The Controversial Ground State of Tetramethyleneethane. An ab Initio CI Study

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Received: January 24, 2000; In Final Form: April 14, 2000

The controversial ground state and conformation of the tetramethyleneethane diradical (TME) are discussed from ab initio calculations including electronic correlation. The results for the singlet−triplet energy gap for different conformations of TME calculated with the difference dedicated configuration interaction method (DDCI) are presented. They support the most reliable experimental hypothesis concerning structures and energetics. The equilibrium geometries of both species have been found to be quite different, of D_{2d} symmetry for the singlet and of D_2 symmetry for the triplet, with dihedral angles between the allyl moieties of 90° and 47°, respectively. Regarding the energies, the singlet always appears to be more stable than the triplet, but the energy difference is so small in the neighborhood of the equilibrium conformation of the triplet, less than 0.3 kcal mol^{-1}, that both states can be considered degenerate at this geometry. The S−T energy difference is tuned by the torsional coordinate, to the extent that the observed state can be modified when the TME is incorporated in a larger structure that rotationally constrains the diradical or when the triplet is produced by the reaction mechanism.

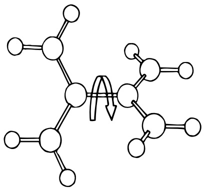
1. Introduction

The field of organic diradicals has been one of long-standing interest for experimental and theoretical chemists. These diradicals may play an important role as intermediates in some thermal and photochemical reactions and can be crucial to the understanding of spin−spin coupling phenomena. One of the basic static features that control many of the properties of these systems is the relative energy of the low-lying singlet and triplet states, which determines the spin of the ground state and so the magnetic properties of the compound and in many cases the reactivity of the diradical species. However, this basic feature is not so easily obtained, neither experimentally nor theoretically, if the magnitude of the energy difference is small. This is the case for tetramethyleneethane (TME), a non-Kékulé molecule for which discrepant or ambiguous results have been obtained for several decades.

The aim of the present work is to elucidate the multiplicity of the ground state of TME using theoretical calculations. We present the results for the singlet−triplet energy gap of different conformations of the TME calculated with a method specifically designed to obtain energy differences, the difference dedicated configuration interaction method (DDCI).[1] This method has already been proven to yield results of very good quality, even in the more severe benchmarks.[2,3,4] The results reported here for TME support the most reliable experimental hypothesis, i.e., the singlet and triplet states are almost degenerate, with the singlet energy being less than 0.3 kcal mol^{-1} lower than the triplet one.

TME can be viewed as being formed by two allyl fragments that can rotate about the central C−C bond, and the variation of this dihedral angle (θ) has been found to tune the relative energy of the low-lying states.

This diradical is assumed to be the central intermediate in the dimerization of allene leading to 1,2-dimethylenecyclobutane[5] and in the thermal rearrangement of this last compound.[6] It is also found incorporated into ring systems, and it is the building block of polymers with useful ferromagnetic or electrically conductive properties. As a prototype of a system with disjoint nonbonding molecular orbitals[7] the singlet state is not destabilized relative to the triplet, so both states have similar energies. It is for this reason that TME can be used as the parent system for series of molecules in which a structural feature (for example a heteroatomic bridge) can be used to gradually change the singlet−triplet gap.[8]



The first direct observation of TME was reported by Dowd in 1970.[9] The temperature dependence of the ESR spectrum intensities[10] agreed with a quasi-degeneracy of triplet and singlet states (ΔE_{S-T}<40 cal mol^{-1}) or with a triplet ground state. On the basis of comparison with restricted analogues, Dowd concluded that the ground state of TME should be a triplet, most probably with a geometry with canted allyl moieties (0° < θ < 90°).[10a]

The studies carried out in 1997 and 1998 by Berson et al.[8] on the ESR spectra of TME derivatives and by Clifford et al.[11] in 1998 on the negative ion photoelectron (NIPE) spectra of TME$^-$, lead to the opposite conclusion, that is, that the singlet state had lower energy than the triplet. The analysis of the data supported the hypothesis that both states can be populated, although the singlet is more stable. From these data, it was also concluded that the equilibrium geometries of the two lowest states of TME (singlet and triplet) have very different torsional angles, of 90° for the singlet (D_{2d} symmetry) and of around 50° for the triplet (D_2 symmetry), so the intersystem crossing

10.1021/jp000278d CCC: $19.00

is controlled by the conformational change. When the decay to the lower singlet is very slow, the triplet state appears as a metastable one and at low temperatures, when the interconversion rate is very small, both states can be populated.

In 1997 and 1998 Matsuda and Iwamura[12] carried out measurements of magnetic susceptibility and magnetization on a conformationally restricted derivative of TME and, in contrast with the interpretation of the former authors, they concluded that singlet and triplet states are almost degenerate, with the singlet slightly lower in energy.

Among the theoretical results, there is no less controversy. In this case, there are two aspects to be analyzed: the equilibrium geometries and the relative energies of both states. In most of these works, the variation of the energy of both states with the torsional angle θ is obtained.

The first calculation on TME carried out by Du and Borden in 1987 using the UHF method[13] yielded the singlet state lower than the triplet by 1.7 kcal mol^{-1}. This small gap would allow the population of the triplet state. The equilibrium geometries that were found corresponded to a dihedral angle of 90° (D_{2d} symmetry) for the singlet and of near 50° (D_2 symmetry) for the triplet, in good agreement with experimental results.

Dowd et al. used different methods (MM2 and UHF in 1988,[14a] CASSCF and SDCI in 1992[14b]). Contrary to the previous results, they found that the triplet was 0.5 kcal mol^{-1} lower than the singlet state. The dihedral angle of the triplet equilibrium geometry was found to be around 50° (D_2 symmetry). Similar results were obtained by Prasad and Radhakrishnan in 1996[15] from AM1/C1 calculations.

In 1997, Havlas and Michl[16] tried to determine the TME equilibrium geometry through the calculation of zero-field splitting parameters. However, the low accuracy of the results obtained did not allow them to draw definite conclusions.

Recently, some density functional theory (DFT) calculations (using spin-restricted ensemble-referenced Kohn−Sham (REKS) method) by Filatov and Shaik[17] have been published. These authors found that the absolute minimum corresponded to the singlet state at a D_{2d} geometry, 1.4 kcal mol^{-1} lower than the triplet state at the same geometry. On the other hand, at the equilibrium geometry of the triplet, with a dihedral angle of 50.1°, this state is lower than the singlet by 0.2 kcal mol^{-1}. This inversion is due to a transition state that the singlet potential energy curve (PEC) shows in this region, which seems to be an artifact of the calculation method. Their conclusions regarding a metastable triplet state in this region are therefore not based on very sound ground.

The analysis of these results leads to the upsetting conclusion that depending on the method, on the basis set used or the corrections considered, not only the magnitude but the sign of the energy gap can change. This variety of theoretical results is due to the fact that, although different methods can provide very satisfactory results for absolute energies, the determination of energy differences is a much more severe test for theoretical calculations because the resulting values are often of the same magnitude as the error of each independent calculation. This is the reason why a specifically oriented method is needed in such cases.

2. Theoretical Methods and Technical Details

As mentioned, the method used in this work is the difference dedicated configuration interaction, DDCI, specifically designed to give energy differences. Let us first recall its main characteristics.

2.1. The DDCI Method to Evaluate Energy Differences. The DDCI method is a variational method in which the configuration interaction (CI) space is selected from second-order perturbation theory considerations. Grounded on the early perturbative calculations of singlet−triplet (S−T) gaps in strongly localized biradicalar systems by De Loth[18] et al., it was first derived to variationally evaluate this specific type of energy gap[19] and was then generalized to optical transitions.[1] Many applications have proven the performance of the method. As examples illustrating its reliability in calculating singlet−triplet gaps, the mean error in a series of carbenes[3] was less than 0.5 kcal mol^{-1}.

The first step in the formal perturbative scheme is the definition of a minimal number of active molecular orbitals (MO), m, allowing a crude zeroth order description of the transition, which gives a small complete active space (CAS) that is taken as model space, S. The external correlation is evaluated in the framework of the quasi-degenerate perturbation theory. At this level of theory, it has been demonstrated[19] that from the double excitations contributing to the second-order development of the effective Hamiltonian built on the previously defined model space, only those involving at least one active orbital (doubly occupied or virtual) are significant for the energy differences. The remaining purely "inactive" pq → rs double excitations (which create two holes, p and q, in the inactive doubly occupied orbitals subset and two particles, r and s, in the inactive virtual orbitals one), although giving very important contributions to the correlation energy, only shift the diagonal elements of the effective Hamiltonian by the same value and, thus, do not contribute to the spectrum. To include higher orders of perturbation, as well as to avoid intruder states, a well-known problem of perturbative effective Hamiltonians, the above perturbative arguments are extrapolated to build a CI space that includes all of the second order excitations that contribute to the spectrum evaluation. It means that the contributors to the spectrum at the perturbative level are included in a CI space, which will be treated variationally. In that way, interactions between double excitations are automatically allowed. This subspace of the CAS single double CI (CAS*SDCI) is then treated variationally. The method gives energy transitions from purely variational calculations. This scheme has been applied successfully in many types of vertical transitions.[19,20] For the specific case of exchange magnetic coupling, some additional restrictions may be added and a smaller differential space, referred as DDCI2, may be used. For more details, see ref 19. Another possibility to reduce the size of the DDCI space when the CAS model space is large is to select the most significant determinants of the CAS and then add up the differential contributions.

Because we deal with a CI space, some additional considerations are to be made. Some complementary determinants are added to ensure the invariance of the wave function under unitary transformations of the active orbitals and to obtain S^2 eigenfunctions. Thus, the DDCI space includes the CAS generated from the n electrons, the m active MOs, and all of the singles and doubles on the CAS involving at least one active MO. The main characteristics of the DDCI method may be summarized in four points: (i) it is a variational method; (ii) for this reason, it is an uncontracted method that allows the external correlation to modify the coefficients of the CAS; (iii) the DDCI matrix is invariant under rotations of the molecular orbitals in the active, doubly occupied, or virtual subsets; and (iv) the number of determinants in the DDCI space is proportional to the cube of the MO set dimension, instead of to the fourth power as it would be in a CAS Single and Doubles CI (CAS*SDCI) calculation.

It is worth mentioning that in DDCI, the most important contribution to the total correlation energy comes from the purely inactive double excitations, which are also the most significant contributor in the size-inconsistency problem. So DDCI is not a strictly size-consistent method, but the size-consistency error is quite small. Several methods have been described to correct the size-inconsistency error in truncated CI calculations, such as the self-consistent size-consistent $(SC)^2$ method. This method consists of adding corrections to the diagonal elements of the CI matrix to cancel the unlinked contributions that are responsible of the size-consistency error. For more details, see ref 21.

Another aspect that must be pointed out is that the arguments that lead to the DDCI selected space are only strictly correct for vertical transitions calculated from a common set of molecular orbitals for all states, but because only a part of the correlation is included, the absolute energies are not well estimated. This means that the method is neither suitable to calculate an isolated potential energy surface nor suitable to optimize geometries, for which purpose other methods must be used instead. Another consequence is that when adiabatic transitions are to be evaluated, the contributions of the neglected double excitations to the correlation energy of each state are to be included. These contributions vary with the geometry and if significant variations of the geometry appear in the different states, their effect must be evaluated and added to the results of the DDCI calculations. In previous works, we proposed that this quantity could be estimated at the MP2 level. In substituted carbenes, in which there are great differences between the geometries of the singlet and the triplet state,[3] this correction gives about 10% of the gap. For cases in which the perturbative estimation is not accurate enough, a previous knowledge of the ground-state potential energy surface is needed (obtained either from an independent, accurate calculation or from experimental information). Then, the transition between the ground state and the excited state(s), calculated at the DDCI level for each geometry is(are) added to the energy of the ground state. Very accurate energy potential curves for K_2 excited states[22] have been calculated in this way.

A last point concerns the choice of the molecular orbitals. Because the results depend on the MOs used in the CI step, an iterative improvement in the active orbitals has been proposed[20a] to avoid this difficulty. Average orbitals iteratively adapted to the states that define the transition may be obtained from a single particle density matrix, $\bar{R}$, obtained by average of the density matrices of the different states, after diagonalizing the DDCI matrix. The procedure (IDDCI) is iterated to self-consistency. To avoid large computational costs, this iterative procedure is shortened by using only the determinants obtained by single excitations over the CAS, CAS*S, because it is the only subset directly coupled to the determinants of the CAS through the single particle density operator. Once the self-consistency has been reached and a new set of orbitals adapted to the calculation of the transition has been obtained, only one diagonalization is performed with the whole DDCI space. The above procedure is not the only way to obtain mean natural orbitals; state averaged CASSCF calculations can also provide active orbitals well suited for determining electronic transitions. However, the general advantage of the IDDCI procedure is that it allows the mixing states belonging to different irreducible representations without any difficulty.

2.2. Calculation Procedure. Because the aim of this work is to obtain the singlet and triplet energy curves as a function of the torsional angle θ with reliable relative energies, one of the curves must be obtained with a different method than the DDCI. The procedure is very similar to that previously described for K_2.[22] The steps followed are three: (i) The critical points of the singlet state potential energy curve are calculated at the CASSCF(6,6)/6-31+G* level, using GAUSSIAN-94.[23] The absolute minimum and several relative minima (restricted geometries, with a fix value of the torsional angle) are obtained. The same set of calculations has been performed for the triplet state, although they are not essential. (ii) The potential energy curve of the singlet state is calculated, with CASSCF(6,6) MOs and a CAS(2,2) reference space, at the singles and doubles CI (SDCI)/triple-ζ+p level, using the MOLCAS-4.0[24] package. The geometry of the absolute minimum of the singlet state found in the first step is used, modifying only the value of the torsional angle θ. (iii) The potential energy curve of the triplet state is calculated, with the same set of MOs as in the preceding step, at the DDCI/triple-ζ+p level, using DDCI+SCIEL[25] programs, coupled to the MOLCAS package after the two-electron integrals transformation. For all of the values of the θ angle, the geometry belongs at least to the D_2 point group, so the singlet and the triplet belong respectively to A and B_1 irreducible representations, IR, and a DDCI space is generated for each one. For each geometry, the vertical energy difference ΔE_{S-T} is calculated and added up to the singlet state energy calculated in the previous step. In this way, it is possible to construct the triplet state energy curve.

In the present case, it would also be possible to determine first of all the PEC of the triplet state and build the PEC of the singlet state in a second step by adding the vertical DDCI energy differences. This reverse procedure is possible given the similarity in the geometrical parameters of the singlet and the triplet minima (with the exception of the dihedral angle). In fact, it could have been simpler, because the triplet state is well described at the CASSCF level. Nevertheless, this reverse procedure is not convenient if the equilibrium geometry of both states involved is dissimilar enough because the absolute minimum of the ground state could be missed.

3. Results

3.1. Preliminary Exploration. Because all of the aspects previously discussed of DDCI show it to be a quite flexible method, the influence of certain factors on the quality of the results for the different types of systems and transitions (magnetic or electronic), such as the model space, the starting MOs, and so forth, is not always predictable. To get the required precision with the minimum cost in a particular case a preliminary analysis is needed. In the case of TME, a previous study was carried out to determine the influence of the several options of the DDCI method on the results, looking for the best quality/cost rate.

Choice of the Model Space. The first premise of the DDCI method is to use a model space as small as possible, provided that it is able to properly describe at the zeroth order the states involved in the transition. Because of the diradical character of TME, the complete active space formed by two electrons in two active orbitals (the HOMO and LUMO) seems to be enough to describe the singlet and triplet states. Nevertheless, some test calculations were performed with a small basis set, a double-ζ+p basis set, comparing the results obtained with a CAS(2,2), a CAS(6,6), and a multireference space, MR, that was generated by enlarging the CAS (2,2) with the additional most contributing

TABLE 1: Approximate Dimension of the Model, DDCI, and DDCI2 Spaces for TME in a D_2 Conformation, Using a Double-ζ+p Basis Set. DDCI2 S−T Separations, ΔE_{S-T} ($E_S - E_T$) in kcal mol^{-1} Are Also Given

	CAS(2,2)	MR	CAS(6,6)
model space[a]	2	5	100
DDCI space[a]	160 000	1 900 000	21 900 000
DDCI2 space[a]	4000	200 000	800 000
ΔE_{S-T}	−0.98	−0.79	−0.89

[a] The CI spaces for *A* and B_1 IR have similar but not strictly identical dimensions. The approximate averaged values are reported.

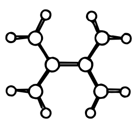
determinants of the CAS(6,6). As shown in Table 1, for a CAS(6,6), the dimension of the DDCI space is around 21 million determinants for this not very large basis set. This enormous size is not easily tractable. Because of the diradicalar character of TME, it is possible to use the DDCI version for strongly localized diradicals (see Section 2), and so we limited this part of the study to DDCI2, which gives much more manageable spaces, as shown in the table. The singlet−triplet separations, ΔE_{S-T} ($E_S - E_T$), calculated at the DDCI2 level for the three model spaces, are so similar that it can be concluded that the CAS(2,2) model space is effectively sufficient to estimate the gap.

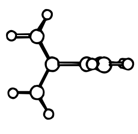
Choice of the Common Set of MOs. The description of the S−T transition within the CAS(2,2) can be improved adapting the molecular orbitals with the IDDCI method, as indicated in Section 2. The improvement has been proven to not be crucial in this case, when the molecular active orbitals optimized for the singlet are used to optimize both states. Nevertheless, IDDCI calculations have been useful to ensure, through the natural occupation numbers, that there were no other orbitals apart from the active ones whose occupations changed noticeably in the transition.

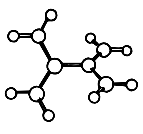
Analysis of the Size-Consistency Error. The DDCI calculations are expected to produce almost negligible size-consistency errors. To verify this aspect, size-consistency corrections were estimated with the (SC)^2 method for some test cases. The mean estimation of this error was 0.01 kcal mol^{-1}, confirming our expectations, so they were not taken into account on the final DDCI results. On the other hand, the ACPF[26] corrections were added to SDCI energies for the singlet potential energy because the size-consistency error in this type of calculation cannot be neglected.

Basis Sets. After the preceding tests, the triple ζ+p basis set of Pierloot[27] was used for caculations performed with MOLCAS 4.0 + DDCI + SCIEL programs. A 6-31+G* basis set, of the same quality, was chosen when the GAUSSIAN-94 package was used.

3.2. Final Results and Discussion. The conformations of TME obtained by rotation around the central C−C bond are of three different symmetries: D_{2h} for the planar conformation ($\theta = 0°$), D_{2d} for a perpendicular one ($\theta = 90°$), and D_2 for any other ($0° < \theta < 90°$).


D_{2h}


D_{2d}


D_2

The active orbitals used for the CASSCF(6,6) geometry optimizations were the 6 π orbitals formed by the 6 p atomic orbitals perpendicular to the allyl planes. At this step, the calculations were performed by using the GAUSSIAN-94 package. The absolute minimum located for the singlet and triplet states were both of D_2 symmetry, with dihedral angles of 44.8° and 50.0°, respectively. Other restricted geometry optimizations were carried out with fixed values of the torsional angle of 0° and 90°. The most important structural data are summarized in Table 2, and the energetics are represented in Figure 1. At this level of calculation, the energy of the singlet state is lower than the triplet one for any conformation. To characterize the critical point located, frequency calculations were performed. A negative value for the lowest frequency was found only for the D_{2h} geometries , which means that only these structures appear to be clear transition states. The small positive values of the first frequency of the D_2 and D_{2d} structures indicate very shallow minima. In Figure 1, this feature is easily observed, mainly in the singlet state curve.

TABLE 2: Main Structural Parameters of the Critical Points Located at the CASSCF(6,6)/6-31+G* Level. Bond-lengths in Ångströms, Angles in Degrees. CASSCF(6,6) and CASPT2 Relative Energies Referred to the D_2 Singlet Minimum, in kcal mol^{-1}

symmetry	state	d_1[a]	d_2[b]	θ	E CAS(6,6)	E CASPT2
D_{2h}	^1A_g	1.49	1.40	0.0	0.98	3.80
	^3A_u	1.51	1.40	0.0	4.83	
D_{2d}	^1A	1.50	1.39	90.0	0.04	−0.05
	$^3A_2$	1.51	1.39	90.0	1.98	
D_2	^1A	1.50	1.40	44.8	0	0
	$^3B_1$	1.50	1.40	50.5	1.32	

[a] Length of the central C−C bond. [b] Length of the allylic C−C bond.

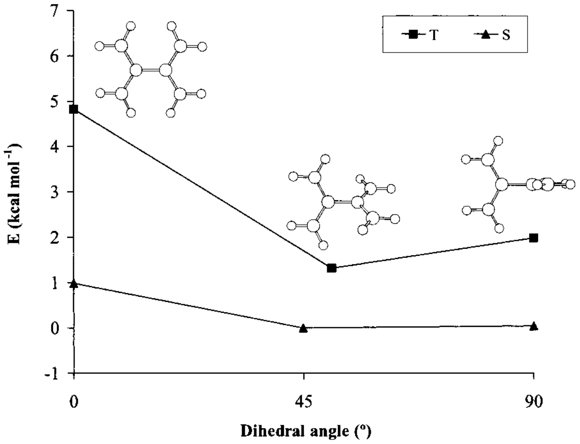


Figure 1. Energies (relative to the singlet minimum) of the singlet (S) and triplet (T) states as a function of the dihedral angle, obtained at the CAS(6,6)/6-31+G* level.

Although the torsional angle for the triplet is in accordance with experimental[8,11] and previous theoretical results,[13−15] the singlet dihedral angle is neither in agreement with the observations of Berson et al.[8] and Clifford et al.[11] nor in agreement with the calculations of Du and Borden,[13] who found a torsion of 90°. To determine if the lack of some correlation is at the origin of this discrepancy, some CASPT2 calculations were performed, with the same active space without optimization, starting with all the minimum geometry parameters of the CASSCF(6,6) singlet, and changing the value of the dihedral angle. The D_{2d} geometry was found to be 0.05 kcal mol^{-1} more stable than the D_2 minimum. The role of the dynamic correlation is thus shown to be important in the optimization of this state. This conclusion will be confirmed in the next paragraph.

To obtain an accurate singlet state potential energy curve, CAS(2,2)*SDCI calculations were performed, using the previous CASSCF(6,6) molecular orbitals and structural parameters of

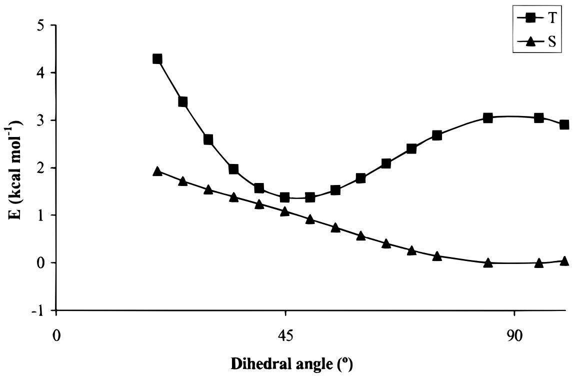


Figure 2. Energies (relative to the singlet minimum) of the singlet (S) and triplet (T) states as a function of the dihedral angle. Singlet energies obtained with CAS(2,2)*SDCI/triple-ζ+p calculations plus ACPF corrections. Triplet energies obtained adding to the previous results the S−T energy gap calculated with the DDCI method.

the singlet D_2 minimum and modifying only the value of the dihedral angle. As mentioned in the previous section, the ACPF size-consistency correction[26] was added to the SDCI energy. The energetics are shown in the potential energy curve represented in Figure 2. As expected from CASPT2 calculations, the minimum energy structure is not any longer that of D_2 symmetry, but the D_{2d} one is significantly more stable, by 1.08 kcal mol^{-1}, with the two allyl moieties perpendicular to each other. Obviously, this point should be confirmed running a geometry optimization at the SDCI level, but this calculation cannot be performed with the distributed versions of the MOLCAS and GAUSSIAN packages. This result is in good agreement with the experimental hypothesis[8,11] and with the calculations of Du and Borden.[13]

To obtain the curve of the triplet state, the singlet−triplet energy gap has been calculated for each geometry of the singlet state potential energy curve. In agreement with the conclusions of the preliminary analysis commented in the former section, DDCI calculations of the S−T energy differences have been carried out over a CAS(2,2) model space. Consistently with the singlet PEC, the basis set and molecular orbitals used are the singlet state CASSCF(6,6) ones. Size-consistency corrections have not been added to the energy difference because it was shown to be almost negligible. The energies of the triplet state are obtained with the addition of the DDCI energy gap to the SDCI energy of the singlet state for each geometry. Let us illustrate this calculation with one example. For the geometry with $\theta = 45°$, the energy for the singlet state, calculated at the CAS(2,2)*SDCI+ACPF correction level, was −232.644 751 hartree. The calculated DDCI energy gap was $\Delta E_{\mathrm{T-S}} = 0.000\,468$ hartree. Adding this difference to the singlet energy led to the absolute energy for the triplet, −232.644 283 hartree. The potential energy curve built in such a way is represented in Figure 2. The equilibrium geometry of this state at this level of calculation is located at a dihedral angle of 47°, not far from the CASSCF(6,6) results. To compare the calculated singlet−triplet energy difference with NIPE results, we have estimated the zero-point energy (ZPE) at the CASSCF level for both minima. Because the ZPE for the singlet and triplet are found to be 75.0 kcal mol^{-1} and 74.8 kcal mol^{-1}, respectively, the overall correction would decrease the energy differences by about 0.2 kcal mol^{-1}. The DDCI vertical $^1A \rightarrow {}^3B_1$ transition is 3.7 kcal mol^{-1} (see Figure 2), around 3.5 kcal mol^{-1} after the ZPE correction, which is in better agreement with the experimental NIPE value of Clifford and Jordan,[11] 3.0 ± 0.3 kcal mol^{-1}, than the last theoretical results by Filatov and Shaik,[17] of 1.4 kcal mol^{-1}. Taking into account the ZPE correction, our adiabatic energy difference is 1.2 kcal mol^{-1}.

The smallest singlet−triplet energy gap appears at the geometry of the triplet minimum and its magnitude, of 0.29 kcal mol^{-1}, is small enough to consider both states almost degenerate at this conformation. On the other hand, the spin−orbit coupling calculated by Michl[16] at this geometry was found to be negligible. It means that, even if both surfaces are very near to each other, there would not be an avoided crossing, and the decay from the triplet to the singlet state will be improbable. In such circumstances, if the mechanism of the reaction that produces the TME diradical leads to triplet products, then this species will be a metastable one, with a noticeable lifetime. Consequently, both triplet and singlet states would be populated with an interconversion process too slow to be detected, and the triplet species could be experimentally observed. As Matsuda and Iwamura have already pointed out,[12] this would be a possible explanation for the contradictory experimental results. Filatov and Shaik[17] also arrive at similar conclusions, but from DFT (REKS) results that differ from ours in several points. The differences arise from the shape of the PEC of the singlet state that, as we and these authors have already mentioned, must be obtained including dynamic correlation in the calculations. The lack or partial inclusion of this correlation leads to curves significantly different, as shown in ref 17 and in this paper. The DFT-REKS curve of the singlet state obtained by Filatov and Shaik shows a transition state at $\theta \approx 40°$, that the authors consider "not to have real chemical significance". If this maximum is an artifact of the calculation method, no comparison of the relative energies is possible in this region. However, the qualitative conclusions are coincident because we all consider nearly degenerate states and very small spin−orbit coupling in this region and agree with the experimental hypothesis of a triplet metastable minimum.

On the other hand, the large difference between the equilibrium geometries of both singlet and triplet states can be the key feature to explain the multiplicity of the ground state of compounds where TME is incorporated. If the conformation of the TME moiety is frozen at a fixed dihedral angle by the rest of the molecule, one state can be strongly favored in front of the other. This means that the torsional coordinate would determine the spin multiplicity of the ground state. The same type of hypothesis was also proposed by Clifford and Jordan.[11]

4. Conclusions

The results presented in this paper offer a satisfactory explanation of the experimental facts concerning the TME diradical. It has been found that the equilibrium geometry obtained for the singlet state at the CASSCF(6,6) level is in contradiction with the results obtained with a higher level of calculation. By adding dynamic correlation at the CASPT2 level, as well as by means of a CAS(2,2)*SDCI calculations, the singlet state potential energy curve indicates that the singlet equilibrium geometry corresponds to a D_{2d} geometry, with a dihedral angle of 90°, whereas for the triplet state, the DDCI curve shows that the equilibrium geometry belongs to D_2 symmetry, with a dihedral angle of around 47°. The singlet state is more stable than the triplet one for any conformation, but the energy difference decreases up to 0.29 kcal mol^{-1} for the structure of the triplet minimum. At this geometry, the singlet and triplet states can be considered degenerate. Despite this quasi-degeneracy, given that the spin−orbit coupling of these states results to be negligible, the decay from the triplet to the singlet must be slow and the triplet state can be populated and consequently experimentally observed. In any case, the S−T energy difference is tuned by the torsional coordinate, to the extent that the ground state can be modified when the TME is incorporated in a larger structure that constrains rotationally the diradical.

Acknowledgment. This work has been supported by DGICYT of the Ministerio de Educación y Ciencia of Spain (Project No. PB98-1216-CO2-02) and by CIRIT of the Generalitat de Catalunya (Grant No. SGR99-182). The authors are indebted to the members of the QUCEX TMR network for fruitful discussions.

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