The Importance of Including Dynamic Electron Correlation in *ab Initio* Calculations

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A very useful simplifying assumption in chemistry is that the electrons in only a small number of orbitals are involved in most molecular processes. For example, the N → V transition in ethylene is usually described as involving the excitation of one electron from the π to the π^* molecular orbital. Similarly, the Jahn−Teller distortions[1] of the radical ions of both aromatic and antiaromatic annulenes (e.g., benzene and cyclobutadiene) are attributed to the presence or absence of a single electron in a degenerate pair of π molecular orbitals (MOs).[2]

Two electrons form the chemical bond in H_2. Other localized chemical bonds, for example, the weak bond in the plane of the ring in 1,2-, 1,3-, and 1,4-dehydrobenzene (**1**−**3**) are also commonly considered to involve just two electrons. The six π electrons in **1**−**3** obviously do not participate in the weak in-plane bonds, because the sextet of π electrons occupy MOs that are orthogonal to the σ framework of the benzene ring.
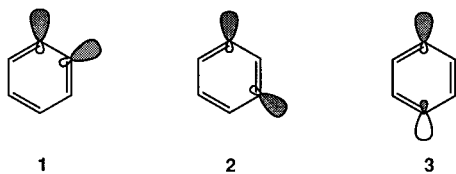
Although more than just one or two electrons are involved in most chemical reactions, the number of electrons that participate is still a small fraction of the total number present in the reactants. For instance, as illustrated for the pericyclic reactions in Figure 1, the electrocyclic ring opening of cyclobutene is considered to involve just four electrons, two in the π bond and two in the scissile σ bond of the reactant. Six electrons, four in the two π bonds of 1,5-hexadiene and two in the C_3−C_4 σ bond, are depicted as participating in the Cope rearrangement. The electrons that

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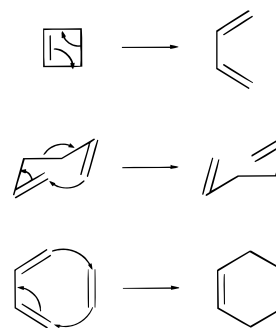

Figure 1. Schematic depiction of three Woodward−Hoffmann allowed, pericyclic reactions: conrotatory electrocyclic ring opening of cyclobutene to 1,3-butadiene, [3,3]sigmatropic, chair Cope rearrangement of 1,5-hexadiene, and Diels−Alder cycloaddition of ethylene and 1,3-butadiene. Each arrow shows how one pair of "active" electrons is redistributed in each reaction.

are "active" in the Diels−Alder reaction between ethylene and butadiene are the six in the three π bonds of the reactants.

It is tempting to attempt to transfer this conceptual simplicity to computational methodology. Indeed, semiempirical theories, such as Pariser−Parr−Pople (PPP), that deal only with the electrons in the π MOs of unsaturated hydrocarbons have been very successful in computing the UV spectra of these molecules.[3] Therefore, one might expect that, in performing *ab initio* calculations on the $\pi \rightarrow \pi^*$ excitation in ethylene, focusing on just the two electrons in the π orbitals would also be successful.

Similarly, since the presence of a single electron in a degenerate pair of π MOs is responsible for the Jahn−Teller distortion that is predicted for cyclobutadiene radical cation (CBD·+), one might also anticipate that an independent particle model should satisfactorily predict whether a rectangle or a parallelogram is the distorted geometry of lower energy. Therefore, Hartree−Fock (HF) calculations, either restricted (RHF) or unrestricted (UHF), would be expected to provide at least the qualitatively correct equilibrium geometry of CBD·+.

HF calculations on the dehydrobenzenes are less likely to be successful, since the weak in-plane bonds in **1**−**3** are expected to have appreciable amounts of diradical character. At least two configurations are necessary to provide correlation between the pair of

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(1) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937,** *161,* 220.

(2) For an excellent discussion of Jahn−Teller distortions in such molecules, see: Liehr, A. *J. Phys. Chem.* **1963,** *67,* 389.

(3) Parr, R. G. *Quantum Theory of Molecular Electronic Structure;* W. A. Benjamin, Inc.: New York, 1963.

electrons in a singlet diradical.[4] Therefore, satisfactory wave functions for the dehydrobenzenes are likely to require two-configuration (TC)SCF calculations that correlate the pairs of electrons which form the weak in-plane bonds in **1−3**.

Although HF calculations should, in principle, furnish a satisfactory description of the symmetry-allowed[5] pathways for the pericyclic reactions in Figure 1, the global potential surfaces for these reactions contain regions where diradical structures exist.[6] Consequently, in order to calculate in an unbiased way the global potential surfaces for these reactions, multiconfigurational wave functions really are necessary.

A logical approach would be to provide correlation for all the electrons that are "active" in these reactions. Complete active space SCF (CASSCF) calculations correlate n "active" electrons ($n = 4$ in cyclobutene ring opening and $n = 6$ in the Cope rearrangement and Diels−Alder reaction) by generating all possible configurations which distribute these electrons among n orbitals.[7] CASSCF wave functions for the "active" electrons in pericyclic reactions might be expected to yield computational results that would be at least qualitatively and, perhaps, even quantitatively correct.

In this Account we describe the results of calculations on the nature of the lowest energy singlet excitation in ethylene[8] and in a much larger molecule, 1,2,4,5-tetramethylenebenzene.[9] We review the computational work on molecular distortions in CBD[•+ 10] and in other radical ions.[11−13] We discuss calculations on the Cope rearrangement,[14−16] cyclobutene ring opening,[17] and the Diels−Alder reaction.[18] Finally, we describe computational investigations of the dehydrobenzenes,[19] the results of which led to a redetermination of the experimental heats of formation of these molecules.[20,21]

The *ab initio* studies discussed in this Account have all shown that computational methodologies which provide correlation for only the "active" electrons give results that are not only quantitatively but, in many cases, also qualitatively *incorrect*. Only when dynamic

(4) See, for example: Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 1.
(5) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
(6) Reviews: Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 213. Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81.
(7) Review: Roos, B. O. In *Ab Initio Methods in Quantum Chemistry II*; Lawley, K. P., Ed.; Wiley: Chichester, 1987; p 399.
(8) Davidson, E. R. *J. Phys. Chem.*, in press.
(9) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 6327.
(10) Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1981**, *103*, 5725.
(11) Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500.
(12) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5330.
(13) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405.
(14) Dupuis, M.; Murray, C.; Davidson, *J. Am. Chem. Soc.* **1991**, *113*, 9756.
(15) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072.
(16) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774.
(17) See footnote 32 of ref 15 and the correction to it, published in *J. Am. Chem. Soc.* **1994**, *116*, 4529.
(18) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478.
(19) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1993**, *115*, 11951. Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11958.
(20) Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 7414.
(21) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401.

correlation (i.e., correlation between the active and inactive electrons) is included do *ab initio* calculations correctly predict: (1) N → V in ethylene is a $\pi \to \pi^*$ valence transition, not an excitation to a Rydberg state.[8] (2) Rectangular CBD[•+] is lower in energy than planar rhomboidal CBD[•+].[10] (3) There is only one C_{2h} stationary point on the potential surface for the chair Cope rearrangement; and it is the "aromatic" transition state for a concerted reaction pathway.[15,16]

Dynamic Electron Correlation in Ethylene

Ethylene is the prototypical molecule for the attempted separation of a many-electron system into two active electrons, with the remaining electrons treated as a passive core. Electronic states of ethylene can be formed by distributing the active electrons between the p−π atomic orbitals (AOs), p_A and p_B, on the two carbon atoms. In valence bond (VB) theory a purely diradical, singlet wave function, Ψ_D, can be written as

$$\Psi_D = (|p_A^{\alpha} p_B^{\beta}\rangle - |p_A^{\beta} p_B^{\alpha}\rangle)/\sqrt{2} \tag{1}$$

where the symbol $|\ \rangle$ stands for a normalized Slater determinant, and α and β are the two possible electron spins. In the wave function for the lowest triplet state, Ψ_T, one electron also occupies each AO, but the electron spins are parallel.

Neither Ψ_D nor Ψ_T contains ionic terms, corresponding to the simultaneous occupancy of the same p−π AO by the two electrons. However, there are two totally ionic, singlet wave functions, which place both electrons on the same atom.

$$\Psi_I = (|p_A^{\alpha} p_A^{\beta}\rangle + |p_B^{\alpha} p_B^{\beta}\rangle)/\sqrt{2} \tag{2}$$

$$\Psi_V = (|p_A^{\alpha} p_A^{\beta}\rangle - |p_B^{\alpha} p_B^{\beta}\rangle)/\sqrt{2} \tag{3}$$

Ψ_V has B_{1u} symmetry and is the wave function for the lower energy excited singlet state of ethylene. Ψ_I, like Ψ_D, has A_g symmetry. The wave function, Ψ_N, for the ground state of ethylene, with energy E_N, contains both diradical and ionic terms; and it can be written as a linear combination of Ψ_D and Ψ_I, with $c_D > c_I$.

$$\Psi_N = c_D \Psi_D + c_I \Psi_I \tag{4}$$

The singlet wave functions—Ψ_D, Ψ_I, and Ψ_V—for the two π electrons in ethylene can also be described in molecular orbital (MO) theory. The bonding and antibonding π MOs in ethylene can be written, respectively, as

$$\pi = (p_A + p_B)/\sqrt{2} \tag{5}$$

$$\pi^* = (p_A - p_B)/\sqrt{2} \tag{6}$$

where, for the sake of simplicity, overlap has been neglected in normalizing the MOs. Using these MOs, three singlet configurations can be constructed. Expressed in terms of these three MO configurations, the

three singlet VB wave functions in eqs 1−3 can be written

$$\Psi_D = (|\pi^\alpha \pi^\beta\rangle - |\pi^{*\alpha} \pi^{*\beta}\rangle)/\sqrt{2} \qquad (7)$$

$$\Psi_I = (|\pi^\alpha \pi^\beta\rangle + |\pi^{*\alpha} \pi^{*\beta}\rangle)/\sqrt{2} \qquad (8)$$

$$\Psi_V = (|\pi^\alpha \pi^{*\beta}\rangle - |\pi^\beta \pi^{*\alpha}\rangle)/\sqrt{2} \qquad (9)$$

In terms of MO configurations, the wave function for the ground state of ethylene thus becomes

$$\Psi_N = c_\pi |\pi^\alpha \pi^\beta\rangle - c_{\pi*} |\pi^{*\alpha} \pi^{*\beta}\rangle \qquad (10)$$

Using eqs 8 and 9 and equating the VB and MO expressions for Ψ_N in eqs 4 and 10 gives

$$c_D = (c_\pi + c_{\pi*})/\sqrt{2} \qquad (11)$$

$$c_I = (c_\pi - c_{\pi*})/\sqrt{2}$$

When, as is the case in Hartree−Fock theory, the wave function for the ground state consists of a single configuration ($c_{\pi*} = 0$ in eq 10), eq 11 shows that the wave function for the ground state in eq 4 is an equal mixture of diradical and ionic terms. In contrast, when $c_\pi = c_{\pi*}$, as would be the case in the transition state for rotation about the double bond in ethylene, where π and π^* are degenerate in energy, eq 11 shows that Ψ_N is a pure diradical wave function and contains no ionic terms.

As indicated by eq 4, the actual wave function for the ground state of ethylene will contain a mixture of diradical and ionic terms, with the former dominant. The ratio of the coefficients, c_D and c_I, depends on the energy difference, $E_I - E_D$, between Ψ_I and Ψ_D and on the size of the matrix element, $\langle \Psi_I | H | \Psi_D \rangle$, that mixes them.

If the two CH$_2$ groups in ethylene were separated by an infinite distance, E_V and E_I would be exactly equal and would differ from E_D by IP − EA, the ionization potential minus electron affinity of each CH$_2$ group. In the PPP model[3] this energy difference is just the Coulomb repulsion energy between a pair of electrons in a p−π AO, which is symbolized as γ_{CC}. In PPP theory γ_{CC} is set equal to the experimental value of 11 eV for IP − EA for the valence state of a free carbon atom. A better model for γ_{CC} in ethylene would be the experimental value of IP − EA for methyl radical, for which IP − EA = 9 eV.

Even at the HF level of *ab initio* theory, the σ electrons in CH$_3^-$, CH$_3^\bullet$, and CH$_3^+$ will all have different wave functions, because of the difference in the number of electrons in the p−π AO. The different electrostatic polarizations of the σ bonds in these three species are easily accommodated in separate *ab initio* calculations on CH$_3^-$, CH$_3^\bullet$, and CH$_3^+$. However, in *ab initio* calculations on ethylene, the σ polarizations in Ψ_I and Ψ_V are more difficult to handle, because they are dynamic (i.e., specific to each of the two p−π AO occupancies in eqs 2 and 3), rather than static (i.e., based on the average π charge distribution for the wave function in each equation).

In Ψ_I and in Ψ_V, as in Ψ_D, there is, *on average*, no net charge on either CH$_2$ group of ethylene. Therefore, if $\Psi_D{}^{core}$ is the wave function for the core of σ electrons that is appropriate for the diradical wave function, Ψ_D, for the two π electrons, $\Psi_D{}^{core}$, or something close to it, will also be the best *average* wave function for Ψ_I and Ψ_V. However, the best total wave function for the *V* state of ethylene is *not* the HF wave function

$$\Psi_V{}^{HF} \approx |\Psi_D{}^{core}\Psi_V\rangle = (|\Psi_D{}^{core} p_A{}^\alpha p_A{}^\beta\rangle - |\Psi_D{}^{core} p_B{}^\alpha p_B{}^\beta\rangle)/\sqrt{2} \quad (12)$$

The HF wave function does not allow the core of σ electrons to become appropriately polarized when both π electrons are in p_A, leaving p_B empty, and *vice versa*. Dynamic polarization requires a wave function in which dynamic correlation between the σ and π electrons is included.

Suppose that, when p_A is doubly occupied and p_B is empty, the appropriately polarized wave function for the σ core is $\Psi_{A^- B^+}{}^{core}$. Then an unnormalized wave function for the *V* state of ethylene which includes dynamic correlation is

$$\Psi_V{}^{dyn} = |\Psi_{A^- B^+}{}^{core} p_A{}^\alpha p_A{}^\beta\rangle - |\Psi_{A^+ B^-}{}^{core} p_B{}^\alpha p_B{}^\beta\rangle \quad (13)$$

$\Psi_D{}^{core}$ in eq 12 is approximately the average of $\Psi_{A^- B^+}{}^{core}$ and $\Psi_{A^+ B^-}{}^{core}$. Also, $(\Psi_{A^- B^+}{}^{core} - \Psi_{A^+ B^-}{}^{core})/2$ can, to a first approximation, be written as a sum of single excitations, $\sum \Psi^*{}_D{}^{core}$, from $\Psi_D{}^{core}$. Thus, the dynamically correlated wave function, $\Psi_V{}^{dyn}$, in eq 13 can be obtained from the HF wave function, $\Psi_V{}^{HF}$, in eq 12 by adding to the latter the terms

$$\Psi_V{}^{dyn} - \Psi_V{}^{HF} = |\sum \Psi^{*core}(p_A{}^\alpha p_A{}^\beta\rangle + p_B{}^\alpha p_B{}^\beta\rangle) = |\sum \Psi^{*core}\Psi_I\rangle = |\sum \Psi^{*core}(\pi^\alpha \pi^\beta\rangle + \pi^{*\alpha} \pi^{*\beta}\rangle) \quad (14)$$

Equation 14 shows that in *ab initio* MO theory provision of dynamic electron correlation for the V state of ethylene involves a sum of double excitations of one core electron and one active electron from the HF wave function for Ψ_V. Since Ψ_V is $^1B_{1u}$, and Ψ_I is ^1A_g, only those terms in $\sum \Psi^{*core}$ that have $^1B_{1u}$ symmetry contribute to eq 14.

A similar expression can be easily derived for the terms that must be added in order to provide dynamic correlation for the ionic component, Ψ_I, of the ground state wave function, Ψ_N, for ethylene.

$$\Psi_I{}^{dyn} - \Psi_I{}^{HF} = |\sum \Psi^{*core}\Psi_V\rangle = |\sum \Psi^{*core}(\pi^\alpha \pi^{*\beta}\rangle - \pi^\beta \pi^{*\alpha}\rangle) \quad (15)$$

As with Ψ_V, provision of dynamic correlation between active and inactive electrons in Ψ_I requires the simultaneous excitation of one electron of each type from the HF wave function. This is generally the case.

Including dynamic electron correlation for Ψ_I would be expected to increase its contribution to Ψ_N, the wave function for the ground state of ethylene. In fact, the ratio $c_{\pi*}/c_\pi$ *decreases* from 0.21 in a CASSCF calculation with a very large basis set to 0.16 in a multireference (MR) configuration interaction (CI) calculation with the same basis set.[8] This change corresponds to an increase in the ratio c_I/c_D from 0.65 to 0.72. The dynamic correlation provided in the

Table 1. Values Obtained[a] from Different Calculations[b] on Ethylene for ΔE (eV), the N → T and N → V Excitation Energies, and for $\langle x^2 \rangle$ (bohr²), the Average of the Square of the Spatial Extent of the Electron Density Out of the Molecular Plane

state	calculation[b]	ΔE	$\langle x^2 \rangle$
T	CASSCF	4.27	11.7
V	CASSCF	8.05	43.4
V	CASSCF (with N MOs)	12.33	10.9
T	π CI	4.34	11.7
V	π CI	8.09	40.1
V	π CI (with N MOs)	8.73	26.3
T	ASSEFAPC	4.41	11.7
V	ASSEFAPC	8.13	18.5
V	ASSEFAPC (with N MOs)	8.06	18.8

[a] Results from ref 8. [b] See the text for descriptions.

MRCI calculation increases the occupancy of the π MO, at the expense of π^*, by stabilizing the ionic terms in the $|\pi^2\rangle$ configuration.

Calculations on Excited States

Ethylene. Dynamic electron correlation should be even more important in Ψ_V than Ψ_N, since the wave function for the π electrons in the first excited singlet state of ethylene is purely ionic. The results of recent *ab initio* calculations on ethylene with a very extended basis set show that whether the V state is computed to be valence or Rydberg depends on whether dynamic electron correlation is included in the wave function for this state.[8,22] Table 1 gives the excitation energies, computed with several different types of wave functions, including wave functions in which the MOs from CASSCF calculations on the ground (N) state were used to construct the wave function for the V excited state.

The CASSCF MOs for V are very different from those for N and T.[23] This is shown by the values of $\langle x^2 \rangle$ for these states in Table 1. The quantity $\langle x^2 \rangle$ for each state gives the spatial extent of the wave function out of the molecular plane and is thus indicative of the size of the π MOs in each state. In the CASSCF wave function, Ψ_N, for the ground state of ethylene, π^* is used to correlate the two electrons in the bonding π MO. Therefore, π^* must overlap effectively with π. Consequently, these two MOs have similar sizes, giving $\langle x^2 \rangle = 10.9$ bohr² for Ψ_N. The CASSCF triplet wave function, Ψ_T,[23] has about the same value of $\langle x^2 \rangle$ as Ψ_N, because the π and π^* MOs in Ψ_T have about the same size as the π and π^* MOs in Ψ_N.[24]

However, in the CASSCF wave function for the excited singlet state, Ψ_V,[23] the value of $\langle x^2 \rangle$ is about 4 times larger than in either Ψ_N or Ψ_T. The reason is that, as shown in eq 3, the two π electrons in Ψ_V are always on the same atom. Therefore, if the sizes of the AOs in the π and π^* MOs were similar, the two π electrons would have a very high probability of simultaneously being in the same region of space and, thus, would have a very high Coulomb repulsion energy. The diffuse, Rydberg-like π^* MO of Ψ_V keeps the electron in this MO confined to a region of space that is quite different from that where the electron in the much more contracted π MO is most likely to be found. Confining electrons of opposite spin to different regions of space minimizes their Coulombic repulsion energy.[1,25]

The results in Table 1 show that the energy of the N → V transition in ethylene depends on the type of MOs used to construct the V excited state. Most dramatic is the finding that using the MOs from the CASSCF (two electrons in two orbitals) calculation on Ψ_N to construct Ψ_V gives a N → V CASSCF excitation energy that is 4.28 eV higher than when a CASSCF calculation is actually performed on the V state.[23]

When full CI is carried out in the π space, the π wave function for the V state would be independent of whether N or V CASSCF MOs were used, *provided* that the CASSCF MOs for the σ cores of the two states were the same. The results in Table 1 show that the σ MOs from these two calculations are obviously quite different. The value of $\langle x^2 \rangle$ for the V state is highly dependent on whether the σ core wave function from the CASSCF calculation on V or N is used in the π CI calculation.

Dynamic correlation between the σ core and the two π electrons can be included by adding single σ excitations to all the π configurations. The resulting AS-SEFAPC (all single σ excitations from all π configurations) CI wave functions for N and V give energies and values of $\langle x^2 \rangle$ that are nearly independent of whether the MOs from the CASSCF calculations on the N or the V state are used. Because dynamic correlation stabilizes ionic terms in the wave function for Ψ_V, π^* has more nearly the same size as π in the ASSEFAPC wave function than in the CASSCF or π CI wave functions.

Using the appropriate CASSCF MOs for *T* and *V*, the vertical excitation energies for these two states are within 0.2 eV of experiment[22h] at all levels of theory in Table 1. However, the predicted nature of the V excited state depends critically on the level of theory used. At the CASSCF and π CI levels the values of $\langle x^2 \rangle$ in Table 1 indicate that the V state of ethylene is a Rydberg state. In contrast, with inclusion of dynamic electron correlation at the ASSEFAPC level, the values of $\langle x^2 \rangle = 18.5-18.8$ for the V state indicate that, although the π^* MO in it is more diffuse than the π^* MO in the T state, the V state of ethylene is not a Rydberg state.

The $S_0 \to S_1$ Excitation in TMB (4). 1,2,4,5-Tetramethylenebenzene (TMB) is a diradical whose nonbonding (NB) MOs can be chosen so that they are essentially those for two pentadienyl radicals and, thus, span disjoint sets of atoms. Consequently, both qualitative considerations[25] and *ab initio* calculations[9,26] predict that TMB will violate Hund's rule[27] by having a singlet ground state. However, when this

(22) Among the most noteworthy of the previous calculations on the N → V ethylene excited state are the following: (a) Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1992**, *83*, 191. (b) Wiberg, K. B.; Hadad, C. M.; Foresman, J. B.; Chupka, W. A. *J. Phys. Chem.* **1992**, *96*, 10756. (c) Cave, R. J. *Chem. Phys.* **1990**, *92*, 2450. (d) Lindh, R.; Roos, B. O. *Int. J. Quantum Chem.* **1989**, *35*, 813. (e) Buenker, R. J.; Shih, S.-K.; Peyerimhoff, S. D. *Chem. Phys.* **1979**, *36*, 97. (f) Brooks, B. R.; Schaefer, H. F., III. *J. Chem. Phys.* **1978**, *68*, 4939. (g) McMurchie, L. E.; Davidson, E. R. *J. Chem. Phys.* **1977**, *66*, 2959. (h) Peyerimhoff, S. D.; Buenker, R. J. *Theor. Chim. Acta.* **1972**, *27*, 243.
(23) (2/2)-CASSCF calculations on the V *and* T states of ethylene each involve a single configuration and, hence, are really ROHF calculations on these states.
(24) Since the Pauli principle prevents the two π electrons in the lowest triplet state from appearing simultaneously in the same region of space, π and π^* can have similar sizes, without engendering a high Coulomb repulsion energy between the electrons in these two MOs.

(25) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. Borden, W. T. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195.
(26) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072.

diradical was first prepared, several observations led Roth and co-workers to identify the triplet as the ground state.[28]
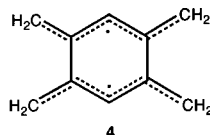
One of these observations was that the UV−vis spectrum of **4** consists of a weak absorption at long wavelengths, followed by a much more intense absorption. Both π CI[26] and CASSCF calculations[9] predict that the lowest energy vertical excitation of singlet TMB is an allowed transition, followed by a forbidden excitation at higher energy. However, the observed spectrum fits the pattern predicted for the triplet by π CI and CASSCF calculations, a weak forbidden absorption followed by a strong allowed absorption.

The excitation energies of singlet and triplet TMB have recently been recalculated at the CASPT2N level of theory.[9] CASPT2N uses second-order Möller−Plesset (MP2) perturbation theory to provide dynamic electron correlation for a CASSCF wave function.[29] A closely related CASMP2 method for adding dynamic correlation to a CASSCF wave function has also been published by one of us.[30]

At the CASPT2N level of theory the vertical excitation $1^1A_g \rightarrow 2^1A_g$, which is forbidden, falls slightly below $1^1A_g \rightarrow {}^1B_{3u}$, which is allowed. Moreover, upon optimization of the geometries of these two excited states, the greater relaxation energy computed for 2^1A_g results in the adiabatic excitation energy for this state being about 0.2 eV lower than that for $^1B_{3u}$. The UV−vis spectrum for singlet TMB, computed by CASPT2N,[9] provides not only a qualitative but also a quantitative fit to the UV−vis spectrum that was observed by Roth and co-workers.[28]

The UV−vis spectrum for the triplet, computed at the CASPT2N level,[9] does not fit the observed spectrum. The CASPT2N calculations thus provide strong evidence that the UV−vis spectrum of TMB belongs to the singlet and not to the triplet. Berson and co-workers[31] have obtained other types of experimental evidence that, as predicted,[9,25,26] the singlet is, in fact, the ground state of TMB.[27]

Radical Cations

Cyclobutadiene Radical Cation (CBD·+). As discussed in the previous section, when the π wave function for an excited state of a neutral molecule contains ionic terms, dynamic electron correlation between π and σ electrons is very important. Therefore, it is not surprising that this type of correlation is also important in conjugated molecules with charged π systems. A good example is provided by CBD·+.[10]

(27) Review: Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.
(28) Roth, W. R.; Langer, R.; Bartmann, M.; Stevermann, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 256.
(29) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.
(30) Kozlowski, P. M.; Davidson, E. R. *J. Chem. Phys.* **1994**, *100*, 3672.
(31) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073.
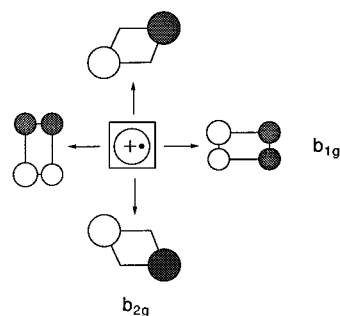
Figure 2. Rectangular (b_{1g}) and rhomboidal (b_{2g}) distortions of D_{4h} CBD·+. Only the top lobes of the p AOs in the π MO that is singly occupied in the ground state at each distorted geometry are drawn. The phase change in the electronic wave function that is necessarily encountered upon completing one pseudorotation circuit about the D_{4h} geometry (Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1975**, *344*, 147) is shown as occurring between the b_{2g} distorted geometry at the bottom of the figure and the b_{1g} distorted geometry at the left.

As shown in Figure 2, square (D_{4h}) CBD·+ can undergo two different types of Jahn−Teller distortions: b_{1g}, which takes the molecule to one of two rectangular geometries, and b_{2g}, which takes it to one of two rhomboidal geometries. The radical cation can pseudorotate from one of these distorted geometries to another, but group theory cannot predict which geometry will be a minimum and which a transition state for pseudorotation.

One might expect that distortion of the D_{4h} bond lengths would provide more stabilization than distortion of the D_{4h} bond angles, and our *ab initio* calculations confirmed that this is, indeed, the case.[10] The b_{1g} distortion lowers the energy by 7.0 kcal/mol, whereas the energy lowering associated with the b_{2g} distortion is only 1.0 kcal/mol. Nevertheless, at many levels of theory, the optimized rhomboidal geometry is lower in energy than the optimized rectangular geometry.

The reconciliation of these two, apparently contradictory, statements is that the energy of the square molecule depends on the type of degenerate MO that is singly occupied. As shown in Figure 2, a rectangular (b_{1g}) distortion requires that the singly occupied NBMO be chosen to span all four atoms, whereas a rhomboidal (b_{2g}) distortion requires that the singly occupied NBMO be confined to two carbons that are diagonally across the ring from each other. Although the computed energy of the square molecule *should* be independent of which type of NBMO is chosen, this does not mean that at approximate levels of theory the computed energy actually exhibits this independence.

At the UHF level the more localized choice for the form of the NBMO that is singly occupied gives an energy for square CBD·+ which is lower by 20.8 kcal/mol than the less localized choice for this NBMO.[10] Without explicit inclusion of electron correlation, localization is favorable, since the other π and σ electrons can adjust their wave functions to capitalize on the localization of spin and charge.

At the ROHF level the dependence of the energy of the square molecule on the type of degenerate NBMO chosen is smaller than at the UHF level, amounting to 7.4 kcal/mol. With inclusion of correlation between the π electrons via full CI in the π space, this difference drops to 4.8 kcal/mol. The existence of this

difference, even when the π electrons are fully correlated, indicates the importance of providing dynamic correlation between the π and σ electrons. When this was done by including all single σ excitations from all π configurations (ASSEFAPC), the dependence of the energy of the square molecule on the form chosen for the singly occupied NBMO decreased to 0.6 kcal/mol, with the less localized NBMO now giving the lower energy.

The symmetry requirement that the energy of square CBD$^{•+}$ should be independent of the type of degenerate NBMO that is occupied provides a convenient test for the quality of different types of wave functions. Testing for artifactual symmetry breaking[32] in this fashion indicates whether the amount of dynamic electron correlation that has been included in the wave function is sufficient to allow the accurate calculation of the energy difference between rectangularly and rhomboidally distorted CBD$^{•+}$.[33]

Cyclooctatetraene Radical Anion (COT$^{•-}$). In COT$^{•-}$ three electrons occupy a pair of degenerate π MOs at the D_{8h} geometry of the planar radical anion. As in CBD$^{•+}$, Jahn−Teller distortions of either the bond lengths or the bond angles of COT$^{•-}$ are possible, with one type of distortion leading to the energy minima along the pathway for pseudorotation and the other leading to the transition states connecting them. Also as in CBD$^{•+}$, calculations on COT$^{•-}$ at the geometry of highest symmetry with two different types of NBMOs provide a test for artifactual symmetry breaking.

Because the π system of COT$^{•-}$ is larger than that of CBD$^{•+}$, at any level of theory the energies computed with the two different types of MOs differ less at the D_{8h} geometry of the former than they do at the D_{4h} geometry of the latter.[11] As expected, ASSEFAPC CI calculations, which provide dynamic correlation between the π and σ electrons, show very little artifactual symmetry breaking. Moreover, ASSEFAPC CI calculations at the bond-alternated, equilibrium, D_{4h} geometry of COT$^{•-}$ give a hyperfine coupling constant of $a_H = -3.21$ G, which is in exact agreement with experiment.[34]

Trimethylenemethane Radical Cation (TMM$^{•+}$). Testing for artifactual symmetry breaking in a molecule, such as TMM$^{•+}$, which has a 3-fold axis of symmetry, is slightly different than in molecules, such as CBD$^{•+}$, with 4-fold symmetry axes.[32] Neither of the degenerate e_x'' and e_y'' π NBMOs in TMM$^{•+}$, shown in Figure 3, individually has D_{3h} symmetry; each has only C_{2v} symmetry. One NBMO belongs to the a_2 representation of C_{2v}; and, when it is singly occupied, the resulting wave function is $^2A_2$. The other NBMO belongs to the b_1 representation and gives rise to a $^2B_1$ state.

The nonuniform distribution of charge and spin in the NBMO of each of these two states affects the σ
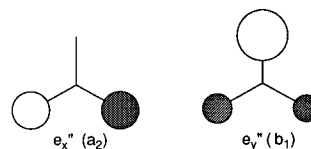

Figure 3. Degenerate e'' MOs in D_{3h} TMM$^{•+}$. Only the top lobes of the p AOs in each π MO are shown. The C_{2v} symmetry designation of each MO is given in parentheses.

and π electrons in planar TMM$^{•+}$ in such a way that both states distort away from a D_{3h} geometry, as predicted by the Jahn−Teller theorem.[1] $^2A_2$ has one short C−C bond and two longer ones, whereas the opposite is the case for $^2B_1$. One of the distorted geometries corresponds to the three minima along the pathway for pseudorotation in planar TMM$^{•+}$ and the other to the three transition states that connect the minima. *Ab initio* calculations were performed to identify which of the two C_{2v} geometries corresponds to which of these two types of stationary points and to compute the energy difference between them.[12]

UHF calculations placed the $^2A_2$ optimized geometry 6.6 kcal/mol below that of $^2B_1$. In contrast, UMP2, ROHF, and SD-CI calculations all found $^2B_1$ to be the lower of the two by, respectively, 5.5, 8.3, and 2.7 kcal/mol. However, when each of these calculations was performed at a D_{3h} geometry, the energy differences found between $^2A_2$ and $^2B_1$ were about the same size as at the optimized C_{2v} geometries for these two states. Of course, pure $^2E_x''$ and $^2E_y''$ states would have had identical energies at D_{3h} geometries.

We had previously used group theory to investigate for the $(NH)_3^{2+}$ diradical what types of dynamic correlation between the σ and π electrons must be included in order to obtain pure $^1E_x'$ and $^1E_y'$ states at D_{3h} geometries.[35] We found that, in order to obtain wave functions which, even to first order, are pure $^1E_x'$ and $^1E_y'$, all single σ excitations from all π configurations (ASSEFAPC) must be included. The same type of analysis shows that the dynamic electron correlation provided by ASSEFAPC CI should also give wave functions that are, at least to first order, pure $^2E_x''$ and $^2E_y''$ states of D_{3h} TMM$^{•+}$.

Indeed, ASSEFAPC CI at D_{3h} geometries of TMM$^{•+}$ gave $^2A_2$ and $^2B_1$ wave functions that differed in energy only by 0.1 kcal/mol. When the Jahn−Teller distorted, C_{2v} geometry of each state was optimized at the ASSEFAPC CI level, the two geometries were computed to have the same energy to within 0.1 kcal/mol. Thus, with proper inclusion of dynamic electron correlation, *ab initio* calculations predict that pseudorotation in TMM$^{•+}$ occurs without any appreciable energy barrier.[12] This prediction is qualitatively different from that which would have been made on the basis of the results of UHF, UMP2, ROHF, or SD-CI calculations.

Trimethylene Radical Cation (TM$^{•+}$) and Related Radicals. Like planar TMM$^{•+}$, which might be formed upon ring opening of methylenecyclopropane radical cation, the (0,0) geometry of TM$^{•+}$ (**6**) might be formed by ring opening of cyclopropane radical

(32) Review: Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

(33) A recent study (Roeselová, M.; Bally, T.; Jungwirth, P.; Cársky, P. *Chem. Phys. Lett.* **1985**, *234*, 395) has found that coupled cluster [CCSD(T)] calculations on CBD$^{•+}$ are relatively free from artifactual symmetry breaking. Calculations at this level found that the optimized rectangular geometry for CBD$^{•+}$ is lower in energy than the optimized planar rhomboidal geometry by 5.3 kcal/mol. However, a puckered rhomboidal geometry, which allows better bonding than a planar geometry between carbons diagonally across the ring, is only 1.7 kcal/mol (0.5 kcal/mol after inclusion of zero-point energy corrections) higher in energy than the rectangular geometry.

(34) Katz, T. J.; Strauss, H. L. *J. Chem. Phys.* **1960**, *32*, 1873.

(35) Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1980**, *102*, 5302. The need for including dynamic correlation between π and σ electrons had become apparent in calculations on another molecule with four π electrons, cyclopentadienyl cation: Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1979**, *101*, 3771.

cation (**5**). We have performed calculations not only on the former reaction[12] but also on the latter.[13]
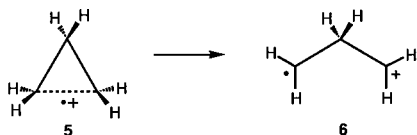
Just as symmetry considerations allow one to test the adequacy of wave functions for CBD$^{\bullet+}$ and TMM$^{\bullet+}$, symmetry also allows one to test the adequacy of wave functions for (0,0)-TM$^{\bullet+}$ (**6**). One can thus determine whether the symmetry breaking calculated for this radical cation at the UHF, ROHF, and CASSCF levels of theory[13] is real or artifactual.[32]

In (0,0)-TM$^{\bullet+}$ the symmetry principle that can be used is that the wave function for a nondegenerate state must have the same symmetry as the molecular geometry. If this is found not to be the case for a particular type of wave function, both the symmetry breaking in the wave function and the molecular distortion to lower symmetry that necessarily accompanies it are clearly artifactual.

In the case of (0,0)-TM$^{\bullet+}$, calculations performed at C_{2v} geometries with UHF, ROHF, and CASSCF wave functions showed the symmetry breaking that they exhibited to be artifactual.[13] In each case a wave function with only C_s symmetry was found to be lower in energy than a wave function on which C_{2v} symmetry was imposed.

None of these wave functions contains dynamic correlation between the electrons in the π MOs and those in the σ MOs. However, when this type of dynamic correlation was provided by ASSEFAPC CI calculations, artifactual symmetry breaking of the wave function was not observed. Moreover, at this level of theory the optimized C_{2v} geometry of (0,0)-TM$^{\bullet+}$ was found to be stable toward lengthening one C−C bond and shortening the other. Thus, when dynamic electron correlation is provided at the AS-SEFAPC level of theory, artifactual symmetry breaking in the wave function disappears, and the radical is stable toward real breaking of the molecular symmetry.

Providing dynamic electron correlation between σ and π electrons through ASSEFAPC CI calculations has also proven important for investigating molecular distortions from C_{2v} to C_s symmetry in other radicals with three π electrons. These include two more radical cations, O(CH$_2$)$_2$$^{\bullet+}$ [36] and CF$_2$$^{\bullet+}$,[37] and neutral formyloxyl radical.[36,38] In each case, without adequate provision of dynamic electron correlation, artifactual symmetry breaking was encountered; and this obscured whether each radical actually preferred a C_{2v} or a C_s geometry.

Potential Energy Surfaces for Pericyclic Reactions

Cope Rearrangement. It is clear why dynamic electron correlation might be important for obtaining qualitatively meaningful results in excited states that
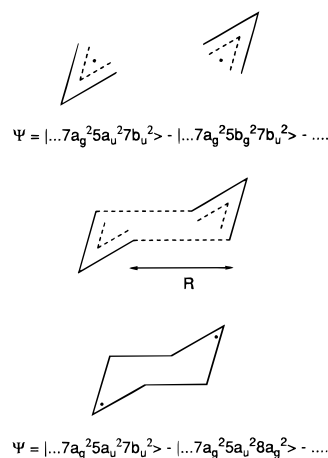

Figure 4. Nature of the C_{2h} species on the PES for the chair Cope rearrangement as the distance, R, between C$_1$ and C$_6$ (and C$_3$ and C$_4$) decreases from the top to the bottom of the figure. The leading terms in the wave functions for the two singlet diradical extremes, two allyls and cyclohexane-1,4-diyl, are given.

have highly ionic π wave functions or in molecules with charged or very polar π systems. However, one might not expect inclusion of dynamic electron correlation to be necessary for calculating the correct potential energy surface for a simple, Woodward−Hoffmann allowed,[5] pericyclic reaction,[6] such as the Cope rearrangement. Nevertheless, recent calculations in both of the authors' research groups have demonstrated clearly that calculations beyond the CASSCF level are necessary to obtain even a qualitatively correct potential energy surface (PES) for this reaction.[15,16]

All calculations agree that the lowest energy pathway for the Cope rearrangement of 1,5-hexadiene passes through a C_{2h} geometry,[6] and discussion of the reaction has focused on the electronic structure and energy of this species and whether it is a minimum or saddle point on the potential energy surface. As shown in Figure 4, at long C$_1$-C$_6$ (and C$_3$-C$_4$) distances, R, the C_{2h} structure separates into two allyl radicals, whose energy is known experimentally to be about 60 kcal/mol above that of 1,5-hexadiene.[39] The singlet wave function for this radical pair consists of the two dominant configurations that are given in Figure 4.

At a C$_1$−C$_6$ distance, R, that is close to a normal C−C single bond length, the C_{2h} structure is a chair diradical, cyclohexane-1,4-diyl. The energy of this diradical is not known experimentally, but thermochemical estimates place it some 40 kcal/mol above 1,5-hexadiene.[40] As shown in Figure 4, although the first configuration in the wave function for this diradical is the same as that for two, singlet-coupled, allyl radicals, the second configuration is not.

The actual transition state for the chair Cope rearrangement has an enthalpy that is 33.5 kcal/mol greater than that of 1,5-hexadiene.[41] The difference between the enthalpy of the transition state and that of each of the two diradical extremes in Figure 4 is the amount by which concerted bond making and bond breaking make the energy of the transition state lower

(36) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513.

(37) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 8034.

(38) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459.

(39) Roth, W. R.; Bauer, F.; Beitat, A.; Ebbrecht, T.; Wüstefeld, M. *Chem. Ber.* **1991**, *124*, 1453.

(40) Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279.

(41) Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.

than each of the two hypothetical transition states in which these two processes are completely decoupled.

A CASSCF wave function for the Cope rearrangement would be expected to have as its three most important configurations

$$\Psi = c_1|...7a_g{}^2 5a_u{}^2 7b_u{}^2\rangle - c_2|...7a_g{}^2 5a_u{}^2 8a_g{}^2\rangle -$$
$$c_3|...7a_g{}^2 5b_g{}^2 7b_u{}^2\rangle - ... \quad (16)$$

Such a wave function has the flexibility to describe both of the diradicals shown in Figure 4, as well as the chair transition state, whose electronic structure is expected to be intermediate betweeen them.

CASSCF/6-31G* calculations on the chair Cope rearrangement find two C_{2h} stationary points: cyclohexane-1,4-diyl, which is a stable intermediate with a short (1.641 Å) C_1-C_6 bond length, and an "aromatic" transition state with a long (2.189 Å) C_1-C_6 bond length.[14] The enthalpies of both are calculated to be more than 10 kcal/mol too high, compared to the experimental value of $\Delta H^{\ddagger} = 33.5$ kcal/mol.[41] At the diyl geometry, $c_2/c_1 = 0.63$, while, at the aromatic transition state, the third configuration in eq 20 becomes slightly more important than the second, and $c_3/c_1 = 0.18$. In C_{2h} symmetry the two stationary points are bond-stretch isomers, separated by a small energy barrier which reaches its maximum height at $R = 1.957$ Å. As would be expected from the discussion given above for ethylene, CASSCF underestimates the importance of the ionic terms in the wave functions for the active electrons. Lack of correlation between the 6 active and 28 inactive valence electrons effectively places the ionic terms too high in energy. Inclusion of this correlation by CASPT2N[15] or CASMP2[16] reduces the importance of the second configuration in eq 16, which removes ionic terms from the first configuration at the geometry of cyclohexane-1,4-diyl.[42]

The CASPT2N and CASMP2 PESs each have a single C_{2h} stationary point at a C_1-C_6 bond length intermediate between the two C_{2h} minima on the CASSCF PES. This single C_{2h} stationary point is the transition state for the Cope rearrangement; and the calculated enthalpy of activation is within about 1 kcal/mol of experiment. There is little qualitative resemblance between the CASSCF results and those obtained from calculations which include dynamic electron correlation.[43]

Other Pericyclic Reactions. The Cope rearrangement is not the only pericyclic reaction for which one must go beyond the CASSCF level in order to correctly predict the reaction pathway. For example, in calculations on the Diels−Alder reaction at the

CASSCF/6-31G* level, Li and Houk found that a diradical intermediate, with just one C−C bond formed between ethylene and butadiene, is 3.1 kcal/mol lower than the concerted transition state.[18] In contrast, at the RQCISD(T) level, in which all the valence electrons are correlated, the concerted transition state is 4.3 kcal/mol lower in energy than the diradical intermediate and 10.2 kcal/mol below the transition state leading to this intermediate. Moreover, the energy of the concerted transition state, relative to the reactants, drops from 43.8 kcal/mol at the CASSCF level to 25.5 kcal/mol at the RQCISD(T) level. The latter is very close to the activation energy measured for this reaction.[18]

For the ring opening of cyclobutene to butadiene, CASSCF and CASPT2N calculations with the 6-31G* basis set give, respectively, 36.6 and 36.3 kcal/mol for the energy difference between cyclobutene and the conrotatory transition state.[17] These values are both close to the "experimental" value of 34.5 kcal/mol.[44] Therefore, it might appear that CASSCF is adequate for this reaction and that inclusion of dynamic electron correlation is unnecessary.

That this is not the case is shown by the calculated energy difference between the transition state and the product, *transoid*-1,3-butadiene. This difference is 55.4 kcal/mol at the CASSCF level and 46.9 kcal/mol at the CASPT2N level. The "experimental" energy difference is 45.4 kcal/mol.[44]

CASSCF gives a satisfactory value for the energy difference between cyclobutene and the transition state for ring opening because (4/4)-CASSCF provides correlation for only one of the four strained σ bonds in cyclobutene. This results in the overestimation of the energy of cyclobutene, relative to that of 1,3-butadiene, by about 8 kcal/mol. The CASSCF overestimation of the energy of cyclobutene balances the 10 kcal/mol overestimation of the energy of the transition state for conrotatory ring opening, caused by the absence of dynamic electron correlation in the CASSCF wave function.

Dehydrobenzenes

In 1,2- and 1,3-dehydrobenzene (**1** and **2**) the additional bonding, not present in benzene, between the "dehydrocarbons" is rather weak. For example, TCSCF/4-31G calculations by Noell and Newton found the energy of **1** and **2** to be, respectively, only 23.3 and 8.8 kcal/mol lower than that of 1,4-dehydrobenzene (**3**).[45] In **3** the through-space interaction between the dehydrocarbons is so weak that the dominant interaction between them is through the C_2-C_3 and C_5-C_6 σ bonds.

TCSCF calculations with basis sets much better than 4-31G give similar results.[19] The TCSCF results are in good agreement with the first set of experimental results on the relative heats of formation of these three isomers, published by Wenthold, Paulino, and Squires.[20]

The TCSCF wave functions correlate the two electrons in the weak σ bond between each pair of dehydrocarbons in **1**−**3**, but these wave functions provide no correlation between the two σ electrons and the six π electrons. Inclusion of the latter type of

(42) Because the first configuration in eq 16 is more dominant in the CASMP2 wave function than in the CASSCF wave function, one might suppose that the CI or perturbation methods that are commonly used for electron correlation in closed-shell systems would work well for the Cope rearrangement. However, only at very high levels of such methods, for instance, at QCISD(T), MP4(SDTQ), and CCSD(T), are results obtained that are comparable to those computed with CASPT2N[15] and CASMP2.[16] In all three of the methods that are based on a single reference configuration, inclusion of triple excitations turns out to have a large effect. The reason is probably that triple excitations from the first configuration in eq 16 are required to provide dynamic electron correlation for the second and third configurations in the CASSCF wave function.

(43) Other calculations on the Cope rearrangement have recently been published: Weist, O.; Black, K. A.; Houk, K. N. *J. Am. Chem Soc.* **1994**, *116*, 10336. Jiao, H.; Schleyer, P. von R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 334.

(44) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412.
(45) Noell, J. O.; Newton, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 51.

correlation should be important, since the required $\sigma \to \sigma^*$, $\pi \to \pi^*$ excitations are relatively low in energy. This type of correlation would be expected to stabilize ionic terms in the wave functions for the two electrons in the weak bonds between the dehydrocarbons in **1** and **2**, thus increasing the occupancy of the bonding σ MOs and resulting in stronger bonds between these carbons.

Calculations that include dynamic correlation between the σ and π electrons have found this to be the case.[19] The weight of the $|...\sigma^{*2}\rangle$ configuration, relative to that of $|...\sigma^2\rangle$, is smaller in these wave functions than in those computed at the CASSCF level; and the heats of formation of **1** and **2** are caclulated to be, respec-

(46) It is well-known that correlated wave functions are also required for the proper description of nonclassical carbocations. (For examples, see: Hehre, W. J.; Radom, L.; Schleyer, P. von R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; pp 379–396. Raghavachari, K.; Haddon, R. C.; Schleyer; P. von R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1983**, *105*, 5915. Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185. Schleyer, P. von R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300. Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112,* 3227.) It seems highly likely that at least some of the electron correlation which must be provided is dynamic in nature. Provision of dynamic correlation also increases the importance of hyperconjugative bonding in the stereomutation of cyclopropane, so that a C_{2v} geometry becomes the transition state for conrotatory ring opening and closure, rather than being a mountaintop, as it is at the (2/2)-CASSCF level. (Getty, S. J.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2085.)

tively, 28−31 and 13−14 kcal/mol lower than that of **3**.

The disagreement between the results of these calculations and the first set of experimental results[20] on the heats of formation of **1**−**3** led Wenthold and Squires to identify a problem in these experiments and to devise a very clever way to circumvent it.[21] A second set of experiments gave heats of formation for **1**−**3** that are in excellent agreement with those predicted by the calculations that included dynamic electron correlation.[19]

Conclusions

A great deal of conceptual simplicity is provided by descriptions of molecules and reactions which focus on just the few electrons that are "active". However, in order to obtain satisfactory results in *ab initio* calculations on excited states that have ionic character, radical ions, pericyclic reactions, and molecules that contain weak bonds, one cannot focus on just the active electrons.[46] Instead, one must go beyond the CASSCF level and include dynamic correlation between the "active" and "inactive" electrons.

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