The Cope Rearrangement Revisited with Multireference Perturbation Theory

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Abstract: Earlier calculations on the Cope rearrangement based on a CASSCF wave function for the six electrons in the rearranging bonds gave reasonable energies at most places on the potential surface except in the crucial region around the chair transition state. Recently developed MP2 methods for multireference wave functions yield greatly improved energies. Using our version of this method, we simultaneously find that the CASSCF wave function overestimates the diradical character of the wave function. When this error is corrected, the Dewar-type diradicaloid stable intermediate no longer occurs as a minimum in the potential surface and the aromatic transition state moves to shorter bond lengths.

Introduction

The Cope rearrangement has been the subject of many semiempirical and *ab initio* studies[1–9] with a variety of results. It is commonly accepted that the reaction passes through a species that has higher symmetry than the reactants or products; however, synchronicity and concertedness in the vicinity of the transition state is the subject of intense debate. The key question in this reaction is whether the rearrangement of 1,5-hexadiene involves formation of a diradicaloid intermediate, or whether the reaction is concerted and passes through a six-electron "aromatic" transition state. In the latter case, bond making and bond breaking occurs synchronously.[10] In this paper, we will focus on the nature of the wave function at the transition state and the reason for the failure of our previous CASSCF calculation to produce a correct description of the electronic structure.

The potential energy surface for this reaction is flat, which indicates that numerical results are very sensitive to the level of theory and quality of calculations. The correct description of bond rearrangement requires the use of a multiconfiguration form for the wave function in order to take into account the significant nondynamical correlation effects. Earlier MCSCF studies were performed by Osamura *et al.*[5] and Morokuma *et al.*[6] The best MCSCF determination of the potential surface has been presented recently by Dupuis, Murray, and Davidson (DMD) based on CASSCF calculations with the 6-31G* basis set[8] for six-electrons in six-orbitals. A total of seven stationary points on the potential energy surface were characterized at this level of theory.

In an attempt to include the effect of dynamical correlation, calculations using the multireference configuration interaction (MRCI) method as well as quasidegenerate variational perturbation theory (QDVARPT) were reported by DMD. The computational evidence still predicted a potential surface with two pathways, one via an aromatic transition state and the other through a cyclohexanediyl intermediate. Because of the large number of valence electrons and large number of basis functions, these calculations were severely truncated and accounted for only a small fraction of the dynamical correlation. Consequently, it was clear that a better computational method was needed that would allow more configurations to be included. Because the variational calculation did not find any configurations with large coefficients outside the list of CASSCF configurations, it appeared that low-order perturbation theory using all configurations would be a better approach. At the time of the DMD publication, MRMP2 programs were not available to us.

These MCSCF calculations gave reasonable relative energies except in the crucial region around the chair transition state. Experimental evidence indicates that the previous calculations gave an energy much too high near this point. Contrary to the expectations of many quantum chemists, the CASSCF potential surface was not sufficiently parallel to the true surface for quantitative conclusions. Hrovat *et al*[9] recently showed that the Roos CASPT2N method[12,13] gives results in much better agreement with experiment.

Further, Hrovat[9] found that the CASSCF potential surface is not even qualitatively correct. In the CASSCF potential surface, the chair transition state had C_{2h} symmetry with a bond length of 2.189 Å for the bonds being broken and formed. There also was a C_{2h} diradicaloid stable intermediate with a bond length of 1.641 Å. These were separated by a low-energy barrier. Hrovat *et al.*[9] reported that the CASPT2N calculations along this C_{2h} cut through the potential energy surface gave only a single minimum near the bond length of the CASSCF barrier.

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Both the long bond transition state and the short bond intermediate disappeared. Hrovat *et al.* also showed that the new C_{2h} constrained minimum they located was a transition state and not a stable intermediate.

As will be described in detail later in this paper, we have developed a somewhat different form of multireference perturbation theory (MRMP2). The most significant difference from the Roos CASPT2N is that the coefficients of the CASSCF configurations are allowed to change due to dynamical correlations with the other electrons. In the context of the Cope rearrangement, this gives additional insight into the reason for the large error in the CASSCF energy. Our MRMP2 method also differs in many other details from the Roos CASPT2 method. Hence, our calculation shows that the results found by Hrovat *et al.* are not sensitive to the details of the multireference second-order perturbation method.

In this paper we report calculations with several variants of our MRMP2 method. We have reevaluated the energy of the seven stationary points obtained previously by DMD.[8] Then we have calculated the energy and wave function at eleven points along a cut of the potential surface joining the loose chair transition state and the Dewar stable intermediate and preserving C_{2h} symmetry. These calculations were done using the 6-31G* basis set. Several points have been re-optimized using an extended basis set.

Methodology

There are many different forms of Møller–Plesset (MP2) theory[11] generalized for the multireference case (MRMP2).[12–27] Many are similar in formulation, differing only in details. Such differences in details are quite frequently responsible for the quality of numerical results. For this reason, we summarize the strategy for MRMP2 employed in the present calculations. Full presentation with a description of computational implementation can be found in ref 26.

The starting point for our calculations was the molecular orbital basis set based on CASSCF calculations for six-electrons in six-orbitals. Our MRMP2 approach requires construction of an effective configuration interaction matrix, H_{eff}, over the model space. Following the Löwdin partitioning technique, the second-order estimate of a matrix element of H_{eff} is given by

$$(H_{\text{eff}})_{\text{PQ}} = H_{\text{PQ}} - \sum_{K}^{\text{SD(CAS)}} \frac{H_{\text{P}K}H_{K\text{Q}}}{E_k^0 - E_0} \qquad \text{P, Q} \in \text{CAS} \tag{1}$$

where the model space contains a CASSCF space of Slater determinants formed from all possible arrangements of the six active electrons among six active optimized canonical orbitals, while K is a Slater determinant in the space of single and double excitations from the model space SD(CAS). An initial zeroth order wave function ψ_0^0 was formed by diagonalization of the model space. From this wave function, a spin-free charge density was formed and used to define F according to the equation

$$F = h + J(\varrho) - {}^1\!/_2K(\varrho) \tag{2}$$

Canonical orbitals were defined so that the inactive, active, and virtual blocks of F were diagonal when F was formed from the CASSCF charge density. Diagonal elements of F were defined to be the orbital energies

$$\epsilon_k = \langle\phi_k|F|\phi_k\rangle \tag{3}$$

The zeroth-order Hamiltonian was then defined as

$$H_0 = \sum n_k\epsilon_k + \sum f(n_k - n_k^0)$$

$$n_k = a_{k\alpha}^\dagger a_{k\alpha} + a_{k\beta}^\dagger a_{k\beta} \tag{4}$$

$$n_k^0 = \langle\Psi_0^0|n_k|\Psi_0^0\rangle$$

where two correction functions $f(n_k - n_k^0)$ were considered. Without this added term, H_0 would be nearly the same as used by Roos and Hirao. In addition to setting f equal to zero (MROPT1 choice) we used the following choice of f, called MROPT2 defined as

$$\langle\Phi_{\text{L}}|f_2(n_k)|\Phi_{\text{L}}\rangle = \begin{cases} {}^1\!/_2(n_k^L - n_k^0)n_k^0K_{kk} & n_k^L > n_k^0 \\ {}^1\!/_2(n_k^0 - n_k^L)(2 - n_k^0)\,K_{kk} & n_k^0 > n_k^L \end{cases} \tag{5}$$

where K_{kk} is the self-exchange integral and Φ_{L} is a Slater determinant. The effect of this added term is to modify the orbital energies so they are more like the orbital energies used in single reference MP2. That is, the negative of the orbital energy for a partially filled orbital becomes more like an ionization potential when excitation from that orbital is considered. Similarly, the orbital energy is shifted to be more like the electron affinity when excitation into the orbital is involved.

The H_{eff} given by eq 1 can be diagonalized to define a corrected ψ_0 and E_{eff} through second order

$$H_{\text{eff}}\psi_0 = E_{\text{eff}}\psi_0 \tag{6}$$

It should be noted that neither ψ_0^0 nor ψ_0 is an eigenfunction of H_0. Consequently, we have the following definition for E_0 and E_1

$$E_0 = \langle\psi_0^0|H_0|\psi_0^0\rangle$$

$$E_0 + E_1 = \langle\psi_0^0|H|{}_0^0\rangle \tag{7}$$

We can also calculate an energy as an expectation value of H_{eff}

$$E_{\text{expect}} = \langle H_{\text{eff}}\rangle_0 = \langle\psi_0^0|H_{\text{eff}}|\psi_0^0\rangle \tag{8}$$

This energy, with MROPT1, is nearly the same as the Roos CASPT2D method.

For good accuracy, the perturbed wave function ψ_0 should not be significantly different from the zeroth-order wave function ψ_0^0. Consequently, we consider an iteration scheme in which we redefine the ψ_0 wave function after diagonalization of the effective hamiltonian to be a new zeroth-order wave function ψ_0^0. This gives a new density matrix and new F according to eq 2. Then a new E_0 and H_0 are defined, and the procedure is repeated until self-consistency is reached. The orbitals are kept fixed in this iteration. At convergence of the iterative procedure, $E_{\text{iter}} = E'_{\text{eff}} = E'_{\text{expect}}$.

All calculations were performed with the use of a recently developed second-order multireference perturbation theory program which is part of the MELD suite of programs[28] and the HONDO program for electronic structure calculations.[29] Both MROPT1 and MROPT2 were

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Table 1. Some Orbital Energies and Occupation Numbers for the Cope Rearrangement[a]

two allyls	loose boat ts	loose chair ts	Dewar ts	tight chair		middle	diene
				exo	endo		
			Virtual				
0.30	0.33	0.34	0.34	0.34	0.35	0.34	0.32
0.30	0.33	0.30	0.31	0.33	0.34	0.31	0.31
0.29	0.28	0.30	0.29	0.31	0.31	0.30	0.30
0.29	0.28	0.28	0.28	0.30	0.29	0.28	0.28
0.26	0.27	0.26	0.26	0.29	0.26	0.26	0.27
0.26	0.24	0.25	0.25	0.24	0.25	0.25	0.26
			Active				
0.27	0.35	0.39	0.60	0.75	0.66	0.45	0.73
(0.1)	(0.1)	(0.1)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
0.27	0.22	0.18	0.42	0.71	0.59	0.29	0.25
(0.1)	(0.1)	(0.1)	(0.0)	(0.0)	(0.0)	(0.1)	(0.1)
−0.09	0.06	0.18	0.06	−0.06	0.01	0.13	0.23
(1.0)	(0.3)	(0.1)	(0.4)	(0.9)	(0.6)	(0.2)	(0.1)
−0.09	−0.22	−0.28	−0.20	−0.09	−0.16	−0.25	−0.34
(1.0)	(1.7)	(1.9)	(1.6)	(1.1)	(1.4)	(1.8)	(1.9)
−0.39	−0.32	−0.30	−0.46	−0.60	−0.54	−0.37	−0.34
(1.9)	(1.9)	(1.9)	(2.0)	(2.0)	(2.0)	(1.9)	(1.9)
−0.39	−0.44	−0.48	−0.58	−0.60	−0.60	−0.51	−0.62
(1.9)	(1.9)	(1.9)	(2.0)	(2.0)	(2.0)	(2.0)	(2.0)
			Filled				
−0.51	−0.49	−0.49	−0.47	−0.44	−0.45	−0.48	−0.47
−0.51	−0.51	−0.50	−0.47	−0.49	−0.47	−0.49	−0.47
−0.53	−0.52	−0.51	−0.51	−0.49	−0.51	−0.50	−0.51
−0.53	−0.53	−0.53	−0.52	−0.53	−0.51	−0.53	−0.54
−0.59	−0.57	−0.57	−0.54	−0.54	−0.53	−0.55	−0.57
−0.59	−0.60	−0.59	−0.60	−0.59	−0.59	−0.60	−0.59

[a] Occupation numbers for the active orbitals are given in parentheses below the orbital energy. All energies are in hartree atomic units. 1 hartree = 627.5 kcal/mol = 27.2 eV.

used, and the three energies E_{expect}, E_{eff}, and E_{iter} were found. For most calculations, the 6-31G* basis was used. Some calculations, with a re-optimized geometry, were repeated with a Dunning triple-ζ correlation consistent basis (with f functions on C and d functions on H omitted).

Numerical Results

Table 1 shows the orbital energies and occupation numbers for the CASSCF orbitals. This table emphasizes the great variation in the wave function between the various stationary points. The highest energies among the inactive orbitals and the lowest virtual orbital energies do not vary much. The active orbital energies tend to be about −0.6 hartree for doubly occupied σ bond orbitals and +0.6 for empty antibonding σ orbitals. Similarly, the energies are about −0.2 hartree for doubly occupied π orbitals and +0.2 hartree for empty antibonding π orbitals. The singly occupied π orbitals have energies near zero because singly occupied orbital energies are approximately defined as the average of ionization potentials and electron affinities. These active orbital energies intrude into the range of inactive and virtual orbitals.

In Table 1, two allyls as a supermolecule have two singly occupied orbitals. The tight chair endo and exo structures are stable intermediates in the CASSCF calculations and are diradicaloids in Dewar's notation. They both have two orbitals that are approximately singly occupied. The loose chair and loose boat structures were reported as aromatic transition states in the previous paper. They have three doubly occupied orbitals with energies in the π range. The starting diene also has two doubly occupied π orbitals and one doubly occupied σ orbital. The middle point was located in the original publication as the relative maximum in the energy separating the loose chair and tight chair endo C_{2h} structures. The wave function at this point resembles the loose chair wave function.

We recomputed the energy of each previously located stationary point on the potential energy surface with the use of second-order multireference perturbation theory. The results of calculations are summarized in Table 2. The results for MROPT1 and MROPT2 are in close agreement. The E_{eff} results from diagonalization of H_{eff} are inconsistent with, and less accurate than, either E_{expect} or E_{iter}. These differences are indicative of large changes in the expansion coefficients for the CAS configurations. E_{expect} and E_{iter} are self-consistent while E_{iter} uses different coefficients to define H_0 than result from diagonalization.

The energies in this table for the loose chair transition state are dramatically improved relative to the CASSCF results. The energy of the tight chair endo stable intermediate is shifted by about the same amount as the loose chair transition state. These two structures have essentially the same relative energy in the MRMP2 calculations, just as they did in the CASSCF calculation. The point labeled "middle" that was the CASSCF optimized maximum between these two structures now appears slightly lower than either of them.

Following the work of Hrovat *et al.*[9] we performed a second series of calculations for eleven points along the cut of the potential energy surface between the tight chair endo stable intermediate (TCSI) and the loose chair transition state (LCTST), such that C_{2h} point group symmetry was preserved. At each point the interallylic C_3-C_4 and C_1-C_6 was fixed and geometry optimized at the six-electron six-orbital CASSCF level of theory with a 6-31G* basis set. According to previous CASSCF calculations there is a maximum between the TCSI and LCTST points, previously called "middle", with two imaginary frequencies. On the basis of those CASSCF calculations we used second-order multireference perturbation theory to improve the description of dynamical as well as nondynamical correlation energy. MRMP2 was used with H_0 defined according to MROPT2 with 20 inactive, 6 active, and 84 virtual orbitals. Results of the calculations are summarized in Figure 1, where E_{CASSCF}, E_{eff}, E_{expect}, and E_{iter} energies are displayed. There was a dramatic change after the application of perturbation theory. Just as was found by Hrovat *et al.*[9] with CASPT2N, the "middle" stationary point vanished and the three CASSCF stationary points collapsed to one stationary point, presumably a transition state for the Cope rearrangement. It is likely that the two mirror image Dewar transition states separating hexadiene from TCSI have also coalesced into this single MRMP2 stationary point.

In order to explain this result, we plot the ratio of C_2/C_1 for the two dominant configurations for the zeroth-order CASSCF wave function, the wave function after diagonalization of H_{eff} and the wave function as a result of iteration. According to Figure 2, the ratio for the zeroth-order wave function is significantly different than that for the others. This ratio measures the extent of diradical character, and the results indicate that diradical character is greatly reduced after diagonalization of H_{eff}.

On the basis of the much smaller value of the second coefficient shown in Figure 2, one might hope that methods that are derived assuming a single dominant configuration would produce the correct result. To test this, we did calculations with MP2,[11] CCD[30] (coupled cluster doubles), and QCISD[31] (quadratic CI with single and double excitations) methods with the

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Table 2. Energies of Structures Considered in the Cope Rearrangement[a,c]

structure	CASSCF	1x	1d	1i	2x	2d	2i	expt[b]
super	54	58	54	57	61	58	60	58
two allyls	54	61	63	56	66	69	62	58
loose boat ts	52	44	34	47	43	32	46	45
loose chair ts	47.7	33	27	34	33	26	34	
Dewar ts[d]	47.1	32	22	32	29	18	31	
tight chair exo	49.2	46	51	45	40	4	49	
tight chair endo	45.8	35	27	34	31	19	33	
middle[e]	48.3	31	24	31	30	23	31	34
diene[f]	−53	−758	−773	−752	−759	−775	−752	

[a] kcal/mol, relative to hexadiene. [b] Expt is for $\Delta H(500)$. See ref 8 for the effect of zero-point and thermal energy. [c] In the column heading, "1" denotes OPT1, "2" denotes OPT2, "x" denotes E_{expect}, from eq 8, "d" denotes E_{eff} from diagonalization in eq 6, "i" denotes E_{iter}. For a more complete description of the stationary points, ref 8. [d] The Dewar transition state separates hexadiene from the tight chair endo stable intermediate. [e] Middle was the geometry of the maximum along the C_{2h} cut of the potential surface connecting the loose chair transition state and the tight chair endo stable intermediate. The experimental activation energy is placed on this line because in the final analysis it has the geometry closest to the MROPT2 calculated transition state. [f] Calculated diene energy in millihartrees, shifted by adding 233000, i.e. $1000(E + 233)$. All MRMP2 energies have uncorrelated ("frozen") cores on all six carbons.

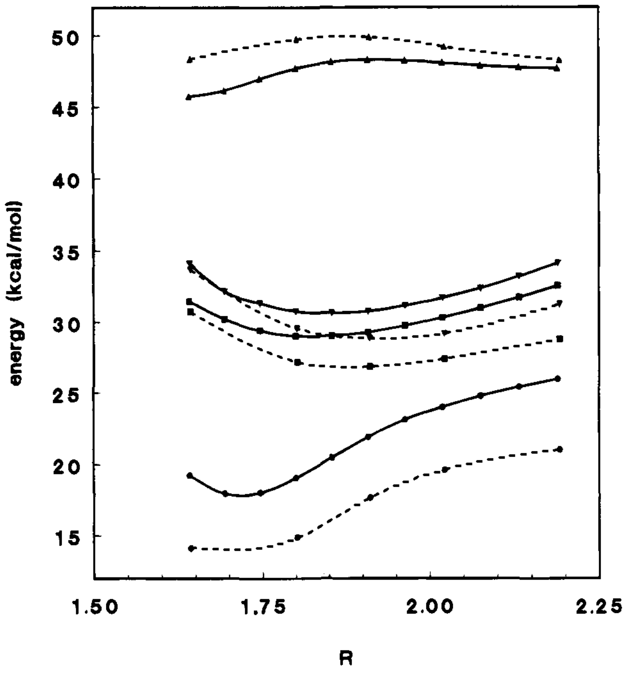

Figure 1. Energy relative to hexadiene along the C_{2h} path connecting the tight chair stable intermediate and the loose chair transition state as a function of $R_{16} = R_{34}$ bond length: (▲) = CASSCF, (●) = E_{eff} (▼) = E_{iter} (■) = E_{expect}. Solid lines are used for the 6-31G* basis and dashed lines for the cc basis.

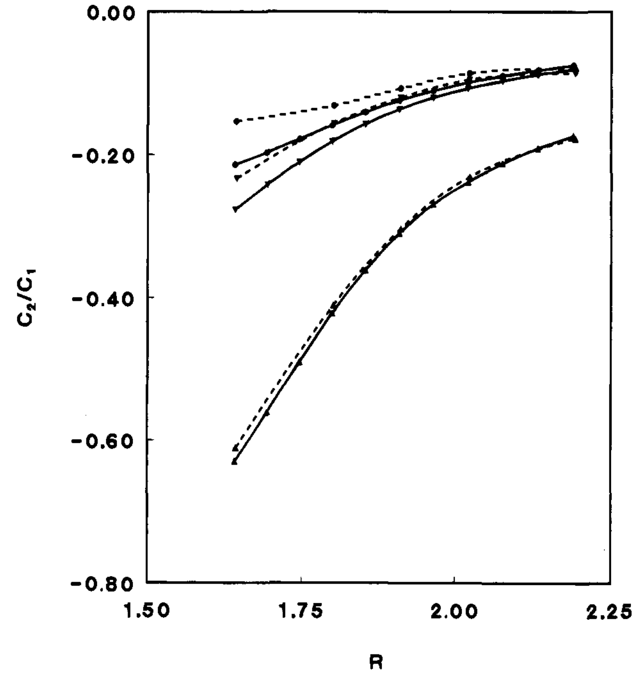

Figure 2. Ratio of the coefficient of the $|a_g{}^2\rangle$ to the $|b_u{}^2\rangle$ configuration along the C_{2h} path of Figure 1: (▲) = CASSCF, (●) = E_{eff} (▼) = E_{iter}. Solid lines are used for the 6-31G* basis and dashed lines for the cc basis.

same 6-31G* basis. Constrained C_{2h} geometry optimization gave a long bond: $R_{16} = R_{34} = 1.873$ Å for CCD, 1.871 Å for QCISD, and 1.783 Å for MP2. These are all close to the value of R, 1.85 Å, giving the lowest energy in Figure 1 without complete optimization of the MRMP2 energy. The absolute energies, when corrected for the difference between frozen and correlated cores, agree well for MRMP2 compared with CCD and QCISD. The MP4SDQ energy also agrees well. Only the MP2 energy was about 25 kcal/mol different. The frequencies from these calculations showed the MP2 calculation had found a stable intermediate with a frequency along the expected reaction coordinate of 112 cm^{-1}. The CCD and QCISD C_{2h} constrained minima, in contrast, were transition states for the Cope rearrangement with imaginary frequencies of magnitude 690 cm^{-1} along the expected reaction coordinate. The CCD and QCISD transition state energies found in this way were both 27 kcal/mol above the hexadiene minimum. We have no program to find frequencies with the MRMP2 program, but we verified that starting from the MP2 minimum and stepping along the lowest frequency normal mode direction (the expected reaction coordinate) the MRMP2 energy went down. Hence, only MP2 seems qualitatively incorrect. All the higher levels of theory discussed here agree that there is only one stationary point along the C_{2h} cut, near $R_{16} = R_{34} = 1.85$ Å, and it is a transition state and not a stable intermediate. The MRMP2 method, however, is the only one giving information about the relative diradical/aromatic nature of the wave function and justifying a single determinant approach after the fact.

Hrovat *et al.*[9] made several tests to establish that their results were converged with respect to basis set. We made a similar test with a basis designated as cc in this paper that was formed from the Dunning[32] triple-ζ correlation consistent cc-pVTZ basis by omitting the f function for C and d function for H. This has one more of each of the s, p, and d functions for C and one more s and two p polarization functions for H compared to the 6-31G* basis. This basis would be the same size as the largest basis, 6-311G (2d,2p), used by Hrovat *et al.*[9] except that we used 6 component d functions where they used 5 components. This effectively adds another s function to every carbon. With

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this basis the CASSCF energy of hexadiene is lowered to −233.118 hartrees compared to −233.053 hartrees with 6-31G*. The dynamic correlation energy is improved even more so the E_{iter} (MRMP2) is −234.037 compared to −233.752 hartrees with 6-31G*.

The loose chair transition state has $R_{16} = 2.192$ Å and the stable intermediate diradicaloid has $R_{16} = 1.643$ Å with the CASSCF wave function for this cc basis in good agreement with the 6-31G* basis. The transition state is 48.3 kcal/mol and the diradicaloid 48.4 kcal/mol above hexadiene in energy, which agrees well with the 6-31G* results in Table 2.

As for the 6-31G* basis, the CASSCF energy was optimized for the cc basis at a few points along the C_{2h} energy cut. The CASSCF and MROPT2 energies are compared with the 6-31G* energies in Figure 1. The results are qualitatively the same, although there are 10% shifts in the calculated energies from each level of theory. The C_2/C_1 ratio shown in Figure 2 is essentially the same for these two basis sets. This is a strong indication that the conclusion from these calculations will not be changed by further improvements in the basis set.

All of the energetic results are in qualitative agreement with Hrovat *et al.*[9] They also concluded that basis set improvement did not change the CASPT2N energy although they did not reoptimize the CASSCF geometry with the larger basis sets.

Discussion

These calculations indicate that (a) electron correlation involving the inactive valence electrons preferentially stabilizes the energy of the CASSCF aromatic wave function compared to the diradical structure and (b) this same electron correlation diminishes the diradical character of the wave function. To the first approximation, the wave function along the C_{2h} cut involves two main configurations. In one configuration, the last two electrons are in a "b_u" orbital given approximately as $p_1 + p_2$ involving orbitals localized on the apical carbons. In the second configuration, the electrons are in an "a_g" orbital given approximately by $p_1 - p_2$. The zeroth-order wave function may be thought of essentially as $C_1|b_u^2\rangle + C_2|a_g^2\rangle$. The $|b_u^2\rangle$ "aromatic" configuration is an equal mixture of diradical and ionic character. When $C_2 = -C_1$, the $|a_g^2\rangle$ configuration cancels the ionic character giving a wave function of pure diradical character. As Figure 2 shows, the CASSCF wave function varies from being largely diradical ($C_2 = -0.6C_1$) for the tight chair structure to being more nearly the $|b_u^2\rangle$ mixture of ionic and diradical character for the loose chair.

Diagonalization of H_{eff} gives a wave function with reduced $|a_g^2\rangle$ character and hence greater ionic character. Examination of the contribution of the SD(CAS) configurations to H_{eff} shows that the most important effect is greatly reducing the effective H_{a^2,b^2} connecting matrix element. This reduces the mixing of these configurations and causes the lower energy $|b_u^2\rangle$ configuration to become more dominant.

If these configurations are transformed to localized orbitals, then the three configurations $|p_1^2\rangle$, $|p_1p_2\rangle$, and $|p_2^2\rangle$ are involved. By symmetry, the ionic configurations $|p_1^2\rangle$ and $|p_2^2\rangle$ enter with equal coefficients. After the transformation, the reduction of H_{a^2,b^2} is seen to be equivalent to preferential lowering of the $|p_1^2\rangle$ and $|p_2^2\rangle$ diagonal elements relative to $|p_1p_2\rangle$. That is "electron correlation" stabilizes the ionic configuration relative to the diradical configuration. This is reasonable in a qualitative sense if these three valence bond configurations are taken literally. The inactive orbitals are determined in the CASSCF in the average field of the active electrons which show no net polarity. Hence, the inactive electron distribution is appropriate for the diradical valence bond configuration. For a configuration like $|p_1^2\rangle$ the inactive orbitals can polarize and substantially lower the energy of the ionic configuration. Hence what appears as "dynamic correlation" in the delocalized picture can be viewed as polarization in a localized picture where each valence bond structure is allowed to have its own most appropriate charge distribution. If this is a valid view, then most CASSCF calculations on molecules in the weak overlap region involving well-separated radical centers will be in error. There is good evidence that this is the case[9,33] at least for transition states.

Further evidence for the generality of this observation can be seen in the choice of parameters for the Pariser−Parr−Pople (PPP) π electron model. The *ab initio* value of the integral representing the repulsion between two electrons in a p orbital on carbon is about 17 eV.[34] This is reduced in the PPP effective hamiltonian to 11.1 eV just to get the correct energy difference between two methyl radicals and the $(CH_3^+)(CH_3^-)$ ion pair.[34] A large part of this change is due to polarization and correlation with the σ electrons.

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