196. *The Allyl Radical and Anion.*

By D. M. Hirst and J. W. Linnett.

Calculations have been carried out for the ground states of the three- and four-π-electron systems of the allyl radical and anion. For treatments assigning electrons to different spatial orbitals, two independent combinations of spin functions (say, Ψ_{I} and Ψ_{II}) are possible for each species. All linear combinations of these $[C\Psi_{\text{I}} + (1 - C)\Psi_{\text{II}}]$ are satisfactory eigenfunctions of S^2; the dependence of the derived energy on C has been investigated and is discussed. For the anion, the proper combination of spin functions for the non-pairing treatment which assigns each electron to a different spatial orbital can be derived from the simple molecular-orbital function by taking into account the effects of electron correlation. For the radical, the spin-density matrices have been calculated for a wide variety of functions and are discussed in relation to Fessenden's experimental results.

This paper deals with the wave functions of the π-electron systems of the ground states of the allyl radical and anion. It has been shown [1] that, for these species, a " non-pairing " treatment which assigns each electron to a different spatial orbital is more successful than the valence-bond or molecular-orbital treatment, when either single or no more than equivalent configurations are used. The non-pairing treatment given by Hirst and Linnett [1] for the radical and anion employed particular combinations of spin functions which were not the only satisfactory ones. In the present paper, all possible satisfactory combinations have been studied and their relative success is examined. For the radical,

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[1] Hirst and Linnett, *J.*, 1962, 1035, 3844.

the calculated spin densities for the different functions are compared with those observed experimentally by Fessenden.[2]

Allyl Radical.—It will be supposed, as before,[1] that the π-orbitals in the molecule can be constructed from the $2p\pi$-orbitals a, b, and c, on the three carbon atoms, b being the central one. The successful non-pairing treatment was based on structure (I), together

$\dot{\mathrm{C}}\mathrm{H_2}\overset{\cdot}{—}\mathrm{CH}\overset{\cdot}{—}\mathrm{CH_2}$ (I)

with its mirror image. In (I), the three orbitals employed are: a, $ka + b$, and $kb + c$ (k being less than one). There are two independent functions, involving the above three orbitals in (I), which are satisfactory eigenfunctions of S^2 for the ground state. They may be represented as $(\alpha\beta\alpha - \alpha\alpha\beta)$ and $(\alpha\beta\alpha - \beta\alpha\alpha)$ in which the spin functions are combined with the above three functions taken in the order listed above. These two functions will be called Ψ_{I} and Ψ_{II} [in these the corresponding mirror image structure to (I) has also been included]. Any combination of Ψ_{I} and Ψ_{II} will be satisfactory; in the previous paper the combination $\Psi_{\mathrm{I}} + \Psi_{\mathrm{II}}$, in which the two exchanges were given equal weight, was used. All combinations of Ψ_{I} and Ψ_{II} have now been tested. On the formulation employed in the previous paper (in which the order of the spin functions is always $\alpha\beta\alpha$), Ψ_{I} and Ψ_{II} are given by:

$$\begin{aligned}\Psi_{\mathrm{I}} &= \{(a,\ ka + b,\ kb + c) + (a,\ kb + c,\ ka + b)\}\\ &\qquad - \{(c,\ b + kc,\ kb + a) + (c,\ a + kb,\ b + kc)\}\\ &= \psi_1 + k\psi_2 + 2k\psi_3 + k^2\psi_4.\end{aligned}$$

and

$$\begin{aligned}\Psi_{\mathrm{II}} &= \{(a,\ ka + b,\ kb + c) + (ka + b,\ a,\ kb + c)\}\\ &\qquad - \{(c,\ b + kc,\ a + kb) + (b + kc,\ c,\ a + kb)\}\\ &= \psi_1 + 2k\psi_2 + k\psi_3 + 2k^2\psi_4.\end{aligned}$$

where k is an adjustable parameter and ψ_1, ψ_2, ψ_3, and ψ_4 have the same meaning as before.

Combinations of Ψ_{I} and Ψ_{II} will be represented by

$$\Psi_+ = C\Psi_{\mathrm{II}} + (1 - C)\Psi_{\mathrm{I}}$$

and

$$\Psi_- = C\Psi_{\mathrm{II}} - (1 - C)\Psi_{\mathrm{I}},$$

both with $0 < C < 1$. For each value of C, the parameter k was chosen to minimise the energy. The energies calculated are shown in Fig. 1 (all numerical quantities used were the same as in the previous paper). The energy is a minimum for $C = 0{\cdot}35$. The results for a number of particular values of C are given in Table 1 where the values of k are also listed. The " best " energy obtainable by using a, b, and c and all possible configurations is also listed.

Allyl Negative Ion.—The " non-pairing " formulation for this ion is based on (II) in which the four orbitals are a, $a + kb$, $kb + c$, and c (k being greater than one). There are

$\dot{\mathrm{C}}\mathrm{H_2}\overset{\cdot}{—}\mathrm{CH}\overset{\cdot}{—}\dot{\mathrm{C}}\mathrm{H_2}$ (II)

two independent eigenfunctions of S^2. These may be taken as $(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\alpha\beta\beta - \beta\beta\alpha\alpha) - \Psi_{\mathrm{I}}^-$ and $(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta) - \Psi_{\mathrm{II}}^-$. On the previous symbolism:

$$\Psi_{\mathrm{I}}^- = k\psi_1^- + 2k^2\psi_2^- + 2\psi_3^-$$

and

$$\Psi_{\mathrm{II}}^- = 2k\psi_1^- + k^2\psi_2^- + 4\psi_3^-,$$

where ψ_1^-, ψ_2^-, and ψ_3^- have the same meaning as in the previous paper. Energies have been calculated for

$$\Psi_+^- = C\Psi_{\mathrm{II}}^- + (1 - C)\Psi_{\mathrm{I}}^-$$

and

$$\Psi_-^- = C\Psi_{\mathrm{II}}^- - (1 - C)\Psi_{\mathrm{I}}^-$$

for $0 < C < 1$. The function used in the previous paper corresponded to $C = 0{\cdot}5$ in

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[2] Fessenden, personal communication.

Ψ_+^- (*i.e.*, to $\Psi_I^- + \Psi_{II}^-$, in which both types of exchange were given equal weight). As with the radical, for each value of C, k was chosen to minimise the energy. The results are shown in Fig. 2. The energy is a minimum for $C = 0{\cdot}8$ in Ψ_-^-; a fairly good energy is obtained with $\Psi_I^- + \Psi_{II}^-$, the function used previously. The results for several particular values of C are shown in Table 2, together with the " best " energy obtainable by using all configurations.

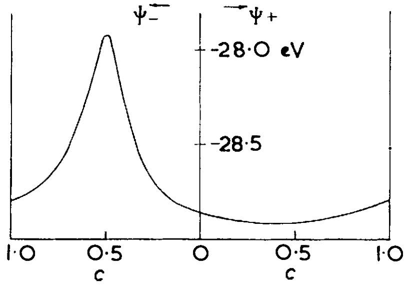

FIG. 1. Dependence of energy on spin combinations for the allyl radical; c measures the mixing of $\Psi_I(\alpha\beta\alpha - \alpha\alpha\beta)$ and $\Psi_{II}(\alpha\beta\alpha - \beta\alpha\alpha)$ (see text).

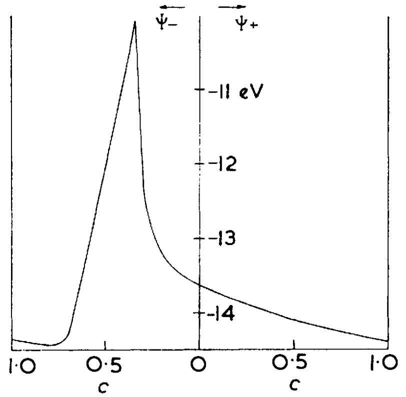

FIG. 2. Dependence of energy on spin combination for the allyl negative ion; c measures the mixing of $\Psi_I^-(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\alpha\beta\beta - \beta\beta\alpha\alpha)$ and $\Psi\Psi_{II}^-(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta)$ (see text).

TABLE 1.

Results for the allyl radical.

Function	Energy (ev)	k
$\alpha\beta\alpha - \alpha\alpha\beta$ (Ψ_I)	$-28{\cdot}859$	0·270
$\alpha\beta\alpha - \beta\alpha\alpha$ (Ψ_{II})	$-28{\cdot}788$	0·239
$\alpha\beta\alpha - \frac{1}{2}\alpha\alpha\beta - \frac{1}{2}\beta\alpha\alpha$ ($\Psi_I + \Psi_{II}$)	$-28{\cdot}904$	0·279
$\alpha\beta\alpha - 0{\cdot}65\alpha\alpha\beta - 0{\cdot}35\beta\alpha\alpha$ ($0{\cdot}65\Psi_I + 0{\cdot}35\Psi_{II}$)	$-28{\cdot}909$	0·282
" Best "	$-28{\cdot}914$	—

Spin Density in the Allyl Radical.—The spin density matrix has been calculated by McConnell's method[3] for a variety of different functions: (1) the best Slater function $0{\cdot}318\psi_1 + 0{\cdot}116\psi_2 + 0{\cdot}142\psi_3 + 0{\cdot}047\psi_4$; McConnell[4] has given figures obtained by using the full molecular-orbital configuration-interaction function of Chalvet and Daudel[5] (these should agree with out " best " figures, which they do); (2) the Heitler–London function (i) with, and (ii) without, overlap; (3) the molecular-orbital function, $k\psi_1 + 2\psi_2 +$

TABLE 2.

Results for the allyl negative ion.

Function	Energy (ev)	k
$\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\alpha\beta\beta - \beta\beta\alpha\alpha$ (Ψ_I^-)	$-13{\cdot}630$	1·123
$\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta$ (Ψ_{II}^-)	$-14{\cdot}378$	2·338
$\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \frac{1}{2}\alpha\alpha\beta\beta - \frac{1}{2}\beta\alpha\alpha - \frac{1}{2}\alpha\beta\beta\alpha - \frac{1}{2}\beta\alpha\alpha\beta$ ($\Psi_I^- + \Psi_{II}^-$)	$-14{\cdot}098$	1·599
$0{\cdot}6\alpha\beta\alpha\beta + 0{\cdot}6\beta\alpha\beta\alpha + 0{\cdot}2\alpha\alpha\beta\beta + 0{\cdot}2\beta\beta\alpha\alpha - 0{\cdot}8\alpha\beta\beta\alpha - 0{\cdot}8\beta\alpha\alpha\beta$ ($0{\cdot}2\Psi_I^- - 0{\cdot}8\Psi_{II}^-$)	$-14{\cdot}448$	3·290
" Best "	$-14{\cdot}506$	

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[3] McConnell, *J. Chem. Phys.*, 1958, **28**, 1188.

[4] McConnell, *J. Chem. Phys.*, 1959, **30**, 328.

[5] Chalvet and Daudel, *J. Chim. phys.*, 1952, **49**, 629.

$k^2\psi_3 + k\psi_4$, in which $k = 1{\cdot}511$ (i) with, and (ii) without, overlap; (4) the Coulson–Fischer function, $(1 + k^2)\psi_1 + 2k\psi_2 + 2k\psi_3$ with $k = 4{\cdot}566$; (5) the non-pairing function $\Psi_{\text{I}} + \Psi_{\text{II}}$ with $k = 0{\cdot}279$; (6) the non-pairing function $0{\cdot}65\Psi_{\text{I}} + 0{\cdot}35\Psi_{\text{II}}$ with $k = 0{\cdot}282$; (7) a molecular-orbital function used by Higuchi,[6] which is described below; (8) results are also listed for some calculations made by McConnell[7] using a similar function due to Berthier;[8] and (9) calculations made by Dearman and Lefebvre[9] using the method of alternant orbitals.

The matrix may be represented as

$$\begin{pmatrix} A_{aa} & A_{ab} & A_{ac} \\ A_{ab} & A_{bb} & A_{bc} \\ A_{ac} & A_{bc} & A_{cc} \end{pmatrix}$$

when a, b, and c refer to the three atomic orbitals. In this matrix, symmetry requires that $A_{aa} = A_{cc}$, and $A_{ab} = A_{bc}$. The results are shown in Table 3.

Higuchi's function[6] was based on the use of the three molecular orbitals $(a + k_1b + c)$, $(a + k_2b + c)$, and $(a - c)$ in which k_1 and k_2 were different. The function actually used by Higuchi was not a satisfactory eigenfunction of S^2. This was corrected; the combination of spin functions used, with the three orbitals in the above order, was $(2\alpha\beta\alpha - \alpha\alpha\beta - \beta\alpha\alpha)$. This leads to

TABLE 3.

Calculated terms in spin density matrix for allyl radical.

Function	A_{aa}	A_{bb}	A_{ab}	A_{ac}
(1) " Best "	0·635	−0·236	−0·013	−0·272
McConnell (Chalvet–Daudel)	0·636	−0·239	−0·011	−0·269
(2) Heitler–London (i)	0·680	−0·313	−0·039	−0·077
(ii)	0·667	−0·333	0	0
(3) Molecular orbital (i)	0·520	0	0	−0·520
(ii)	0·500	0	0	−0·500
(4) Coulson–Fischer	0·646	−0·248	−0·027	−0·208
(5) $\Psi_{\text{I}} + \Psi_{\text{II}}$	0·639	−0·235	−0·021	−0·260
(6) $0{\cdot}65\Psi_{\text{I}} + 0{\cdot}35\,\Psi_{\text{II}}$	0·637	−0·239	−0·014	−0·259
(7) Higuchi	0·618	−0·201	−0·009	−0·320
(8) McConnell–Berthier	0·609	−0·185	−0·005	−0·345
(9) Dearman–Lefebvre	0·639	−0·265	−0·103	−0·242

$$\Psi = (2k_2 + k_1)\psi_1 + 6\psi_2 + 3k_1k_2\psi_3 + 3k_1\psi_4,$$

which gives an energy of $3W_{2p} - 28{\cdot}759$ ev, compared with $3W_{2p} - 28{\cdot}914$ ev calculated by using the " best " function. This is not nearly as good as the non-pairing treatment. McConnell and Berthier's calculations are similar but a bond length of 1·35 Å was used instead of 1·39 Å.

Fessenden observed the electron-spin resonance spectrum of the allyl radical. The observed spin densities were: *a* 0·581; *b* −0·162; *c* 0·581.

McLachlan,[10] using a semi-empirical self-consistent-field molecular-orbital treatment calculated them to be 0·594, −0·187, 0·594, respectively (cf. Higuchi, and McConnell and Berthier).

Discussion.—The spin densities in the allyl radical will be discussed first. The Heitler–London treatment predicts too much negative spin density on the central atom and too much positive spin density on the end carbon atoms. This is a consequence of the

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[6] Higuchi, *J. Chem. Phys.*, 1957, **26**, 151.

[7] McConnell, *J. Chem. Phys.*, 1958, **29**, 244.

[8] Berthier, *J. Chim. phys.*, 1955, **52**, 141.

[9] Dearman and Lefebvre, *J. Chem. Phys.*, 1961, **34**, 72.

[10] McLachlan, *Mol. Phys.*, 1960, **3**, 233.

absence of ionic terms from this type of function and because it involves too great a separation of spin. On the other hand, the molecular-orbital treatment underestimates the spin densities, and even gives a zero spin density to the central atom. The experimental result is between the two. The " best " function, the Coulson–Fischer function, and the non-pairing functions all give approximately equal results and, since the last two both constitute a localised-orbital approach, they show the same feature as the Heitler-London function in giving spin densities which are too high, but they are much smaller than those calculated by using a Heitler–London function. Higuchi's correlated molecular-orbital function (cf. also McLachlan, and McConnell and Berthier) is the most successful though, even with this, the densities are too large; in this it differs greatly from the ordinary molecular–orbital treatment. In assessing fully the true significance of these results, it is difficult to know what allowance, if any, ought to be made for spin polarisation in the σ-orbitals.

By making calculations with different spin combinations for the allyl radical and anion, it has been possible to improve the energy compared with that obtained in the previous paper. With the radical the improvement is small, and the combination of spin functions that had been used was the best simple one that could have been selected. However, the situation is very different for the anion. In that case, Ψ_{II}^- alone would have been much better than $\Psi_{\text{I}}^- + \Psi_{\text{II}}^-$ which was used. The combination, $0{\cdot}2\Psi_{\text{I}}^- - 0{\cdot}8\Psi_{\text{II}}^-$, is better still and gives an energy only about 1 kcal./g.-ion greater than the best treatment. With the anion the energy, and the value of k needed to minimise it, are much more dependent on C than they are with the radical (see Tables 1 and 2). This is presumably because the presence of four electrons makes inter-electron repulsion in the anion much more important than in the radical. Consequently changes in inter-electron correlation are more important, and those are affected both by changes in the combination of spin functions and by changes in k.

It is important to try to understand why Ψ_{II}^- is better than Ψ_{I}^-, $\Psi_{\text{I}}^- + \Psi_{\text{II}}^-$, or any other simple combination of spin functions. This can be done by starting with the general molecular-orbital description and modifying it to take account of charge correlation. The simple molecular-orbital wave function for the ground state is:

$$[(a + kb + c)\alpha,\ (a - c)\alpha,\ (a + kb + c)\beta,\ (a - c)\beta]. \tag{1}$$

This may be transformed into an equal determinant made up of equivalent orbitals:

$$[(2a + kb)\alpha,\ (kb + 2c)\alpha,\ (2a + kb)\beta,\ (kb + 2c)\beta]. \tag{2}$$

Let us replace the first function by $[a + (a + kb)]$ and the second by $[c + (c + kb)]$. Multiplying these together we obtain four types of terms ac, $a(c + kb)$, $(a + kb)c$, and $(a + kb)(c + kb)$. Similarly we will obtain a similar four types for the third and fourth functions in (2). The whole determinant (1) may now be replaced by products of terms derived by multiplying these together. Let us do this but, in order to take account of electron correlation, all terms which assign two electrons to the same spatial orbital will be omitted. This gives the following sum:

$$\begin{aligned}&[a\alpha,\ c\alpha,\ (a + kb)\beta,\ (c + kb)\beta] + [a\alpha,\ (c + kb)\alpha,\ (a + kb)\beta,\ c\beta]\\ &+ [(a + kb)\alpha,\ c\alpha,\ a\beta,\ (c + kb)\beta] + [(a + kb)\alpha,\ (c + kb)\alpha,\ a\beta,\ c\beta].\end{aligned}$$

This is equal to:

$$\begin{aligned}&[a\alpha,\ (a + kb)\beta,\ (c + kb)\beta,\ c\alpha] - [a\alpha,\ (a + kb)\beta,\ (c + kb)\alpha,\ c\beta]\\ &- [a\beta,\ (a + kb)\alpha,\ (c + kb)\beta,\ c\alpha] + [a\beta,\ (a + kb)\alpha,\ (c + kb)\alpha,\ c\beta].\end{aligned}$$

This is $-\Psi_{\text{II}}^-$. A reason why Ψ_{II}^- is the best simple spin combination is therefore provided. Because of spin correlation it would not be possible for the molecular orbital to give, by any analogous transformation, terms of the kind $\alpha\alpha\beta\beta$ or $\beta\beta\alpha\alpha$ since they correspond to the orbitals at one end of the molecule associated with one spin function and those at the other with the other spin function.

It is possible to derive the non-pairing function for the allyl radical similarly, but the argument is less satisfactory because it is more arbitrary.

It is apparent that a major difficulty that arises when every electron is assigned to a different spatial orbital is that, for a given set of space functions, there are a number of combinations of spin assignments which produce eigenfunctions in S^2. It is not always possible to decide simply which will give the lowest energy. This paper shows that further work is needed because this problem will arise frequently when attempts are made to allow for electron correlation by modifying the functions of simple molecular-orbital treatments to account for the effect of electrons on one another.

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INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, July 27th,* 1962.]