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Reply to Comment "Electronic Reorganization in 1,3-Dipolar Cycloaddition of Fulminic Acid to Acetylene"

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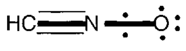
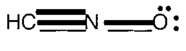
1. The Harcourt−Schulz (HS) valence bond (VB) calculations and theory[1] show that increased-valence structure **12** involves a lower energy than does resonance between the nonclassical structures **10** and **11**. Nguyen et al. (NCSU)[2] use the equivalent of one of the latter two structures, which they represent as **A**, to formulate their reaction mechanisms in each of their schemes I−III and elsewhere. NCUS have not given consideration to the possible use of **12** as the primary VB structure.



12

10



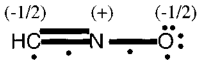
11

A

2. NCUS claim HS had concluded that the electronic reorganization proceeds according to the "more classical VB scheme I" of the NCUS Comment. Scheme I of the Comment corresponds to the HS scheme D of Figure 1.[1] The HS preference was for scheme A, not scheme D of this figure.

3. NCUS frame their discussion in terms of the movement of electron pairs. This begs the question. One-electron transfers, as in the HS scheme A, need also to be considered.

4. As discussed on many occasions (see for example refs 3−5), the results of VB calculations, both of the "classical" and GVB type, indicate that 1,3-dipolar molecules, with one or more 4-electron 3-center bonding units, can involve appreciable singlet diradical character.[6] A variety of VB structures can be constructed in order to make explicit the presence of the singlet diradical character.[3,5,6b,7,8] For HCNO, one such approach[9] involves resonance between increased-valence structure **12** of HS and the HCNO analogues of the N_2O increased-valence structures **24**, **26**, and **28** of HS. The nonpaired spatial orbital VB structure,[10] **B** (+ mirror image) for HCNO, also makes explicit the presence of singlet diradical character. Structure **C** is an example of one Lewis type of singlet diradical structure.[3,5,7b,8]



B

C

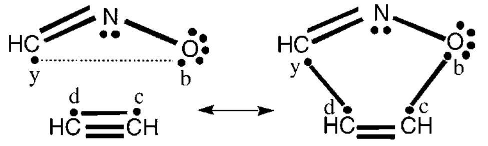
5. In a variety of publications we have utilized the singlet diradical character that is present in different types of VB structural representations of 1,3-dipoles to develop concerted diradical[7,8,11] VB formulations of 1,3-dipolar cycloaddition reactions. Without reference to refs 7, 8, and 11 here, Robb et al. have also provided the equivalent of a concerted diradical formulation.[12] Neither NUCS, nor any of the publications cited by them (except for HS), give consideration to the concerted diradical mechanism.

6. For reasons discussed in ref 7, the concerted diradical mechanism differs from the two-step diradical mechanism proposed by Firestone.[10] However, when a 1,3-dipolar molecule reacts with a hetero-dipolarophile via the concerted diradical mechanism, Firestone's electrostatic rationalization for regioselectivity, giving two transition states, designated as **TSn** and **TSr** by NCUS, is appropriate, and provides an alternative to the NCUS donor and acceptor considerations.

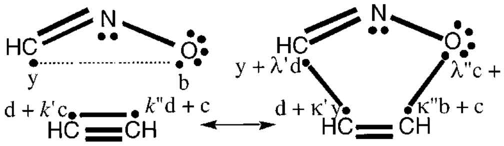
7. For illustrative purposes only, HS used the primary increased-valence structure **12** to formulate the concerted diradical cycloaddition of scheme A in Figure 1 of HS.[1] But as indicated in ref 7a, for example (see also refs 8a and 11a), the less-important increased-valence structures can also be included in the formulation. Use of **12** alone shows that the oxygen atom of HCNO has the primary radical-like character.

8. Charge transfer between the reactants introduces secondary VB structures,[8b] which do not contribute to the VB description of the separated reactants. These structures can contribute via covalent-ionic resonance, i.e., $AB \leftrightarrow A^-B^+ \leftrightarrow A^+B^-$ with A = HCNO and B = HCCH, for example, to the VB descriptions of the nonseparated reactants throughout the cycloaddition.

Use of Coulson−Fischer orbitals[13] rather than AOs to formulate Heitler−London type wavefunctions for electron-pair bonds in VB structures permits additional Lewis VB structures to be included in the equivalent canonical Lewis structure resonance scheme. The mechanism of scheme A of Figure 1 in HS can then accommodate some charge transfer between the reactants, but this effect is more easily illustrated here by using the singlet diradical structure **C** for HCNO. In **D** ↔ **E**, the AO formulation involves no charge transfer between the reactants. The Coulson−Fischer orbital formulations are those of **F** for a reactant-like entity and of **G** for a product-like entity, respectively. Such a formulation[14] still involves the singlet diradical character in the development of a VB representation for the concerted diradical mechanism.

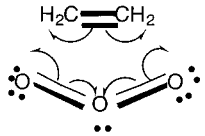


D **E**

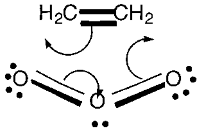


F **G**

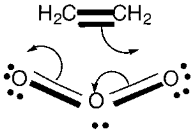
9. A further point for consideration is the following: When an ozonide is formed in the first step of the Criegee mechanism[15] for the ozonolysis of ethene, each of the NCUS formulations I−III would be represented as follows.



(I)



(II)



(III)

The O_3 VB structure is the nonclassical structure in which the four π electrons occupy two non-orthogonal 2-center MOs (cf. VB structure **26** of ref 6c). Due to symmetry, II and III are equally probable. Therefore, there is no preferred direction for electron flow when these two structures participate in resonance,

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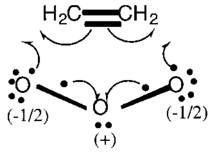
i.e., 1,3-dipolar cycloaddition cannot occur via II ↔ III. In contrast, the one-electron transfer of each of I and IV (which uses a nonpaired spatial orbital structure for O_3) permits cycloaddition.



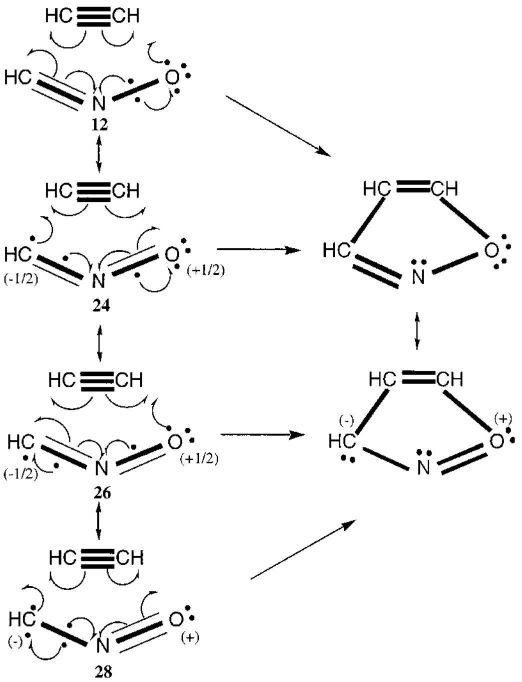
(**IV**)

The O_3 VB structure of IV makes explicit the presence of singlet diradical character on the terminal oxygen atoms. This structure is a special case of structure I, and therefore I also involves singlet diradical character (cf. ref 6b), although the diradical character is disguised. In the cycloadditions of I and IV, the presence of singlet diradical character in O_3 is utilized, as it is in the GVB studies of Goddard and co-workers.[16]

With regard to electronic reorganization during cycloaddition, each of the singlet diradical VB formulations can participate in resonance with the types II and III formulations. But the singlet-diradical formulation will be the primary contributor to the resonance scheme. Also, unless a MO wavefunction is analyzed in terms of VB structures, VB-type conclusions that are obtained from MO calculations may not be soundly based.

Note Added in Proof

Use of the HS increased-valence structures[1] of types **12**, **24**, **26**, and **28** for HCNO to provide a more-complete VB representation of cycloaddition is displayed here. The development of any increased-valence in the VB structures for the isoxazole product is not indicated.



References and Notes

(1) Harcourt, R. D.; Schulz, A. *J. Phys. Chem. A* **2000**, *104*, 6510. In ref 25, change “1.24 Å” to “1.20 Å”, and in line 8 below Figure 1, change “F_2NO” to “F_2N_2O”.

(2) Nguyen, M. T.; Chandra, A. K.; Uchimaru, T.; Sakai, S. *J. Phys. Chem. A* **2001**, *105*, 10943.

(3) Harcourt, R. D. *Qualitative Valence-Bond Descriptions of Electron-Rich Molecules*; Lecture Notes in Chemistry; Springer-Verlag: Berlin, 1982; Vol. 30.

(4) Harcourt, R. D. In *Pauling's Legacy—Modern Theory (Modelling) of Chemical Bonding;* Maksić, Z. B., Orville-Thomas, W. J., Eds.; Elsevier: New York, 1999; p 449, refs 39-45 therein.

(5) Harcourt, R. D. *Eur. J. Inorg. Chem.* **2000**, 1901 and refs 27-29, 36, 41 therein.

(6) To varying degrees, singlet diradical character is always present in any 4-electron 3-center bonding unit,[3−5] although its presence is disguised when either a delocalized or a localized MO formulation of this bonding unit is provided. See for example: (a) Coulson, C. A. *J. Chem. Soc.* **1964**, 1444. (b) Harcourt, R. D.; Harcourt, A. G. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 743. (c) Harcourt, R. D. *J. Mol. Struct. (THEOCHEM)* **1992**, *259*, 155. It is partly disguised in each of the increased-valence structures, but inclusion of all such structures in a resonance scheme makes its presence explicit.

(7) Harcourt, R. D. (a) *J. Mol. Struct.* **1972**, 12, 351. (b) *Tetrahedron* **1978**, *34*, 3125; **1979**, *35*, 910. See also: Haque, M. S. *J. Chem. Educ.* **1984**, *61*, 490. A recent summary of MO and VB studies of concerted vs stepwise diradical 1,3-dipolar cycloadditions has been provided: Di Valentin, C.; Freccero, M.; Gandolfi, R.; Rastelli, A. *J. Org. Chem.* **2000**, *65*, 6112.

(8) (a) Harcourt R. D.; Roso, W. *Can. J. Chem.* **1978**, *56*, 1059. (b) Harcourt, R. D.; Little, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 41.

(9) Note that singlet diradical character is absent from the HCNO analogues of the familiar N_2O Lewis structures **5**, **23**, **25**, and **27** of HS.[1] It is also absent from Huisgen's earlier VB formulation (Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565) of the electronic structures of 1,3-dipolar molecules. Huisgen includes it later (Huisgen, R. *J. Org. Chem.* **1976**, *41*, 404).

(10) Firestone, R. A. (a) *J. Org. Chem.* **1972**, *37*, 2181. (b) *Tetrahedron* **1977**, *33*, 3009. Structures **B** and **C** are particular forms of structure **12**.

(11) (a) Harcourt, R. D. *Qualitative Valence-Bond Descriptions of Electron-Rich Molecules*; Lecture Notes in Chemistry; Springer-Verlag: Berlin, 1982; Vol. 30, pp 175, 239. (b) Harcourt, R. D. *J. Mol. Struct. (THEOCHEM)* **1997**, *398-399*, 93 and refs 13 and 26 therein.

(12) (a) Bernardi, F.; Olivucci, M.; McDouall, J. J. W.; Robb, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 544. (b) Cooper, D. L.; Robb, M. A.; Williams, I. *Chem. Br.* **1990**, *26*, 1085 in which their Scheme 3 for 1,3-dipolar cycloadditions, which uses structure **C**, is identical to that described in ref 8b above.

(13) Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386.

(14) At each stage along the reaction coordinate, an approximate wavefunction is $\Psi = C_1(\Psi_{\mathbf{F}})_R + C_2(\Psi_{\mathbf{G}})_P$, in which the “R” and “P” refer to the “reactant-like” and “product-like” singlet spin-pairings; cf. refs 7, 8b, and 11a. This wavefunction involves seven independent variational parameters. A more complete wavefunction is $\Psi = C_1(\Psi_{\mathbf{F}})_R + C_2(\Psi_{\mathbf{G}})_P + C_3(\Psi_{\mathbf{F}})_P + C_4(\Psi_{\mathbf{G}})_R$, with 15 independent variational parameters. With 14 Lewis-type VB structures possible (four “covalent” and ten “ionic”), this wavefunction has sufficient flexibility to accommodate the variationally-best resonance between these 14 structures. The ten “ionic” structures involve one $A^{2+}B^{2-}$, one $A^{2-}B^{2+}$, four A^+B^-, and four A^-B^+ structures.

(15) Criegie, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745.

(16) (a) Wadt, W. R.; Goddard, W.A., III. *J. Am. Chem. Soc.* **1975**, *97*, 3004. (b) Walch S .P.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1975**, *97*, 5319. (c) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180. See also: Hiberty, P. C. *Isr. J. Chem.* **1983**, *23*, 10.