Molecular Constants and Chemical Theories II. Additive Molecular Constants and Chemical Structures

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All additive molecular constants, besides parachor and molecular refractivities (Part I), in particular also dipole moments, bond distances, and energies of formation (or bond energies) may be separated into individual (atomic or bond) contributions according to different proposed structures of a covalent molecule or different chemical theories on which these structures are based. Such constants do not therefore possess diagnostic qualities as to the nature of different covalent bonds, and different theories or concepts based on them, by necessity are inconclusive. A number of standard examples of molecules formed by a marked central atom are considered, which often are assumed to establish the existence of a second variety of covalent linkage, i.e., coordinate bonds, or its wave mechanical counterpart, i.e., enhanced resonance of covalent and ionic (or other) forms. For all of them, all the above molecular constants are in perfect agreement also with the older classical formulae, including those of pentacovalent nitrogen. Again wave mechanics does not offer any objections but is in full accord with these classical structures. While a decision between different sets of formulae and concepts cannot be reached by means of any of these additive molecular constants, spectroscopical evidence is leading farther and appears to favor the older classical system and its underlying concepts.

INTRODUCTION

THE first part of this paper[1] has shown an additive molecular constant, to wit the parachor, a function of the molecular volume, to be adaptable to two entirely different sets of chemical formulae. Additivity of the atomic or bond constants is achieved on either basis, although the concepts underlying the two sets of structures are entirely different. One of them works on the basis of different types of covalent linkage, directly or by virtue of resonance of different structures, while the other recognizes only one type of non-electrostatic bond. If no *raison d'être* was left for the classical structures, as often assumed, we are faced indeed with a situation as mysterious as it is logically unsatisfactory. At this juncture evidently a re-examination of the relation of both chemical theories with other additive molecular constants is called for. It will be seen that neither dipole moments (Section 3 of this paper) nor heats of formation (Section 5) nor bond distances (Section 4), etc., are able to distinguish between different theories or conceptions of the covalent linkage. In each case the grand total of a certain physical property of a molecule is measured, but the separation into atomic or bond constants is not an observed fact but an inferred deduction and therefore may be adjusted to any preconceived reasonable struc-

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

ture of the molecule. A simple physical reason can be suggested for this behavior (Section 6), but in any case it is obvious that such constants do not possess any diagnostic value as to different theories or types of the covalent bond.

Furthermore, the two chemical theories have to be compared with their wave mechanical equivalent (Sections 1 and 2). It will be seen (Section 6) that certain complications may be unified and simplified because the experimental basis on account of which they had been introduced does not stand up to a re-examining analysis and in fact does not exist. All this refers to molecules which belong to Werner's first order, and are formed by a definite central atom. They are energetically different from resonating aromatic or conjugate structures and the body of spectroscopical evidence appears to favor the classical formulae (Section 6).

In order to obtain a more clearly defined basis and terminology for the discussion of dipole moments, etc., most of the theoretical argument is taken up first and follows immediately (Sections 1 and 2).

1. WAVE MECHANICAL INTERPRETATIONS OF POLARITY AND OF DIFFERENT TYPES OF COVALENT BONDS

Different interpretations of the wave functions of a particular molecule are possible in wave mechanics; they are entirely compatible with

each other and are in fact made use of by different schools of thought or by the same for different purposes. It might be as well to define clearly from the beginning which interpretation and hence which terminology is used in the following paragraphs.

Before doing so, however, another salient point of theoretical development might be recalled at the very outset, namely, that wave mechanics only knows one type of covalent linkage and does not recognize the concepts of the semipolar double bond or the singlet linkage. These concepts have been introduced into chemistry originally to save the so-called Octet rule (Lewis,* Langmuir, Lowry, Sidgwick, Sugden, et al.) and it is now often believed that wave mechanics has definitely established their existence in the form of resonance between covalent and electrovalent structures. However, a moment's reflection will show that this is not so. To be sure, resonance exists and, as the wave function of a molecule because of incomplete localization of the electrons between the nuclei, also contains a hybridization with ionic terms, the resulting linear combination may be interpreted as a resonance between covalent and electrovalent structures. But this is decidedly true of *all* covalent bonds, and only the contributions of the structures vary according to the ratio of the coefficients of their normalized functions. In this interpretation resonance with ionic parent structures does take place not only for molecules frequently described by means of a semipolar double bond, $-NO_2$, CO, $-NC$, etc., but for HCl, CH_4, H_2, and all others as well. The difference is not one of quality but of degree only, and sometimes not even that. We may call the bonds by whatever name we choose, but we are not entitled to differentiate between two groups and assume different kinds of linkage in them. Hence, the larger bond moment (to take this as an example of an additive molecular constant) of $N=O$ in the nitro group as compared with the nitroso stage may be ascribed to a larger ionic contribution, but not to a different type of linkage.

However, the description of the molecules as resonating between different structures, is only one of different but entirely equivalent interpretations.** As is well known, in an abbreviated form sufficient for our purpose the same wave function of the molecule AB may be written[2] either according to the view of the theory of molecular orbitals (of Herzberg, Hund, Lennard-Jones, and Mulliken) as

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

and according to the requirements of the (Heitler-London, Slater, Pauling) electron pair bond theory of linkage the function is then written as

$$\Psi_{AB} = ab\{\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)\}$$
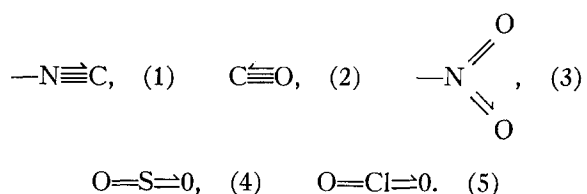$$+ \{a^2\psi_A(1)\psi_A(2) + b^2\psi_B(1)\psi_B(2)\}.$$

Of these identical expressions, the second represents the molecule as resonating between the covalent structure $A : B$ and the ions B^+A^- and A^+B^- while the coefficients a and b determine the contributions of these structures. In the first the linkage is described as an ordinary covalent bond of a certain polarity. As the fields of the two nuclei, or rather of the two cores, are not identical, the field of the molecule possesses a certain dissymmetry, the analytical expression of which again is the ratio of the normalizing factors. This may be visualized as the electron pair being shifted slightly towards the negative partner, or belonging more to it in time, and if needs be it may be written, as has been done sometimes, as $A^{+\delta} - B^{-\delta}$, indicating a differential fractional charge. However, there is really no

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* However, Lewis himself always maintained the Doublet rule to be of vastly greater importance than the Octet rule.

** The possibility of different but entirely equivalent theories of valency is particularly clearly expressed by Pauling [L. Pauling, *The Nature of the Chemical Bond* (1938), p. 47]: "It is possible, on the other hand, to develop (at least in principle) a complete discussion of the structure of a molecule from either the purely ionic point of view (with extreme polarization or deformation of the ions), or the covalent point of view, provided that all the unstable atomic orbitals are used in the discussion. No treatment of either of these types has been carried out for molecules ·of any complexity, however, whereas the reasonable procedure which forms the basic of our argument has found extensive application to the problems of structural chemistry." The point of view adopted in this paper may be said to approach the second of the alternatives mentioned by him.

[2] Full details and references will be found in standard texts, e.g., in J. H. Van Vleck and A. Sherman's important summary in Rev. Mod. Phys. **7**, 167 (1935). Cf. also literature in H. Lessheim and R. Samuel, Proc. Ind. Acad. Sci. **1**, 623 (1935).

need for such a symbol. The formula cannot be supposed to indicate all properties of the molecule at a glance. Exactly as we do not indicate variations of bond energy by the different length of the printed line, we also refrain from indicating variations of polarity. The symbol $A-B$ therefore is understood to imply some polarity as long as the two atoms are not identical. The same physical fact, namely, the dissymmetry of the field, is described by both interpretations in a different way, and therefore each of the two wordings "covalent-ionic hybrid" or "polar covalent bond" explains or expresses not more and not less, but exactly as much as the other. The ratio of the coefficient of the normalized functions also measures the degree of non-localization of the binding electrons. That is why the polarity of the molecule may be interpreted in these different ways. This also appears to be the underlying reason for the great difference of behavior between molecules formed by a marked central atom, under discussion here, and structures like the aromatic rings to which this paper does not apply. The latter are distinguished by non-localized electrons and rigorously identical energy values of the resonating structures; the former are best described by means of localized electrons and the energy differences between the resonating configurations are very large (cf. Section 6).

In this paper the first interpretation and terminology are made the basis of discussion. The reasons for this choice will become apparent below. At this stage attention may be drawn only to its greater simplicity. In Sidgwick's theory of coordinated bonds of simple inorganic structures the following molecules have to be written with a semipolar double bond thus:

$$-N\overset{\leftarrow}{\equiv}C, \quad (1) \qquad C\overset{\leftarrow}{\equiv}O, \quad (2) \qquad -N\overset{\nearrow O}{\underset{\searrow O}{}}, \quad (3)$$

$$O=S\overset{\leftarrow}{=}O, \quad (4) \qquad O=Cl\overset{\leftarrow}{=}O. \quad (5)$$

If it is now attempted to embody as much as possible of these chemical concepts into a physical theory following the second interpretation, as has been done so carefully and ingen-

iously by Pauling,[3] the result is that the first of these structures is a hybrid between a covalent (electron pair bond) and only one ionic form, as expected. For the second, resonance of the covalent with two ionic forms obtains, which later cancel each other out, for (3) resonance of two ionic forms without any covalent structure, for (4) resonance between a covalent double and a covalent single bond, and for (5) a three-electron bond. To our mind there is nothing in the observable properties of the so-called coordinate bonds which calls for a separate and individual explanation of each or the introduction of a second variety of linkage.[3a] But if there should be, it is obvious that the interpretation on the basis of resonance with ionic structures does not yield a uniform theory, which would at least explain the additivity of molecular constants.

Another, and to our mind much more serious, discrepancy between both interpretations is the following: Both describe in different ways the same polarity of the molecule and therefore should arrive at identical expressions for the percentage of ionic contributions. But in many actual cases the results are widely different. In the above example for the orbital method the same ratio of the coefficients applies to both electrons in the same way, both the electrons being shifted towards the negative partner. Two electrons of 4.8×10^{-10} e.s.u. charge, shifted $0.1A = 0.1 \times 10^{-8}$ cm will produce an electric moment of about 1×10^{-18} or 1 Debye unit. For gaseous HCl, the experimental moment of 1.28D therefore represents a shift of the bonding electron pair of 0.13A, which is about 10 percent of the internuclear distance of 1.28A. The orbital method therefore could be said to describe the molecule as 90 percent covalent and 10 percent ionic. From the pair bond view Pauling has made the same calculation, comparing the actual moment with that produced by the hydrogen electron, if transferred over the whole length of the internuclear distance, and obtains 17 percent

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[3] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1938). (For details of structures, e.g., $-NC$, also literature mentioned therein.)

[3a] Physical properties are discussed in this paper and those referred to. An analysis of the chemical properties may be found in R. F. Hunter and R. Samuel, J. Chem. Soc., p. 1180 (1934); Chem. and Ind. 54, 31, 467, 635 (1935).

ionic contribution. Such a calculation cannot be more than a rough estimate. Thus, the hydrogen electron could approach the Cl nucleus to its M shell only, while on the other hand the charge density distribution of the Cl⁻ ion still shows a considerable value at 1.28A distance from the nucleus, or, in other words, the radius of the Cl⁻ ion is larger than the bond distance of the HCl molecule. The estimate on the basis of the orbital method is not affected by such difficulties and therefore most probably more reliable, but under such conditions it is sufficient that both approximations lead to the same order of magnitude, indicating that both methods are in essential agreement as to the description of the observable facts in such an unambiguous case.

However, even the highest dipole moments recorded for polar covalent molecules fall into the order of 1.5 to 2D for a single and 3 to 4D for a double bond. For the latter, the shift of two pairs or 4 electronic charges has to be taken into consideration from the point of view of the orbital method. With the known internuclear distances, even the most favorable examples do not yield more than 10 to 15 percent ionic contributions according to the view of this theory, while 30 to 40 percent have been calculated for the description of the same molecules by means of resonating structures.

In some cases the uncertainty of experimental values will be responsible for this serious discrepancy, as is shown below (Section 5) for the carbonyl group. For another large class of molecules, formed by nitrogen, it is due to the fact that nitrogen is assumed to be not more than tetracovalent, and structures with pentacovalent nitrogen are excluded from consideration. The discussion of this assumption follows immediately (Section 2).

2. THE PENTACOVALENCY OF NITROGEN

If it were not for the purpose of establishing a clear terminology beforehand, the discussion of the pentacovalency of nitrogen would have been taken up at the end of this paper. The question is opened here not for the sake of an arbitrary supposition but because we are led to it by necessity. It will be seen below that all the physical constants of molecules formed by nitrogen, such as dipole moment, bond distance,

and bond energy, behave similarly to the parachor, already dealt with in the preceding part of this paper. They can be represented as the sum of additive contributions of the constituent atoms on the basis of their classical formulae, if nitrogen is assumed to be pentacovalent. Again the pentacovalency of nitrogen is necessary to reconcile the findings of the pair bond theory and the molecular orbital theory as to the degree of polarity, as has already been indicated above. The results as to the additive molecular constants are sufficiently consistent not to take this situation as accidental, but to reconsider this question from its beginning.

Pentacovalency of nitrogen would originate from the excited electron configuration sp^4, similar to the sp^3 configuration of tetravalent carbon. As London[4] has shown, 2 of the p electrons would be chemically inactive, as they must be paired already in the atom on account of Pauli's exclusion principle, while d orbitals do not yet exist in this period. However, this is not so for polyatomic molecules where entirely different statements are derived from Pauli's principle on account of the axial symmetry of the field. It amounts to the simple fact that the possibilities for uncoupling the spin vectors of p electrons, originally paired in the atom, increase step by step from the atom to the diatomic, triatomic, polyatomic molecule. We may say that the l and λ properties of the electrons are successively lost in the formation of di- and polyatomic molecules. Another way of putting it is to count the number of free p orbitals, which increases step by step with the number of the constituent atoms, because the chemically active atoms always possess less p electrons than the following rare gas. However, just these points of view have been discussed earlier in detail[5] and a brief description of the formation of such a molecule by means of the orbital method will be sufficient here.

The combination of two unexcited N atoms in the configuration $(2s^2, 2p^3 - {}^4S)$ leads to the following configuration of the ground state of N_2:

$$\sigma^2(2s), \ \sigma^{*2}(2s), \ \pi^4(2p), \ \sigma^2(2p),$$
$$\{\pi^{*0}(2p), \ \sigma^{*0}(2p)\} - {}^1\Sigma.$$

[4] F. London, Zeits. f. Physik **46**, 455 (1928).
[5] H. Lessheim and R. Samuel, Phil. Mag. **25**, 664 (1938).

In the atom, each of the three p electrons occupies one of the two places in one of the orbitals $\lambda = +1, 0, -1$, as shown by the ^4S term. In the molecule, these electrons are shared in the corresponding $\pi(2p)$ and $\sigma(2p)$ orbitals which together represent the triple bond. But the free places of the atomic orbitals also have been "shared," and now form the premoted orbitals. These can be used again for the uncoupling of any pair. They have been added here, in parenthesis, marked by an asterisk for promotion and the superscript zero to indicate that they are unoccupied as long as N_2 is unexcited. If now an unexcited N atom combines with an excited one in the configuration $(2s, 2p^4, -{}^4P)$, i.e., posessing one s electron less and one p electron more, the following excited term of N_2 results:

$$\sigma^2(2s),\ \sigma^*(2s),\ \pi^4(2p),\ \sigma^2(2p),\ \pi^*(2p).$$

A singlet and a triplet Π term are formed, $^3\Pi$ being the lower one. The two unpaired electrons $\sigma(2s)$ and $\pi^*(2p)$ now may share their orbital with electrons of a third atom. One of them certainly is a premoted electron and we shall have to inquire presently whether it possesses bonding power, particularly in a polyatomic molecule. However, the first part of the argument is perfectly obvious: The two electrons which by necessity have been paired in the $2p^4$ configuration of the atom* have become uncoupled in the diatomic molecule. The excitation of the N_2 molecule by which this is brought about is in any case necessary, because unexcited N_2 and unexcited O could not combine to give the diamagnetic ground level of N_2O.

It may be mentioned that such a simple description would not be possible on the basis of the pair bond theory. Oxygen possesses the same $2p^4$ configuration of its p electrons in its unexcited state, and the above procedure essentially is nothing else but the building up of the ground state of O_2 from two unexcited atoms. The same process of uncoupling of electrons obtains for each of the two atoms and a configuration $[\ldots \pi^{*2}(2p) - {}^3\Sigma]$ results, which now contains two similarly unpaired electrons (one each being in π_+ and π_-). Indeed, the paramagnetism of the oxygen molecule is the direct experimental proof of this process of uncoupling of electrons previously paired in the separated atoms, exactly as the existence of the ozone molecule indicates the pentacovalency of nitrogen later on. The correct description of the oxygen molecule has been one of the early triumphs of the orbital method, but, as is well known, the pair bond theory could not obtain a paramagnetic O_2 molecule without resort to higher approximation. These may be gained[6] by considering the interaction of the normal with an excited term of the O atom, or of the corresponding electron configurations. Without too much inaccuracy these treatments may be described as making use of simultaneous but different distributions of the four p electrons over the three p orbitals. In this way, none of the three p orbitals is permanently taken up by a pair of electrons, but each of them alternatingly is occupied by a pair and by a single electron in the different distributions or terms. It appears evident that the same procedure applied to the excited sp^4 nitrogen atom instead of to s^2p^4 oxygen, will lead to a pentacovalent nitrogen atom, i.e., an excited N_2 molecule possessing two unpaired electrons.

Finally we have to investigate whether the unpaired but premoted electron of the excited N_2 molecule possesses bonding power. Here it should be recalled that all theories of valency in existence are only extrapolations of those few examples of molecules for which it has been possible to carry through the actual wave mechanical calculation. In order to be able to distinguish between established and assumed elements of these theories, we have to revert to the fundamentals on which they are based. Some of the points have already been discussed in greater detail elsewhere.[7]

Because the theories of valency cannot be established directly, but are generalizations only, however plausible, this process of extrapolation has to be guided and constantly corrected by experimental facts. Among them, of course, are such as known from band spectra, dipole moments, etc. But chemistry too has built up a

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* As distinct from those of an s^2 group, which of course remain chemically inactive until the group is split by excitation.

[6] W. Heitler and G. Poeschl, Nature 133, 833 (1934). G. Nordheim-Poeschl, Ann. d. Physik 26, 258 (1936). G. W. Wheland, Trans. Faraday Soc. 33, 1499 (1937).

[7] a. H. Lessheim and R. Samuel, Proc. Ind. Acad. Sci. 1, 623 (1935). b. R. F. Hunter and R. Samuel, Nature 138, 411 (1936); R. Samuel, Cur. Sci. 4, 762 (1936).

large body of facts which also must play a leading role in the selection of those features of the simple molecules which should be extrapolated into a general theory of valency. In the chemistry of inorganic first-order molecules, numerical valency is a definite property of the free atom. It indicates its possibilities of reactions, although not all of them will lead to chemically stable molecules on energetical grounds. Characteristically, it is always in best agreement with the number and subdivision of the outside electrons of the atom. A theory of valency in which almost each molecular type needs special considerations to such an extent that the numerical valency of the atom occurs almost as a mere incident of the process of molecule formation—such a theory to the present writer at least appears to be less desirable than any other possible extrapolation in which the numerical valency of the free atom is one of the component assumptions by which the generalized theory is instituted.

While the electron pair bond theory essentially is a generalization from the point of view of the H_2 molecule, the orbital theory extrapolates the H_2^+ ion. To this fact is due the great importance as well as the great weakness of the latter. It permits the description of electronic configurations in terms of single electrons, but the bonding effect of the H_2^+ ion is due to the degeneracy of the two nuclear fields, and disappears the more the fields of the two atoms become unequal. It is therefore not the bonding effect which chemistry calls valency. Chemical covalency is produced by the degeneracy due to the identity of the electrons, which is always present, for equal and unequal atoms alike. Its prototype is the electron "resonance" of H_2 and because this effect is necessarily missing in the orbital theory, the latter is not a theory of valency at all, but essentially a description of the electron configuration of the completed molecule. As such it is greatly superior to the pair bond theory as the example of the O_2 molecule has shown. But because the electrons are treated essentially as independent, it leads (as is well known) to an entirely incorrect description of the process of formation (or, what is the same, of dissociation) of the molecule. Slater and Van Vleck* have

demonstrated this in the example of H_2 and CH_4, which according to the orbital theory would be formed to 50 percent and to 73 percent, respectively, not from atoms but from ions. In order to convert the orbital method into a theory of valency, an additional assumption is necessary, and it is for this reason that the postulate has been introduced, according to which premoted electrons act antibonding. This can hardly be called even a generalization of H_2^+. Indeed, in the ground state of this molecule the electron is on a non-premoted orbital, but all the other terms of H_2^+ are unstable and not bonding* no matter whether the electron occupies a premoted or non-premoted group. To be sure, the premoted electron goes into an orbital of higher energy on decrease of the internuclear distance, and as in the united atom, it is bound with less energy to the molecule than the corresponding non-premoted electron. However, in a polyelectronic molecule, we do not know whether both the premoted and the corresponding non-premoted electron together are bound with more or less energy than in the correlated separated atoms. Or in other words, we do not know, whether compared with the corresponding non-premoted one, the premoted electron is bonding and contributes a smaller but positive amount to the energy of formation, or is antibonding, contributing a negative amount.

In most simple diatomic molecules only the lower premoted orbitals are occupied and a direct comparison with experimental evidence has not been possible so far. However, there is at least one excited term known, i.e., the $C^2\Sigma$ term of N_2^+, which appears to contradict this postulate.[8] In this term the molecule possesses an energy of dissociation which considerably exceeds that of the ground term. It is brought about by an excitation of the odd electron from the orbital $3s\sigma(2p)$ of the ground state to $3d\sigma(3s)$ of the excited level. Hence it furnishes an example of a non-premoted and therefore presumable bonding electron, whose excitation to an orbital of higher energy nevertheless strengthens the bond. This would appear not to be compatible with the basic

* Cf. reference 2.

* With one accidental exception at large internuclear distances.
[8] R. K. Asumdi and R. Samuel, Proc. Ind. Acad. Sci. 3, 244 (1937). The term was found by W. W. Watson and G. P. Koontz, Phys. Rev. 46, 32 (1934).

concept of the above postulate, according to which the change of energy of the system on the formation of the molecule is sufficiently described by the sum of such changes of the individual and independent electrons.

The introduction of the postulate of bonding and non-bonding electrons also does not fully permit the orbital theory to become a theory of valency, which represents the facts of covalent linkage as accumulated by chemistry. It clearly leads to the assumption, that all molecules with equal numbers of s and p electrons are bound by the same number of valencies. Thus BF possesses the same six p electrons on exactly the same orbitals as N_2 and the fact that either atom contributes three of them in the latter case, while one is supplied by B and five by F in the former is not taken into account. In order to do so, some special assumption has to be made, such as the higher nuclear charge of F keeping four of them on atomic orbitals. But then almost each molecule needs special considerations and explanations, and the simple system of inorganic chemistry is destroyed. Even so, the bonding effect of the degeneracy of the nuclear fields in H_2^+ makes the valency of an atom dependent on its partner not only in an energetic but also in a numerical sense, and the greater the difference of the nuclear fields the smaller must be the distance between them to bring about this bonding effect. This is certainly empirically not true, as a glance at the bond distances of the oxides of a period will show.

It is then simpler and clearer to follow an earlier suggestion of Hund,[7] to count as covalent bonds only those bonding pairs to which electrons are contributed by *different* atoms. In the frame work of the orbital theory this, of course, again is a postulate because this theory *per se* is unable to make any statement concerning the system of separated atoms, i.e., the completely dissociated molecule. But just for this reason some postulate is necessary if the orbital method shall be considered as a theory of valency, and this particular assumption does nothing less but to engraft into the orbital method the results of the pair bond theory, especially the electron "resonance" valency of Heitler and London. This way of

counting immediately distinguishes the triple link of N_2 from the single link of BF, in spite of the identical electron configuration of both.* To the present writer this appears to be the procedure which is most economical in the number of assumptions, but permits the combination of results of the pair bond method at large internuclear distances with those of the orbital method at small ones, where it is supreme.

In such a procedure the energy of formation is due to the Heitler-London effect in the first instance, while premotion of electrons is a secondary effect by which it may be modified. It is of interest now to consider a pair of electrons, one from either atom, which together occupy a premoted orbital. If premotion was the only bonding effect, they should not constitute a link but act repulsively only. If it is a secondary effect, we may go one step further than Hund and expect a decreased bonding effect also in this case in which both the effects of electron degeneracy and of premotion counteract each other. Again only comparisons with experimental evidence can decide. Among the low terms of the light molecules only one is known suitable for this purpose, i.e., the double-excited term $2p\sigma_u^2 - {}^1\Sigma_g$ of H_2. It is stable, the energy of formation being about 50 percent smaller than in the ground state $\sigma_g^2 - {}^1\Sigma_g$. Here a pair of premoted electrons acts bonding, and (with the optimism recommended by Van Vleck and Sherman as a necessary ingredient of any theory of valency) the existence of this stable term might be generalized as well as that of the ground levels of H_2 or H_2^+. However, as the situation is complicated by the additional rigorous degeneracy of the nuclear fields, we confine ourselves to the statement that as far as diatomic molecules are concerned the identification of premoted with antibonding electrons is not a necessary part of the orbital theory, but has been introduced as an additional postulate. As that, it agrees neither with the well-established concepts of chemical valency nor with some of the experimental facts of band spectroscopy.

For polyatomic molecules the contention of pentacovalency of nitrogen becomes even more

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[9] F. Hund, Zeits. f. Physik **73**, 1 (1931); **74**, 429 (1932).

* It should be noted that C in CO is divalent according to Hund's theory, in agreement with its parachor (Part I of this paper), its electric moment, bond distance, and bond energy (cf. Sections 4 to 6 below).
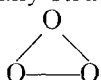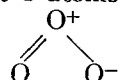
evident. As pointed out above, the kinematical nature of the quantum numbers of the electrons becomes less and less known, and with it the description and designation of the electrons at small internuclear distances less and less possible. It becomes less and less possible to predict whether the terms omitted in a simplified theory are not of importance, or else whether some of the higher roots of the secular equation classified as non-bonding are not actually such as to favor the binding of additional atoms. Hence two remarks may be sufficient to characterize the situation. First Mulliken's procedure[10] may be used to describe the electronic configuration from the point of view of a particular atom. In the above example of the excited N_2 molecule (containing one N atom excited to the pentacovalent state) the two unpaired electrons might be shared by a divalent atom, as in N_2O or in the similar case of $-NO_2$. Whether in such a molecule the electrons remain premoted ones from the viewpoint of the central N atom is difficult to decide; e.g., when replacing the two N atoms by the "united atom" Si, the two $3p$ electrons would be the shared ones of SiO, both being non-premoted. But without going into details, one point is clear, namely, that from the point of view of the O atom they form the fifth and sixth $2p$ electrons which are non-premoted. Furthermore, premotion, as well as being a statement about the energy by which the electron is bound to the nuclei, has also another physical meaning. The distribution of electric charge produced by the premoted electron between the nuclei is decreased when compared with that of the corresponding non-premoted one, the wave function of the former possessing at least one additional node between the nuclei. This is illustrated by the well-known Heitler-London diagram of the charge distribution of two repelling hydrogen atoms and may be considered as the origin of the postulate of the antibonding character of such electrons. But by virtue of the same argument, the charge distribution is particularly concentrated on the opposite side of the nuclei, and therefore in the polyatomic molecule such premoted electrons are particularly suited to be shared by additional atoms. Again this has been

pointed out for certain cases by Mulliken in the same early paper.

The mechanism described here agrees with London's original paper[4] insofar as the higher valencies of atoms with three p electrons or more are not developed in the free and isolated atom itself. They can become active only in the stage of the triatomic molecule. Indeed the highest valency known in diatomic molecules and radicals is three; higher ones occur in polyatomic structures only. But once they have been developed, they are indistinguishable from the lower ones. The five bonds in N_2O are due to one s electron and four p electrons of the central N atom, hybridized similarly as in the case of tetravalent carbon. This view is entirely congruous with all the results of actual wave mechanical calculations. It differs from others only in the choice among the features presented for extrapolation by the simple molecules, one of which has to be generalized in order to span the gulf to the more complex ones. For all atoms maximal covalency immediately becomes identical with the number of their valence electrons in their outer shell, in agreement with the observed facts of chemistry.

Finally, after these theoretical remarks, attention may be drawn to the ozone molecule. Once more, as for O_2, the electron configuration (s^2p^4) of the O atom makes tetracovalency of O the equivalent of the pentacovalency of $N(sp^4)$. Recently Stand and Spurr[11] have shown that ozone forms an isosceles triangle with an angle of 122° at the apex. Together with the fact that a dipole moment of 0.5D has been observed[12] for it, this excludes any structure with equivalent O atoms such as $\begin{smallmatrix} & O & \\ \diagup & & \diagdown \\ O & \!\!-\!\!-\!\! & O \end{smallmatrix}$. A structure like $\begin{smallmatrix} & O^+ & \\ \diagup\!\!\diagup & & \diagdown \\ O & & O^- \end{smallmatrix}$ would possess a several times larger dipole moment.* But a structure with tretacovalent

[10] E.g., R. S. Mulliken, Phys. Rev. **40**, 55 (1932).

[11] W. Stand and R. A. Spurr, J. Am. Chem. Soc. **65**, 179 (1943).
[12] C. P. Smith and G. L. Lewis, J. Am. Chem. Soc. **61**, 3063 (1938).
* A resonance structure similar to that suggested by Pauling for SO_2, i.e., $[O-O=O, O=O-O]$ might be possible, but there is no chemical indication that atoms of group VI act trivalent, and the paramagnetic term belonging to such a configuration should be the lowest one both for O_3 and SO_2. It is therefore difficult to accept it on the strength of the valence angle and bond distance alone. However, no low d orbitals exist for the O atom and by virtue of the same arguments by which N can be tetra-

oxygen at the apex, i.e.,
$$\begin{array}{c} O \\ \diagup \diagdown \\ O \quad O \end{array}$$
is in best agreement with both (cf. Section 3). The structure of ozone may be considered as the direct experimental evidence for the pentacovalency of nitrogen. The premotion of the unpaired electrons of O_2 finds its expression in the decrease of the bond energy of the second double bond compared with the first one. (But already for SO_2, on account of the larger internuclear distance, this effect has almost vanished, as the atomic heat of formation of SO_2 is about twice that of SO.)

Summing up the argument, we may say that there is nothing in wave mechanical theories which prevents pentacovalency of nitrogen. The paired p electrons of its excited (sp^4) configuration become unpaired already in the diatomic molecule, as shown by the ground level of O_2. The antibonding character of its one premoted electron is the result of an additional assumption, the validity of which is highly doubtful already for diatomic molecules. For polyatomic molecules the bonding character of this electron (with respect to a third atom) appears to be evident even on the basis of this postulate. The ozone molecule seems directly to establish this contention.

Under these circumstances, approaching the empirical evidence without any preconceived view and taking it at its face value, it is difficult not to treat nitrogen as pentacovalent in such compounds as N_2O_5, exactly as on account of the divalency of oxygen boron is treated as trivalent in B_2O_3 or phosphorus pentavalent in P_2O_5, and chlorine heptavalent in Cl_2O_7. As B possesses 3, N and P 5, and Cl 7 valence electrons, this is indeed the much more consistent and satisfactory procedure. Nitrogen is pentacovalent only, it is true, if the atoms attached to it or at least most of them, belong to the second period, in combinations like $>C=N\equiv N$, $-N=N\equiv N$, $-O-NO_2$ (and may be NF_5 the existence of which has
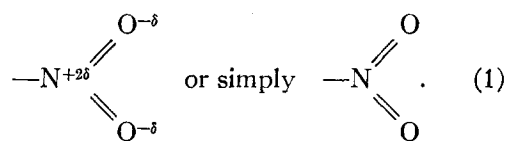
covalent only, the maximal covalency of O is two, and tricovalent as well as tetracovalent oxygen would establish the possibility of pentacovalency of nitrogen. For SO_2 and SO_3, G. E. Kimball [J. Chem. Phys. **8**, 188 (1940)] obtains structures and covalent double bonds, but with the help of d electrons, which in first approximation are not necessary in the present view and do not exist for oxygen as the central atom.

been reported).* But this is due to the great energy necessary for the transition from the s^2p^3 to the sp^4 configuration, the energy of fission of the s^2 group increasing from C towards F. This energy can be obtained only in conjunction with partners contributing the highest bond energies, and for the same reason oxygen never reaches the higher valence states of sulphur, and sulphur itself is hexavalent only in combination with O and F, but not with Cl or Br. These energetical conditions suggest themselves immediately as the true reason, if we compare the maximal valencies exhibited, e.g., by the atoms of the sulphur family against halides. They are:

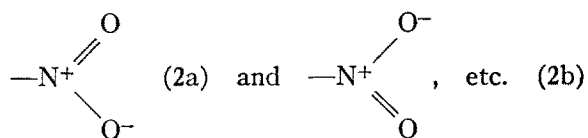|			
OF_2	SF_6	SeF_6	TeF_6
OCl_2	SCl_4	$SeCl_4$	$TeCl_4$
...	...	$SeBr_4$	$TeBr_4$
...	...	...	TeI_4.

As the single-bond energy decreases from O to Te and from F to I, as well as the energy of fission of the s^2 group, it is apparent that only F provides sufficient energy to form hexavalent compounds of the heavier atoms. The other halides only come up to tetravalency, Cl from S onwards, Br only in combination with Se and Te, I with Te only. From Cl onwards they do not provide sufficient energy to obtain a positive energy balance for hexavalency and although the energy to be overcome includes the heats of sublimation and the dissociation energies of the diatomic molecules, most of it has to be ascribed to the fission of the s^2 group of the positive partner. No wonder that the even higher excitation energy of O is not overcome by any.

Accepting the pentacovalency of nitrogen, the structure, for instance, of the nitro group is

$$-N^{+2\delta} \diagup\!\!\!\diagup \overset{O^{-\delta}}{\underset{O^{-\delta}}{\diagdown\!\!\!\diagdown}} \quad \text{or simply} \quad -N \diagup\!\!\!\diagup \overset{O}{\underset{O}{\diagdown\!\!\!\diagdown}} . \quad (1)$$

* L. Staub, Dissertation, Breslau, and private communication of Miss Staub. Along with nitrates of a number of metals, also ammonium nitrate has been found to be entirely covalent in the vapor state (below M.P.), and again for the ammonium nitrogen no other but a pentacovalent formula appears possible. [M. I. Haq and R. Samuel, Proc. Ind. Acad. Sci. **3**, 487 (1936).] NH_4Cl obtains one electrovalent bond by the intersection of the covalent with the ionic potential curve (as HCl or AgCl in solution), the additional energies of solvation, lattice, etc., being indispensable for this process. [Cf., e.g., R. F. Hunter and R. Samuel, Chem. and Ind. **55**, 733 (1936).]

The N=O bond is a simple covalent bond, i.e., two electron pairs, with a certain polarity superimposed according to the ratio of the coefficient of the normalized wave function; or in other words, according to the dissymmetry of the fields which itself is measured by the ionization potential and electron affinity of N and O. For the bond distance of structure (1) a theoretical value of 1.18A obtains (for the normal covalent double bond) according to Pauling's table,[3] in good agreement with the empirical value of 1.21 ± 0.02A. Its polarity may as well be termed resonance with the structures

$$-N^+ \overset{\displaystyle O}{\underset{\displaystyle O^-}{\diagup\!\!\!\diagup \atop \diagdown}} \quad (2a) \quad \text{and} \quad -N^+ \overset{\displaystyle O^-}{\underset{\displaystyle O}{\diagup \atop \diagdown\!\!\!\diagdown}} \quad , \text{ etc.} \quad (2b)$$

But these structures (2) are the only ones possible according to Sidgwick's theory and therefore the only ones recognized by Pauling. They form, however, much higher excited terms of the system. The level (sp^3) of N^+ needed for the ionic structure (2) lies 22.1 ev or about 500 kcal./mole above the term (sp^4) of N, required for the covalent structure (2), which amount is reduced to about 450 kcal./mole by the first electron affinity of O. The energy of formation of a semipolar bond $N^+ - O^+$ may be estimated as the sum of the covalent $N - O$ single bond of organic nitrates, plus an electrovalent bond such as LiF of the same period, or about 175 kcal./mole in all. Structure (2) therefore lies about 275 kcal./mole above structure (1) even without taking $D(N^5 = O)$ into account. Hence the contributions of parent structures (2) are very small and the molecule is overwhelmingly represented by the classical structure (1). That is the inherent reason why the classical structures permit representation of the physical properties of the molecules, measured as additive molecular constants. This has already been seen for the parachor and will be shown also for the dipole moments and other similar constants. If nitrogen was not pentacovalent, all this indeed would hardly be understandable. At the same time it is evident how such a case of resonance differs entirely from the resonance, say, of the two Kekulé structures of benzene, in which latter case the two terms or electronic configurations indeed are associated

with identical energy values. The resonance between covalent and ionic parent structures of inorganic molecules, which is the main subject of this paper, nowhere approaches this criterion. The two corresponding terms of the system are always separated by a considerable energy of excitation (often of the order of one or several bond energies). That is why the terminology of resonance is avoided here and instead that of the polar covalent bond (as defined in Section 1) is used throughout. According to the bond moment of 3.3D, the four binding electrons of each N=O bond of the nitro group are shifted from the center of electrical symmetry by 0.165A or 13 percent of the bond distance (1.21A) only. This may be taken as the order of the contribution of the parent structure (2).

3. DIPOLE MOMENTS AND BOND DISTANCES OF SOME TYPICAL MOLECULES

Dipole moments and the bond moments derived therefrom have been used in quite a number of attempts to establish the existence of the semipolar double bond and are assumed to establish large contributions of ionic structures justifying such formulae.[13] It is impossible to deal with all of them, as that would imply setting up in its entirety an alternative theory or system of bond moments. In such a theory *the change of valency* of the central atom would be responsible for any change of moment between the same atoms in different structures other than those due to a solvent or an induction effect of one moment on the other.* For outside reasons it appears impossible to work out such a system in all its details at this time, but a few examples will be sufficient to show such a theory to be entirely practicable.** Most of the typical structures whose electric moments have been discussed in connection with the coordinate linkage appear to involve the carbon and nitrogen atom

[13] For different opinions cf., e.g., the remarks on parachor and dipole moments of organic sulphur compounds in E. Bergmann, L. Engel, and S. Sandor, Zeits. f. physik. Chemie **B10**, 397 (1930).

* These two effects (of which only the former may be excluded in time by sufficient measurements in the gaseous phase) constitute inherent difficulties for any theory of bond moments and no greater or stricter additivity can be expected for one system, than for another.

** *Note added in proof:* A paper on bond moments and higher valence states is in preparation, which appears to lead to similar conclusions as have been obtained for the parachor in Part I.

and we shall confine ourselves to a discussion of the influence on the dipole moments exerted by a change of valency of these two atoms in a number of molecules.†
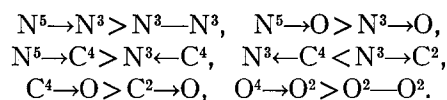
It may be seen from a comparison of the one radical the moment of which we know experimentally, i.e., nitric oxide, with the nitroso group, that this effect, which forms the basis of discussion here, really exists. The NO molecule differs from the $-N{=}O$ group by possessing a free odd p electron while for the latter the same electron is shared by another atom. The dipole moment of nitric oxide is 0.1D or less, the bond moment of the nitroso group is 2.0D. The transfer of a single electron of the N atom to an orbital on which it links another atom and is shared by it, reduces the negative charge on the positive end of the moment to such an extent that the latter is increased by 2 units.

The ozone molecule forms another typical example. From the discussion of the preceding section it has been seen that the dipole moment of 0.5D is too small for a semipolar double bond (or a resonance formula involving more than about 3 percent of an ionic parent structure), but its existence also rules out any formula based on three equivalent O atoms. The molecule therefore shows the existence of a moment between two oxygen atoms, one being in the divalent, the other in the tetravalent state. Because the ionization potential of oxygen is higher than that of sulphur, the dipole moment is quantitatively lower but otherwise similar to that of SO_2. Quite generally, namely, as long as bond angles, etc., remain unchanged, the bond moments should increase with the higher electron affinity of the negative and/or the lower ionization potential of the positive partner (e.g., $H-Cl=1.03>H-Br=0.78$, but $As-Cl=1.64 <Sb-Cl=2.6$).

From the point of view of the orbital method, the existence of this type of moment always has been evident. The polarity of the bond can be obtained from the sum of ionization potential
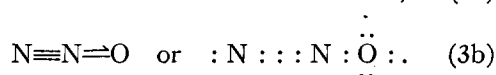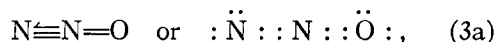
plus electron affinity of either atom, and the ionization potential of an atom obviously varies in different states of valency, in which different groups of electrons are involved. Indeed, the effect which is made the basis of discussion here is intimately related to the procedure successfully used by Mulliken[14] for the calculation of electro-affinities and for related problems. In the following it is attempted to find a qualitative understanding of the additivity of bond moments on the basis of classical structures.

As both the ionization potential and the electron affinity change in the same sense, in a homologous series a comparison of the former is sufficient to estimate the change of dissymmetry of the field and therefore the polarity of the bond. The mean ionization potentials again may conveniently be used, and a glance at the table in Part I of this paper shows, that the following moments will exist (here and later the superscripts designate different states of covalency, not ionic charges!):

$$N^5{\to}N^3 > N^3{-}N^3, \quad N^5{\to}O > N^3{\to}O,$$
$$N^5{\to}C^4 > N^3{\leftarrow}C^4, \quad N^3{\leftarrow}C^4 < N^3{\to}C^2,$$
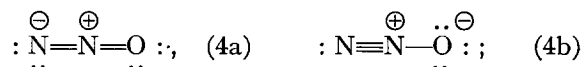$$C^4{\to}O > C^2{\to}O, \quad O^4{\to}O^2 > O^2{-}O^2.$$

This method of estimating the polarity of the bond by means of the dissymmetry of the axial field has the advantage of being based on directly observed quantities.

Nitrous oxide will serve as a typical starting point. Its electric moment is low, $\mu=0.1$ to 0.2D. As the moment of N_2 is of course zero, while the NO structure shows quite a large moment in the nitroso group ($\mu=1.65$ to 2.0D) the small moment of N_2O was thought to require special explanations. Thus Sutton[15] gives the two formulae (3a) and (3b).

$$N{\equiv}N{=}O \quad \text{or} \quad :\overset{..}{N}::N::\overset{..}{O}:, \quad (3a)$$

$$N{\equiv}N{=}O \quad \text{or} \quad :N:::N:\overset{..}{O}:. \quad (3b)$$

Pauling[3] accepts these two structures, but writes them closer to Lowry's concept of the semipolar double bond thus:

$$\overset{\ominus}{:}\overset{\oplus}{N}{=}N{=}O:, \quad (4a) \qquad :N{\equiv}\overset{\oplus}{N}\overset{..\ominus}{-}O:; \quad (4b)$$

† All dipole moments of molecules mentioned without reference are taken from the compilations in Trans. Faraday Soc. 30 (1934). All bond moments for which no reference is given refer to those calculated by C. P. Smyth [J. Am. Chem. Soc. 60, 183 (1938) and earlier] which have been used as the basis of the following calculations. Inter-nuclear distances are taken from L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936), if not mentioned otherwise.

14 R. S. Mulliken, J. Chem. Phys. 3, 573 (1935).
15 L. E. Sutton, Trans. Faraday Soc. 30, 789 (1943).

showing more clearly that the semipolar double bond involves the complete transfer of an electron from one atom to another. On the basis of known or plausible internuclear distances the bond moment of these forms may be computed. For N_2O only the sum of both distances has been measured to $2.38 \pm 0.05A$ by electron diffraction and 2.31A from spectroscopic data.[16] However, this is sufficiently near to the sum of Pauling's covalent radii, *viz.*, 1.10 for $N \equiv N$ and 1.18 for $N = O$. Using such values Sutton is able to calculate the moments of the two structures thus:

$$\overset{\ominus}{:}\overset{\oplus}{N} = N = O : \quad (4a) \quad \text{and} \quad : N \equiv N - \overset{\oplus}{O} \overset{..}{:} \overset{\ominus}{} \quad (4b)$$
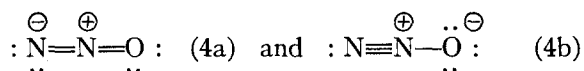
$$\overset{+\!\!\!+ \quad +\!\!\!\!\rightarrow}{\mu = 5.3 - 1.65 = 3.65} \quad \overset{+\!\!\!\!\rightarrow +\!\!\!\!\rightarrow}{\mu = 0 - 5.8 - 0.8 = -6.6.^*}$$

It is now assumed that resonance exists between the two structures, (a) contributing so much more that the small moment of about $\mu = 0.1$ is observed. Agreement with experimental facts of course can always be achieved this way.

In the alternate theory nitrous oxide possess the simple structure $N \equiv N = O$, or, as electronic formula

$$: N ::: N :: \overset{..}{O} : \quad (5)$$
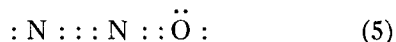
in which the triple and double bond consists of 3 and 2 pairs of electrons, half being contributed by either atom. However, comparing N_2

$$: N ::: N : \quad (6)$$

with (6) it is immediately evident that an electric moment is produced by the change of the valence state of N. In the transition from N_2 to N_2O, the central N atom partially loses two electrons now shared with O; it becomes a center of positive polarity and the $N^3 \equiv N^5$ group is no longer symmetrical but will possess an electric moment of considerable strength. At the same time and for the same reason the moment of the $N^5 = O$ group must be much larger than that of the $N^3 = O$ group, the positive character of N being enhanced by the partial removal of

two electrons. Taking the experimental results at their face value, the dipole moment of nitrous oxide can be used to determine the moment of the $N^3 \equiv N^5$ group. The N^5 atom being the positive center, the small moment of N_2O is but the very natural result of two opposing moments. The $N^5 = O$ moment cannot be that of the nitroso group in which N is trivalent. The nitro group exhibits about the same internuclear distance (1.21A) as $N = O$ in N_2O, and its moment of 3.3D will be that of the $N^5 = O$ bond. It is larger than the $N^3 = O$ moment of the nitroso group quite in keeping with the view developed here.

The moment of N_2O may now be described thus:

$$N^3 \equiv N^5 = O$$
$$\overset{+\!\!\!+ \quad +\!\!\!\!\rightarrow}{\mu = -3.1 + 3.3 = 0.2,}$$

and there remains only to show that this is not an assumption *ad hoc*, but that a similar moment of $\mu = 3.1$ is associated with the group $N^5 \equiv N^3$ in other molecules too.

Attention may therefore be drawn to the organic azides and diazo compounds both frequently quoted as standard examples of molecules containing the semipolar double bond or resonating between corresponding ionic parent structures. The older structural formula $R - N = N \equiv N$ has already been found entirely sufficient to calculate the molecular parachor (Part I of this paper). It will be seen that this formula and the related one $R_2 = C = N \equiv N$ for the diazo compounds are entirely sufficient to describe their dipole moments and also the internuclear distances.

For this purpose, however, it is necessary first to evaluate the bond moments of the groups $N^5 = N^3$ and $N^5 = C$. It should be possible to calculate these directly from the known moments of normal and iso-azoxybenzene, and of the N ethers of the benzaldoximes, used by Sutton and Taylor[17] to determine the isomeric forms. But the uncertainty as to valence angles prevents such a calculation without further experimental data.* Fortunately rough values of bond mo-

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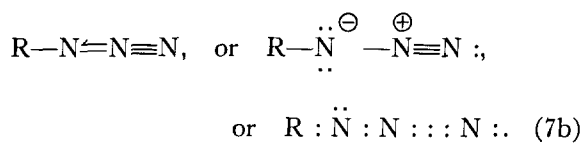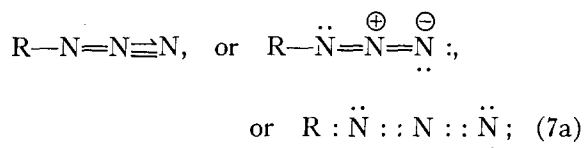[16] E. K. Plyler and E. F. Barker, Phys. Rev. **38**, 1827 (1931).

* The moments 5.3×10^{-18} and 5.8×10^{-18} are the charge of the electron, 4.8×10^{-10} multiplied with the distances 1.1×10^{-8} and 1.2×10^{-8}, respectively, $\mu = 1.65$ is the moment of the nitroso group $R - N = O$, $\mu = 0.8$ half of it, the double bond being replaced by a single bond.

[17] L. E. Sutton and T. W. J. Taylor, J. Chem. Soc., p. 2190 (1931); p. 63 (1933).

* Substituting a few extreme values of the valence angle, it can be seen that the $N^5 = N^3$ moment probably will be between 1.5 and 2.0D, directed against N^3, the $C^4 = N^5$ moment between 1.0 and 1.5D pointing against C, both directions in agreement with the present view.

ments, as so often in the past, can be obtained by a number of different extrapolations. For the $N^5=N^3$ moment a rough value would be two thirds of the $N^5\equiv N^3$ moment, or 2.0D. But as the polarity depends on the ionization potentials and electron affinity, a better way is offered by the great similarity of the positive atoms C^4 and N^5 and the negative atoms O^2 and N^3. As $\mu(C^4=O)$ is higher than $\mu(C^4=N^3)$ by $2.5-0.9 = 1.6$, and as the same factors are working in both cases, $\mu(N^5=O)$ should be about as much higher than $\mu(N^5=N^3)$ and the latter therefore about 1.7D, particularly as the internuclear distance of both are almost identical. The moment of $N^5=C$ cannot be obtained this way, because the mean ionization potential indicates a change of sign, if compared with $N^3=C$. Hence, falling back to the first procedure, we calculate $\mu(N^5=C)$ by adding two thirds of 3.1 for the valence change to $\mu(N^3=C)$, $-0.9+2.0 = 1.1$, and adding an allowance for the increase of bond distance as compared with $N\equiv N$, we choose 1.5D as a rough final value.

The dipole moments of the azides, to which we now may turn, have been determined by Sidgwick, Sutton, and Thomas[18] to between 1.4 and 1.6D pointing away from the organic radical. Sidgwick[19] and Pauling[3] again assume resonance between two structures, which may be written in different ways as follows:

$$R-N=N\rightleftharpoons N, \quad \text{or} \quad R-\overset{\cdot\cdot}{\underset{}{N}}=N=\overset{\oplus}{N}\overset{\ominus}{\underset{\cdot\cdot}{}} :,$$

$$\text{or} \quad R : \overset{\cdot\cdot}{N} : : N : : \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}; \quad (7a)$$

$$R-N\rightleftharpoons N\equiv N, \quad \text{or} \quad R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}\overset{\ominus}{}\quad-\overset{\oplus}{N}\equiv N :,$$

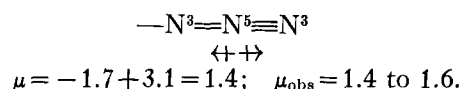$$\text{or} \quad R : \overset{\cdot\cdot}{N} : N : : : N :. \quad (7b)$$

As for N_2O, opposing moments of the order of $\mu=4$ are estimated, both contributing to the empirical value. In the present view the azides have to be represented by the formula:

$$R-N^3=N^5\equiv N^3 \quad (8)$$
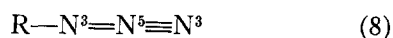
[18] N. V. Sidgwick, L. E. Sutton, and W. Thomas, J. Chem. Soc., p. 406 (1933).
[19] N. V. Sidgwick, Trans. Faraday Soc. 30, 801 (1934); Chem. Rev. 19, 183 (1936).

and their moment by

$$-N^3=N^5\equiv N^3$$
$$\overset{\leftarrow+\,\rightarrow}{}$$
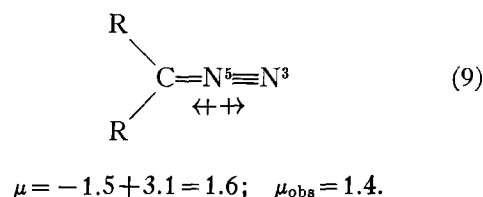$$\mu = -1.7+3.1 = 1.4; \quad \mu_{obs} = 1.4 \text{ to } 1.6.$$

A better agreement cannot be expected. The internuclear distances have been measured by electron diffraction and agree perfectly well with those calculated on the basis of the formula (8) thus:

$$H_3C-N=N\equiv N$$

r [observed]:	1.47	1.24	1.10	±0.02A.
r [calc. for (8)]	1.47	1.22	1.10.	
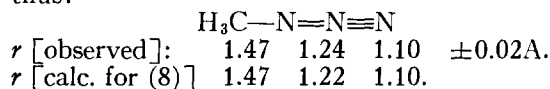
Bond distance, bond moments, and parachor agree exceedingly well with formula (8). Any other one being a highly excited term of the molecule, it seems to be overwhelmingly represented by this classical structure.

The aromatic diazo compounds R_2CN_2 suggest themselves as a further instance to check the present procedure. Their dipole moments have been determined by Sidgwick, Sutton, and Thomas[18] ($\mu=1.4$) and their formula has been discussed by Sidgwick[19] at various occasions on the basis of coordinate or resonating structures, similar to those of the azides. Without repeating the previous argument their structure and moments may be represented immediately by the classical formula thus:

$$\begin{array}{c} R \\ \diagdown \\ C=N^5\equiv N^3 \quad (9) \\ \diagup \quad \overset{\leftarrow+\,\rightarrow}{} \\ R \end{array}$$

$$\mu = -1.5+3.1 = 1.6; \quad \mu_{obs} = 1.4.$$

A better agreement could not be expected. As to the bond distances, a linear structure with $r(CN) = 1.34\pm0.05$A and $r(NN) = 1.13\pm0.04$A has been observed, against 1.28 and 1.10A, respectively, calculated for structure (9). Again it is obvious that this classical formula agrees perfectly well with both molecular constants and there is no need to amend it in any way.

At the same time it is shown that the moment of 3.1D, produced by the change in the state of valency, is constant and definitely associated with the $N^5\equiv N^3$ structure both for the azides and diazo derivatives.
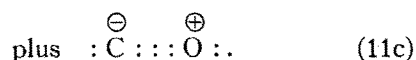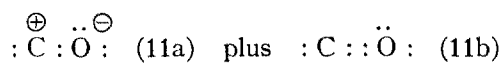
The second group of molecules most often said

to establish the existence of a semipolar double bond or the fact of enhanced resonance in simple inorganic molecules is that formed by divalent carbon. In the same way the change of bond moments produced by the change of valency of this atom may be used to throw light upon their structure.

The bond moment of carbon monoxide is small, $\mu = 0.1$, that of the carbonyl group large, $\mu = 2.5$. Hence for the former the formula

$$\overset{\ominus}{C} \overset{\oplus}{\equiv} O \quad \text{or} \quad : \overset{\ominus}{C} = \overset{\oplus}{O} : \quad \text{or} \quad : C ::: O : \quad (10)$$
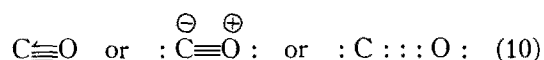
has been suggested.[20] Pauling[3] assumes resonance between this structure, the ordinary structure $C^2 = O$, and a third one in which C is a positive and O a negative ion, linked by a single bond, thus

$$\overset{\oplus}{:} C : \overset{..}{\underset{..}{O}} : \overset{\ominus}{} \quad (11a) \quad \text{plus} \quad : C :: \overset{..}{O} : \quad (11b)$$

$$\text{plus} \quad : \overset{\ominus}{C} ::: \overset{\oplus}{O} : . \quad (11c)$$
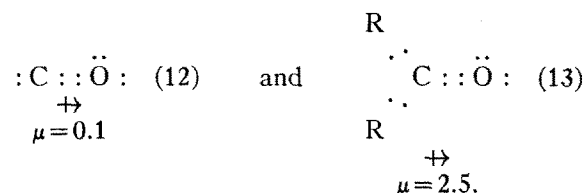
One of the reasons for introducing the third structure (11a) is the good agreement between the observed internuclear distance of 1.13A with the sum of the covalent radii for the old formula (11b), which is 1.15A. This indicates structure (11b) as the only one present; any resonance of $C = O$ (11b) with $C \equiv O$ (11c) makes the straightforward empirical result not understandable. Therefore, a third structure (11a) has to be assumed in such a way that (11a) and (11c) cancel each other out entirely [both together representing a molecule with $\frac{1}{2}(1+3) = 2$ normal covalent bonds and no charges on either atom]. All three together in reality amount only to the classical formula (11b). This structure, to our mind, is in entire agreement with the electron configuration of C $(s^2 p^2)$, only the p electrons being active, as in N^3, etc., and the chemical and physical properties of the molecule. If therefore it could be shown that the dipole moment does not force resonance upon the carbon monoxide molecule, nothing would prevent the acceptance of the old formula $C^2 = O$.

This can in fact be done, the only difficulty

[20] D. L. Hammick, R. G. A. New, N. V. Sidgwick, and L. E. Sutton, J. Chem. Soc., p. 1876 (1930). Cf. references 15 and 19.

being the small number of compounds formed by divalent carbon. The best way therefore appears to calculate the effect of the change of valency from C^4 to C^2 as indicated by CO, and then to see whether a similar value again occurs in the isocyanides $R - N = C^2$.

Again taken as they are found, and without any theoretical assumption as to a change of linkage, the empirical results of dipole measurements lead to the following simple structures for the CO group in carbon monoxide (12) and in the carbonyl radical (13):

$$: C :: \overset{..}{O} : \quad (12)$$
$$\overset{+\!\!\!+}{}$$
$$\mu = 0.1$$

$$\text{and} \quad \begin{matrix} R \\ \overset{..}{} \\ \overset{.}{C} :: \overset{..}{O} : \quad (13) \\ \\ R \\ \overset{+\!\!\!+}{} \\ \mu = 2.5. \end{matrix}$$

In the first, the C atom forms the positive end of the moment, but only its p electrons are chemically active, the two remaining electrons of its symmetrical s^2 group still screen the nuclear charge. The four bonding electrons are in the field of O^{6+}, screened by 4, and C^{4+} screened by 2 electrons, the dissymetry of the axial field is therefore slight. In the other structure, the two s electrons (one having been excited) now are chemically active, i.e., occupy molecular instead of atomic orbitals. They belong partially to the organic radicals; their screening effect has diminished almost to the vanishing point. This amounts to a large positive charge having been added to the positive end of the $C = O$ dipole. No special theoretical concept is necessary to understand fully the difference of moment. Therefore, it may be stated, that this difference most certainly does not provide evidence for the existence of resonance of the CO molecule with ionic parent structures, in which more than 2 of the p electrons of oxygen take part in the linkage.

From this it would appear that the valence change of C produces an increase of the $C = O$ moment of 2.4D. While the moment calculated for the $N^5 \equiv N^3$ group in one molecule could be shown to exist also in others, such a simple procedure is not possible in the case of $C^2 = O$, the carbon atom being divalent only in the combinations $C = O$ and $C = N -$. This new value therefore has to be compared with the bond

moment of the iso-cyanides. Although the molecule CO and the radical C≡N— are quite similar in some respects, they are not identical. In particular, the internuclear distance is 1.13A in CO and 1.17A in CN—, and the moment as the product of both, charge and distance, is as sensitive to the one as to the other. Two pairs of electrons shifted a distance of 0.04A would produce an addition to the moment of 0.8D. Added to the above value, 3.2D obtains, and the moment of —N^3≡C^2 in the isocyanides should be smaller by this amount than that of —N^3≡C^4= of the isocyanates.

The isocyanides form straight chains,* and their dipole moments have been measured by Hammick, New, Sidgwick, and Sutton,[20] together with their parachors, which have been discussed in Part I of this paper. Their measurements on substituted benzenes show clearly that the NC bond moment points toward C and for the moment of the isocyanide group a value of 2.3D is obtained. They formulate the group as

$$-N≡C \quad \text{or} \quad -\overset{\oplus}{N} ::: \overset{\ominus}{C} : \qquad (14)$$
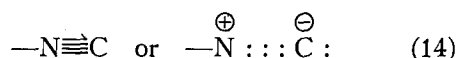
and consider the moment as that of the cyanide group superimposed on a second one of opposite sign produced by the transfer of an electron along the whole internuclear distance. Pauling believes the radical to resonate between this structure (14) and the older Nef formula

$$-N=C^2 \quad \text{or} \quad -\overset{..}{N}::\overset{..}{C}. \qquad (15)$$
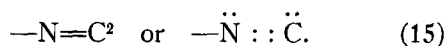
Incidentally, the internuclear distance is observed to 1.17± 0.02A; the sum of Pauling's covalent radii (with the usual allowance for the incomplete valence shell of C) comes to 1.19. Hence even on this basis and taking the internuclear distance as the main indicator, no resonance with (14) is required and the sole use of the Nef formula is entirely justified.

On the basis of the formula —N^3≡C^2, the bond moment may be compared with that of —N^3≡C^4, thus:

O :: C :: N̈—R   C̈ :: N̈—
    ⇥   ⇤
$\mu = 0.9$ $\mu = 0.9 - 3.2 = -2.3$;
                      $\mu_{obs} = -2.3.$

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* As carbon is divalent, they are entirely different from the oximes and no conclusion as to the type of linkage could be based on a comparison of the valence angles of both.

In other words, the return of two previously shared electrons into the s^2 group of the C atom, when becoming divalent, screens the field of the C^4 nucleus and adds additional negative charge to the C— end of the moment. Using for the latter the figure calculated from carbon monoxide, a moment obtains which has the correct numerical value and the right direction. Although this is a very simple and straightforward interpretation, the scarcity of molecules formed by divalent carbon with which to compare molecular constants makes a further and a more conclusive analysis impossible.

The numerical values used here certainly are very rough, and the preceding calculations do not pretend to be more than a short preview of a future detailed calculation. But even so these few examples are sufficient to show a separation of dipole moments into bond moments according to the state of valency of the positive atom to be entirely practicable and workable. This may be said with even greater confidence as the molecules chosen here are just those often considered as standard examples for the existence of additional varieties of covalent bonds.

The fundamental difference of the two representations may be demonstrated by considering again the linkage of the simple molecule CO. The observed fact is that the moment is smaller than that of the carbonyl group. According to Sidgwick it is a triple bond, the third link produced by 2 additional electrons of oxygen. In Pauling's terminology this bond is represented by resonance with a structure in which C is a negative, O a positive ion. In the present representation the greater negativity of C as compared with the carbonyl carbon is produced by its own s^2 electrons. Therefore only two and not four electrons of the oxygen take part in the linkage at any time. The bond is an ordinary covalent double bond. The polarity of this bond is very slight because the fields of the two nuclei are very similar as long as C is divalent. This may be represented by an exceedingly slight resonance of the Nef structure (12) with Pauling's structure (11a), but not with (11c). The almost vanishing smallness of the ionic contribution is again indicated by the bond distance calculated for the Nef structure, being almost identical with the observed one. This representation is not only

in accordance with all observed facts, straightforward and simple, but it also has the additional advantage that oxygen in linkage with carbon has not suddenly become the positive partner, entirely contrary to its electron affinity and to the observable and known ionization potentials of both.

It is beyond the scope of this paper to extend this procedure to other molecules, determining, for example, the different values of the S=O bond moment according to the valence state of S. The differences will be less marked, as can be seen from the ionization potentials, but a similar set of values could be derived. However, attention should be drawn in passing to the new evidence brought forward recently by Sutton et al., indicating very definitely that such bonds are ordinary covalent double bonds.[21] Bond distances of 1.4, 1.5, and 1.9A having been observed[22] for S=O, P=O, and P=S, respectively, it has been computed that their moments should be 6.9 to 9.3D if they are semipolar double bonds, i.e., structures with large ionic contributions. The experimental bond moments are only 2.16, 3.5, and 2.5D in solution[23] and 2.0 to 2.5, 3.5, and 2.5D, respectively, in the gaseous state.[24] Conditions are similar for N=O in trimethylamine oxide.[25] Although these calculations of the bond moments neglect by necessity the ordinary induction effect and also that of the change of valency, the order of magnitude must be correct, and no such objection can be raised against the low value of the S=O moment in SO₂. The dipole moment therefore again decides against the coordinate linkage or enhanced resonance with ionic structures in such molecules as SO_2, $SOCl_2$, $POCl_3$, etc., which have been taken as its prototype for such a long time.

Polarity and resonance are made use of in

modern physico-chemical theories for the rationalization of such concepts as acid strength or reactivity. It is not likely that excessive changes would be brought about in these theories by the present interpretation. The electric moments are observed facts and the results of their working cannot be affected by the causes to which we attribute their existence. We may obtain a different theoretical model but similar results of actual calculation. Thus, the ionic contributions (viewed either as resonance with ionic parent structures or as an electric strain of the covalent bond) in the present view is much reduced for a great class of molecules, e.g., for the nitro group from 100 percent to 13 percent. In theories of acid strength, to take these as an example, the "resonance" factor would almost vanish but the new effect of valence change will take its place. The effective field of the central atom will increase its strength in the higher valencies compared with the lower ones, where it is screened by its two s electrons. A general shift of the electrons in the direction of the central atom results. This may be added to the inductive effect, and different inductive factors for the same atom in different states of valency will take the place of the resonance factor. Such a model automatically should work just as well as the description by means of resonance because both are equivalent interpretations of the same fundamental wave mechanical concepts.

4. BOND DISTANCES

The bond distances again belong to the class of additive constants of the molecules which is discussed here. The distance between the nuclei, it is true, is directly observed, but any conclusion as to the chemical structure of the molecule is based on the separation of the bond distance into contributions of the constituent atoms.[26] Although conditions are slightly different for the bond distances than for other constants, it happens that one constant per atom is not sufficient to represent the experimental values and therefore different subdivisions according to various theoretical viewpoints are again pos-

[21] L. E. Sutton, Ann. Repts. **37**, 74 ff. (1940), London, 1941.
[22] Cf. literature in reference 21.
[23] C. P. Smyth, J. Am. Chem. Soc. **60**, 183 (1938); C. P. Smyth, G. L. Lewis, A. J. Grossman, and F. B. Jennings, *ibid.* **62**, 1219 (1940).
[24] I. E. Coop and L. E. Sutton, Trans. Faraday Soc. **35**, 505 (1939).
[25] Cf. reference 21. As compared with the nitro group, the bond distance is increased from 1.21 to 1.36A. Hence the increase of the moment from 3.3 to 4.38D does not call for a special explanation by means of an enhanced contribution of an ionic structure. This moment represents a shift of two pairs by about 16 percent of the bond distance.
[26] Values of a covalent radii are taken from Pauling, reference 3. Cf. also V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941) for influence of polarity.

sible. Besides the different values of the additive covalent radii for multiple bonds, a number of factors have been made responsible for the deviations between the observed and calculated values, among them the variations of polarity or of the contributions of different structures, an incomplete valence shell (which amounts, e.g., for C to different radii for different valence states), and different quantum numbers of the binding electrons. The change of valence state, of course, has often been considered as a decisive factor, and might be called upon to solve a number of difficulties if considered *in conjunction* with a polarity factor and with the different role of an atom as the positive or negative partner in a molecule.

The discussion of this particular property of the molecules is made more difficult at this time because the experimental evidence is still rapidly changing. New evidence brought forward recently[21] has shown the whole question to be more complex than originally thought. Very roughly the present situation may be described as follows: Among organic molecules the observed bond distances agree with the theoretical ones with the exception of some molecules of enhanced polarity [cf. fluorides or the differences of the $N^5{=}O$ distance in the nitro group (1.21A) and amine oxide (1.36A)].

Among the organic molecules some indication of an influence of different states of valency is apparent, e.g., Pauling's reduction of 0.09 for C in CO as allowance for incomplete valence shell. If, however, the experimental CO distance in the carbonyl group is compared directly with that in carbon monoxide without regard to the theoretical value, it is found that it sometimes has the same value (CO_2, CH_2O, CH_3COCl) and sometimes the higher theoretical value ($COCl_2$, CH_3CHO).

Among inorganic molecules, i.e., taking into consideration a greater number of different atoms, the bond distance is found to be remarkably insensitive to a change of valence. For instance, the SO distance is identical in SO_2, $SOCl_2$, SO_3, SO_2Cl_2, and even agrees not too badly with the spectroscopical value of SO. On the other hand the bond distances do not agree well with the theoretical values any longer, some being too large and most of them too small. The discussion

has not reached a definite conclusion; serious objections have been raised against various suggested explanations. It appears to be evident, however, that the polarity of the bond is one of the determining factors, although perhaps not the only one. Another simply might be that the additive covalent radius say of S, obtained from S_8 molecules, works satisfactorily only in simple organic molecules in which this atom almost invariably is the divalent negative partner, but not in SO_2, where it forms the positive end of the dipole and is tetravalent. An introduction of a polarity factor, while improving some of the older agreements, impairs others. But this may be recorrected by a constant for valence change.

TABLE I.

Molecule	Bond	Bond distance observed	calculated for the classical structure of column 1
$-N^5{\displaystyle\nwarrow^{O}_{O}}$	$N^5{=}O$	1.21±0.02	1.18
$N^3{\equiv}N^5{=}O$	$NN{+}NO$	2.31 to 2.38	2.28
$-N^3{=}N^5{\equiv}N^3$	$-N^3{=}N^5$	1.24±0.02	1.22
	$N^5{\equiv}N^3$	1.10±0.02	1.10
$>C{=}N^5{\equiv}N^3$	$C{=}N^5$	1.34±0.05	1.28
	$N^5{\equiv}N^3$	1.13±0.04	1.10
$C^2{=}O$		1.13	1.15
$-N^3{=}C^2$		1.17±0.02	1.19

In this rather complicated situation it is not easy to appeal to the bond distance for definite guidance as to the structure of a molecule for which different concepts are possible. We confine ourselves therefore to the statement that in all those standard examples which we have considered (Section 3), i.e., the molecules $-NO_2$, $N{\equiv}N{=}O$, $-N{=}N{\equiv}N$, $>C{=}N{\equiv}N$, $C{=}O$, and $-N{=}C$, the bond distances are in excellent agreement with these classical structures. They are summarized in Table I (in which the superscripts again mark the state of valency, not electric charges).

In the case of resonance of two structures, of which the first has a higher and the other a lower theoretical value if compared with the experi-

mental one, agreement can always be achieved by assuming an appropriate percentage contribution of each form. This is not possible if only one classical formula serves as the basis of calculation and this surprising agreement is therefore even more convincing. It appears therefore extremely difficult to avoid the conclusion that no objections can be raised on the grounds of bond distance against an interpretation which considers the classical structures (including those of pentacovalent nitrogen) as the nearest approach to reality.

5. BOND ENERGIES

Finally, the bond energies have to be discussed. However, only a few words are necessary here. The experimental facts are similar to those observed for other molecular constants. If from the heat of formation the heat of dissociation D of the gaseous molecule into gaseous atoms is calculated,[27] e.g., for PCl_3 a value of 343 kcal./mole obtains, i.e., an average bond energy D_B of the $P-Cl$ bond of 87. The same procedure gives the smaller value of $D_B = 69$ for the $P-Cl$ bond in PCl_5. One way to account for this difference is to assume two of the chlorine atoms to be linked to phosphorus differently as compared with the others. However, the other alternative is to consider the valence change of the central atom. While the Cl atoms in PCl_3 are linked by the three p electrons, for the transition to PCl_5 the two inert s electrons have to be activated. The fission of the s^2 group, i.e., an excitation of the PCl_3 molecule, absorbs energy to such a considerable extent that the ground level of PCl_5 lies much closer to that of PCl_3 as it would do if PCl_5 were formed by a combination of unexcited PCl_3 and two unexcited Cl atoms. This has been discussed at length in connection with the dissociation spectra of a great number of inorganic and organic molecules;[27, 28] a general rule applicable for every spectrum investigated so far, could be formulated, and in the case of SO, SO_2, and

SO_3 where most spectroscopical data are available, an energetical interpretation of what is called the semipolar double bond could be given.[29] According to this interpretation the true bond energy of $S=O$ in SO_3 is not diminished, but the energy of the reaction SO_2+O does not measure it, because the ground level of SO_2 is not the term from which that of SO_3 originates. To our mind this interpretation is definitely established, because this energetical relation of the ground levels of SO_2 and SO_3 is independently confirmed. If, for instance, unexcited (diamagnetic) SO_2 and unexcited (paramagnetic) O would combine to give the ground level of SO_3, this would be a paramagnetic molecule. But as is well known, all the molecules to which this reasoning applies, i.e., PCl_5, $POCl_3$, $PSCl_3$, SO_3, $SOCl_2$, Cl_2O_7, etc., are diamagnetic.

The bond energies therefore constitute a molecular constant which again could be divided into additive increments in different ways and in accordance with either of two discordant chemical theories, only that in this case the one favoring the coordinate bond of such molecules appears to be ruled out by conflict with the experimental spectroscopical and magnetic evidence.

A short discussion of Pauling's procedure to calculate directly the contributions of the ionic structures to the energies of the various bonds may be inserted at this point. It has been pointed out above (Section 1) that such estimates according to different theories do not agree for a number of typical molecules. It can be seen that this is due to certain basic energy values. Their determination in our view has not reached a point where conclusive deductions could be reached for these controversial structures.

First of all, Pauling's system of electronegativities is based on a set of single bond energies stated to be devised for use in connection with what is called the "normal" covalence of the atoms. These are 4 for C, 3 for N and P, etc., in contradistinction, e.g., to pentavalency of P. Hence, for instance, the (mean) single bond energy of $N-H$ is taken from the atomic heat of formation of NH_3, and in its ground level this molecule dissociates indeed into unexcited N and

[27] R. Samuel, "Report on absorption spectra and chemical linkage," Ind. Acad. Sci. (Bangalore, 1935). R. K. Asundi and R. Samuel, Proc. Phys. Soc. (London) **48**, 28 (1936). Asundi, Samuel, and Jan-Khan, Proc. Roy. Soc. **A157**, 28 (1936). R. Samuel *et al.*, Proc. Phys. Soc. (London) **48**, 626 (1936); **49**, 679, 568 (1937); E. Bergmann and R. Samuel, J. Org. Chem. **6**, 1 (1941).
[28] K. Butkow, Zeits. f. Physik **90**, 810 (1934).

[29] R. Samuel, Proc. Ind. Acad. Sci. **6**, 257 (1937).

3 unexcited H atoms. The bond energy therefore is identical with the adiabatic energy of dissociation. But this is not the case for CH_4 or SiH_4 as has been discussed above. The atomic heat of formation refers again to a system of unexcited atoms, but the ground level of CH_4 does not originate in the term of $C(s^2p^2)$ but of $C(sp^3)$, i.e., a highly excited term of the radical CH_2. What is called bond energy in such a case is not the energy necessary to remove H from C by an adiabatic excitation of the vibrational levels as before. It is a contribution to the heat of reaction counted from the (more or less arbitrary) level of the unexcited atoms.

From these remarks it is evident that we can safely compare the atomic energies of dissociation of bonds formed by C^2, N^3, S^2, and S^4, etc., among themselves, and probably also of those formed by C^4, Si^4, N^5, P^5, S^6, etc., among themselves. But as one group of values represents real energies of adiabatic dissociation, the other does not, it is by no means obvious whether a comparison from one group to the other is permissible.

Another point to be considered is the actual values of the single bond energies used. Only one of them may be mentioned here, i.e., that of the $C-O$ bond. It is particularly interesting because on its value is based the calculation of the partial ionic character of many important molecules. As the $C-O$ bond shows 22 percent ionic character, that of the $C=O$ bond in the ketones, for example, is assumed to be about 44 percent. The ionic resonance energy of $C-O$ is calculated as the difference of $D(C-O)$ with the mean of the $C-C$ and $O-O$ bond and for the latter a value of 34.9 is calculated from $D(H_2O_2)$. However, this value is evidently unacceptable. The single bond energies of $S-S$ and $Se-Se$ are calculated to be 63.8 and 57.6, respectively, and there is only one sequence possible, that in which $D(O-O)$ is higher than both. The dissociation energies of the double-bonded diatomic molecules* are directly known from the band spectra as $D(O_2) = 117.4$, $D(S_2) = 43.7$, i.e., in their proper order. As is well known from band spectra, hydrides behave differently from other molecules

and exhibit an electron configuration closely approaching that of the "united atom." The too low value in H_2O_2 therefore probably is due to its bond energy bearing no relation to the linkages of oxygen to heavier atoms. As that of the $S-S$ bond is independently calculated by Pauling from the S_8 molecule (that of $Se-Se$ appears to be less certain), we may estimate $D(O-O)$ as about three-quarters of $D(O_2)$ or about 72 kcal./mole. With such a value the ionic character of the $C-O$ bond would be about 7 percent only.

A similar argument concerns the direct calculation of the resonance energy of the $C=O$ double bond of the carbonyl group. The above value of $D(O_2)$ is that of the $^3\Sigma$ ground level, i.e., a structure with two unpaired electrons such as $-O=O-$ or $>O=O$. We are not able to consider such a structure as partially due to a three-electron bond, but as a normal covalent bond disturbed and weakened by the unpaired electrons. This conception has been used to explain the strange increase of bond energy on excitation, known from the band spectra of many molecules. The excitation of an unpaired electron always increases the energy of formation of the molecule[30] whether such an electron is premoted (as in NO) or non-premoted (e.g., N_2^+), whether the nuclear fields are (nearly) equal and permit an explanation by means of a three-electron bond changing into another one, or whether the fields are unequal (e.g., AlO, AsO, SiF, SnCl, BeF, etc.) and no three-electron bond is possible. Hence, considering the $^3\Sigma$ term of O_2 not as a special case but as one of a great number of molecules with unpaired electrons, we shall estimate for the undisturbed structure $: \overset{..}{O}=\overset{..}{O} :$ ($^1\Sigma$) a value not lower but higher than $D(O_2)$, and according to the behavior of NO, a very considerable increase may be expected, again decreasing the ionic character of $C=O$ to about 10 to 20 percent. Such a figure can be verified from the bond moment ($\mu = 2.5D$) of the carbonyl group. To produce this moment, the group of 4 binding electrons has to be shifted 0.13A towards the O atom, or about 11 percent of the distance. To our

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* In literature sometimes slightly different values are used for S_2. Cf. R. K. Asundi and R. Samuel, Proc. Ind. Acad. Sci. 3, 466 (1936) and later references (27 and 29) for the above values.

[30] H. Lessheim and R. Samuel, Zeits. f. Physik 84, 637 (1933); Phil. Mag. 21, 41 (1936). R. K. Asundi and R. Samuel, Proc. Ind. Acad. Sci. 3, 346, 467 (1936); 5, 244 (1937).

mind, such bonds therefore are best described as covalent bonds with a slight polarity superimposed on them.

6. NATURE OF THE SPECTROSCOPICAL EVIDENCE

At the end of this necessarily lengthy analysis, the position which emerges from the maze of molecular constants, their working, and their separation into different additive components is quite clearly this: Neither the parachor (molecular volume), nor molecular refractivities, nor dipole moments, nor bond distances, nor bond energies are capable by themselves of distinguishing between different covalent chemical structures or the chemical theories (classical or wave mechanical) on which they are based. In all cases a grand total is observed empirically and in order to make any theoretical progress, it has to be divided into constituent increments for the individual atoms or bonds. This can be done in different ways and the resultant system of atom or bond constants is then automatically but arbitrarily adjusted to one out of two or more equivalent sets of chemical structures and equivalent chemical theories. It is possible unambiguously to differentiate between electrovalent and covalent linkage. But it is also quite evident that such molecular constants do not possess any diagnostic quality by which different types of covalent linkage could be discovered. This situation in fact has been predicted as an *a priori* probability some time ago[7b] and the reason given for it may now be assumed to have acquired some significance. Molecular constants like those mentioned are always due to the outside electrons of the molecule. Its "volume" is determined by its attractive and repulsive potential, its dipole moment by the dissymmetrical shift of the whole electron cloud, its internuclear distance is adjusted in such a way that the energy liberated on account of the interaction of the binding electrons becomes a maximum, etc. Such molecular constants therefore always measure some property of the molecule which is determined by and is a function of *all* its electrons or at least *all* its bonding electrons. But different types of the covalent linkage are distinguished by *an individual* electron playing a different role. Hence only such experiments *a priori* are capable of differentiating between them which permit us to observe the different parts taken up by an individual electron. Up till now such experiments are known only to spectroscopy where a particular spectrum is associated with the excitation of a single electron.

In this connection it is interesting to note that those additive molecular constants lead us further which permit us to utilize spectroscopical knowledge. The dissociation energy of a gaseous molecule like SO_2 or $SOCl_2$ into gaseous atoms may be determined thermochemically and then broken up into bond increments in various ways. But the dissociation spectra of these molecules which permit observation of the rupture of the individual bond directly select for us the correct among the possible systems of subdividing the total into additive bond energies. Again electric moments of organic molecules have been separated into bond moments only because one of them, the $C-H$ moment, has been determined directly. Experimentally, this has been done, e.g., by Rollefson and Havens[31] from the variation of refractive index in the neighborhood of certain spectral lines, as suggested by Van Vleck.[32] Such a method utilizes rotational or vibrational but not electronic spectra. Consequently it may yield direct information on individual bond moments, yet it is incapable of giving a decision in such cases where the bond moment itself is well known, say of CO or $-NC$, but different interpretations are possible according to different theories involving the role of particular electrons.

Very similar conditions are met with in the attempt to utilize Raman spectra to distinguish between different structures. The Raman spectrum is useful to help to determine an unknown structure and will reveal whether, e.g., a particular double bond exists in the molecule. But again it is often unable to differentiate between two discordant interpretations of the same structure. A case in point is the Raman frequency of CO which is practically identical with that of N_2. Hence it was assumed to establish a triple bond between C and O, according to the formula $C\equiv O$. However, as was pointed out[33] this is entirely inconclusive as the Raman frequency is

[31] R. Rollefson and R. Havens, Phys. Rev. 57, 710 (1940).
[32] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).
[33] R. F. Hunter and R. Samuel, Chem. and Ind. 54, 635 (1935).

that of an harmonic oscillator, which of course the molecule is not. In reality the force constant also depends on the anharmonic constant which can be measured only in the electronic spectrum. If this is taken into account, the bond energy (and together with it the true force constant of CO) turns out to be about 30 percent larger than that of N_2. Hence a triple bond for CO cannot be established this way, the only definite conclusion being that bond energies of oxides and nitrides are not commensurable.

From this follows that only electronic spectra are qualified to distinguish between different possible structures, as in principle they determine the electron configuration of the undisturbed molecule and give a description of the process of dissociation or formation.

On the other hand, on account of this intrinsic difficulty any inference as to different covalent structures of a particular molecule and its classical or wave mechanical interpretation by necessity must be inconclusive if based on measurements of such additive molecular constants. With very sincere respect for the great ingenuity exercised in the construction of such concepts, to our mind it is not acceptable to make these additive constants or some of them the sole arbiter either for the structure of a particular molecule or for a theory of valency.

Spectroscopical evidence is yet by no means complete, particularly as far as polyatomic molecules are concerned. Still, a definite body of facts already exists. For instance, the dissociation energy determined by spectroscopical means has the same value of about 116 kcal./mole for the S=O bond in the molecules SO, SO_2, $SOCl_2$, $SOBr_2$.[27] The valence vibration is about the same in SO and SO_2, both in the ground level and the first excited state, and the energy of excitation itself very nearly the same.[34] The same valence vibration even persists as Raman frequency of $SOCl_2$. Conditions are similar, e.g., for the S—Cl bond of the same molecules as also for other bonds in molecules formed by a central atom of another family. Even for radicals, i.e., molecules unknown to the chemist like SiCl and $SiCl_2$, the same close relation of bond energy, bond frequency, and energy of excitation appears to

persist.[35] In our view it is therefore impossible to avoid the conclusion, that, for instance, the S=O bond is exactly of the same nature in SO, SO_2, and $SOCl_2$. This would exclude the three-electron bond for SO, formulae like $: \overset{..}{O} : : \overset{..}{S} : \overset{..}{O} :$ or the resonance formula* $\{O=S-O, O-S=O\}$, and other similar ones. The classical structures

$$S=O, \quad O=S=O, \quad O=S\overset{\displaystyle \diagup Cl}{\diagdown Cl}$$
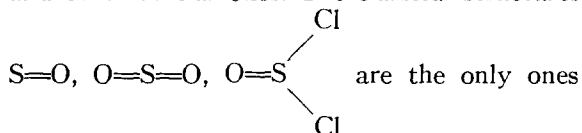
are the only ones which seem to meet the case. The experimental facts indicate electron-pair bonds, which are firmly localized between S and O. This also excludes any high ionic contribution, which is compatible only with fairly non-localized electrons. Indeed the bond moment of about 1.7D of SO_2 shows that the four binding electrons are shifted from the position of exact electrical symmetry towards O by 0.09A or about 6 percent of the bond distance.

All the other possible structures are suggested by particular values of additive molecular constants which are capable of different interpretations and therefore not conclusive. In such a case of conflicting results, to us it appears wiser to rely on the direct spectroscopical evidence and to accept the classical structures.

It is interesting to note that all such molecules for which similar conditions obtain, all for which we have direct spectroscopical evidence to this effect, and all of which are treated in this paper, are molecules formed by a definite and marked central atom (which mostly is capable of exercising different numerical valencies). Their behavior appears to be entirely different from that of the aromatic ring structures or others with conjugated double bonds, where only resonance formulae give a good approximation and where for this reason non-localized electrons exist. There appears to be some theoretical possibility of distinguishing between the wave functions of these two types;[7a] one great difference, however, is immediately evident. For the two resonating Kekulé formulae the energy difference is indeed

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[34] Reference 27 and N. Metropolis, Phys. Rev. **60**, 295 (1941).

[35] R. K. Asundi, M. Karim, and R. Samuel, Proc. Phys. Soc. (London) **50**, 581 (1938).
* Cf. asterisk footnote on pages 187–188.

nil, but for the different structures formed by a central atom it is always several ev, and sometimes much more. Yet one or two ev are already of the order of some of the normal bond energies, like $S-Cl$, $C-I$, $As-I$, etc. It is therefore most probably not a good approximation to call structures with such a term difference energetically degenerated. It may well be that discordant interpretations of essentially the same concepts are caused by nothing more than that an energy difference of 1 ev seems small to the mathematical physicist, while 23 kcal./mole loom large in the mind of the spectroscopist or the physicochemist.

In accepting the classical structures, we also adopt its corollary, namely, that there exists only one kind of covalent linkage in this type of molecules. No proof of a coordinate or of any other second variety of covalent bond can be obtained from their chemical[3a] or physical behavior. The polarity which is always superimposed on the covalent bond by the dissymmetry of the nuclear fields is of the same order for all of them and constitutes a secondary effect at that. It does not justify the restoration of coordinate formulae by means of enhanced resonance.

This small polarity hardly appears to exceed 15 percent of ionic character at its very best. On this reduced basis the two concepts of a slight resonance with ionic structures or of a slight shift of the electrons towards the negative partner are of course equivalent. Which to employ is a question of usefulness. It may well be that the chemist concerned with the actions of the molecule prefers to depict it as resonating between two structures, each of which explains some of the reactions, while the physicist, observing one definite property of the undisturbed molecule such as its band spectrum, finds the other alternative more serviceable.

7. SUMMARY

(i). If additive molecular constants like molecular volume (parachor), molecular refractivity, dipole moments, bond distances, or bond energies are used to determine the structure of a molecule, the respective property of the molecule as a whole is measured and then separated into contributions of the constituent atoms or bonds. It is shown that this second step is arbitrary. All

these constants retain their additive character even if entirely different structures of the molecule are assumed for the purpose of this separation.

(ii). In particular, all these constants are unable to distinguish between the set of classical structures recognizing only one type of covalent bond, and that of the theory of coordination in which some are described as semipolar double bonds, i.e., due to enhanced wave mechanical resonance with ionic parent structures. It is therefore not possible to differentiate between these two concepts or chemical theories by means of any of these constants.

(iii). This lack of diagnostic quality appears to have its origin in the fact that molecular volume or refractivity, electric moment, bond distance, and bond energy all are due to the action of *all* the electrons or at least *all* the binding electrons of the molecule. On the other hand, the difference between a normal covalent bond and a semipolar double bond, or the difference between resonating covalent or ionic structures, are due to the different part played by *a single*, individual electron, the action of which therefore cannot be observed or measured by such physico-chemical effects. The only experimental approach to such problems would then be through electronic band spectra which directly observe the different functional role of the single electron.

(iv). Among the structures which permit the perfect additive working of all these molecular constants are also those formed by pentacovalent nitrogen. As this hardly can be considered as a coincidence, the question as to whether pentacovalency of nitrogen is ruled out by wave mechanics is reinvestigated anew. It is shown that this is not so. The supposed covalency maximum of four of nitrogen is not established by any fundamental wave mechanical calculation, but is due to various assumptions or postulates introduced into the wave mechanical theory of valency in order to expand it from the calculable simple molecules to the more complex ones for which no calculation has been carried through. These assumptions may be replaced by similar ones which will permit the existence of pentacovalent nitrogen.

(v). The classical structures therefore appear to be entirely equivalent with any other set of

formulae. They are congruous with all observed facts and the results of actual wave mechanical calculation. They are favored by the results of spectroscopy which appear of particular importance. This paper is not concerned with aromatic or conjugated structures in which genuine resonance exists as the result of rigorous energetic degeneracy on account of non-localized electrons. But for (Werner's first-order) molecules marked by a distinct central atom—for which spectroscopy appears to indicate firm localization of the electrons—it is suggested that the classical formulae after all are the nearest approach to reality.

(vi). Consequently, for such molecules every bond is considered as a normal covalent bond. Its polarity now appears much reduced, e.g., to 13 percent ionic character in the nitro group or to 11 percent for the carbonyl radical. The polarity is therefore of the same order for all covalent bonds in such molecules and it is not possible to restore the concept of coordinate bonds for some of them on the basis of enhanced resonance with ionic structures.