962. *Molecules and Ions containing an Odd Number of Electrons.*

By M. Green and J. W. Linnett.

The electronic distribution in simple diatomic systems containing unpaired electrons is discussed in terms of bond order and electronegativity, and shown to be consistent with the differing susceptibilities of species, such as CN and NO, towards dimerization. A supposition is derived, in the light of which molecules such as NO_2 and ClO_2 are examined. A suggestion is offered to account for the failure to observe OF. The stabilities of various related systems, such as O_2^-, HO_2, $C_2O_4^{2-}$, and B_2F_4 are discussed. Finally, the general implications of the spin distributions induced are considered.

THE molecule, NO, contains an odd number of electrons; yet it neither readily dimerizes nor decomposes to nitrogen and oxygen. On the other hand, systems such as CN and OF are unstable, even though they are formed from elements in adjacent groups of the first short period, as NO is. The triatomic molecules, NO_2 and ClO_2, also contain an odd number of electrons. NO_2, like NO, is relatively stable; it has a slightly greater tendency to dimerize, but bonding between the NO_2 groups is, nevertheless, weak. ClO_2 does not dimerize at all. The oxalate ion, $C_2O_4^{2-}$, which is isoelectronic with N_2O_4, shows no tendency to dissociate into monomeric CO_2^-.

The object of this paper is to examine the extent to which these observations can be explained. We will make use of two postulates: (A) that an electron shared by two atoms tends to be associated more closely with the one having the higher electronegativity, and (B) that an increase in total bond order involves a rise in overall binding energy. These two postulates will be referred to as A and B.

The Formal Representation of NO.—According to the molecular-orbital method, the electronic structure of NO is $KK\ \sigma 2s^2\sigma^*2s^2\pi 2p^4\sigma 2p^2\pi^*2p$. In this representation, the orbitals $\sigma 2s$ and $\sigma 2p$ are depicted as independent, though they are, of course, of the same symmetry and may mix. In addition the NO linkage is of bond order $2\frac{1}{2}$, since the number of electrons in bonding orbitals exceeds that in antibonding ones by five. If one denotes the π-orbitals by π_+ and π_-, the representation becomes $KK\ \sigma 2s^2\sigma^*2s^2\pi_-2p^2\pi_+2p^2\sigma 2p^2\pi_+{}^*2p$, in which $\pi_+2p^2\pi_+{}^*2p$ is what is usually called the " three-electron bond."

The simplest of molecular-orbital methods uses linear combinations of atomic orbitals. If t_A and t_B represent atomic orbitals on atoms A and B in a diatomic molecule AB, and if τ and τ^* represent corresponding bonding and antibonding molecular orbitals, it follows that, when this treatment is used, $\tau\tau^* \equiv t_At_B$, provided that the orbitals contain electrons of the same spin (see, *e.g.*, Linnett [1]). Therefore in NO, if the L.C.A.O. method is justified, $\sigma 2s^2\sigma^*2s^2 \equiv 2s_N{}^2 2s_O{}^2$ and $\pi_+2p^2\pi_+{}^*2p \equiv 2p_{+N}2p_{+O}\pi 2p$. Hence, in the three-electron bond, one electron appears to be associated primarily with the nitrogen atom, one primarily with the oxygen, while the third is mainly in the region between them, *i.e.*, in the bond. It seems to us that this is best represented by $\dot{N}\cdot\dot{O}$, the molecule being depicted by $-\dot{N}\doteq\dot{O}-$,

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[1] Linnett, *J.*, 1956, 275.

where a line represents an electron pair. The validity of this formation is emphasized by separating spins in the representation:

$KK\ 2s_{\mathrm{N}}2s_{\mathrm{O}}2p_{+\mathrm{N}}2p_{+\mathrm{O}}\pi_{-}2p\sigma 2p$ (which is the grouping for a double bond and having, let us say, α-spin)

$KK\ 2s_{\mathrm{N}}2s_{\mathrm{O}}\pi_{+}2p\pi_{-}2p\sigma 2p$ (which is the grouping for a triple bond and having, let us say, β-spin)

It becomes clear that all the electrons in the system are " paired," except for those in the orbitals, $2p_{+\mathrm{N}}2p_{+\mathrm{O}}\pi 2p$, *viz.*, $-\dot{\mathrm{N}}\overset{\times}{=}\dot{\mathrm{O}}-$, where the dot and cross represent electrons with opposed spins, and lines represent electron pairs. Secondly, the bond order of $2\frac{1}{2}$ is again demonstrated. In the next section, it will be shown that experimental evidence supports this order of bond, which indicates that the L.C.A.O. treatment is justified here.

In valence-bond nomenclature, NO has been represented [2] $-\mathrm{N}\overset{\cdots}{=}\mathrm{O}-$. Our representation, however, makes it clear why the strength of a three-electron bond, which really only involves one bonding electron, is about half that of a conventional bond using the electron pair.

CN *and* NO.—The simplest structure of the CN radical in the molecular-orbital method is $KK\ \sigma 2s^2\sigma^*2s^2\pi 2p^4\sigma 2p$. There are thus five more electrons in bonding orbitals than in antibonding ones, giving a bond order of $2\frac{1}{2}$. The corresponding valence-bond picture is $-\mathrm{C}\overset{\cdot}{=}\mathrm{N}-$. However, configurational interaction could occur between the wave function above and $KK\ \sigma 2s\sigma^*2s^2\pi 2p^4\sigma 2p^2$, which has a higher bond order. In valence-bond terms, the new wave function corresponds roughly to a hybrid of $\cdot\mathrm{C}{\equiv}\mathrm{N}-$ and $-\mathrm{C}{\equiv}\mathrm{N}\cdot$. The higher bond order ought to make these structures quite significant (see postulate B). However, the first is more likely to be a contributing structure for it does not contravene postulate A in the way the second does. The closeness to a bond order of three in CN is shown by the C–N distance of 1·17 Å found in the radical, compared with 1·15 Å in $\mathrm{HC{\equiv}N}$ and 1·27 Å in $(\mathrm{CH_3{\cdot}C{=}N{\cdot}OH})_2$. (Bond lengths, unless otherwise stated, are taken from Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions." The Chemical Society, London, 1958.) The structure $\cdot\mathrm{C}{\equiv}\mathrm{N}-$ derived from the postulates is thus supported by experimental evidence, so that one may say that in the CN radical, the " odd " electron tends to be localized on the carbon atom.

In NO, configurational interaction (or resonance) could conceivably occur also, *viz.*:

$KK\ \sigma 2s^2\sigma^*2s^2\pi 2p^4\sigma 2p^2\pi^*2p$ or $-\dot{\mathrm{N}}\overset{\cdot}{=}\dot{\mathrm{O}}-$

$KK\ \sigma 2s^2\sigma^*2s\pi 2p^4\sigma 2p^2\pi^*2p\sigma^*2p$ corresponding roughly to $-\dot{\mathrm{N}}{=}\mathrm{O}{=}$ and ${=}\mathrm{N}{=}\dot{\mathrm{O}}-$

In the second group of representations there is a lower bond order than in the first, so that they will tend to be unimportant (postulate B). The bond length of 1·15 Å in NO, compared with 1·06 Å in $\mathrm{NO^+}$, supports a bond order of $2\frac{1}{2}$. Thus postulate B is supported at the expense of A. However, the difference in electronegativity between nitrogen and oxygen [3] is only 0·5. We will show later that postulate A becomes important only when the electronegativity difference becomes one or greater. The bond order of $2\frac{1}{2}$ demonstrates that an L.C.A.O. treatment such as is given in the previous section is sound and that the pictorial representation we have suggested is realistic, if the difference in electronegativity in the molecule concerned is not too great.

Dimerization of CN *and* NO.—When two CN radicals dimerize to cyanogen, *viz.*:

$$2{\cdot}\mathrm{C}{\equiv}\mathrm{N}-\ (\text{or } -\mathrm{C}\overset{\cdot}{=}\mathrm{N}-) \longrightarrow \mathrm{N}{\equiv}\mathrm{C}{-}\mathrm{C}{\equiv}\mathrm{N}$$

there is an increase of at least one in the total number of bonds. It is not surprising that cyanogen is much more stable at ordinary temperatures than the radical (see postulate B).

[2] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1960, p. 344.

[3] Ref. 2, p. 90.

However, nitric oxide hardly associates to N_2O_2 at all in the gas phase, though on liquefaction a dimer is formed.[4] The bond is weak; $\Delta H = 3{\cdot}7$ kcal./mole (Smith and Johnston [5]). Dulmage, Meyers, and Lipscomb [6] have shown the dimer to be planar; they find that the mean distance between the NO monomers is 2·40 Å, but were unable to tell whether the structure is shaped like a rectangle, parallelogram, or trapezium. Nor were they able to discover whether the long bonds were between N and N, or between N and O. Fateley, Bent, and Crawford [7] have detected spectroscopically *cis*- and *trans*-dimers, ONNO, using a matrix technique. One would expect the dimer to have the structure $=O=\overset{|}{N}-\overset{|}{N}=O=$, since then each atom exerts its conventional valency and carries a formal charge of zero, which is not possible in NONO or NOON. This molecule involves five bonds, which is the same as that in two molecules of nitric oxide:

$$2{-}\dot{N}\doteq\dot{O}{-} \longrightarrow O{=}\overset{|}{N}{-}\overset{|}{N}{=}O$$

It is not surprising that the energy of reaction is so small (postulate B).

Alternatively, the situation may be regarded in the following way. To form the N–N bond each nitrogen atom must assume a share of an additional electron from the other nitrogen atom. However, if there were no adjustment of electronic structure this would result in each nitrogen's having a valency shell of nine electrons. This shell is reduced to eight by transferring one of the NO bonding electrons to the oxygen atom. Therefore the N–N bond can only be formed by weakening the two NO bonds by an equivalent amount. In CN dimerization, no "weakening" occurs; the association is much more akin to the combination of two chlorine atoms or two methyl radicals.

The Oxygen Molecule.—The molecular-orbital representation of the ground state of O_2 is:

$$KK\ \sigma2s^2\sigma^*2s^2\pi2p^4\sigma2p^2\pi^*2p^2$$

which is equivalent to:

$$KK\ 2s_A{}^2 2s_B{}^2 2p_{+A}2p_{+B}2p_{-A}2p_{-B}\pi_+2p\pi\_2p\sigma2p^2$$

This can be split according to spin into:

$$\begin{array}{ll} KK\ 2s_A 2s_B 2p_{+A}2p_{+B}2p_{-A}2p_{-B}\sigma2p & \vdots O\cdot O\vdots \\ KK\ 2s_A 2s_B\pi_+2p\pi\_2p\sigma2p & \cdot O\vdots O\cdot \end{array}$$

Hence the best simple diagram of the structure of the ground state of O_2 is $-\dot{\underset{\cdot}{O}}\div\dot{\underset{\cdot}{O}}-$, a modified form of $-O\overset{\cdot\cdot\cdot}{\underset{\cdot\cdot\cdot}{-}}O-$, suggested by Pauling.[8] Any dimer of O_2 would be expected to be weak, for the reasons already given in the section on NO. Lewis [9] has estimated the energy of dimerization of O_2 to be 128 cal./mole.

The diatomic molecule NF is isoelectronic with O_2. It does not exist, though the dimer F–N=N–F is known. From the structure of O_2 and our supposition, the electronic structure of NF would be expected to be $-\dot{\underset{\cdot}{N}}\div\dot{\underset{\cdot}{F}}-$. This structure, like O_2, would be reluctant to dimerize as there would be no rise in bond order during the process (postulate B). However, the difference in electronegativity [3] between the atoms of NF is 1·0, as opposed to 0·5 in NO. This large difference makes it very likely that some localization of the unpaired electrons occurs on to the fluorine atom, so that structures $-\dot{\underset{\cdot}{N}}\dot{-}\dot{F}=$ and even $-\dot{\underset{\cdot}{N}}-F\equiv$ are more important in the resonant hybrid, in spite of the reduction of bond order

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[4] Smith, Keller, and Johnson, *J. Chem. Phys.*, 1951, **19**, 189).

[5] Smith and Johnson, *J. Amer. Chem. Soc.*, 1952, **74**, 4696.

[6] Dulmage, Meyers, and Lipscomb, *Acta Cryst.*, 1953, **6**, 760.

[7] Fateley, Bent, and Crawford, *J. Chem. Phys.*, 1959, **31**, 204.

[8] Ref. 2, p. 353.

[9] Lewis, *J. Amer. Chem. Soc.*, 1924, **46**, 2027.

involved and contravention of postulate A. On dimerization of either of these last two forms, there would be an increase in bond order (postulate B).

It is now possible to formulate a supposition: that in a molecule containing one or more unpaired electrons, the unpaired electron tends to be localized on one atom if there is a consequent increase in bond order or if that atom has a high electronegativity relative to the others, otherwise it tends to be delocalized. In practice a high electronegativity difference appears to be unity or greater. The supposition is seen to follow from postulates A and B.

Either directly from the supposition or indirectly by means of the postulates, as has already been shown, it follows that the structures below predominate in the respective forms of CN, NO, and NF: $\cdot\mathrm{C}{\equiv}\mathrm{N}{-}$, $-\dot{\mathrm{N}}\overset{\cdot}{=}\dot{\mathrm{O}}-$, $-\underset{\cdot}{\dot{\mathrm{N}}}\overset{\cdot}{-}\dot{\mathrm{F}}=$ (or $-\underset{\cdot}{\dot{\mathrm{N}}}-\mathrm{F}\equiv$). The electronic distribution in these structures determines the bond order of the monomeric form. The order of magnitude of the dimerization is decided by the change in bond order, when association occurs. The validity of the supposition will now be tested by application to other systems.

Application of the Supposition.—In the ion, O_2^-, there is no difference in electronegativity between the atoms. The supposition therefore indicates a structure $=\dot{\mathrm{O}}\overset{\cdot}{-}\dot{\mathrm{O}}=$ with a bond of order of $1\frac{1}{2}$, as opposed to a hybrid of $=\dot{\mathrm{O}}-\mathrm{O}\equiv$ and $\equiv\mathrm{O}-\dot{\mathrm{O}}=$. Dimerization would not be accompanied by a rise in total bond order and so would not be expected (postulate B). In KO_2, the anion is in fact O_2^-, not O_4^{2-}, which explains the paramagnetism shown by the substance. The bond length of 1·28 Å, which is intermediate between that in HO–OH (1·48 Å) and in O_2 (1·21 Å), supports the order of $1\frac{1}{2}$.

The radical OF is isoelectronic with O_2^-. The electronegativities of nitrogen, oxygen, and fluorine are 3·0, 3·5, and 4·0 respectively.[3] The radical OF would be expected to have the structure $=\dot{\mathrm{O}}\overset{\cdot}{-}\dot{\mathrm{F}}=$, which would be analogous to $-\dot{\mathrm{N}}\overset{\cdot}{=}\dot{\mathrm{O}}-$. As for NO and O_2^-, dimerization would involve no rise in overall bond order. The dimer O_2F_2 can be kept at temperatures below $-100°$.[10] Like N_2O_2, it is unstable at room temperatures. However the products of decomposition are O_2 and F_2, not OF. The radical OF has never in fact been observed.[11] The failure to detect it is discussed below.

The radical HO_2, believed to be a fairly stable intermediate in the hydrogen–oxygen reaction, is the conjugate acid of O_2^-. If the bond order in O_2^- is $1\frac{1}{2}$ and the electron distribution for electrons of each spin round each oxygen atom is tetrahedral, then there will be electrons of opposed spins at an angle of 55° ($\frac{1}{2} \times 109\frac{1}{2}°$) and at 70° (*i.e.*, $180°—109\frac{1}{2}°$) to the O–O axis. They would be placed sufficiently close to hold a proton without reduction of the OO bond order. Thus HO_2 is not very different from O_2^- in electron distribution.

The ion CO^- is isoelectronic with NO. Of the contributing structures $-\dot{\mathrm{C}}\overset{\cdot}{=}\dot{\mathrm{O}}-$ and $-\dot{\mathrm{C}}=\mathrm{O}=$, the greater electronegativity difference between C and O than between N and O, would probably make the second the more important (cf. the supposition). Dimerization would, therefore, be likely as there would be an increase in total bond order (postulate B). In $(=\mathrm{O}=\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}=\mathrm{O}=)^{2-}$ the negative charge formally resides entirely on the carbon atoms, which therefore show a great affinity for protons, glyoxal being formed. It seems thus unlikely that CO^- or its dimer will be prepared.

It would be interesting to know whether the ion OF^+ is stable, for in it the electronegativity difference between the two atoms is less than in NF. The most important structure would be $-\underset{\cdot}{\dot{\mathrm{O}}}\div\underset{\cdot}{\dot{\mathrm{F}}}-$, according to the supposition. It is intended to investigate whether OF^+ can be shown to exist in some suitable solvent.

The Stabilities of NO *and* OF.—At room temperature, NO is observed, even though it is thermodynamically unstable. OF, however, has not been detected. This failure to

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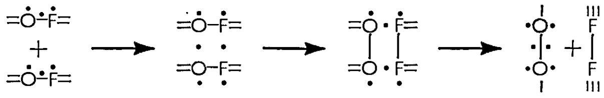
[10] Ruff and Menzel, *Z. anorg. Chem.*, 1933, **211**, 204.

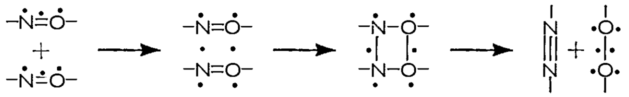
[11] Frisch and Schumacher, *Z. anorg. Chem.*, 1936, **229**, 423.

observe OF suggests that there is a reaction course open to it, over which NO cannot pass. A four-centre transition state would satisfy this requirement:



The difference in order of individual links between the two transition states is only ½, so that a change from one to the other ought not to be difficult. (There could even be a resonance hybrid of the two forms, which would further lower the energy of activation.)

A four-centre mechanism involving NO would follow a course:



In this case there is a large change in bond distribution during the transition, so the reaction seems unlikely.

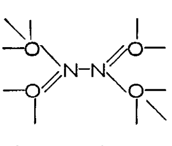
HO_2 is isoelectronic with OF. The former has been identified but not the latter. HO_2 is fairly readily " reflected " by glass surfaces. However, fluorine compounds such as F_2 and HF attack glass. A similar behaviour by OF would make it much more difficult to detect than HO_2, for it would be destroyed at the wall of the reaction vessel.

It is notable that the O_2^- ion, except in the strong electron-donating atmosphere of one of the heavier metals from Group IA, yields O_2 and O_2^{2-}. The reaction is electronically similar to OF, giving O_2 and F_2.

The Molecule NO_2.—If our supposition is extended from diatomic molecules to triatomic, no localization of unpaired electrons is to be expected in cases where electronegativity differences are small, *e.g.*, in NO_2 and ClO_2, but it is probable if the difference is larger, *e.g.*, in the hypothetical ion CO_2^-.

A molecular-orbital treatment of NO_2 has been carried out in a previous paper,[12] in which it was shown that the unpaired electron is most probably in an a_1-orbital. The valence-bond hybrid consists of several forms. Application of our supposition leads to $=\dot{O}\overset{\bullet}{-}\dot{N}=O=$ and $=O=\dot{N}\overset{\bullet}{-}\dot{O}=$ as the most probable forms, for in them the bond orders are higher than in the other structures. The electronegativity difference between nitrogen and oxygen is not great enough to offset the fall in bond order in $\equiv O-\dot{N}=O=$ and $=O=\dot{N}-O\equiv$. In $=\dot{O}-\overset{|}{N}=O=$ and $=O=\overset{|}{N}-\dot{O}=$ localization has occurred on to the more electropositive atom. Therefore, these last two pairs of structures seem unlikely.

Dimerization occurs by the formation of a long (1·75 Å) weak N–N bond; [13] the energy of dimerization [14] is 12·9 kcal./mole. Our molecular-orbital treatment indicated that the N–N bond was primarily a σ-bond, though interactions between the π-electrons on the two NO_2 groups would keep the molecule planar. The valence-bond approximation would describe the dimer as inset, involving resonance with three other equivalent structures. However, they have the unsatisfactory feature that the nitrogen atoms both carry a formal charge of +1.



The behaviour of NO_2 is very like that of NO. Both molecules contain an unpaired electron, which is not localized on any atom, *viz.*, $=O=\dot{N}\overset{\bullet}{-}\dot{O}=$ (resonating with $=\dot{O}\overset{\bullet}{-}\dot{N}=O=$) and $-\dot{N}\overset{\bullet}{=}\dot{O}-$. In both systems, dimerization leaves the bond order unchanged (five for

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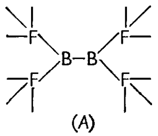
[12] Green and Linnett, *Trans. Faraday Soc.*, submitted for publication.
[13] Smith and Hedberg, *J. Chem. Phys.*, 1956, **25**, 1282.
[14] Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

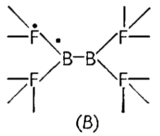
$2NO \longrightarrow N_2O_2$ and seven for $2NO_2 \longrightarrow N_2O_4$). It is not surprising that the energy of dimerization in each case is small. In NO_2 the electrons of one spin have the configuration ⁚O⁚N⁚O⁚, corresponding to (let us say) a total α-electron bond order of 4, while those of β-spin are distributed ⁝O·N⁚O⁚ (or ⁚O⁚N·O⁝) giving an order of 3. The mean is thus $3\frac{1}{2}$. The electrons around the nitrogen atom in the first case can only have a tetrahedral distribution in a linear molecule, so that when the molecule is bent, the total bond order effectively falls below $3\frac{1}{2}$. This may explain why the energy of dimerization of NO_2 is larger than that of NO.

The oxalate ion $C_2O_4^{2-}$, which is isoelectronic with N_2O_4, shows no tendency to dissociate into CO_2^-. The C–C bond has a normal length of 1·54 Å. In the hypothetical monomer CO_2^- the difference in electronegativity between carbon and oxygen is greater than that between nitrogen and oxygen. Therefore, our supposition indicates that some localization of the unpaired electron system will occur. Hence $\equiv O-\dot{C}=O=$ becomes more important than $=O=\dot{C}\overset{\cdot}{-}\dot{O}=$, as compared with NO_2 where the situation is reversed. The ion CO_2^- thus would have a total bond order tending towards three. As the oxalate ion has an overall bond order of seven, it is not surprising that it is stable.

The molecule B_2F_4 is isoelectronic with N_2O_4 and $C_2O_4^{2-}$. It is planar in the crystal state when the B–B and B–F bond lengths are 1·67 and 1·32 Å respectively.[15] In CH_3BF_2 the C–B and B–F bond lengths are 1·60 ± 0·03 and 1·30 ± 0·02 Å, so that there seems to be little difference between the BF bond lengths in the two compounds. If it is supposed that the normal single-bond radius of carbon is 0·77 Å, then in CH_3BF_2 boron is apparently exhibiting a single-bond radius of 0·83 Å which means that the normal B–B distance to be expected in B_2F_4 would be 1·66 Å, agreeing satisfactorily with the observed length of 1·67 Å. There does not, therefore, seem any reason to regard B_2F_4 as anything other than (*A*), though there may be some increase in the strength of BF bonds in B_2F_4 by contributions from structures such as (*B*) and (*C*). This does not affect the order of the B–B bond directly. The planarity may be due to crystal forces, for B_2Cl_4 is planar in the solid state,[16] but " skew " in the liquid and the gas phase.[17]



(A)



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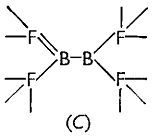

(C)

Chlorine Dioxide.—Our supposition would not localize the unpaired electron system in ClO_2, so this molecule would not be expected to dimerize easily. However, the position may be complicated by *d*-orbitals. If, however, one neglects these, the unpaired electron can be placed by using a suitable correlation diagram. Mulliken,[18] Walsh,[19] and we ourselves [12] all place it in a b_1-orbital, *i.e.*, one having the plane of the molecule as a node. Pairing of this electron could only result in a π-bond. Therefore, it is not surprising that Cl_2O_4 does not exist.

Electron Distribution.—It has been shown that in a three-electron bond, it is reasonable to think of the electrons as being widely spaced in some molecules, such as NO, in which the total spin is larger than zero. Now one of the limitations of the valence-bond method is that paired electrons are not allowed sufficient freedom of independent " movement," in the way in which they are in a molecular-orbital description. One could overcome this difficulty to some extent by supposing that electrons were not necessarily paired, even in

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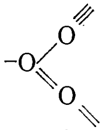
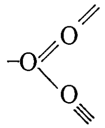
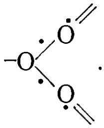
[15] Trefonas and Wheatley, *J. Chem. Phys.*, 1958, **28**, 54.
[16] Atoji, Wheatley, and Lipscomb, *J. Chem. Phys.*, 1957, **27**, 196.
[17] Mann and Fano, *J. Chem. Phys.*, 1957, **26**, 1665.
[18] Mulliken, *Rev. Mod. Phys.*, 1942, **14**, 204.
[19] Walsh, *J.*, 1953, 2266.

systems where the total spin was zero. Thus in the resonance hybrid of O_3, one might include in addition to  and  a structure such as . The last type of form, as well as allowing electrons greater " independence," would give a clearer impression of the bond order. It is inevitable in molecules such as NO, and it is very possible that it should not be overlooked in systems containing an even number of electrons.

Conclusion.—In this paper, it has been demonstrated that one can explain the behaviour of simple radicals and molecules containing unpaired electrons by means of two simple postulates, namely, A and B, stated in the introduction. Moreover these postulates are in themselves reasonable. They are combined to form a supposition, which determines electronic pattern. The electronic patterns derived give bond orders which are consistent with observed bond lengths. It is possible next to decide whether the energy of dimerization will be large or small depending whether there is an overall increase in bond order or not when the process occurs. Though electronic distribution, bond order, and bond energy are different concepts, they are nevertheless concomitant. We have shown that it is possible to induce from simple concepts electronic patterns compatible with energies of dimerization that are observed.

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[*Received, March* 28*th*, 1960.]