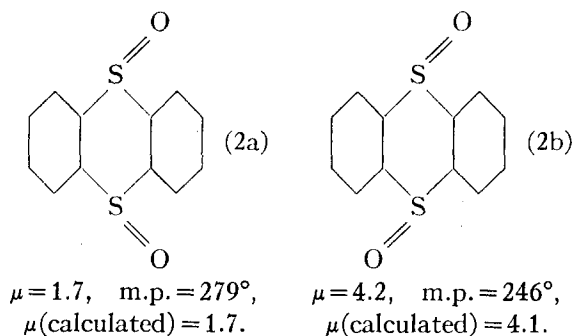
$$\mu(\text{calculated}) = 3.3, \mu(\text{observed}) = 3.9,$$

p, p'-dichloro diphenyl sulfoxide:

$$\mu(\text{calculated}) = 2.4, \mu(\text{observed}) = 2.7.$$

The slight difference between calculated and observed values may be due to induction. It will be seen that such discrepancies are particularly persistent for halogen substituted phenyl groups.

These bond moments may now be applied to the two isomers of thianthrene sulfoxide, the moments of which have been measured by Bergmann and Tschudnowsky⁵ as $\mu = 1.7$ and $\mu = 4.2$ for the two forms with melting points of 279° and 246° , respectively. Like thianthrene



⁵ E. Bergmann and M. Tschudnowsky, Ber. d. D. Chem. Ges. **65**, 467 (1932).

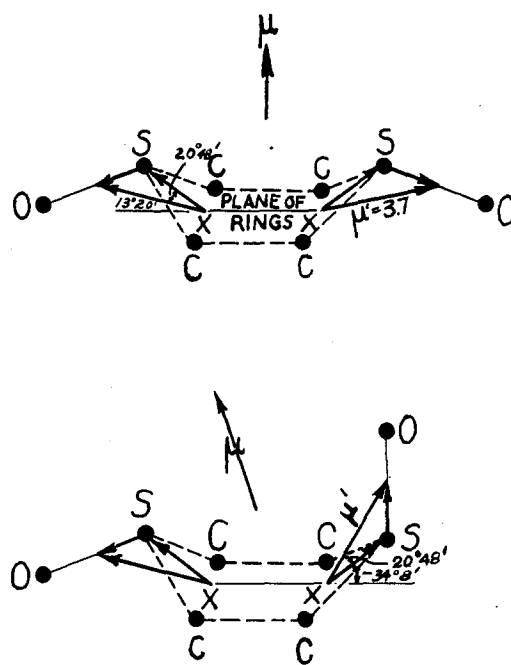


FIG. 1. Cross section of the two forms of thianthrene sulfoxide in the $(O-S \cdots S-O)$ plane. Broken lines refer to planes normal to that of the paper. The internuclear distances are drawn to scale, i.e., $(S=O) = 1.4\text{\AA}$, $(X-X) = (C_{AR}-C_{AR}) = 1.4\text{\AA}$, $(S-X) = 1.03\text{\AA}$ follows from $(S-C) = 1.8\text{\AA}$. The scale of the moment vector (arrows) is independent of that of the distances and chosen to make the $S-X$ vector as long as the $S-X$ distance. All angles follow from simple geometrical calculations under the one assumption that the valence angle (CSC) is 110° .

itself, they cannot be planar if the valence angle (CSC) be maintained at 110° . The $S-C$ bonds are 1.8\AA and the projection of S in the plane of the rings must form an angle of 120° with the two neighboring C atoms. Then the (CSC) plane forms with that of the rings an angle of $34^\circ 8'$ and this is, therefore, also its angle with the bisector of the angle (CSC). On the other hand, as the four $(C-H)$ moments cancel out, we have only to consider the moments $(S^{IV} \leftarrow C)$. With the valence angle of 110° at S, they form a resultant of 2.5D. The $(S^{IV} \rightarrow O)$ moment of 1.6 added under an angle of 125° produces a total moment of each (OSC_2) structure of 3.7D, and this vector forms an angle of $20^\circ 48'$ with the bisector of (CSC). Its angle against the plane of the rings (Fig. 1) is $34^\circ 8' - 20^\circ 48' = 13^\circ 20'$. The vector sum of two such moments, which now meet under an angle of $(180^\circ - 2 \times 13^\circ 20' =) 153^\circ 20'$, is 1.7D, exactly as observed for form (2a). Rotating one $S=O$ bond by 180° into the other possible position makes the

angle between the two 3.7 vectors $153^\circ 20' - 2 \times 20^\circ 48' = 111^\circ 44'$. The vector sum of these two is then 4.1, while 4.2 has been observed for form (2b). Because the shift of the ($S^{IV} \rightarrow O$) vector affects only the direction of the two weaker ones of the four composing moments and as they do not compensate, thianthrene sulphoxide provides an exceptional case, in which the *cis*-form (2a) exhibits a weaker moment than the *trans*-form (2b) and the lower melting point of the *trans*-form, therefore, is associated with the higher moment. The easy representation appears to confirm the numerical values and the directions of the two moments ($S^{IV} \rightarrow O$) and ($C \rightarrow S^{IV}$), and also the contention that a moment like the former, originally taken from SO_2 , remains constant and additive as long as sulphur is tetravalent.

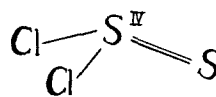
Next we turn to the molecules S_2Cl_2 and Se_2Cl_2 . The results of electron diffraction measurements on sulphur monochloride⁴ have been interpreted as indicating an extended structure $Cl-S-S-Cl$. However, the absorption spectra⁶ of the vapors clearly indicate the existence of a double bond $S=S$ in this molecule and of a $Se=Se$ bond in both selenium monochloride and selenium monobromide. To the present writer the very careful investigation of the Raman effect⁷ of $SOCl_2$ and S_2Cl_2 appears to be decisive, which goes to show that both molecules possess the same branched structure. On account of the larger distances the repulsive forces again should be slightly reduced as compared with $SOCl_2$. For S_2Cl_2 we assume the same value of 114° for the angle ($ClSCl$), but the slightly reduced value of 115° for its bisecting line against $S=S$. For Se_2Cl_2 both angles are taken as 110° . Slight changes would hardly affect the results. The bond moment of $S^{IV}=S^{II}$ will have the same ratio against $S^{IV}=O$ as for instance $C^{IV}-S$ against $C^{IV}-O$, and $\mu(S^{IV}=S) = 0.94\mu(S^{IV}=O)$ is taken as 1.5D.* Extrapolation by means of $\mu(Se^{IV}=Se) : \mu(Se^{IV}=O) = \mu(S^{IV}=S) : \mu(S^{IV}=O) = 0.94$ gives $(Se^{IV}=Se^{II}) = 2.0$.

* R. K. Asundi and R. Samuel, Proc. Rphys. Soc. London **48**, 28 (1935); S. L. Hussain and R. Samuel, *ibid.* **49**, 679 (1937); cf. M. Jan-Khan and R. Samuel, *ibid.* **48**, 626 (1936).

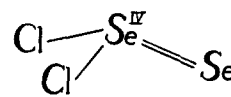
⁷ F. Matossi and H. Aderhold, Zeits. f. Physik **68**, 683 (1931).

* The value of $\mu(C^{IV}-S^{II}) = 0.74$ has been used which follows from that of $(C_2H_5)_2S$, $\mu = 1.58$, if the correct value of 92° is employed for the valence angle.

Using these values together with those derived for $S^{IV}-Cl$ and $Se^{IV}-Cl$ in the oxychlorides, we obtain:



$$\begin{aligned} \mu(\text{calculated}) &= 1.5, \\ \mu(\text{observed}) &= 1.6. \end{aligned}$$



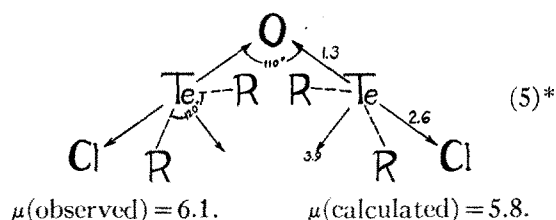
$$\begin{aligned} \mu(\text{calculated}) &= 2.1, \\ \mu(\text{observed}) &= 2.1. \end{aligned}$$

Finally, the moments of molecules of the type Ph_2SeCl_2 have been measured recently⁸ and may now be considered. Pauling⁹ suggests for them the structure of a trigonal bipyramid, in which the "lone pair" of tetravalent sulphur or selenium occupies one of the equatorial positions. Although in the present view the *d* electrons are needed for the formation of a bond only in a higher approximation,¹ this appears to be the most plausible structure. It follows that the two moments directed towards the apices compensate, and the other two will form an angle of approximately 120° . If the phenyl groups take up the apical positions the moments of Se^{IV} and Te^{IV} against C cannot be determined. However, a survey of the moments shows that in all likelihood this cannot be so. For Ph_2SeCl_2 and Ph_2SeBr_2 , for instance, the moments are observed as 3.2 and 3.4D. Their difference is too small and their absolute value much too high for such a structure, but both agree with one in which the halogens are at the apex and the radicals in the equatorial position. The small difference between them is then due to solvation or to the ($XSeX$) angle being slightly less than 180° , and the small resultant then opposes that of the ($PhSePh$) structure. As the angle of the latter is supposed to be 120° , the total moment of the molecule is identical with that of the bond against the phenyl radical, and we obtain immediately the following values:

$$\begin{aligned} Ph_2SeBr_2 &= 3.4, & (Se^{IV} \rightarrow Ph) &= 3.4, \\ & & (Se^{IV} \rightarrow C_{AR}) &= 3.8, \\ (p-MeC_6H_4)TeBr_2 &= 3.2, & (Te^{IV} \rightarrow R) &= 3.2, \\ & & (Te^{IV} \rightarrow C_{AR}) &= 3.9, \\ TeCl_4 &= 2.6, & (Te^{IV} \rightarrow Cl) &= 2.6. \end{aligned}$$

⁸ K. A. Jensen, Zeits. f. anorg. allgem. Chemie **250**, 245, 257, 268 (1943).

⁹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1944), second edition.



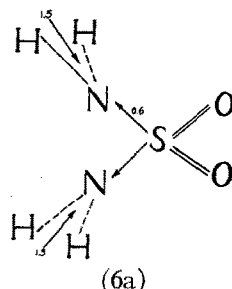
The molecule $[(p\text{-Me-C}_6\text{H}_4)_2\text{TeCl}]_2\text{O}$ may be used to verify these structures and values. The two reduced bipyramids have a common apex at the O atom (5)* and the two Cl—Te—O axes enclose the valence angle of oxygen of about 110° . The two Te—tolyl bonds at each Te atom, each possessing approximately $\mu = 3.9$, form a resultant each of the same value 3.9. These resultants, both normal to (O—Te—Cl), enclose an angle of 110° and their vector sum is 4.3. The two Te—Cl moments (also 110°) produce a resultant of 3.0 in the same direction. The Te—O bonds (according to the conditions found in dimethyl sulphite) will possess a moment of about half that of $\text{Te}^{\text{IV}}\text{—Cl}$ or about 1.3. Their resultant is 1.5, pointing in the opposite direction. Hence, we obtain for the total moment of the molecule $4.3 + 3.0 - 1.5 = 5.8\text{D}$, the observed value is 6.1D . Considering the scarcity of data and necessity of extrapolations, the agreement is very good indeed. It shows again the bond moments to be constant from molecule to molecule. Incidentally it also shows that the $(\text{Se}^{\text{IV}}\text{—C})$ and $(\text{Te}^{\text{IV}}\text{—C})$ moments point in the direction of the carbon atom. As to diphenyl selenoxide, the individual bond moments now being established, it is concluded from the moment $\mu(\text{Ph}_2\text{SeO}) = 4.4$, that the angle (Ph Se Ph) probably lies between 95° and 110° , that of its bisector against Se=O between 110° and 120° . However, these geometrical structures are not always the most stable ones. Among these molecules and even more so among those formed by the pentavalent atoms (discussed below) which form similar bipyramids, complete changes appear to occur frequently. Thus, the high value of $\mu = 4.4$ appears to indicate that in dibenzyl sulphide diiodide $(\text{C}_7\text{H}_7)_2\text{SI}_2$ the lone pair takes the place on the apex. The moment calculated for such a structure (with $\mu(\text{S}^{\text{IV}}\text{—I}) = 1.1$) comes to 4.0D .

* The broken lines refer to a plane normal to that of the paper.

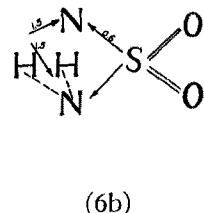
BOND MOMENTS OF HEXAVALENT SULPHUR

The natural starting point for molecules formed by hexavalent sulphur is sulphuryl chloride, $\mu(\text{SO}_2\text{Cl}_2) = 1.8$. Its structure is almost exactly that of the regular tetrahedron,¹⁰ and as the sulphate ion also possesses tetrahedral structure, this structure is assumed for such molecules in general. Using again the ratio $\mu(\text{S}^{\text{VI}}\text{—Cl}) : \mu(\text{S}^{\text{VI}}\text{=O}) = 3:5$ the moments $\mu(\text{S}^{\text{VI}}\text{—Cl}) = 2.4$ and $\mu(\text{S}^{\text{VI}}\text{=O}) = 3.9$ are obtained. From diethyl sulphone a value of 0.4 can then be calculated for $\mu(\text{S}^{\text{VI}}\text{—C})$. It is, however, doubtful whether heavier organic sulphones possess the same geometric structure, and at this time it is sufficient to know that the moment of this bond contributes a small positive amount.

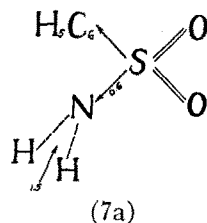
If we estimate the moment of $\text{S}^{\text{VI}}\text{—N}^{\text{III}}$ by means of the ratio $\mu(\text{C}^{\text{IV}}\text{—Cl}) : \mu(\text{C}^{\text{IV}}\text{—N}) = \mu(\text{S}^{\text{VI}}\text{—Cl}) : \mu(\text{S}^{\text{VI}}\text{—N}^{\text{III}}) = 3.5$, the sulphone amide permits us to verify the values for both $\text{S}^{\text{VI}}\text{=O}$ and $\text{S}^{\text{VI}}\text{—Cl}$ simultaneously. For $\text{S}^{\text{VI}}\text{—N}$, 0.6D results, and for the amide, according to formula (6a) and the ammonia angles, the moment is 3.9, precisely the observed value. Rotation of the N—H_2 moment by 180° about the S—N axis (6b) would lead to 2.2D, and the position of (6a) is the preferred one. For benzene



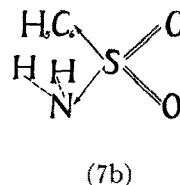
$\mu(\text{calculated}) = 3.9,$
 $\mu(\text{observed}) = 3.9.$



$\mu(\text{calculated}) = 2.2.$



$\mu(\text{calculated}) = 2.9.$



$\mu(\text{calculated}) = 5.1,$
 $\mu(\text{observed}) = 5.09.$

¹⁰ K. J. Palmer, J. Am. Chem. Soc. **60**, 2360 (1938).

sulphone amide,¹¹ the observed value obtains for form (7b). For both molecules the influence of free rotation appears to be negligible. The two prevailing forms are characterized by the repulsion of the hydrogen atoms in sulphonamide, and attraction of the hydrogens to the phenyl ring in benzene sulphonamide. The reason probably is the positive charges at the hydrogen atoms and the negative charges at the ring.

BOND MOMENT OF PENTAVALENT PHOSPHORUS

Not much is known about the electric moments of molecules formed by the atoms of the fifth family in their state of maximal valency. Ph_3AsCl_2 , Ph_3SbCl_2 , Ph_3BiCl_2 possess no definite dipole moments⁸ and, probably, form trigonal bipyramids with the chlorine atoms at the apices. The structure of POCl_3 and PSeCl_3 approaches that of the regular tetrahedron.¹² But the moments of Ph_3PO , Ph_3PS , and Ph_3PSe (4.3, 4.7, 4.8, respectively) cannot be explained on such a basis. Their difference appears to be too small and their increase in the wrong direction for the PO (S, Se) moment to oppose the vector sum of the others. Such moments as $\text{Ph}_3\text{As} \cdot (\text{OH}) \cdot \text{Cl}$ ($\mu = 9.2$) and $\text{Ph}_3\text{Sb} \cdot (\text{OH}) \cdot \text{Cl}$ ($\mu = 3.0$) appear to be incompatible for the same geometric structure. Apparently the chlorine atom and the phenyl radical exchange their position frequently. SbCl_5 possesses a moment in some solvents, but not in others. A more detailed analysis (including that of amine oxide, mentioned earlier¹) appears premature.

Hence, we confine ourselves to calculating $\mu(\text{P}^{\text{V}}=\text{O}) = 6.2$ and $\mu(\text{P}^{\text{V}}-\text{Cl}) = 3.7$ from $\mu(\text{POCl}_3) = 2.4$, assuming again the ratio of 5:3 between them. Thus, again extrapolating $\mu(\text{P}^{\text{V}}=\text{S})$ as slightly less than $0.9 \times \mu(\text{P}^{\text{V}}=\text{O})$, we take it as 5.4D and calculate the moment of (PSeCl_3) to be $5.4 - 3.7 = 1.7$, while the observed value is 1.4D. The moment $(\text{P}^{\text{V}} \rightarrow \text{Ph})$ probably will lie between 1.5 and 2D, pointing towards Ph.

BOND MOMENTS OF PENTAVALENT NITROGEN

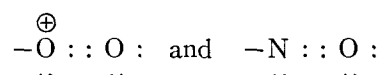
In the following molecules nitrogen is taken as pentavalent according to the classical

¹¹ W. D. Kumler and I. F. Halberstadt, J. Am. Chem. Soc. **63**, 2182 (1941).

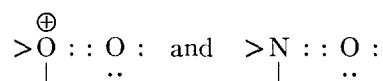
¹² L. O. Brookway and J. Y. Beach, J. Am. Chem. Soc. **60**, 1836 (1938); J. Y. Beach and D. P. Stevenson, J. Chem. Phys. **6**, 75 (1938).

structures. It has been shown previously¹ that neither band spectra nor wave-mechanical treatment provides a basis for the hypothesis of a covalency maximum of four of this atom. London's early remark¹³ about the uncoupling of p electrons concerns only the isolated atom but not the molecule, as already in the diatomic molecule twice the number of p orbitals are available for this process. While in the oxygen atom two of the four p electrons are paired, they become uncoupled in the oxygen molecule as shown by its paramagnetic ground level $^3\Sigma$. If we indicate those electrons which are uncoupled and available for molecular formation by lines, and by dots those which are paired in the atom or by sharing, the electronic formula is $\text{>O} :: \text{O} :$

If now one of these free p electrons is removed by ionization, the electron configuration of O_2^+ and, therefore, of NO obtains, which is that of the nitroso stage, i.e.,



If, however, one of the s electrons is removed, an excited O_2^+ or NO is produced (formed by O or N in sp^4), with three free valencies,



Two of these three electrons are those originally unpaired in the ground level of O_2 , the third loses its partner through ionization. Hence, as both wave-mechanical treatments satisfactorily account for the paramagnetic ground level of O_2 , they also automatically both establish and prove the existence of a nitrogen atom with five electrons capable of linking other atoms. The full number of five is developed from the stage of the diatomic molecule onwards. The bonding character of these electrons in the theory of molecular orbitals has been discussed previously;¹ in the electron-pair bond theory this question does not arise. A comparison of the configurations of O_2 and excited NO with those of O_2^+ and unexcited NO and with those of O_2^{2+} , NO^+ , and CO will show that the unpaired electrons of excited NO are those of the N atom.

¹³ F. London, Zeits. f. Physik **46**, 455 (1938).

Some bond moments of pentavalent nitrogen have been considered in Part II of this series.¹ The calculations were based on Smyth's value of 3.3D for the $N^V=O$ bond in the nitro group.² This figure, however, is derived under the assumption that the C—N bond of the group points against nitrogen and is in fact the same as the C— N^{III} bond, e.g., of the amines. However, the basic concept of a change of polarity with change of valency has to be applied uniformly here as elsewhere, and the C— N^{III} and the C— N^V bond cannot be considered as identical. The moment of $C=N^V$ shows that the C— N^V single bond too will be directed against the carbon atom, and although the figures involved are not high, this makes necessary a recalculation of the moments of bonds involving pentavalent nitrogen. The essential features of Part II (Section 3) remain unchanged, as there only linear molecules with two opposing moments have been considered.

For the nitro group a number of experimental values have been observed, which vary from 3.2 and 3.8D of nitro methane in solution and the gaseous phase, respectively, to 3.9 and 4.2D of nitrobenzene in the same conditions. For the nitro group proper this leads to values between 3.4 and 4.5D. If we take a mean value of 4.0 as the basis of calculation, we derive by the same process as previously¹ the following bond moments, the N^V atom always being the positive partner:

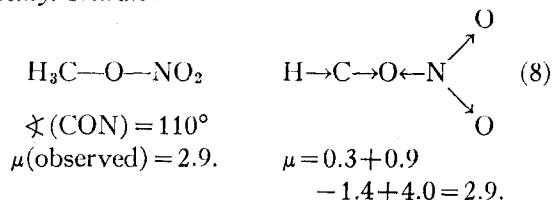
$$\begin{array}{lll} N^V=O & 4.4, & N^V\equiv N^{III} & 4.2, & N^V=C & 2.6, \\ N^V-O & 1.4, & N^V=N^{III} & 2.8, & N^V-C & \sim 1.0. \end{array}$$

These values may now be verified by calculating the moments of a great number of molecules. Some of them are given here, and for this purpose particularly those have been selected for which up till now no calculation has been possible at all. The valence angle ($C=N^V-O$) has been taken as that of ($O=N^V-O$), i.e., 127° . For the angle ($Ph-N^{III}-N^V$) of the azoxybenzene and its derivatives that of 120° has been used as observed between a single and a double bond at N^{III} in the azides. A small change would not affect the results appreciably.* For $\mu(N^{III}-Ph)$

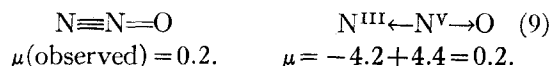
* In NOCl this angle has been observed to be 116° and such a value would change the following calculated moments by about 0.1D.

Sutton's value¹⁴ of 1.3D has been adopted, leading to about 0.9 for $\mu(N^{III}-C_{Ar})$.

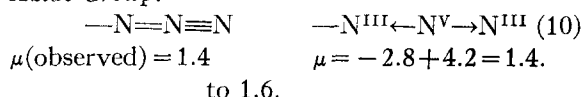
Methyl Nitrate:



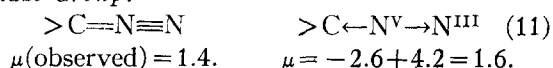
Nitrous Oxide:



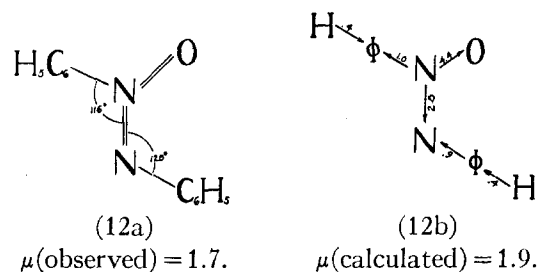
Azide Group:



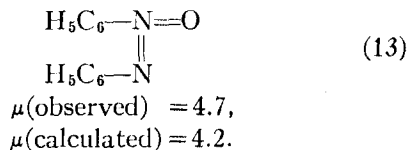
Diazo Group:



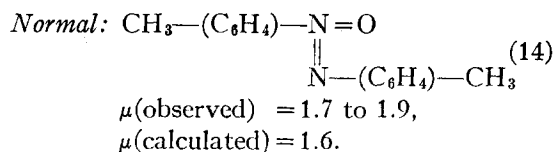
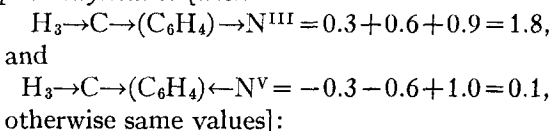
Azoxybenzene:



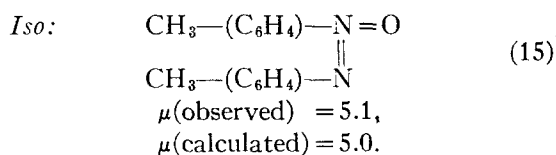
Iso-Azoxybenzene (with same angles and bond moments):



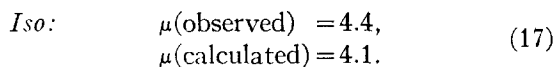
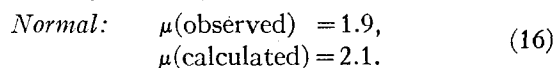
p,p'-Azoxytoluene [with



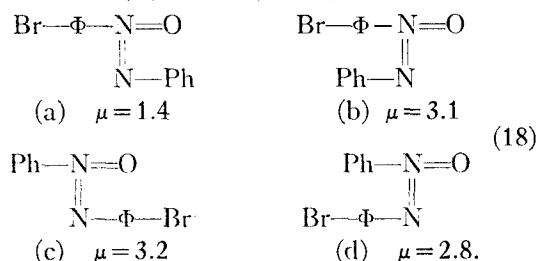
¹⁴ L. E. Sutton, Trans. Faraday Soc. 30, 789 (1934).



o,o'-Azoxytoluene (calculated for free rotation of the tolyl radical):

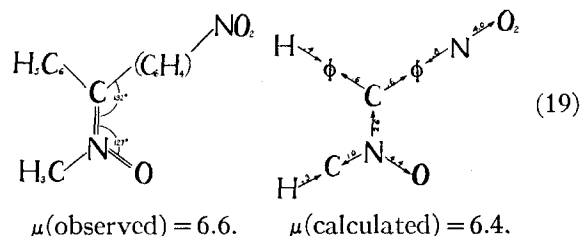


Mono-p-bromo Azoxybenzene: For the four possible structures the following moments are calculated ($\mu(\text{Br}-\text{C}_{\text{AR}}) = 1.1$):

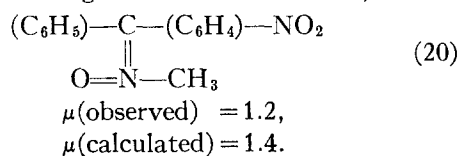


For two of them the moments have been observed as 0.9 and 2.6D, and these probably will have been structure (a) and (d). The induction of the halogen upon the ring is again apparent.

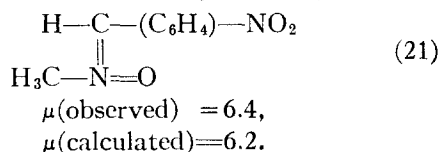
p-Nitrobenzophenone α -Oxime *N*-Methyl ether:



p-Nitrobenzophenone β -Oxime *N*-Methyl ether (with same angles and bond moments):



p-Nitrobenzaldoxime *N*-Methyl ether (α):



The agreement is very good, particularly as the bond moments used cannot be more (and do not claim to be more) than the very first rough evaluations and as individual changes of valence angles are bound to occur in such molecules. The result is the more remarkable, as among the more complex molecules are those whose electric moments have remained unexplained up till now. For the classical structures and their bond moments, however, no difficulty exists at all and they fall into line automatically. The dipole moments of molecules formed by pentavalent nitrogen would appear to make any other theoretical concept untenable. This paper set out (Part I and Part II) to show that physicochemical measurements such as these by their very nature are unable to distinguish between different types of covalent linkage. It would appear as if we have defeated our own ends; for these molecules, the dipole moments would seem definitely to decide in favor of the classical structures and against formulae containing a coordinate bond. Therefore, it may as well be admitted that with a sufficient number of resonance forms a description of any moment may be obtained. This is particularly so, as the percentage contribution of the parent structures is a variable factor. Such an adjustable element in a theory naturally makes it possible to represent any measured quantity, but by the same token it makes it impossible to prove the theory as such. For a theory which, by assuming different percentages of contributions of different forms, automatically can represent any experimental result, a crucial experimental test does not exist. The classical structures do not possess this advantage, but, on the other hand, representations such as this of the observed moments, for this very reason establish their validity and their inner congruence. Such an extremely simple and straightforward description of the electric properties of the molecules by means of definite additive bond moments for each valence state is, therefore, superior at least by virtue of the principle of economy of hypotheses.

BOND MOMENTS AND ATOMIC NUMBER

The bond moments derived so far, together with some calculated by Smyth² for the lower valence states, are collected in Table I. Mostly they represent values taken from one particular

TABLE I. Bond moments.

| | | | | | | | |
|---------------------|-------|-----------------|--------|-------------------|------------------|--------------|-----|
| $N^{III}-C$ | -0.5 | | | | | | |
| $N^{III}=C$ | -0.9 | | | | | | |
| $N^{III}=O$ | 2.0 | | | | | | |
| N^V-C | (1.0) | $P^{III}-Cl$ | 0.8 | | | | |
| $N^V=C$ | 2.6 | P^V-C | (~1.3) | | | | |
| $N^V=N^{III}$ | 2.8 | | | | | | |
| $N^V\equiv N^{III}$ | 4.2 | | | | | | |
| N^V-O | 1.4 | | | | | | |
| $N^V=O$ | 4.4 | $P^V=O$ | 6.2 | | | | |
| | | $P^V=S$ | 5.4 | | | | |
| | | P^V-Cl | 3.7 | | | | |
| | | $S^{II}-C$ | -0.7 | | | | |
| | | $S^{II}-Cl$ | 0.6 | | | | |
| | | $S^{IV}-C_{AR}$ | -2.2 | $Se^{IV}-C_{AR}$ | (~3.8) | | |
| | | $S^{IV}-O$ | 0.6 | | $Te^{IV}-C_{AR}$ | (~3.9) | |
| $O^{IV}=O$ | 0.6 | $S^{IV}=O$ | 1.6 | $Se^{IV}=O$ | 2.1 | | |
| | | $S^{IV}=S^{II}$ | 1.5 | $Se^{IV}=Se^{II}$ | 2.0 | | |
| | | $S^{IV}-Cl$ | 1.1 | $Se^{IV}-Cl$ | 1.4 | $Te^{IV}-Cl$ | 2.6 |
| | | $S^{VI}-C$ | 0.4 | | | | |
| | | $S^{VI}-N$ | 0.6 | | | | |
| | | $S^{VI}=O$ | 3.9 | | | | |
| | | $S^{VI}-Cl$ | 2.4 | | | | |

molecule and measurement, and are still unnecessarily afflicted by fortuitous errors. They could be improved by taking the average of several observations of a number of similar molecules. However, this method of direct comparison without taking means appeared better suited for the present purpose, namely, to demonstrate the existence of constant and additive bond moments according to the state of valency. It will be seen that they are governed by three rules: (1) In an homologous series such as $S^{IV}-Cl$, $Se^{IV}-Cl$, $Te^{IV}-Cl$, the moment increases in this order. (2) In a series $S^{IV}=O$, $S^{IV}=S$, in which the negative atom varies, the bond moment decreases in the same direction. (3) A change of valency increases the moment, as shown by such examples as $\mu(P^{III}-Cl)=0.8$ and $\mu(P^V-Cl)=3.7$, $\mu(N^{III}=O)=2.0$ and $\mu(N^V=O)=4.4$, or $\mu(N^{III}-C)=-0.5$ and $\mu(N^V-C)=1.0$, reversing the direction. An exception to these rules appears to be offered only by the moment $\mu(S^{IV}-C)=-2.2$.

The absolute values even in the highest valence states are not very high. According to the basic concept as discussed in Part II, the

values per electron pair have to be compared. For the nitro group this value is 2.2, not much higher than for HCl or H_2O , particularly if the bond distance is taken into account.

The electric moment measures the dissymmetry of the nuclear fields, and Mulliken¹⁵ has suggested that this dissymmetry may be expressed in terms of the ionization potential (I) and the electron affinity (E). Accordingly in a bond $A-B$ the quantities $[I(A)+E(A)]/2$ and $[I(B)+E(B)]/2$ describe the dissymmetry of the fields, and their ratio, therefore, the polarity of the bond. In the preliminary discussion of Part II of this series,¹ this concept has been used, and indeed these three empirical rules could be stated as follows: (1) In comparing, e.g., $S^{IV}-Cl$ and $Se^{IV}-Cl$, the ionization potential of Se^{IV} is smaller than that of S^{IV} , the electron affinity and ionization potential of Cl remain unchanged, hence, the moment increases from S to Se . (2) Conversely, the electron affinity and ionization potentials of O^{II} are larger than those of S^{II} , hence, $S^{IV}=O$ exhibits a larger moment than $S^{IV}=S$. (3) In the transition to a

¹⁵ R. S. Mulliken, J. Chem. Phys. 2, 782 (1934); 3, 573, 586 (1935).

higher state of valency the mean ionization potential of the central atom increases as two electrons are transferred from atomic to molecular orbitals and the field of the core becomes vastly more positive.

A more detailed discussion, however, reveals at once that this concept is only approximately valid. Its physical meaning is that the binding electrons are shifted in the direction of the nucleus with the stronger electric field. Already in molecules like PCl_3 it is in reality the P atom which is surrounded by the stronger field, but the moment points in the direction of the Cl atom and special further assumptions have to be introduced. In the cases under discussion here, the higher the valence state, the higher the nuclear field of the central atom. But empirically the moment always points away from it, with the one exception of the $\text{Si}^{\text{IV}}-\text{C}$ moment. The reason for this discrepancy is that ionization potential and electron affinity measure the strength of the nuclear fields only when the atoms are at infinite separation, but not in the completed molecule at small internuclear distance, or rather they do so only in the first approximation.

If the wave function of the molecule AB be written according to the method of molecular orbitals, namely, as

$$\psi_{AB} = \{a\psi_A(1) + b\psi_B(1)\} \{a\psi_A(2) + b\psi_B(2)\},$$

the dissymmetry of the fields is expressed by the ratio of the coefficient a^2 and b^2 . But these can be expressed as simple functions of ionization potential and electron affinity only, as long as non-localized molecular orbitals are used (Mulliken) or the interaction of the electrons is omitted (Hund). In both procedures as pointed out before,¹ the resonance effect of Heitler and London is neglected, and we obtain a description of the electron configuration and term system of the molecule, but no valid statements can be made as to its energies. Hence, all questions as to valency and the formation of the molecule remain unanswered, among them that of the polarity of the bond. If written according to the requirements of the electron-pair bond theory as:

$$\begin{aligned} \psi_{AB} &= ab\{\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)\} \\ &\quad + a^2\{\psi_A(1)\psi_A(2)\} + b^2\{\psi_B(1)\psi_B(2)\} \\ &= ab\psi(A-B) + a^2\psi(B^+A^-) + b^2\psi(A^+B^-), \end{aligned}$$

the ratio of the normalizing factors a^2 and b^2 again measures the polarity of the bond. But here, both a and b themselves depend on the internuclear distance. They are simple functions of ionization potential and electron affinity only for separated atoms at infinite distance; otherwise, indeed the bond moment always would be directed against that atom whose core has the stronger field in the isolated state. Then, of course, the interaction of the atoms vanishes and the same result obtains as before, namely, that a^2 and b^2 are proportional to the sum of ionization potential and electron affinity only, when the electron resonance is not present.

However, as the second function also represents Pauling's resonance concept, we may measure the ratio of a^2 and b^2 by means of the energy differences between the energy level which constitutes the molecule $A-B$ and those of the forms (B^+A^-) and (A^+B^-) . For reasons discussed earlier, which are even more valid for these higher valence states, we do not attempt to formulate absolute values. Nevertheless, one relation is obvious. The energy difference between $(A-B)$ and (A^+B^-) is an energy of "excitation" between two terms of the same molecule, and applying the well-known band spectroscopical equation which expresses the energy of the (O, O) band of a band system in terms of the atomic excitation and the dissociation energies (D) of lower and higher state, we may write for the energy difference of the completed molecules at small internuclear distance $\Delta = I(A) - E(B) + D(A-B) - D(A^+B^-)$. If the ground level of the molecule is $(A-B)$, then the lower the excited term with the electron configuration (A^+B^-) (i.e., the more the electrons shifted towards B), the larger will be the coefficient b^2 . Hence, Δ should be proportional to $1/b^2$. A similar simplified relation obtains for a^2 , and the dissymmetry of the fields will be characterized by:

$$\frac{b^2}{a^2} \sim \frac{I(B) - E(A) + D(A-B) - D(A^+B^-)}{I(A) - E(B) + D(A-B) - D(A^+B^-)}.$$

In such a formula, the dissociation energies include the missing terms of the electron resonance.

Often the dissociation energies $D(A-B)$, $D(A^+B^-)$, and $D(A^-B^+)$, although different, still will be of the same order, and will compensate or

nearly so. This is the case in simple molecules like HCl. The two ionic terms will nearly counter-balance each other also in simple molecules with double bonds, like CO or SO. In each case the polarity may still be considered as proportional to the ratio of ionization energy plus electron affinity of both atoms.

However, when proceeding to higher valencies, e.g., from SO to SO₂, conditions change. In a bond such as S^{IV}=O, four valence electrons are in the fields of S⁴⁺ and O²⁺. The term (A^+B^-), therefore, contains, among others, contributions of forms in which all four electrons are with O, i.e., of ($S^{4+}O^{2-}$). The corresponding term of (A^-B^+) contains forms in which all four electrons are with S, but this gives us (SO^{2+}). The dissociation energy of such a molecule comprising a neutral atom and an ion, is of the order of the van der Waals or association bonds, while $D(S^{4+}O^{2-})$ is overwhelmingly larger. Their difference easily can be greater than that of ($I(S^{4+}) - E(O^{2-}) - I(O^{2+})$). As a matter of fact, if $D(S^{4+}O^{2-})$ is taken as twice that of ($Ca^{2+}O^{2-}$), which has a similar internuclear distance, the level ($S^{4+}O^{2-}$) will be several electron volts below that of (SO^{2+}), although for the separated systems ($S^{4+} + O^{2-}$) and ($S + O^{2+}$) the former is much higher than the latter on account of the high ionization energy of S⁴⁺. Hence, in such a case, b^2 is larger than a^2 in spite of $I(B)$ being smaller than $I(A)$, and the moment points away from the central atom. If, however, oxygen is replaced by CH₃ with its low ionization potential of 11 ev, the energy difference between the separated systems becomes so large that an intersection of the terms on decreasing internuclear distance cannot come to pass, and a^2 remains larger than b^2 , i.e., the moment points towards the central atom as in the sulphoxides.

These conditions may be expressed slightly differently in the language of the resonance concept. If $A-B$ is a simple molecule like HCl or SO, then the forms (A^+B^-), e.g., (H^+Cl^-), or (S^+O^-) and ($S^{2+}O^{2-}$), and the forms (A^-B^+), e.g., H^-Cl^+ or (S^-O^+) and ($S^{2-}O^{2+}$), may already be markedly different in their energetic contributions, but are still of the same order. For higher valence states, in which the positive atom A carries a much higher positive charge than the

negative atom B , this is not so, and the contributions of (A^+B^-), among them such as ($S^{4+}O^{2-}$), are not in the least compensated by those of the forms (A^-B^+). Hence, the forms (A^+B^-) play the much greater role and direct the bond moment against B , although the stronger field goes with A . It is this feature which may be expressed¹ as the addition of a positive charge to the plus end of the dipole at the transition of the central atom to a higher valence state, without corresponding shift of the electrons.

CONCLUSION

For simple molecules formed by a central atom in a higher state of valency, a number of bond moments have been calculated on the basis of the classical formulae. These are then applied to other more complicated molecules. For each combination of two atoms a definite bond moment obtains, which remains unchanged for this combination as long as the state of valency and the multiplicity of the bond remain the same. The bond moments are additive in the same molecule and are constant from one molecule to the other. As a matter of fact, they remain more constant than might have been expected under the varying effects of induction, solvation, and slight changes of the valence angles. This indicates all such bonds to be of the type of ordinary covalency, the valence electrons firmly localized between two atoms.

The dipole moments of a considerable number of these molecules have not been rationally explained before. It would be possible, therefore, to conclude that these classical structures are a better approach to reality than any other concept. In any case, they describe the electric properties of the molecules at least as well as any other theory. Hence, it is obvious that dipole moments do not possess any diagnostic quality, which permits them to distinguish between semipolar or normal covalency, or between two different theories of the covalent linkage. For molecules of Werner's first order, formed by a marked central atom, dipole moments, therefore, do not provide evidence for the existence of semipolar bonds or of enhanced resonance with ionic parent structures.