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Diradical Character of the Cope Rearrangement Transition State

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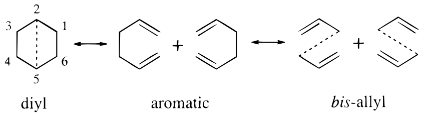
The mechanism of the Cope rearrangement, the [3,3]-sigmatropic rearrangement of 1,5-hexadiene, is believed to involve a chairlike transition state of C_{2h} symmetry.$^{1-4}$ In a simple valence bond perspective, the wave function at each point on the potential energy surface (PES) may be regarded as a resonance hybrid of the five ways of coupling the six active electrons to form a singlet state. Along a C_{2h} cut of the PES, as the distance R between atoms C1 and C6 increases, the wave function changes from predominantly 1,4-cyclohexanediyl to aromatic to predominantly bis-allyl. Most ab initio methods employing at least the 6-31G* basis set lead to the conclusion that the actual transition state is dominated by the "aromatic" combination of two resonance structures, the best estimates of the C1−C6 bond length being near 1.8 Å.^{1,2} Several experimental$^{5-9}$ and, more recently, computational$^{10-13}$ studies concern the effects of various radical stabilizing substituents on the geometry and "diradical character" of the Cope rearrangement transition structure. Here we propose a one-particle density function, $u(\mathbf{r})$, which reflects the extent of the radical character in molecules of any spin multiplicity, including singlets. By computing this electron distribution for the Cope rearrangement of 1,5-hexadiene, we show that, along a C_{2h} cut of the PES, the extent of diradical character reaches a minimum near the transition state geometry.



The term "diradical" is broadly applied to any species which is believed to contain two unpaired electrons. In a more restricted sense, a diradical is a molecule in which unpaired electrons are, on the average, separated by a large distance and, as a result, are only weakly coupled.[14] Despite intense speculation in the past about the extent of "diradical character" of the Cope rearrangement transition state, it is unclear how one would count unpaired electrons, if any, in this system.[15] Indeed, the exact uncompensated spin density, $\rho_u(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$, contains no indication of the presence of unpaired electrons because, in a singlet system, $\rho_u(\mathbf{r})$ is zero at all positions in space. So far, assessment of the extent to which a particular Cope rearrangement geometry is a diradical has been based on such computational evidence as (i) magnetic properties suggesting the presence or absence of ring current effects characteristic of aromatic structures,[3] (ii) the ratio of the coefficients of leading configurations in a configuration interaction (CI) expansion,[4] and (iii) the magnitude of $\langle S^2 \rangle$ for a broken spin, symmetry-unrestricted calculation (for example, UB3LYP).[12,16]

The radical character of individual atoms can be characterized by various indices extracted in an electron population analysis, as for instance, the free valence index of Mayer[17] generalized to post-Hartree−Fock wave functions. However, such indices suffer from all the shortcomings of the adopted population analysis scheme. We propose a continuous distribution, called the "density of effectively unpaired electrons", defined as

$$u(\mathbf{r}) = 2\rho(\mathbf{r}) - \int \rho(\mathbf{r}|\mathbf{r}')\rho(\mathbf{r}'|\mathbf{r})\,\mathrm{d}\mathbf{r}' \tag{1}$$

where $\rho(\mathbf{r})$ is the charge density and $\rho(\mathbf{r}|\mathbf{r}')$ is the spin-free first-order reduced density matrix.[18] The function $u(\mathbf{r})$ describes the spatial distribution of electrons of either spin in orbitals not matched by orbitals with electrons of the opposite spin. If the wave function is a single spin-restricted Slater determinant (RHF), then one can show that $u(\mathbf{r})$ is identical to the usual spin density, $\rho_u(\mathbf{r})$. That is, $u(\mathbf{r}) = 0$ for a single closed-shell determinant and $u(\mathbf{r}) = \rho_u(\mathbf{r})$ for a restricted high-spin open-shell determinant. However, for a general CI wave function, $u(\mathbf{r})$ is *not* equivalent to $\rho_u(\mathbf{r})$, and this furnishes new information about the distribution of electrons with opposing spins and, hence, the radical character of the system. A Mulliken population analysis scheme applied to $u(\mathbf{r}|\mathbf{r}')$ gives effective numbers of unpaired electrons associated with each atom. These coincide with Mayer's free valence in the case of RHF and CI wave functions for singlet states but differ in all cases of a nonzero spin density.

The integral of $u(\mathbf{r})$ over the entire space,

$$n = \int u(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{2}$$

gives the total number of effectively unpaired electrons. It can be shown[19] that, for an unrestricted Hartree−Fock (UHF) wave function, one has $n = 2[\langle S^2 \rangle - M^2]$, where $\langle S^2 \rangle$ is the average value of the total spin squared and M is the spin projection quantum number. For a pair of widely separated hydrogen atoms, coupled as either singlet or triplet and described with either a UHF or a CI wave function, the definition gives $n = 2$, as should be expected.

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(1) (a) Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336−10337. (b) Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378−8388.

(2) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072−1076.

(3) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 334−337.

(4) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774−778.

(5) Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4417−4424.

(6) Wehrli, R.; Schmid, H.; Bellus, D.; Hansen, H.-J. *Helv. Chim. Acta* **1977**, 60, 1325−1356.

(7) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693−6704.

(8) Wessel, T. E.; Berson, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 495−505.

(9) Doering, W. v. E.; Birladeanu, L.; Sarma, K.; Teles, J. H.; Klärner, F.-G.; Gehrke, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 4289−4297.

(10) Hrovat, D. A.; Borden, W. T.; Vance, R. L.; Rondan, N. G.; Houk, K. N.; Morokuma, K. *J. Am. Chem. Soc.* **1990**, *112*, 2018−2019.

(11) Black, K. A.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 5622−5627.

(12) Hrovat, D. A.; Duncan, J. A.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 169−175.

(13) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, H.-Y.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 10529−10537.

(14) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*; John Wiley & Sons: New York, 1994.

(15) In this connection, Dewar and Healy used the term "diradicaloid", defined as "a closed shell species derived from a singlet diradical by a weak interaction between the radical centers": Dewar, M. J. S.; Healy, E. F. *Chem. Phys. Lett.* **1987**, *141*, 521−524.

(16) This approach is based on the fact that, for a single Slater determinant description of a singlet diradical, the unrestricted method gives a much better PES than the restricted one. However, it also yields a totally wrong (nonzero) spin density. Moreover, the range of stability of a Slater determinant to spin-symmetry breaking on the PES strongly depends on the type of the unrestricted method: Davidson, E. R. *Chem. Phys. Lett.* **1998**, 284, 301−307.

(17) (a) Mayer, I. *Int. J. Quantum Chem.* **1986**, 29, 73−84. (b) Mayer, I. *Int. J. Quantum Chem.* **1986**, 29, 477−483.

(18) More generally, we define the corresponding reduced density matrix, $u(\mathbf{r}|\mathbf{r}') = 2\rho(\mathbf{r}|\mathbf{r}') - \int \rho(\mathbf{r}|\mathbf{r}'')\rho(\mathbf{r}''|\mathbf{r}')\,\mathrm{d}\mathbf{r}''$.

(19) Staroverov, V. N.; Davidson, E. R. *Int. J. Quantum Chem.*, accepted.

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Table 1. Effective Number of Unpaired Electrons (n) and CASSCF Mulliken Unpaired Electron Populations (n_C^{CASSCF}) at Selected Cope Rearrangement Geometries along C_{2h} Cut of PES

		n		n_C^{CASSCF}	
R, Å	CASSCF[a]	MRCI[b]	UHF[c]	C2,5	C1,3,4,6
1.54	1.99	2.80	2.03	0.86	0.05
1.75	1.38	1.89	1.83	0.47	0.11
1.966	1.05	1.55	1.45	0.24	0.14
2.0	1.05	1.55	1.41	0.22	0.15
2.25	1.17	1.58	1.80	0.17	0.21
2.50	1.49	1.73	2.35	0.17	0.29
3.00	2.23	2.37	2.76	0.18	0.47
3.50	2.62	3.07	2.85	0.19	0.56
4.00	2.74	3.26	2.87	0.19	0.59

[a] The 6e$^-$/6 orbital CAS includes 52 spin-adapted configurations. [b] MRCI wave functions include from 221 444 to 451 207 spin-adapted configurations. [c] Broken symmetry UHF solution in C_s. Here, $n = 2\langle S^2 \rangle$.

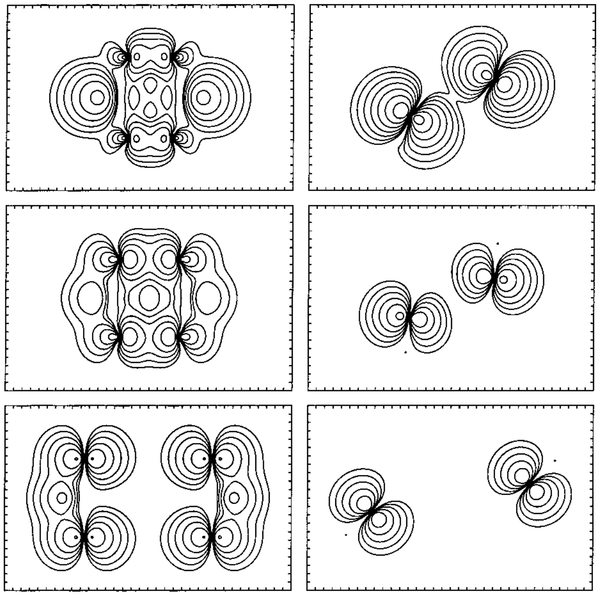

Figure 1. Density $u(\mathbf{r})$ computed with CASSCF wave functions at selected geometries along the C_{2h} cut. The plots are in the C1−C3−C4−C6 plane (left panels) and the perpendicular mirror plane drawn through C2 and C5 (right panels). From top to bottom: $R = 1.54$ Å, $R^{\ddagger} = 1.966$ Å, and $R = 4.0$ Å. The same set of density levels is used for all panels. The outermost contour corresponds to 0.001 e/a_0^3. Densities of consecutive levels differ by a factor of $10^{1/3}$.

We computed the density matrix $u(\mathbf{r}|\mathbf{r}')$ associated with $u(\mathbf{r})$ for several possible geometries of the Cope reaction along the C_{2h} cut representing diyl, aromatic, and bis-allyl structures. All geometries were optimized with Gaussian 98 at the UB3LYP/6-31G* level using the integration grid having 99 radial shells and 974 angular points per shell.[20] In our calculations, the transition state appears as a relative energy minimum along the C_{2h} cut of the PES at the C1−C6 distance $R^{\ddagger} = 1.966$ Å. The diyl is represented by the C_{2h} structure optimized with the distance C1−C6 frozen at $R = 1.54$ Å (the typical C−C bond length in alkanes) and having a pseudoaxial orientation of the hydrogens attached to C2 and C5. The bis-allyl is the structure optimized with R frozen at 4.0 Å, and is essentially a complex of two nearly planar allyl fragments. Near $R^{\ddagger}$, unrestricted and restricted density functional theory (DFT) calculations give the same result, i.e., $\langle S^2 \rangle_{UB3LYP} = 0$. Density matrices $u(\mathbf{r}|\mathbf{r}')$ were generated in the 6-31G* basis from 6e$^-$/6 orbital complete active space self-consistent field (CASSCF), multireference configuration interaction (MRCI, perturbatively selected single and double excitations from the 6e$^-$/6 orbital CAS), and broken symmetry UHF wave functions. The MELD[21] series of programs was used for these steps, except that the CASSCF wave functions were obtained with the HONDO[22] program. Note that DFT does not produce a meaningful density matrix and would have given $u(\mathbf{r}) \equiv 0$ at the transition state.

Total numbers of effectively unpaired electrons computed with these wave functions and CASSCF Mulliken unpaired electron populations on carbons are summarized in Table 1. The contour plots of $u(\mathbf{r})$ from the CASSCF wave function for the diyl, aromatic, and bis-allyl structures are shown in Figure 1. At $R = 1.54$ Å, the shape of the unpaired electron distribution closely resembles p orbitals localized on atoms C2 and C5. Considering that Table 1 shows 0.86 unpaired electron on both atoms C2 and C5 and little on the other carbons, this structure has all the expected diradical features of 1,4-cyclohexanediyl.[23]

The structures near $R^{\ddagger}$ exhibit a relatively low unpaired electron density with comparable populations on all carbons. This cyclic delocalization of unpaired electrons suggests domination of the "aromatic character".[24] As the distance between the allyl groups is increased to near the dissociation limit, the distribution becomes similar to that for a pair of free allyl radicals: a depletion of $u(\mathbf{r})$ in the mirror plane drawn through C2−C5 is accompanied by an accumulation in the C1−C3−C4−C6 plane with 0.59 unpaired electron on each of the atoms C1, C3, C4, and C6. Because of the high spin-polarization at the central carbon of allyl, the unpaired electron population at C2 and C5 remains appreciable in bis-allyl. As documented in the Supporting Information, Mulliken unpaired electron populations are not drastically affected by the type of the wave function employed. The CASSCF, UHF, and MRCI results show the same trend. Remarkably, this is also the trend found for absolute values of Mulliken atomic spin densities from the UHF wave function (see Supporting Information).

In summary, this study demonstrates that the unpaired electron character of singlet diradicals can be described in a rigorous manner. In the example of the Cope rearrangement PES, the total number of effectively unpaired electrons passes through a minimum near the predicted transition state geometry. As the two allyl groups are brought close together or moved apart, a redistribution of effectively unpaired electrons takes place, and the overall number of such electrons increases. Thus, the Cope rearrangement transition state can be justly referred to as predominantly aromatic. This conclusion has been also confirmed by calculations of magnetic susceptibility exaltations.[3]

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Supporting Information Available: **Z** matrices for the structures shown in Figure 1, and complete tables of energies, values of n, $\langle S^2 \rangle_{UHF}$, Mulliken unpaired electron populations for CASSCF, MRCI, and UHF wave functions, and atomic spin densities from UHF (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S., Ochterski, J.; Petersson, G. A..; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L., Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) McMurchie, L. E.; Elbert, S. T.; Langhoff, S. R.; Feller, D.; Rawlings, D. C.; Davidson, E. R. The MELD series of electronic structure codes.

(22) Dupuis, M.; Marquez, A.; Davidson, E. R. HONDO 99.6; IBM Corp.: Neighborhood Road, Kingston, NY 12401; 1999.

(23) Contributions of the hydrogen atoms to the total n are relatively small even in the tightest structure and decrease with larger R. In the short-R structures, where the hydrogen atoms bonded to C1, C3, C4, and C6 can be classified as equatorial and axial, the axial ones consistently have larger unpaired electron populations because of hyperconjugation; hydrogens at C2 and C5 bear the smallest populations.

(24) For comparison, in the much tighter structure of benzene, a similar CASSCF/6-31G* calculation gives 0.15 unpaired electron on each carbon.