

A RE-STATEMENT OF THE CONCERTED-DIRADICAL MECHANISM FOR 1,3-DIPOLAR CYCLOADDITION REACTIONS

RICHARD D. HARCOURT*

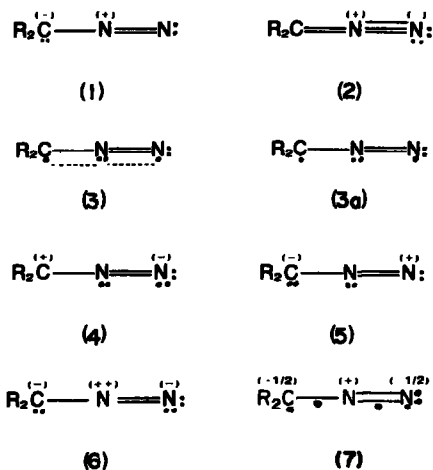
Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

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Abstract—Valence-bond theory is presented for a concerted-diradical mechanism of 1,3-dipolar cycloaddition reactions. Particular attention is given to the importance of "long-bond" (or spin-paired diradical) structures for describing the electronic structures of 1,3-dipolar molecules, and the use of them to provide valence-bond descriptions of concerted 1,3-dipolar cycloadditions.

Firestone¹ has recently provided a comparison of the step-wise diradical and concerted mechanisms of 1,3-dipolar cycloadditions, and has concluded that "the experimental facts for the field as a whole favor the diradical mechanism". The contrary conclusion is held by Huisgen.² In an earlier publication,³ an attempt was made to reconcile the conflicting points of view expressed previously by Huisgen⁴ and Firestone.⁵ A quantum mechanical justification was provided³ for the hypothesis that 1,3 dipolar cycloadditions could have both concerted and (spin-paired) diradical characteristics simultaneously. The theory for Ref. 3 focussed attention on some aspects of valence-bond theory that have not been effectively considered by Firestone¹ and Huisgen.² These include the importance of "long-bond" structures for describing the electronic structure of the 1,3-dipolar molecule, and the development of "increased-valence" in the transition state. It is therefore worthwhile here to restate and elaborate on the concerted diradical mechanism of 1,3-dipolar cycloaddition. In doing so, particular attention will be given to the mechanism when Linnett-type⁶ structures are used to represent the electronic structure of the 1,3-dipole. Firestone^{1,5} has used the Linnett structures to form the theoretical basis for his step-wise diradical mechanism.

We shall use diazomethane as an example of a 1,3-dipolar molecule. For it there are six (singlet-spin) valence-bond structures (1-6) that differ in the locations of four $2p\pi$ -electrons amongst three $2p\pi$ atomic orbitals. The structures 1-3 obey the octet rule for the C and N atoms, whereas 4-6 involve a sextet rather than an octet of valence-shell electrons disposed around the kernel for one of these atoms. Structures 1 and 2 are the zwitterionic structures, and structure 3 is a "long-bond" or spin-paired diradical structure. Because the "long-bond" between the C and terminal N atoms of 3 is formed by the overlap of singly-occupied atomic orbitals located on non-adjacent atoms, this bond is extremely weak; some workers^{2,7,8} choose not to indicate the presence of this weak bond in the valence structures, and write 3 as 3a. For the present purpose it is irrelevant which of 3 or 3a is used; the essential point to note is that each of them has opposed spins for the singly-occupied π orbitals, and therefore it is able to participate in resonance with the remaining structures. Structures 4 (in particular) and 5 are the 1,3 dipolar



structures that Huisgen has implicated in his electronic mechanism for cycloaddition.

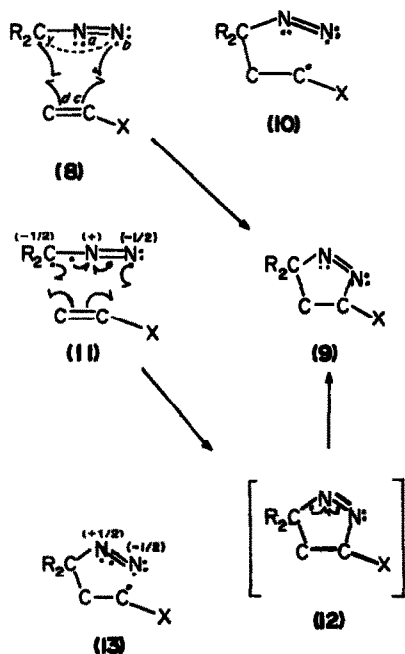
The results of a number of valence-bond calculations indicate that 3 makes an important contribution to the ground-state resonance description of the electronic structure of CH_2N_2 . For valence-bond structures (1-5), Roso⁹ has calculated bond-eigenfunction coefficients of 0.31, 0.23, 0.38, 0.05 and 0.10, and Hiberty and Le Forestier⁸ have calculated weights of 0.16, 0.41, 0.28, 0.04 and 0.01. The generalized valence-bond calculations of Walch and Goddard⁷ indicate that CH_2N_2 resembles more a diradical (i.e. 3) rather than a zwitterion. Although there may still be some uncertainty as to which is the most-important of these structures, it is clear that 3 must be given rather more attention than what has been allowed for by Huisgen.^{2,4}

Firestone^{1,5} has used the Linnett valence structure 7 to represent the electronic structure of CR_2N_2 . (For illustrative purposes only, formal charges in 7 are assigned on the assumption that bonding electrons are shared equally by pairs of adjacent atoms.³) The wave-function for 7 may be expressed as a linear combination of the bond-eigenfunctions for structures 1, 2, 3 and 6, i.e. 7 summarizes resonance between these latter four structures.^{3,6} The (spin-paired) diradical character of 7 is

made evident due to the presence of fractional odd-electron charges on the C and terminal N atoms.

If we use 3 alone to represent the electronic structure of CR_2N_2 then a concerted cycloaddition mechanism may easily be devised,⁹ namely that of 8→9. If the $2p\pi$ -atomic orbitals of the reactants are designated as y , a , b , c and d (as in 8), the (singlet-spin) wave-function for 9 may be expressed (see appendix) as $\Psi_1 = [(y^+d^+ - y^-d^-)(a^+a^+)(b^-c^- - b^+c^+)]$. In this wave function, α and β are the spin wave-functions, and the y and b electrons of R_2CN_2 are respectively spin-paired (in a Heitler-London sense) with the d and c electrons of the olefin to form CC and NC σ -bonds between the reactants. For the well-separated reactants, a similar wave function is $\Psi_2 = [(y^+b^+ - y^-b^-)(a^+a^+)(c^-d^- - c^+d^+)]$ for which spin-pairing occurs within the reactants. The linear combination $\Psi = C_1\Psi_1 + C_2\Psi_2$ may therefore be constructed^{3,10} to describe the approach of the reactants, with $|C_1| \ll |C_2|$ and $|C_1| \gg |C_2|$ respectively near the commencement and completion of the cycloaddition. For this description it is not obvious why Firestone¹ should require that only one bond (the CC σ -bond) be formed between the reactants to generate the singlet diradical (10).

If 7 is used to represent the electronic structure of CR_2N_2 , then the above description will still be relevant except for the replacement of (a^+a^+) by $(\psi_{ya}^+ \psi_{ab}^+ - \psi_{ya}^- \psi_{ab}^-)$ in the two wave-functions. (The $\psi_{ya} = y + ka$ and $\psi_{ab} = b + k'a$ are CN and NN bonding molecular orbitals, which are singly occupied in 7). The cycloaddition mechanism of 11→12→9 may then be constructed

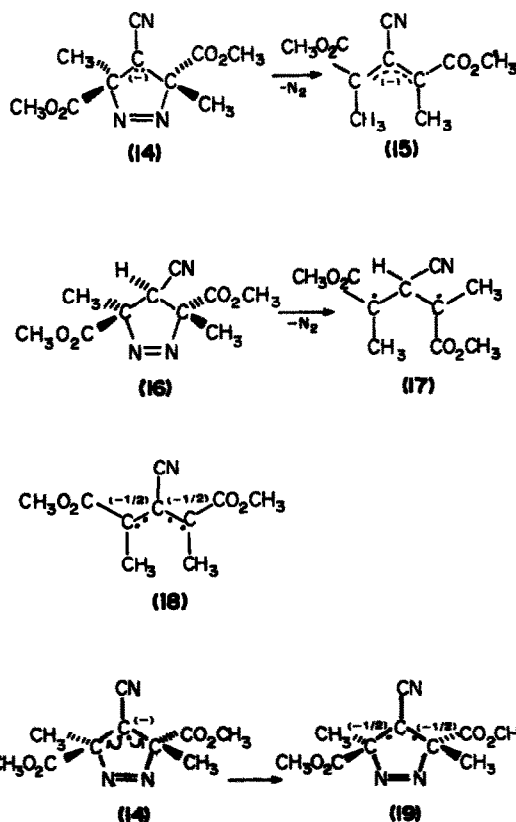


which utilizes the (spin-paired) diradical character present in valence structure 7. Firestone's spin-paired diradical structure 13 can be seen to be a special form of 12 with the parameter $k = \infty$ in ψ_{ya} and the spin-pairing that must occur between the b and c electrons (because their orbitals overlap) not displayed in the valence structure. The transition state (12) is an example of an "increased-valence" structure¹¹ because for it more electrons participate in bonding than does occur in the octet

structure 9. Firestone has not taken account of the possibility that "increased-valence" may occur in the transition state, and Huisgen has rejected the possibility that spin-paired diradical structures may make important contributions to the ground-state resonance description of a "1,3-dipolar" molecule.

If the above theory is valid for CH_2N_2 and other "1,3-dipolar" molecules, it is suggested that a more appropriate name for this class of molecule is "zwitterionic diradical hybrid"^{3,9,11} thereby emphasizing the important components of the valence-bond descriptions for these molecules. For all neutral "1,3-dipolar" molecules, there exists a "long-bond" structure (for example, 3) with zero formal charges on all atoms. An appeal to the electroneutrality principle suggests that such structures can make an important contribution to the ground-state resonance description of the electronic structure. The results of a number of valence-bond studies from different laboratories^{7-9,12} support this hypothesis.

Huisgen has commented² that "the rate ratio of $\geq 10^{20}$ between the reactions 14→15 (concerted cycloreversion 5→3+2) and 16→17 (formation of a trimethylene) at -197° illustrates the energetic advantage of the allyl anion bond system over the long-bond trimethylene species". We disagree. Huisgen has conceded (see Ref. 12 of his paper) that the allyl anion bond system of 15 can have diradical character, and this is made evident in the Linnert structure 18. As a consequence of electron delocalization from the negatively-charged C atom of 14, this type of electron distribution can also be generated from 14, as is shown in "increased-valence" structure 19. This leads to a weakening of the CN bonds of 14 relative to those of 16. We ascribe the increase in rate for 14→15 as due to a greater ability to acquire the diradical character



of 18, rather than to the greater stability of the allyl anion bond system.

Firestone¹ and Huisgen² agree that the formation of oximes and hydrazones from the 1,3-additions of nitrile oxides and nitrile imines to aryl acetylenes¹³ proceeds by means of a two-step mechanism for these reactions. Firestone's two-step diradical mechanism seems to be electronically viable.

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See also Refs. 1, 6, 7, 12, 17 and 19 of Ref. 9.

¹³See Refs. 181–184 of Ref. 1, or 167–173 of Ref. 2.

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APPENDIX

Construction of $S=0$ wave function

The $S=0$ wave functions Ψ_1 and Ψ_2 may be constructed by multiplying each of the spatial orbital wave-functions $y(1)d(2)a(3)a(4)b(5)c(6)$ and $y(1)b(2)a(3)a(4)c(5)d(6)$ by the $S=0$ spin wave-function $\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}\{\alpha(3)\beta(4) - \beta(3)\alpha(4)\}\{\alpha(5)\beta(6) - \beta(5)\alpha(6)\}$ and then antisymmetrizing.¹⁴ The Slater determinantal wave functions of the text are thereby obtained in which $y^a d^b$ is equivalent to $y(i)\alpha(i)d(j)\beta(j)$ etc. A similar procedure may also be used to construct $S=0$ wave functions when $a(3)a(4)$ is replaced by $\psi_a(3)\psi_b(4)$ in the spatial orbital products.

The Ψ_1 and Ψ_2 wave-functions may be expanded to give the following linear combinations of Slater determinants:

$$\begin{aligned}\Psi_1 &= |y^a d^b a^c a^b b^c c^a| + |y^b d^a a^c a^b b^c c^a| \\ &\quad - |y^c d^b a^c a^b b^c c^a| - |y^b d^a a^c a^b b^c c^a| \\ \Psi_2 &= |y^a b^b a^c a^b c^a d^a| + |y^b b^a a^c a^b c^a d^a| \\ &\quad - |y^a b^b a^c a^b c^a d^a| - |y^b b^a a^c a^b c^a d^a|\end{aligned}$$

For the four singly-occupied spatial orbitals y , b , c and d , the branching diagram^{14b} indicates that there are two $S=0$ spin eigenfunctions, and the above expressions for Ψ_1 and Ψ_2 correspond to a (non-orthogonal) set of these functions.¹⁵