## 194. *Electronic Structures and Formulæ: the Allyl Cation, Radical, and Anion.*

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Calculations have been carried out for the π-electron systems of the allyl cation, radical, and anion, which contain 2, 3, and 4 electrons, respectively. For the cation and anion, which contain an even number of electrons, formulæ which do not involve electron pairing in bonds, or on atoms, provide the best simple representation of the electronic structure, being markedly better than those based on the molecular orbital, or the conventional Pauling-type resonance approximation involving Lewis structures, both of which pair-off electrons in orbitals as far as possible. For the radical, which contains an odd number of electrons, the best result is similar, a resonance hybrid of $CH_2\!\cdot\!-\!CH\!\cdot\!-\!\dot{C}H_2$ and $\dot{C}H_2\!-\!\cdot\!CH\!-\!\cdot\!CH_2$ providing a better wave function than a resonance hybrid of $CH_2\!=\!CH\!-\!\dot{C}H_2$ and $\dot{C}H_2\!-\!CH\!=\!CH_2$. For the radical, the results obtained by using wave functions that are rather severely restricted are misleading. It is necessary to examine wave functions which provide a good approximation to the " best " solution. The implications of these results in molecules such as ozone, and ions such as nitrite and acetate, as well as in other species are discussed briefly.

THE object of the calculations in this paper is an investigation of relative merits of different methods of describing the electronic structures of molecules. The most common of these are the molecular orbital and valence-bond methods, but recently one of us [1] has suggested a formulation that may be regarded as additional and different from both these. The various methods may be illustrated by considering the nitrite ion. By the valence-bond approach, the simplest description is that in terms of a resonance hybrid of (I) and (II),
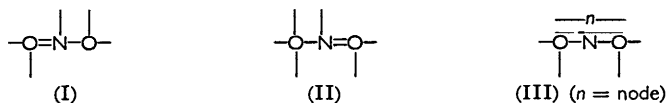
the wave functions describing each of the structures making an equal contribution to the overall wave function. The molecular-orbital description may be represented by (III) in which the short lines represent electron pairs in σ-orbitals (bonding and lone pair) and the long lines represent the two π-orbitals in which there are four electrons. One of these (indicated by the lower long line) has no node other than the molecular plane while the other (indicated by the upper line) has a central nodal plane. The third (double-quartet or non-pairing) representation is that shown by (IV) in which the dots represent single electrons. An attempt to be more detailed is in (IVa) where the circles represent electrons of one spin and the crosses electrons of the other spin. (For further discussion of spin see below.) Representation (IVa) is a single structure in which the electrons of one spin have the pattern of the pairs in (I), while those of the other have the pattern of the pairs in (II). The structure (IV) is different from a resonance hybrid of (I) and (II). In (IV)
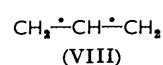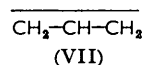

the electrons are not entirely grouped in pairs. The test of the relative merits of these three types of formula has been made by means of calculations carried out on the electrons in the π-orbitals of the allyl cation $C_3H_5^+$, radical $C_3H_5\cdot$, and anion $C_3H_5^-$ which have 2, 3, and 4 electrons, respectively, in π-orbitals. There are three reasons for choosing these

[1] Linnett, *Nature*, 1960, **187**, 859; *J. Amer. Chem. Soc.*, 1961, **83**, 2643.

species for the test. The first is that reliable published values of the integrals required for the calculation are available.[2] The second is that the literature contains calculations for these systems which enable checks to be made, so ensuring that the results obtained are free from error. The third is that the anion is isoelectronic with NO_2^- and O_3, and is closely related to other species such as $R \cdot CO_2^-$, while the cation and the radical provide valency situations of a simple and instructive kind, as will be seen below.

As stated above, a number of calculations have been published on the π-electron systems of $C_3H_5^+$, C_3H_5, and $C_3H_5^-$.[3,4] Our results agree with these, except for certain small differences arising from the use of slightly different values for the integrals, etc. In one case, there was a larger discrepancy but this resulted from an error in the published calculations. In this instance, our figures were in substantial agreement with one of the other published sets of results. Higuchi[4] has made the most thorough examination of these systems, testing the relative success of a wide variety of functions. Some of these have also been tested by us. Our figures for such functions have been included in this paper so that a direct comparison with our other functions is possible. However, all the functions tested by Higuchi retained to a greater or smaller degree the idea that the electrons should be considered as far as possible in pairs. It is the conclusion of this paper that it is possible to obtain much better approximate wave functions for all three species if, for the electrons in the π-orbitals, the concept of pairing is discarded. As a result we have found it possible to suggest simple functions which are more successful than the best tested by Higuchi.

Outline of Treatment.—For all three species a quantum-mechanical treatment of the same type has been carried out. This may be illustrated by considering the cation in which there are two electrons occupying the π-orbitals. It will be supposed that these orbitals can be described as combinations derived solely from the three $2p\pi$-orbitals on the three carbon atoms. There are nine states which can be formed by such combinations, namely, three triplet and six singlet states. Any complete treatment (*i.e.*, either valence-bond with resonance among all states, or molecular-orbital including interactions among all configurations) will lead to the " best " set of wave functions for describing these nine states within two limitations: (i) that only certain particular carbon $2p\pi$-atomic orbitals have been used as basic functions and (ii) that the potential field for the π-electrons is, in effect, approximated. When these " best " wave functions have been obtained, it is possible to see which of the approximate procedures provides wave functions closest to them. In a later paper a comparison will be made for excited states, but here our main concern will be for the three ground states. For instance, for the ground state of the allyl positive ion, we shall be interested in which of the following simple methods produces wave functions which are closest to the " best ": (*a*) the valence-bond methods using a

$$CH_2=CH-\overset{+}{C}H_2 \qquad \overset{+}{C}H_2-CH=CH_2 \qquad \overline{CH_2-CH-CH_2} \qquad CH_2\overset{\cdot}{-}CH\overset{\cdot}{-}CH_2$$
$$\text{(V)} \qquad\qquad \text{(VI)} \qquad\qquad \text{(VII)} \qquad\qquad \text{(VIII)}$$
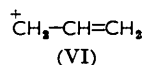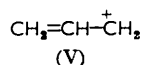
resonance hybrid of (V) and (VI); (*b*) a molecular-orbital representation (VII); or (*c*) a method based on structure (VIII), in which the two bonding electrons are in different bonds. (Several functions corresponding to each type will be tested.) We shall find that (VIII) is clearly the best. An outline of the results obtained will now be presented; the calculations involved the use of Hamiltonians of the type introduced by Goeppert-Mayer and Sklar[5] and integrals evaluated by Parr *et al.*[2]

[2] Parr and Crawford, *J. Chem. Phys.*, 1948, **16**, 526, 1049; Parr, Craig, and Ross, *ibid.*, 1950, **18**, 1561.
[3] Chalvet, *Compt. rend.*, 1952, **234**, 2369; *Ann. Chim. (France)*, 1954, **9**, 97; Chalvet and Daudel, *J. Chim. phys.*, 1952, **49**, 629; Moffitt, *Proc. Roy. Soc.*, 1953, *A*, **218**, 486; Berthier, *Compt. rend.*, 1954, **238**, 91; *J. Chim. phys.*, 1955, **52**, 141; Lefkovits, Fain, and Matsen, *J. Chem. Phys.*, 1955, **23**, 1690; Hunt, Peterson, and Simpson, *ibid.*, 1957, **27**, 20.
[4] Higuchi, *J. Chem. Phys.*, 1957, **26**, 151, 825.
[5] Goeppert-Mayer and Sklar, *J. Chem. Phys.*, 1938, **6**, 645.

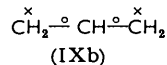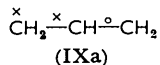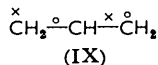*Electron spin.* In the later parts of this paper it will be necessary to consider the spin of the electrons and to ensure that the wave functions describe states in such a way that

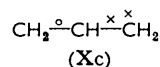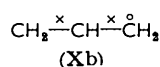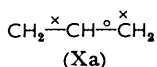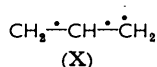$$CH_2\overset{x}{-}CH\overset{o}{-}CH_2 \quad \text{(VIIIa)}$$
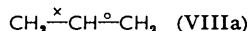
the spin is appropriately quantised. For formula (VIII) for the ground state of the allyl positive ion, the spin situation could be described by using (VIIIa). The wave function would be separable into two parts and would involve two determinants: for one $\times$ would represent a spin quantum number of $+\frac{1}{2}$, and $\circ$ one of $-\frac{1}{2}$; for the other the symbolism would be reversed. The orbitals occupied by the two electrons would be some form of bond orbitals, there being one electron to each orbital.

For the allyl negative ion, formula (IX), analogous to (IVa) for NO_2^-, might be written as (IX). As for the positive ion, this represents two spin distributions (*i.e.*, two 4 by 4

$$\overset{x}{CH_2}\overset{o}{-}CH\overset{x}{-}\overset{o}{CH_2} \qquad \overset{x}{CH_2}\overset{x}{-}CH\overset{o}{-}CH_2 \qquad \overset{x}{CH_2}\overset{o}{-} CH\overset{o}{-}\overset{x}{CH_2}$$
$$\text{(IX)} \qquad\qquad\qquad \text{(IXa)} \qquad\qquad\qquad \text{(IXb)}$$

determinants; the functions in the four columns would be two atomic and two bond orbitals). However, in general, the wave function which corresponds to formulation (IX) will involve too great a restriction on spin distribution (*i.e.*, it is not an eigenfunction of S^2). For a satisfactory description, corresponding to the proper quantisation of spin, it is necessary to include also other spin distributions (IXa and IXb). In this paper, the combination that has been used is the following: the determinants corresponding to (IX), in which the spins alternate along the molecule, have been given the greatest weight, the determinants corresponding to the other spin distributions (IXa and IXb) being given (*a*) equal weight, and (*b*) a total weight equal to that of the functions in which the spins alternate along the molecule (*i.e.*, IX). So the final function used combines (IX), (IXa), and (IXb) with the relative weights 1, $\frac{1}{4}$, $\frac{1}{4}$ (this is an eigenfunction of S^2). However, it is found that, if bond orbitals are described by linear combinations of the atomic orbitals of the component atoms associated with the one-electron bond, the wave function derived from (IX) alone is equal to that derived from the above combination. So, with this bond function, structure (IX) does provide a satisfactory wave function, though with other formulations of the bond functions it might not.

For the allyl radical, formula (X) will be examined. In this case, the contributing structures in which the spin distributions are specified are (Xa, b, and c). These are combined in the same way as for the negative ion, so that they have the relative weights 1, $\frac{1}{2}$, $\frac{1}{2}$ [in this case (Xa) alone does not provide a satisfactory function]. Because the

$$CH_2\overset{.}{-}CH\overset{.}{-}\dot{C}H_2 \qquad CH_2\overset{x}{-}CH\overset{x}{-}\overset{x}{C}H_2 \qquad CH_2\overset{x}{-}CH\overset{x}{-}\overset{o}{C}H_2 \qquad CH_2\overset{o}{-}CH\overset{x}{-}\overset{x}{C}H_2$$
$$\text{(X)} \qquad\qquad\qquad \text{(Xa)} \qquad\qquad\qquad \text{(Xb)} \qquad\qquad\qquad \text{(Xc)}$$

contributions of the different spin distributions are combined in a specified manner, formulæ such as (X), in which dots only are used, serve, so far as this paper is concerned, to describe a function completely, once the form of the bond orbitals has been decided.

RESULTS OF CALCULATIONS

Allyl Positive Ion.—Within the limitations referred to above, the nine states of this ion for which $S_z = 0$,* but which involve different dispositions of the two electrons among π-type orbitals, can be described by various combinations of the following nine simple determinantal wave functions:

$$\phi_1 = (a\alpha, b\beta); \qquad \phi_2 = (b\alpha, a\beta); \qquad \phi_3 = (a\alpha, c\beta);$$
$$\phi_4 = (c\alpha, a\beta); \qquad \phi_5 = (b\alpha, c\beta); \qquad \phi_6 = (c\alpha, b\beta);$$
$$\phi_7 = (a\alpha, a\beta); \qquad \phi_8 = (b\alpha, b\beta); \qquad \phi_9 = (c\alpha, c\beta);$$

* $S_z = 0$ means that an equal number of electrons must be assigned α- and β-spin wave functions so that the magnitude of the spin angular momentum about the specified (z) direction is zero.

a, *b*, and *c* designate the $2p\pi$-orbitals on the three carbon atoms (*b* refers to the central atom). α and β are the spin wave functions corresponding to $S_z = +\frac{1}{2}$ and $-\frac{1}{2}$. The symbol $(a\alpha,b\beta)$ represents the determinantal function:

$$\frac{1}{\sqrt{2}} \begin{vmatrix} a(1)\ \alpha(1) & b(1)\ \beta(1) \\ a(2)\ \alpha(2) & b(2)\ \beta(2) \end{vmatrix}$$

where the two electrons are described as 1 and 2. We shall further abbreviate $(a\alpha, b\beta)$ to (a,b) it being understood that always the α spin wave function is associated with the first orbital and the β spin wave function with the second. The symmetry of the system, and the requirement that the wave functions must describe states for which the resultant spin angular momentum is quantised, limit the combinations of the above functions that are allowed. For instance, there are four combinations that correspond to states which have totally symmetric wave functions and a zero resultant spin angular momentum (singlet state) usually described as $^1A_1$. These are

$$\psi_1^+ = (a,b) + (b,a) + (b,c) + (c,b); \qquad \psi_2^+ = (a,c) + (c,a);$$

$$\psi_3^+ = (a,a) + (c,c); \qquad \psi_4^+ = (b,b).$$

The other three classes ($^3A_1$, $^1B_2$, and $^3B_2$) include the following combinations:

$$^3A_1\ \psi_5^+ = (a,b) - (b,a) - (b,c) + (c,b).$$

$$^1B_2\ \psi_6^+ = (a,b) + (b,a) - (b,c) - (c,b); \qquad \psi_7^+ = (a,a) - (c,c).$$

$$^3B_2\ \psi_8^+ = (a,b) - (b,a) + (b,c) - (c,b); \qquad \psi_9^+ = (a,c) - (c,a).$$

We have carried out calculations like those of Lefkovits, Fain, and Matsen [3] to determine the linear combinations of the above functions (ψ_1^+, ψ_2^+, etc.) which describe the nine states most satisfactorily. These functions will be given by expressions of the following type: *e.g.*, for a member of the $^1A_1$ class

$$C_1^+\psi_1^+ + C_2^+\psi_2^+ + C_3^+\psi_3^+ + C_4^+\psi_4^+.$$

The results are summarised in Table 1 which lists the energies calculated for the nine states, and the coefficients C_1^+, C_2^+ ... C_9^+, which are the coefficients in the expressions for the corresponding wave functions. The energies listed are relative to the energy of two electrons in orbitals on separate carbon atoms, $2W_{2p}$.

TABLE 1.

Energies (*E*) and coefficients of component functions for "best" wave functions for the allyl positive ion.

Symmetry type	$E - 2W_{2p}$			Coefficients	
$^1A_1$	(ev)	C_1^+	C_2^+	C_3^+	C_4^+
	$-30\cdot396$	$0\cdot313$	$0\cdot250$	$0\cdot026$	$0\cdot233$
	$-22\cdot785$	$-0\cdot161$	$0\cdot661$	$-0\cdot036$	$-0\cdot399$
	$-16\cdot247$	$-0\cdot323$	$0\cdot229$	$-0\cdot261$	$0\cdot957$
	$-10\cdot460$	$-0\cdot362$	$0\cdot158$	$0\cdot712$	$0\cdot438$

Symmetry type	$E - 2W_{2p}$		Symmetry type	$E - 2W_{2p}$	Coefficients	
		C_5^+	$^1B_2$	(ev)	C_6^+	C_7^+
$^3A_1$	$-24\cdot435$	$0\cdot526$		$-25\cdot642$	$0\cdot486$	$0\cdot082$
				$-11\cdot282$	$-0\cdot251$	$0\cdot754$

Symmetry type	$E - 2W_{2p}$	C_8^+	C_9^+
$^3B_2$	$-28\cdot236$	$0\cdot326$	$0\cdot404$
	$-20\cdot316$	$-0\cdot439$	$0\cdot642$

Allyl Radical.—The same procedure as before was employed with this species. The basic set of functions used was: (a,b,c), (a,c,b), (b,a,c), (a,a,c), (c,c,a), (a,b,b), (b,b,c), (a,a,b), and (b,c,c).

In these determinants it is supposed that the three atomic functions in the above are associated with α, β, and α spin functions in that order. As with the ion, only certain combinations of the above are possible and these fall into the various symmetry classes as follows:

$$^2A_2: \quad \psi_1 = 2(a,b,c) + (a,c,b) + (b,a,c) \qquad ^2B_1: \quad \psi_5 = (b,a,c) - (a,c,b)$$

$$\psi_2 = (a,a,c) + (a,c,c) \qquad\qquad \psi_6 = (a,a,c) + (c,c,a)$$

$$\psi_3 = (a,b,b) + (b,b,c) \qquad\qquad \psi_7 = (a,b,b) - (b,b,c)$$

$$\psi_4 = (a,a,b) + (b,c,c) \qquad\qquad \psi_8 = (a,a,b) - (b,c,c)$$

$$^4A_2 \quad \psi_9 = (a,b,c) - (a,c,b) - (b,a,c)$$

The " best " combinations of the above functions and the corresponding energies have been determined in the same manner as for the allyl ion and are summarised in Table 2. They are discussed below.

TABLE 2.

Energies (E) and coefficients of component functions for " best " wave functions for the allyl radical.

Symmetry type	$E - 3W_{2p}$	Coefficients			
$^2A_2$	(ev)	C_1	C_2	C_3	C_4
	$-28\cdot914$	$0\cdot318$	$0\cdot116$	$0\cdot142$	$0\cdot047$
	$-16\cdot422$	$-0\cdot144$	$-0\cdot296$	$0\cdot628$	$0\cdot244$
	$-15\cdot972$	$-0\cdot204$	$0\cdot482$	$-0\cdot027$	$0\cdot397$
	$-8\cdot943$	$0\cdot255$	$-0\cdot519$	$-0\cdot521$	$0\cdot613$
$^2B_1$		C_5	C_6	C_7	C_8
	$-26\cdot482$	$0\cdot665$	$0\cdot099$	$-0\cdot113$	$0\cdot008$
	$-19\cdot123$	$0\cdot031$	$0\cdot353$	$0\cdot435$	$0\cdot314$
	$-14\cdot562$	$0\cdot426$	$-0\cdot565$	$0\cdot546$	$-0\cdot035$
	$-10\cdot315$	$0\cdot006$	$-0\cdot398$	$-0\cdot384$	$1\cdot719$
$^4A_2$		C_9			
	$-24\cdot950$	$0\cdot620$			

Allyl Negative Ion.—The same procedure was employed with the negative ion. The basic set of determinantal functions used was: (a,a,b,c), (a,a,c,b), (a,b,c,c), (b,a,c,c), (a,c,b,b), (c,a,b,b), (a,a,c,c), (a,a,b,b), and (b,b,c,c). In these determinants the four atomic functions are associated with α, β, α, and β spin functions in that order. As with the negative ion and the radical only certain combinations of the above are allowed, and these fall into the various symmetry classes as shown.

$$^1A_1: \quad \psi_1^- = (a,a,b,c) + (a,a,c,b) + (a,b,c,c) + (b,a,c,c)$$

$$\psi_2^- = (a,b,b,c) + (c,b,b,a)$$

$$\psi_3^- = (a,a,c,c)$$

$$\psi_4^- = (a,a,b,b) + (b,b,c,c)$$

$$^3A_1: \quad \psi_5^- = (a,a,b,c) - (a,a,c,b) - (a,b,c,c) + (b,a,c,c)$$

$$^1B_2: \quad \psi_6^- = (a,a,b,c) + (a,a,c,b) - (a,b,c,c) - (b,a,c,c)$$

$$\psi_7^- = (a,a,b,b) - (b,b,c,c)$$

$$^3B_2: \quad \psi_8^- = (a,a,b,c) - (a,a,c,b) + (a,b,c,c) - (b,a,c,c)$$

$$\psi_9^- = (a,c,b,b) - (c,a,b,b)$$

The " best " combination of the above functions, and the corresponding state energies, have been determined as for the other two species and are summarised in Table 3 which also tabulates the constants in the wave function. These results also are discussed below.

TABLE 3.

Energies (E) and coefficients of components for " best " wave functions for the allyl negative ion.

Symmetry type $^1A_1$	$E - 4W_{2p}$ (ev)	Coefficients			
		C_1^-	C_2^-	C_3^-	C_4^-
	$-14 \cdot 506$	$0 \cdot 319$	$0 \cdot 304$	$0 \cdot 195$	$0 \cdot 045$
	$-6 \cdot 481$	$0 \cdot 198$	$-0 \cdot 700$	$0 \cdot 383$	$0 \cdot 033$
	$0 \cdot 475$	$-0 \cdot 292$	$0 \cdot 218$	$0 \cdot 934$	$-0 \cdot 338$
	$+5 \cdot 748$	$-0 \cdot 404$	$0 \cdot 183$	$0 \cdot 519$	$0 \cdot 739$

Symmetry type $^3A_1$	$E - 4W_{2p}$	C_5^-	Symmetry type $^1B_2$	$E - 4W_{2p}$ (ev)	Coefficients	
					C_6^-	C_7^-
	$-8 \cdot 099$	$0 \cdot 547$		$-9 \cdot 194$	$0 \cdot 495$	$0 \cdot 107$
				$+4 \cdot 920$	$-0 \cdot 271$	$0 \cdot 806$

Symmetry type $^3B_2$		C_8^-	C_9^-
	$-12 \cdot 268$	$-0 \cdot 315$	$0 \cdot 466$
	$-3 \cdot 834$	$0 \cdot 468$	$0 \cdot 666$

EXAMINATION OF RESULTS

In this section the results that have been obtained for the ground states of the three species will now be examined, and the " best " functions and calculated energies will be compared with results obtained by using various approximate procedures.

Allyl Positive Ion.—For the $^1A_1$ ground state of the allyl positive ion the wave function might be constructed on the valence-bond basis as a resonance hybrid of structures (V) and (VI). If the Heitler–London method of constructing the wave functions of electron-pair bonds is used the resulting wave function would be

$$\{(a,b) + (b,a)\} + \{(b,c) + (c,b)\} = \psi_1^+.$$

If bond orbitals (*i.e.*, $a + b$, and $c + d$) were used, the wave function would be

$$(a + b, a + b) + (b + c, b + c)$$
$$= \{(a,b) + (b,a) + (b,c) + (c,b)\} + \{(a,a) + (c,c)\} + 2\{(b,b)\}$$
$$= \psi_1^+ + \psi_3^+ + 2\psi_4^+.$$

On the other hand, the two-electron wave function might be constructed according to the molecular-orbital approximation (VII); in which case, if the simplest possible molecular orbital which has no adjustable constant, $a + b + c$, is used, the function would be:

$$(a + b + c, a + b + c)$$
$$= \{(a,b) + (b,a) + (b,c) + (c,b)\} + \{(a,c) + (c,a)\} + \{(a,a) + (c,c)\} + \{(b,b)\}$$
$$= \psi_1^+ + \psi_2^+ + \psi_3^+ + \psi_4^+.$$

Alternatively, the simple Hückel form for the molecular orbital, $a + b\sqrt{2} + c$, might be used, in which case the wave function becomes

$$(a + b\sqrt{2} + c, a + b\sqrt{2} + c) = \psi_1\sqrt{2}^+ + \psi_2^+ + \psi_3^+ + 2\psi_4^+.$$

Finally, a wave function constructed on the basis of the non-pairing formula (VIII) (or VIIIa) may be tested. When bond orbitals are used, this would be

$$(a + b, b + c) + (b + c, a + b)$$
$$= \{(a,b) + (b,a) + (b,c) + (c,b)\} + \{(a,c) + (c,a)\} + 2\{(b,b)\}$$
$$= \psi_1^+ + \psi_2^+ + 2\psi_4^+.$$

In fact, the " best " wave function for the ground state is

$$0 \cdot 313\psi_1^+ + 0 \cdot 250\psi_2^+ + 0 \cdot 026\psi_3^+ + 0 \cdot 233\psi_4^+.$$

It is immediately apparent that the formula based on (VIII) comes closest to this. The Heitler–London valence-bond function is too limited, being just ψ_1^+. The bond-orbital valence-bond function is unsatisfactory because the coefficient of ψ_2^+ is small and that of ψ_3^+ considerable, which is the reverse of what is found for the " best " function. The molecular-orbital approximations also fail to predict the small value found for C_3^+. On the other hand, the formula based on (VIII) does predict that C_3^+ should be small, and that C_1^+, C_2^+, and C_4^+ should be comparable, which is the pattern of the constants in the " best " function. A comparison of the merits of the various functions may be tested by comparing the " energies " calculated from them. These are listed in the middle column of Table 4, where the energies are given as differences from $2W_{2p}$ (*i.e.*, $E - 2W_{2p}$; cf. Table 1).

TABLE 4.

Results for the allyl positive ion obtained by using various functions having no adjustable constants.

Functions	Energy (ev)	Overlap
Valence bond (bond orbitals)	-27.642	0.871
Valence bond (Heitler–London)	-28.678	0.929
Molecular orbital $(a + b + c)$	-28.830	0.958
Molecular orbital $(a + b\sqrt{2} + c)$	-29.402	0.969
Non-pairing formula (VIII)	-29.696	0.974
" Best " function	-30.396	1.000

This Table shows that, by this criterion, the molecular-orbital (with $a + b + c$) and the valence-bond (Heitler–London) method are approximately equally good (energy about 1·7 ev greater than the " best "). Hückel orbitals, which were obtained by a simple variation treatment of the one-electron problem, are somewhat better. However, the wave function based on (VIII) yields an energy only 0·7 ev (16 kcal./mole) greater than the " best " value. That is, the new approximation, which locates one electron of the π-system in each bond, is the best of the five.

The extent to which these five functions resemble the " best " one may also be tested by evaluating for each the overlap integrals $\int \Psi \Phi d\tau$ where Ψ and Φ are both normalised, and are respectively the " best " and the approximate functions. The results are shown in the last column of Table 4. This test places the five functions in the same order as does the energies, though the spacing is not quite the same. The non-pairing formula remains clearly better than the others and would probably, therefore, also be better for calculation of other molecular properties.

The five functions so far discussed, and for which results were given in Table 4, contained no adjustable constants. In order to give each of the three types (valence bond, molecular orbital, and non-pairing formula) an equal chance of improvement the following five functions, each containing one adjustable constant, were tested:

Valence bond:

　A: $(a + kb, a + kb) + (c + kb, c + kb)$
　　$= k\psi_1^+ + \psi_3^+ + 2k^2\psi_4^+.$

　B (cf. ref. 6): $(ka + b, a + kb) + (a + kb, ka + b) + (kc + b, c + kb) + (c + kb, kc + b)$
　　$= (1 + k^2)\psi_1^+ + 2k\psi_3^+ + 4k\psi_4^+.$

Molecular orbital:

　$(a + kb, + c, a + kb + c) = k\psi_1^+ + \psi_2^+ + \psi_3^+ + k^2\psi_4^+.$

Non-pairing formula (VIII):

　A: $(a + kb, c + kb) + (c + kb, a + kb)$
　　$= k\psi_1^+ + \psi_2^+ + 2k^2\psi_4^+.$

　B: $(a + kb, b + kc) + (b + kc, a + kb) + (c + kb, b + ka) + (b + ka, c + kb)$
　　$= (1 + k^2)\psi_1^+ + 2k\psi_2^+ + 4k\psi_4^+.$

M M

(In these formulæ it is again presumed that the α and the β spin function are associated with the orbitals in that order; cf. above.) Table 5 presents the results, listing the lowest energies (*i.e.*, $E - 2W_{2p}$) obtainable with these functions, the values of k that give these energies, and

the magnitudes of the overlap integral, $\int \Psi' \Phi d\tau$ (see earlier).

TABLE 5.

Results for the allyl positive ion obtained by using various functions having one adjustable constant.

Functions	Energy (ev)	k	Overlap
Valence bond (A)	$-27 \cdot 842$	$1 \cdot 235$	$0 \cdot 869$
Valence bond (B)	$-29 \cdot 302$	$0 \cdot 1222$	$0 \cdot 932$
Molecular orbital	$-29 \cdot 434$	$1 \cdot 563$	$0 \cdot 966$
Non-pairing (A)	$-30 \cdot 038$	$0 \cdot 711$	$0 \cdot 986$
Non-pairing (B)	$-30 \cdot 201$	$0 \cdot 252$	$0 \cdot 988$
" Best " function	$-30 \cdot 396$	—	$1 \cdot 000$

The order remains the same, the better non-pairing formula giving an energy only 0·2 ev (about 4½ kcal./mole) greater than the " best " energy, and the overlap integral is 0·988. The molecular orbital remains better than the better valence-bond formula. Of the two valence-bond formulæ, B is markedly better than A, as would be expected, because it increases the mean inter-electron separation by reducing the importance of " ionic " terms and by bringing the valence-bond (bond-orbital) representation towards the Heitler–London formulation. Both the non-pairing formulæ are very successful, as judged by both energy and overlap. The reason why B is better than A is that it increases the probability of one electron's being in the orbital on atom b. This produces a lowering of the energy because the central atom has, in effect, a greater electronegativity than the outer ones, having two near-neighbour carbon atoms which exert some attractive effect on the electron whereas the outer atoms have only one near-neighbour each. This outweighs the effect of reducing the mean inter-electron separation.

Allyl Radical.—The radical has been examined in the same way as the positive ion. The main formulæ that have been tested are represented by:

Valence bond:

A: $\{(a + kb, a + kb, c)\} - \{(c + kb, c + kb, a)\} = k\,\psi_1{}^+ + \psi_2 + k_2\psi_3$.

B (ref. 6): $\{(a + kb, ka + b, c) + (ka + b, a + kb, c)\}$
$\qquad\qquad\qquad - \{(c + kb, kc + b, a) + (kc + b, c + kb, a)\}$
$= (1 + k^2)\psi_1 + 2k\psi_2 + 2k\psi_3$.

Molecular orbital:

$\{(a + kb + c, a + kb + c, c - a)\} = k\psi_1 + 2\psi_2 + k^2\psi_3 + k\psi_4$.

Non-pairing:

$\{2(a + kb, b + kc, c) + (b + kc, a + kb, c) + (a + kb, c, b + kc)\} - \{2(c + kb, b + ka, a)$
$\qquad\qquad\qquad + (b + ka, c + kb, a) + (c + kb, a, b + ka)\}$
$= 3[\tfrac{2}{3}\psi_1 + k\psi_2 + k\psi_3 + k^2\psi_4]$.

The valence-bond formulæ describe the resonance hybrid of (XIa and b). In the molecular-orbital descriptions, two electrons are in the·bonding orbital while the third is in what is essentially a non-bonding orbital. The non-pairing formula describes a resonance hybrid of

$$(XIa)\quad \overset{\bullet}{C}H_2{-}CH{=}CH_2 \qquad\qquad CH_2{=}CH{-}\overset{\bullet}{C}H_2 \quad (XIb)$$
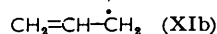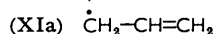
(X) and its mirror image. With each, the three different spin distributions (Xa, b, c) must be included with appropriate relative weights.

Tests were first made by using no adjustable constants. The Heitler–London function was tested ($k = 0$ in valence bond B above). As an alternative, bond orbitals were used ($k = 1$ in B). The molecular-orbital formula was tested with $k = 1$ and with $k = \sqrt{2}$ (Hückel). The non-pairing formula (X) was tested with $k = 1$ (simple bond orbitals). The " best " solution is $0 \cdot 318\psi_1 + 0 \cdot 116\psi_2 + 0 \cdot 142\psi_3 + 0 \cdot 047\psi_4$. The results are presented in Table 6 where the " energies " are $E - 3W_{2p}$ (cf. Table 2).

⁶ Coulson and Fischer, *Phil. Mag.*, 1949, **40**, 386.

TABLE 6.

Results for the allyl radical obtained by using various functions having no adjustable constants.

Functions	Energy (ev)	Overlap
Non-pairing formula	−26·409	0·897
Molecular orbital $(a + b + c)$	−26·600	0·908
Molecular orbital $(a + b\sqrt{2} + c)$	−27·110	0·942
Valence bond (Heitler–London)	−27·996	0·967
Valence bond (bond orbital)	−28·229	0·980
" Best " function	−28·914	1·000

The " energy test " and " overlap test " place the five schemes in the same order; this order is discussed below.

The results obtained when each type of function is allowed one adjustable constant (*i.e.*, k in each is chosen to minimise the energy) are listed in Table 7 (the energies are $E - 3W_{2p}$). These results are somewhat disconcerting because, while the valence-bond and the molecular-orbital method have retained the order of merit that they had in the simpler treatment (Table 6), the non-pairing formula surpasses them all and its results are very close to the " best " function (see below).

For completeness two other functions were tested but, because of their lack of success, the results obtained by means of them are not included in Table 7. One was a third valence-bond function constructed in a manner similar to B above, except that c in the first pair of terms was replaced by $(c + kb)$, and a in the second pair by $(a + kb)$. The minimised energy was

TABLE 7.

Results for the allyl radical obtained by using various functions having one adjustable constant.

Functions	Energy (ev)	k	Overlap
Molecular orbital	−27·124	1·511	0·945
Valence bond (A)	−28·240	1·061	0·981
Valence bond (B)	−28·849	0·2212	0·998
Non-pairing	−28·904	0·2790	0·9996
" Best " function	−28·914	—	1·000

−28·848 with $k = 0.1830$, the overlap being 0·998. The performance is, therefore, almost as good as that of valence bond B, though k is, as would be expected by considering inter-electron repulsion, less in this case than for B. The second was another non-pairing formula, in which the first term in the non-pairing formula above was changed to $(a + kb, c + kb, c)$, and subsequent terms were modified correspondingly. The performance of this was very little better than that of the non-pairing formula having $k = 1$ (Table 6). The energy was minimised with $k = 1.080$ at −26·424 ev and the overlap was 0·898. If we consider the functions that have been tested, it seems unlikely that any simple one having only one adjustable constant will provide an improvement on the non-pairing formula (X), the results for which are given in Table 7.

Allyl Negative Ion.—The ion has been examined in the same way as the other two species. The various formulæ that have been tested may be represented by:

Valence bond:

A: $\{(a + kb, a + kb, c, c)\} + \{(c + kb, c + kb, a, a)\}$
$= k\psi_1^+ + 2\psi_3^+ + k^2\psi_4^-$.

B (ref. 6): $\{(a + kb, ka + b, c, c) + (ka + b, a + kb, c, c)\}$
$+ \{(c + kb, kc + b, a, a) + (kc + b, c + kb, a, a)\}$
$= (1 + k^2)\psi_1^- + 4k\psi_3^- + 2k\psi_4^-$.

Molecular orbital:

$(a + kb + c, a + kb + c, c - a, c - a) = 2k\psi_1^- + k^2\psi_2^- + 4\psi_3^- + k^2\psi_4^-$.

Non-pairing:

$\{(a, a + kb, kb + c, c) + (c, c + kb, kb + a, a)\} = k\psi_1^- + k^2\psi_2^- + 2\psi_3^-.$ *

* This shows that formula (IX) leads to a satisfactory function; see " Electron Spin " section.

In the first place, tests were made with no adjustable constants, *i.e.*, the valence-bond formula B with $k = 0$ (Heitler–London) and $k = 1$ (bond orbital) were tested. The molecular-orbital formula was tested with $k = 1$ and $k = \sqrt{2}$ (Hückel). The non-pairing formula (based on IX) was tested with $k = 1$ (bond orbitals).

The " best " formula was found to be $0.319\psi_1^- + 0.304\psi_2^- + 0.195\psi_3^- + 0.045\psi_4^-$. It is clear that the best of the above formulæ (with no adjustable constant) is the non-pairing one, as it leads to a solution which makes the coefficient of ψ_4^- zero, and this is, in fact, found to be very small. Both the valence-bond (bond orbital) and the molecular-orbital method give quite the wrong pattern of coefficients, in particular overestimating the contribution of ψ_3^- and ψ_4^-. The valence-bond (Heitler–London) method is, of course, over-restrictive. The results for all these functions are listed in Table 8. The " energies " are $E - 4W_{2p}$ (cf. Table 3). The results are similar to those obtained for the positive ion, though, in this case, the energy

TABLE 8.

Results for the allyl negative ion obtained by using various functions having no adjustable constants.

Functions	Energy (ev)	Overlap
Valence bond (bond orbital)	−11·440	0·854
Valence bond (Heitler–London)	−12·570	0·918
Molecular orbital $(a + b + c)$	−12·968	0·929
Molecular-orbital $(a + b\sqrt{2} + c)$	−13·432	0·956
Non-pairing	−13·416	0·958
" Best " function	−14·506	1·000

derived by using the Hückel molecular orbitals is lower than that derived by using the non-pairing function. The difference is very small and the non-pairing formula overlaps the " best " function better.

The results obtained when each type of function is allowed one adjustable constant are listed in Table 9 (the energies are $E - 4W_{2p}$). The order is now the same as that obtained

TABLE 9.

Results for the allyl negative ion obtained by using various functions having one adjustable constant.

Functions	Energy (ev)	k	Overlap
Valence bond (A)	−11·495	0·8965	0·851
Valence bond (B)	−13·206	0·1195	0·924
Molecular orbital	−13·438	1·4767	0·962
Non-pairing	−14·098	1·5991	0·984
" Best " function	−14·506	—	1·000

with the positive ion, and the non-pairing formulation leads to a markedly better result than does the best molecular-orbital representation. The energy obtained by using the non-pairing function is about 10 kcal. per g.-ion greater than that obtained by using the " best " function. This is not quite as good as for the positive ion.
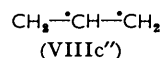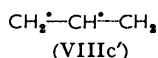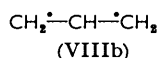
For all three species, the most satisfactory formulation is one that is of a bond-type but discards (for electrons in π-orbitals) the idea of pairing electrons in the same orbital or the same bond. That is, the representations are radically different from those obtained by the ordinary molecular-orbital method and also from those obtained by the ordinary valence-bond method which employs Lewis–Langmuir component structures as the basis.

DISCUSSION

The cation and anion will be considered first. For the cation the calculations for the ground state have shown that formula (VIII) (non-pairing) represents the electronic structure better than does (VII) (molecular orbital) or a resonance hybrid of (V) and (VI) (conventional valence bond with Pauling-type resonance). Though formulæ of this type do not seem to have been suggested previously, it is to be expected that (VIII) should have a lower energy than a hybrid of (V) and (VI) because all these have two electrons of the π-system in bond regions but (VIII) separates the two electrons more than do (V) and (VI). Therefore, for structure (VIII), inter-electron repulsion will be less than for (V) and (VI), and
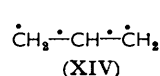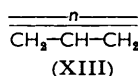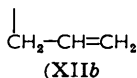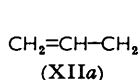
hence structure (VIII) has a lower energy. It is interesting that structure (VIII) and the resonance hybrid of (V) and (VI) both describe the two π-bonds as half-bonds. However, the hybrid achieves this by describing each bond as a combination of a single π-bond for one structure and a zero π-bond for the other, the two structures having equal probability. On the other hand, (VIII) is a structure for which the two bonds are simultaneously half-bonds. The molecular-orbital formula (VII) gives equal probability to the distribution in which the two electrons are in separate bonds and to those in which they are in the same bond. Consequently, as might be expected, it is less good than the non-pairing formula (VIII) but better than the valence-bond (resonance) description (V and VI) which puts both electrons in the same bond.

The wave function corresponding to the non-pairing structure (VIII) was allowed one adjustable constant in two ways. The first, A, is made of separate parts which are themselves symmetrical, but the second, B, is made up of parts which are unsymmetrical.

$$CH_2\overset{\bullet}{-}CH-\overset{\bullet}{-}CH_2 \qquad CH_2\overset{\bullet}{-}CH\overset{\bullet}{-}CH_2 \qquad CH_2\overset{\bullet}{-}CH\overset{\bullet}{-}CH_2$$
$$\text{(VIIIb)} \qquad\qquad \text{(VIIIc')} \qquad\qquad \text{(VIIIc'')}$$

The first may be represented by (VIIIb) and the second by (VIIIc' and c'').* Of these, the second (B) is definitely the better. For A, the energy E is minimised with ($a + 0.711b$, $c + 0.711b$), etc. This is to be expected since it separates the electrons. But it reduces the probability of the electrons' being near the central atom, which, as pointed out above, has a greater effective electronegativity than the outer atoms. For B, the energy E is minimised with ($a + 0.252b$, $b + 0.252c$), etc., and the greater success of this function shows clearly the effect of the greater effective electronegativity of the central atom.

For the negative ion the valence-bond description may be represented diagrammatically as a resonance hybrid of (XIIa and b). The molecular-orbital formula is (XIII), which is

$$CH_2=CH-CH_2 \qquad \overset{|}{C}H_2-CH=CH_2 \qquad \overline{\overset{\overline{n}}{CH_2-CH-CH_2}} \qquad \overset{\bullet}{C}H_2\overset{\bullet}{-}CH\overset{\bullet}{-}\overset{\bullet}{C}H_2$$
$$\text{(XIIa)} \qquad\qquad \text{(XIIb} \qquad\qquad \text{(XIII)} \qquad\qquad \text{(XIV)}$$

analogous to (III) for the NO_2^- ion. The non-pairing formula is (XIV). As described above, the two most important structures are those described by (IX). For the same reasons as for the positive ion, (XIV) is a better description than the resonance hybrid of (XIIa and b), and it is also better than (XIII). Again the balancing effects of increasing the binding and decreasing the inter-electron repulsion are apparent. In the wave function for the non-pairing formula which has one adjustable constant, the simple bond orbital ($a + b$) is replaced by ($a + 1.5996b$). In this case, both inter-electron repulsion and the effect of electronegativity favour $k > 1$, which is a little different from the situation in the positive ion. Therefore a formula analogous to (VIIIb, c', and c'') which were drawn for the cation would be (XIVa) which gives rather more information than (XIV).

$$\overset{\bullet}{C}H_2\overset{\bullet}{-}CH\overset{\bullet}{-}CH_2 \qquad \text{(XIVa)}$$
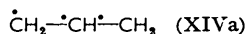
Though this formulation also has severe limitations, it stresses the fact that terms such as *aabb* and *bbcc* have little importance in the wave function, whereas the valence-bond-resonance description gives them as much weight together as *aacc*—this is its major fault.

The radical presents for discussion a more difficult problem than that for the two ions. On the other hand, for it, the best approximate function is very close indeed to the " best " function (overlap 0.9996). There is here a matter of principle. Looking at the performance of the functions with no adjustable constants (Table 6), we should conclude that

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* In formulæ VIIIb, c', and c'', the position of the dot is used to indicate which atomic orbital makes the bigger contribution to the bond orbital. Thus, in the function represented by (VIIIb), the orbitals on the outer atoms make larger contributions. This type of formula clearly has limitations but it is also useful in the present discussion.

the valence-bond description is much the best, being much better than that based on the non-pairing or double-quartet formulation. But when one adjustable constant is allowed the relative merits are reversed (Table 7). This means that the conclusion derived from the more approximate approach is almost certainly wrong. It means that, with this degree of limitation (*i.e.*, no adjustable constant) placed on the functions, the best electron distribution that can be obtained is that provided by the valence-bond method. However, this does not prove that the valence-bond method provides a very good description, because the limitation that has been imposed on the functions apparently precludes any approximate solution from approaching the true one closely. Because the results obtained with the non-pairing formula containing one adjustable constant are so good, little significance can be attached to the conclusions based on the simpler treatment. Therefore we conclude that the best representation of the structure is a hybrid of (XVa and b) rather than a hybrid of (XVIa and b).

(XVa) $\overset{\bullet}{C}H_2\overset{\bullet}{\text{---}}CH\overset{\bullet}{\text{---}}CH_2$ $CH_2\overset{\bullet}{\text{---}}CH\overset{\bullet}{\text{---}}\overset{\bullet}{C}H_2$ (XVb)

(XVIa) $\overset{\bullet}{C}H_2\text{---}CH\overset{\bullet}{\text{---}}CH_2$ $CH_2\overset{\bullet}{\text{---}}CH\text{---}\overset{\bullet}{C}H_2$ (XVIb)

On the basis of achieving a balance between chemical binding and inter-electron repulsion (as has been discussed above) this can be readily understood.

For the radical, the molecular-orbital method produces a poor description, a conclusion with which the results in Tables 6 and 7 are in accord. A further indication that the radical presents a somewhat different problem from the two ions and is not necessarily intermediate between them is provided by the values of the three constants required to minimise the energies in the valence-bond formulations. They are: cation 0·1222; radical 0·2212; anion 0·1195. This difference is clearly because a high value of this constant introduces, for the ions, terms that are wanted (*e.g.*, *bb* for the cation) and terms that are not wanted (*e.g.*, *aa* and *cc* for the cation), whereas, for the radical, it brings in only terms that are wanted (*e.g.*, *aab* type and *abb* type).

Perhaps the π-binding in the allyl radical should be considered in the following way. The distribution (XVII) would provide some binding because the energy of an electron

$\overset{\bullet}{C}H_2\text{---}\overset{\bullet}{C}H\text{---}\overset{\bullet}{C}H_2$ (XVII)
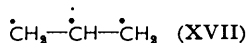
in a $2p\pi$-orbital on, for example, the CH group is lower in the system CH_2–CH–CH_2 than in the isolated CH group. But, in addition, there is an increased lowering of the energy because of electron drifts in the two directions in the molecule of the type represented by (XVa and b).

Lastly, certain implications of these results will be mentioned though it must be stressed that they constitute extrapolations of what has been found for the allyl systems. For the nitrite ion it would seem that (IV) is likely to be the best simple formula. Similarly, for ozone the best formula is almost certainly (XVIII) rather than the combination of the two valence-bond-resonance structures or the molecular orbital-formulation. Similarly
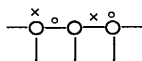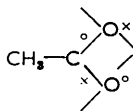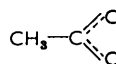
(XVIII)   (XIX)   (XX)

the acetate ion would presumably be written better as (XIX). Often the electronic structure of the acetate ion is represented by (XX), but this is used either as an abbreviation for the Pauling-type resonance pair of structures or to indicate that the two bonds are equal, without implying anything in particular about the wave function (this vagueness is, of course, most unsatisfactory and should be avoided, because it means that the formula has no real or definite meaning).

In the allyl positive ion there are two σ-bonds and two electrons in the π-system, and it is found that the ground state involves two simultaneous π-half-bonds, rather than the Pauling-type resonance between single and zero-π-bonds. This suggests that for benzene, in which there are six electrons in π-orbitals and six σ-bonds, the structure will consist of six simultaneous π-half-bonds, the formula being (XXI).[7] This, and the other systems mentioned above, as well as a number of others, are being examined along similar lines and the results will be presented in future papers.

(XXI)

[7] Dewar and Schmeising, *Tetrahedron*, 1960, **11**, 96.