

METHODOLOGICAL TRAPS ENCOUNTERED IN THEORETICAL TREATMENTS OF THE PHOTOISOMERIZATION OF TRIPLET BUTADIENE

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(Received November 13, 1984; in revised form January 23, 1985)

Summary

The relative triplet energies of various conformations of butadiene were computed with reference to the ground state using a variety of conventional unrestricted Hartree-Fock (UHF) and restricted Hartree-Fock (RHF) methodologies correlationally corrected at the Møller-Plesset second- and third-order levels. It is shown that the geometries and relative energies of the various triplet species cannot be adequately estimated at either the UHF or the RHF level alone. In particular, at the RHF open-shell level, the geometry of the singly-twisted allyl-methylene diradical triplet shows the same properties as those encountered in the classic RHF instability of the allyl radical. However, the relative energies computed at the UHF level alone are poor, possibly reflecting the differing levels of spin contamination obtained for different geometries. Therefore, in contrast to the case of the ethylene triplet, where the relative energies of the triplet conformations are not correlation sensitive, the relative energies of the various conformations of the butadiene triplet require a correlation-energy correction.

1. Introduction

The triplet-sensitized photochemistry of dienes has long been of interest to both experimental and theoretical chemists [1 - 7]. In this work our attention is directed towards what we shall show is a methodological problem in the treatment of the triplet-sensitized photochemistry of 2,4-hexadienes (Fig. 1). Saltiel and coworkers and Hindman *et al.* [2, 8 - 11] have shown that the *cis-trans* isomerization of the *trans-trans-* (TT), *trans-cis-* (TC) and *cis-cis-* (CC) 2,4-hexadienes occurs through the commonly accessible twisted triplet states ${}^3T-90^\circ$ and ${}^3C-90^\circ$. The temperature dependence of the isomerization yields can be most easily interpreted by assuming that

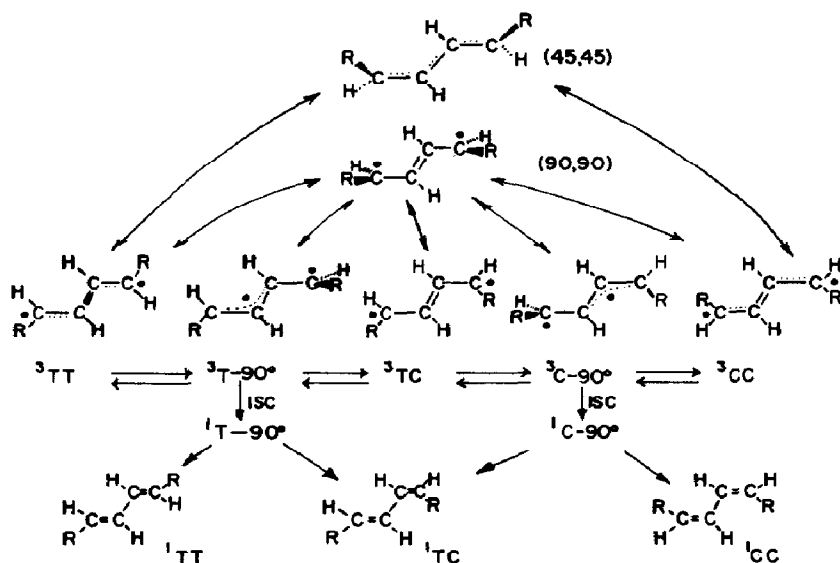


Fig. 1. The various possible intermediates in the triplet-sensitized photoisomerization of 2,4-hexatriene. Intersystem crossing (ISC) is assumed to occur mostly from a singly-twisted intermediate (either ${}^3T-90^\circ$ or ${}^3C-90^\circ$). See ref. 2 for a complete discussion of the mechanism.

these two twisted species have an energy difference of only $0.3 \text{ kcal mol}^{-1}$ with an activation energy of $3.5 \text{ kcal mol}^{-1}$ [10, 11]. In this model it is not necessary to assume that the various planar triplets 3TT , 3TC and 3CC are other than communicating transition states between ${}^3T-90^\circ$ and ${}^3C-90^\circ$. Therefore, the relative energies of these planar triplet structures in relationship to the singly- 90° -twisted conformations can be assumed to be of the order of $3.5 \text{ kcal mol}^{-1}$. There is also the possibility of a concerted double-isomerization mechanism in which the transition states could have either a double- 90° structure (Fig. 2, $\theta_1, \theta_2 = 90^\circ$) or approximately $45^\circ, 45^\circ$ (or $-45^\circ, 45^\circ$, depending on the direction of rotation). However, the hypothesis that only singly-twisted and planar triplet conformations play a role in the photoisomerization is sufficient to explain the experimental results. In any case, the experimental aspects of this problem seem clear and no revision in their interpretation is necessary.

As we show below, the theoretical aspects of the triplet-photoisomerization mechanism in 2,4-hexadienes are not well understood. A number of *ab initio* theoretical studies [4 - 7] have now been performed on the butadiene triplet which has been used as a model for acyclic dienes. The first *ab initio* study was performed by Bonacic-Koutecky and Ishimaru using a 2×2 configuration interaction (CI) on wavefunctions obtained from an open-shell self-consistent field (SCF) Nesbet hamiltonian [4]. However, the Nesbet hamiltonian is not restricted Hartree-Fock (RHF) in character within the criteria imposed by the generalized Brillouin theorem [12]. In particular, CI matrix elements will exist between the parent Nesbet SCF

wavefunction and other single replacement configurations. This will not occur in the case of a true RHF-SCF parent having the same open-shell electronic configuration using a proper open-shell RHF operator [12]. Therefore, the first-order single configuration energy computed for the Nesbet parent will have some unknown energy above the true open-shell RHF. The Nesbet energy difference between the planar ($0^\circ, 0^\circ$) and singly-twisted ($0^\circ, 90^\circ$) triplets is $2.8 \text{ kcal mol}^{-1}$ using optimized C—C bond distances [4]. Since this energy difference is close to the $3.5 \text{ kcal mol}^{-1}$ activation energy found in hexadiene isomerization, it might be concluded that the theoretical aspects of this problem have been resolved. However, one serious problem still remains in these calculations which indicates a methodological fault which may be serious. The optimized geometry of the twisted ($0^\circ, 90^\circ$) structure showed a large asymmetry in the C—C distances in the allyl portion of the triplet allyl-methylene diradical [4] (C_3 — C_5 , 1.332 \AA ; C_3 — C_2 , 1.447 \AA). This large asymmetry in the allyl-radical portion of the singly-twisted butadiene triplet is similar to that found for the allyl radical itself computed at the RHF level [13, 14]. This asymmetry does not occur in the allyl radical computed at the unrestricted Hartree-Fock (UHF) and multiconfiguration self-consistent field (MCSCF) levels and is related to the much-discussed [13] Hartree-Fock (HF) instability of RHF treatments of three electron-three orbital systems. Therefore, there is the distinct risk that the singly-twisted butadiene triplet cannot be adequately treated at the first-order level using any restricted open shell (Nesbet or RHF) methodology. Ironically, this critique might not apply to the planar RHF triplet. Therefore, there is the possibility that the computed SCF-level energy difference found between the planar and the $0^\circ, 90^\circ$ -twisted butadiene triplets is too small because the latter more stable structure would be computed to be even more stable at the correctly optimized geometry.

Another set of *ab initio* calculations at the same 4-31G basis-set level were performed by Ohmine and Morokuma [5, 6] using a UHF methodology. First of all, as is discussed below, the UHF methodology yields wavefunctions having values of S^2 that are sometimes very far (2.2) from the pure triplet value of 2. In the case of the planar butadiene triplet, we have found two minima, one having a symmetric C_{2h} structure (conceptually a $\cdot\text{CH}_2$ — $\text{CH}=\text{CH}$ — $\text{CH}_2\cdot$ triplet diradical), and the other a slightly more stable C_s structure having an allyl-methylene planar diradical character (the C—C bond lengths are 1.510 , 1.361 and 1.408 \AA). The optimized $0, 90^\circ$ -singly-twisted UHF triplet had what can be termed a pure allyl-methylene diradical character (the C—C bond lengths are 1.398 and 1.387 \AA in the allyl portion). However, the UHF energy of this latter twisted species was approximately 10 kcal mol^{-1} below that of the planar triplets. Within the context of condensed-phase photochemistry where vibrational relaxation can be assumed to be complete within the known lifetime of triplet 2,4-hexadiene (32 ns) [15], this energy difference is too great to permit more than a single isomerization about one of the double bonds. Another disturbing element in these UHF-level calculations is that the C_s asymmetric planar configuration

and the 0° , 90° -twisted configuration are heavily spin contaminated, while the planar C_{2h} triplet is not. Therefore both the RHF- and UHF-level computations seem to be methodologically flawed.

Malrieu and coworkers [7] have very recently perfected an effective valence-bond Heisenberg hamiltonian which permits the use of high level *ab initio* CI computations to parameterize the geometry-optimized energies of non-ionic excited states. Their results gave symmetric C_{2h} geometries for the planar butadiene triplet and symmetric C—C distances in the allyl portion of the 0° , 90° -twisted configuration. In addition, they found an energy difference of $4.2 \text{ kcal mol}^{-1}$ between the planar and more stable 0° , 90° -configuration. Since we can find no basis on which to criticize this new work, we feel that these results can be used as a standard with which conventional methodologies should be compared. Our principal goal in this work is to reinvestigate the problem posed above within the context of the methodologies that are available to experimental chemists who wish to exploit these as a "black box". However, at the same time we wish to warn non-theoreticians of the methodological traps which may be encountered in using these techniques blindly. We have analysed the cost of performing these calculations at the lowest level necessary to obtain adequate results.

2. Technical details

Three computer programs were used in the work presented here. The preliminary work was done using the "Gaussian-70, Nesbet + CI" program discussed by Bonacic-Koutecky and Ishimaru [4]. The June, 1981 version of Monstergauss [16] was used to perform standard gaussian-type closed- and open-shell RHF- as well as UHF-geometry-optimized computations. However, the single- and double-CI packages were limited to 40 gaussian-type orbitals (GTOs) and were not directly applicable to the orbital size of 48 in the 3-21G level computations on butadiene. The Pople group Gaussian 80 is available through the Quantum Chemistry Package Exchange, University of Indiana, Bloomington, IN. Both programs have comparable central processing unit (CPU) times for standard calculations. However, Gaussian 80 is about ten times more input/output (IO) active (disc communication) than Monstergauss and about three times more expensive to exploit at our particular computing centre. Therefore, geometry optimizations [17] were performed using Monstergauss while the Møller-Plesset (MP) calculations were performed using Gaussian 80. The Møller-Plesset calculations were performed on the closed-shell butadiene ground state (MP2, MP3 (MP, many-body perturbation; 2, second order; 3, third order)) but only for the UHF solution of the triplet states (UMP2, UMP3 (U, unrestricted)). There is no open-shell RHF Møller-Plesset option in Gaussian 80. However, some UHF UMP2, UMP3 computations were performed on the RHF triplet-optimized geometries.

The split 3-21G is the basis generally employed in this work [18]. In fact, we did perform calculations on the UHF-energy differences between the C_{2h} planar and C_s 0° , 90° -twisted configurations at the 4-31G and 6-31G levels and found these to be the same as that at the 3-21G level. We did not consider going to the 6-31G* or higher levels because these bases are expensive at the MP3 levels. In addition, a recent SCF study on the configurations of ground-state butadiene [19] did not indicate that any improvement would be obtained at these higher levels of basis set in this study. As we show below for ethylene and also in a paper [20] based on a study of the bond-rupture surfaces in triplet propene, 3-21G calculations give acceptable results. However, we warn the non-theoretician that this basis set is minimal for this kind of problem.

3. Results and discussion

3.1. Cost analysis

The calculations presented here were performed using an NAS 9080. Although the machine is quoted as having a speed of 8 million instructions per second (MIPS), comparable standard calculations using Gaussian 80 actually showed it to be 16 times faster than a VAX 11/780 (1 MIPS). Maximum CPU times on the NAS 9080 were: (i) RHF or UHF, 2 min; (ii) geometry optimization in 18 degrees of freedom, UHF butadiene triplet, 15 min; (iii) UHF (single point) plus UMP2, 6 min, and UMP3, 25 min. These are for the most time-consuming cases. The total time expenditure on this project was about 6 h of CPU time. This time expenditure was equivalent to about 75% of the yearly total available to a CNRS scientist. According to the above examples, a project of similar scope would cost about 80 h on a VAX 11/780 and about 40 h on an SEL-32-97. These are considered pessimistic estimations and include the errors in input and rejected and exploratory calculations.

3.2. Comparative calculations on the ground-state ethylene and triplet ethylene energy differences

In order to obtain some idea of the reliability of the basis set and methodological level of treatment we have reinvestigated the ethylene system. Computations which employ very high-level large basis sets and are optimized and correlationally corrected have been carried out on the energy difference between planar ground-state ethylene and the twisted triplet [7, 21]. Table 1 shows the 3-21G level RHF/UHF calculations on ethylene followed by MP2, 3-UMP2, 3 corrections. The most important feature in Table 1 is that the difference in energy between S_0 and $T_a(90^\circ)$ is 65 kcal mol⁻¹, this being comparable with the best literature values, *i.e.* 62 - 67 kcal mol⁻¹ [7, 21]. This can be considered as partially fortuitous since no subsequent CI optimizations were performed on S_0 and $T_a(90^\circ)$. Within the triplet manifold itself, the relaxation energies in going from the vertical triplet to

TABLE 1
Ground- and triplet-energy calculations on ethylene^a

Structure computed	RHF or UHF	Energy (au)	
		MP2 or UMP3	MP3 or UMP3
S ₀ , ground state ethylene: CC = 1.315 Å; CH = 1.073 Å; CĈH = 121.9°	-77.60100	-77.78013	-77.79702
T _v , vertical triplet (same geometry as S ₀)	-77.46570 (2.02) ^b	-77.60112 (2.01)	-77.62138 (NC)
T _p , planar relaxed triplet: CC = 1.55 Å; CH = 1.071 Å; CĈH = 120.0°	-77.50733 (2.02)	-77.64602 (2.00)	-77.66670 (NC)
T _a , 90°-relaxed triplet: CC = 1.474 Å; CH = 1.074 Å; CĈH = 121.0°	-77.53160 (2.01)	-77.67322 (2.00)	-77.69338 (NC)
<i>Energy changes^c</i>			
S ₀ → T _v	84.9	112.3	110.2
S ₀ → T _p	58.7	84.1	81.8
S ₀ → T _a	43.5	67.1	65.0
T _v → T _p	-26.1	-28.2	-28.4
T _p → T _v	-15.3	-17.1	-16.7

^aThis is at the 3-21G level.

^bNumerals in parentheses are the values of S^2 ; NC, not calculated.

^cUnits, kcal mol⁻¹.

v, vertical; p, planar relaxed; a, adiabatic.

the planar relaxed triplet and finally to the 90°-twisted configuration are essentially correlation insensitive, being the same at the UHF and UMP3/UHF levels. These energy differences also match those found using higher basis sets [7, 21].

Methodologically, the most worrisome feature of the calculations presented in Table 1 are that they involve comparisons between ground-state ethylene, computed using an RHF-MP3 technique, and triplet ethylene, using a UHF-UMP3 method. However, since the S^2 values of all computed triplets in Table 1 were close to 2, the (principally) quintet contaminations were small. We shall return to this point later in discussing UMP3 calculations on highly-contaminated UHF functions in some of the structures of the butadiene triplet.

The overall correlation energy for ground-state ethylene is 0.197 au, which is similar to that normally found at this level of basis set (0.19) [22]. This is approximately 0.03 au per valence bond, since the carbon 1s-core molecular orbitals are frozen in these calculations.

3.3. Butadiene ground state

The geometry conventions used in these calculations are those of DeMaré and Neisus [19] (Fig. 2). Table 2 shows the RHF-MP2, MP3 level

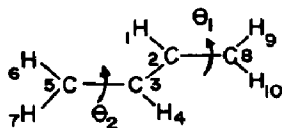


Fig. 2. Geometry convention used in the calculations where θ_2 and θ_1 represent rotation angles around the C—C terminal bonds. This geometry convention is taken from ref. 19.

TABLE 2

Ground- and triplet-state energies of butadiene computed using 3-21G SCF level ground-state optimized geometries

State (θ_1, θ_2)	Energies at various levels of computation (au)		
	RHF or UHF	MP2 or UMP2	MP3 or UMP3
$S_0(0^\circ, 0^\circ)$, ground state	-154.059456 ^a	-154.40966	-154.43716
$T_v(0^\circ, 0^\circ)$, vertical triplet	-154.94360 (2.02) ^b	-154.26831 (2.00)	-154.29678 (NC)

See Fig. 2 for definition of geometry.

^aCalculated using the geometry reported in ref. 19.

^bNumerals in parentheses are the values of S^2 ; NC, not computed.

computations on the 3-21G-optimized geometry [19] of ground-state butadiene. The MP3 correlation energy (0.38 au) is about that expected for 11 valence bonds having approximately 0.03 au per valence bond [22] at the double-zeta (DZ) level.

3.4. Butadiene triplet structures at the UHF and RHF single configuration level

Table 2 shows the UHF, UMP2 and UMP3 energies of the vertical triplet $T_v(90^\circ, 90^\circ)$ having the same geometry as the ground state. Table 3 shows the UHF and RHF level computations on the optimized planar restrained structures and those obtained by a single 90° twist around one of the terminal double bonds.

With respect to the planar restrained UHF and RHF calculations, two local planar minima are found, in agreement with the 4-31G UHF results of Ohmine and Morokuma [5, 6]. The structure having C_{2h} symmetry has a low spin contamination ($S^2 = 2.02$) while the other lower-energy structure has a high spin contamination ($S^2 = 2.16$). Open-shell RHF triplet optimization yielded only the C_{2h} structure, which has essentially the same geometry as the UHF structure.

Table 3 also shows the $T(0^\circ, 90^\circ)$ -optimized structures obtained from both methodologies. The C_s $T(0^\circ, 90^\circ)$ structure obtained by UHF optimization is heavily spin contaminated ($S^2 = 2.22$) and has nearly equal CC bond lengths in the allyl moiety of the allyl-radical part of the allyl-methylene structure. This is the same result as that obtained by Ohmine and Morokuma [5, 6]. The RHF C_s $T_a(0^\circ, 90^\circ)$ structure has a large asymmetry in the allyl-radical portion of the twisted triplet state; this is similar to the optimized

TABLE 3

Optimized structures of planar and singly-terminal-90°-twisted triplet butadiene using UHF and RHF methodologies and their respective correlatively corrected energies using a 3-21G basis

Geometry elements optimized	Planar			90° Terminal twist	
	<i>C</i> _{2h} UHF	<i>C</i> _{2h} RHF	<i>C</i> _s UHF	<i>C</i> _s UHF	<i>C</i> _s RHF
C ₂ —C ₈	1.471 ^a	1.469	1.520	1.481	1.472
C ₃ —C ₅	1.471	1.469	1.412	1.389	1.330
C ₂ —C ₃	1.327	1.327	1.358	1.389	1.438
C ₈ —H ₁₀	1.073	1.072	1.072	1.074	1.074
C ₅ —H ₆	1.073	1.072	1.074	1.074	1.074
C ₈ —H ₉	1.071	1.070	1.074	1.074	1.074
C ₅ —H ₇	1.071	1.070	1.072	1.074	1.074
C ₂ —H ₁	1.076	1.076	1.074	1.077	1.076
C ₂ —H ₄	1.076	1.076	1.077	1.076	1.076
C ₈ —C ₂ —C ₃	124.3 ^a	124.3	123.1	123.1	122.5
C ₂ —C ₃ —C ₅	124.3	124.3	124.7	124.3	124.3
C ₂ —C ₈ —H ₉	120.8	120.8	120.4	120.8	121.0
C ₃ —C ₅ —H ₇	120.8	120.8	121.1	121.4	121.8
C ₂ —C ₈ —H ₁₀	120.5	120.0	120.0	120.8	121.0
C ₃ —C ₅ —H ₆	120.5	120.0	121.0	121.2	121.7
C ₃ —C ₂ —H ₁	119.3	119.3	120.0	118.9	118.4
C ₂ —C ₃ —H ₄	119.3	119.3	118.2	117.6	116.3
<i>E</i> (SCF)	−153.99464 (2.02) ^b	−153.98852 (2.00)	−153.99689 (2.16)	−154.01217 (2.22)	−153.98934 ^a (2.00)
<i>E</i> (UMP2)	−154.30930 (2.01)	NC —	−154.29945 (2.10)	−154.31182 (2.15)	−154.30825 ^c (2.13)
<i>E</i> (UMP3)	−154.34021	NC	−154.331901	−154.34443	−154.34067 ^c

^aUnits, ångströms for bond lengths and degrees for bond angles.

^bNumerals in parentheses are the values of *S*².

^cFrom an UHF/UMP2, 3 computation at RHF geometry.

Nesbet triplet structure reported by Bonacic-Koutecky and Ishimaru [4]. If the RHF-optimized structure is computed using UHF methodology, the resulting energy is only 2.6 kcal mol^{−1} higher, but the *S*² value is too high (2.20).

Three other triplet-butadiene conformations were computed and the results are shown in Table 4. The T(90°, 90°) structure where both terminal C—C bonds are twisted by 90° has an energy (Table 5) about 18 kcal mol^{−1} above the global minimum for T_a(0°, 90°). Likewise, both the double-45°-twisted species appear to be well above the global minimum. However, the results change when reference is made to either the planar UHF minimum or the vertical triplet T_v(0°, 0°).

TABLE 4

Partially optimized doubly-twisted structures of the butadiene triplet

Geometry elements optimized ^a	θ_1, θ_2 ^b		
	C_{2h} $90^\circ, 90^\circ$	C_2 $45^\circ, 45^\circ$	C_1 $-45^\circ, 45^\circ$
C_2-C_8	1.483 ^c	1.473	1.471
C_2-C_3	1.319	1.323	1.327
C_8-H_9	1.074	1.073	1.073
C_2-H_1	1.079	1.078	1.077
$C_8-C_2-C_3$	124.0 ^c	124.2	124.3
$C_2-C_8-H_9$	120.8	121.1	121.1
$C_2-C_8-H_{10}$	120.8	120.4	120.4
$C_3-C_2-H_1$	119.1	119.1	119.1
UHF-level SCF energy	-153.98316 (2.02)	-153.99013 (2.02)	-153.99058 (2.02)
UMP2 energy	-154.29711	-154.30512	NC ^d

^aEquivalent elements are not shown.^bSee Fig. 2. Restrained symmetry elements are θ_1, θ_2 and the overall symmetry of the species treated.^cUnits, ångströms for bond lengths and degrees for bond angles.^dNC, not computed.

With respect to the critical issue of the energy difference between the planar and singly-twisted butadiene triplet, the UHF-energy differences shown in Table 5 are 11 kcal mol⁻¹ and 9.6 kcal mol⁻¹ depending on whether one chooses the planar triplet having C_{2h} or C_s symmetry. These numbers are the same as those obtained at the 4-31G level by Ohmine and Morokuma [5, 6]. The RHF-level energy difference is 0.5 kcal mol⁻¹. As we have argued above no confidence can be placed in either sets of numbers.

3.5. Butadiene triplet energies at the MP2 and MP3 levels

As indicated above we were stimulated to investigate this particular problem by our suspicion that the Nesbet-optimized 2×2 CI structure of $T_a(0^\circ, 90^\circ)$ obtained by Bonacic-Koutecky and Ishimaru was wrong [4]. In fact, in a preliminary study using the same method but performing an after 20×20 CI optimization of the C—C bonds in this structure we found nearly symmetric CC distances (1.380 and 1.379 Å) in the allyl moiety. This indicated that the asymmetric solution found by these authors was a methodological artifact. As shown in Table 5, at the UMP3 level the lowest triplet structure $T_a(0^\circ, 90^\circ)$ is still that obtained at the UHF level. However, for the planar structure, the C_{2h} structure is now 5.2 times more stable than the C_s planar structure whereas it was 1.4 kcal mol⁻¹ less stable at the UHF level only. This probably indicates that the C_s planar structure is also a methodological artifact. Most importantly, whereas the energy difference between

the C_{2h} planar and C_s structures is $11.0 \text{ kcal mol}^{-1}$ at the UHF level, this is reduced to $2.6 \text{ kcal mol}^{-1}$ at the UMP3 level. Normally, this amount of correlation-energy gain in what is essentially a monoconfigurational correlation-insensitive transformation is inordinately large. Before entering into this problem we had not anticipated that the relative effects in the triplet manifold would be more than several kilocalories per mole, similar to that found in the triplet-ethylene transformations. At this point we attribute the correlation effect to the different spin contaminations in the UHF functions having C_{2h} planar and C_s non-planar conformations.

With regard to some of the other structures computed in Table 4, Table 5 shows that at the UMP2 level the $T(45^\circ, 45^\circ)$ -structure is, as at the UHF level, only several kilocalories per mole above the planar C_{2h} structure. Since these structures have about an equal and low spin contamination, this energy difference will probably be maintained at the UMP3 levels, even at higher levels of basis set. However if this is not the case, a concerted double-isomerization contribution could play a role together with the sequential mechanism involving passing through a planar transition state from ${}^3T-90^\circ$ to ${}^3C-90^\circ$ in the 2,4-hexadiene isomerization. Based on the energies shown in Table 5 we would exclude a double- 90° transition state from playing a role in isomerizations except in gas-phase-sensitized processes [6].

TABLE 5

Energies of the various triplet conformations of butadiene relative to the ground state at various methodological levels

State $(\theta_1, \theta_2)^a$, symmetry	Geometry optimization level ^b	Energies at various levels of computation (kcal mol ⁻¹)		
		RHF* or UHF	MP2* or UMP2	MP3* or UMP3
$S_0(0^\circ, 0^\circ)$, planar C_{2h}	CS-RHF	0*	0*	0* ^c
$T_v(0^\circ, 0^\circ)$, planar C_{2h}	UHF	72.7	88.7	88.0 ^c
$T_a(0^\circ, 0^\circ)$, planar C_{2h}	UHF	40.7	63.0	60.8 ^d
$T_a(0^\circ, 0^\circ)$, planar C_{2h}	OS-RHF	44.5*	NC	NC ^{d, e}
$T_a(0^\circ, 0^\circ)$, planar C_s	UHF	39.3	69.1	66.0 ^c
$T_a(0^\circ, 90^\circ)$, twisted C_s	UHF	29.7	61.4	58.2 ^c
$T_a(0^\circ, 90^\circ)$, twisted C_s	OS-RHF	44.0*	NC	NC
$T_a(0^\circ, 90^\circ)$, twisted C_s	UHF//RHF ^g	32.3	63.6	60.5
$T(90^\circ, 90^\circ)$, double-twisted C_{2h}	UHF	47.9	70.6	NC ^f
$T(45^\circ, 45^\circ)$, double-twisted C_2	UHF	43.5	65.6	NC ^f
$T(-45^\circ, 45^\circ)$, double-twisted C_i	UHF	42.6	NC	NC ^f

S_0 , ground state; T_v and T_a , vertical and adiabatic triplets respectively.

^aSee Fig. 2.

^bCS, closed shell; OS, open shell.

^cSee Table 2.

^dSee Table 3.

^eNC, not computed.

^fSee Table 4.

^gUHF//RHF, UHF computation done at the RHF-optimized geometry.

3.6. Some observations on the absolute energies of butadiene triplets

From our computation on the ground state of butadiene we conclude that the energies shown in Table 5 have some relationship to the experimental energies. The $T_a(0^\circ, 0^\circ)$ energy corresponds to the 0-0 transition energies in dienes. The value computed here of $60.8 \text{ kcal mol}^{-1}$ lies slightly above the values found experimentally of $59 - 60 \text{ kcal mol}^{-1}$ [23]. However, the experimental spectra show a long tailing region and there is no guarantee that the last reported peak in this absorption is the 0-0 band. The most recent study [24] of the thermal isomerization of *trans-trans*-2,4-hexadiene to the *cis-trans*- compound gives an activation energy of $53 \pm 2 \text{ kcal mol}^{-1}$, which is within the region of that of the sensitized photoisomerization. Assuming that the energy of the singlet and triplet allyl-methylene twisted diradical triplet states are the same, the experimental energy of $T_a(0^\circ, 90^\circ)$ is 53 kcal mol^{-1} . This value is about 5 kcal mol^{-1} below our estimate. However, Malrieu and coworkers [7] recently found this energy to be 52 kcal mol^{-1} . A recent multireference CI study on the butadiene triplet and singlet manifold [25] at the DZ level yielded a $T(0^\circ, 90^\circ)$ value of about 60 kcal mol^{-1} . It should be noted that this is not a "black box" method. We suspect that at this point in the development of this kind of calculation, further energy gains using conventional methodologies can only be made at a greatly increased cost in going to larger basis sets and performing the correlation correction at the UMP4 level. If this is so, the results of Malrieu and coworkers provide an opportunity to examine a number of related systems with reasonable precision and cost. The level of treatment we have presented here can be extended to slightly larger systems.

4. Concluding remarks

We have shown that for the butadiene triplet both the single-configuration RHF and the UHF methodologies in certain cases yield results that are artifacts. Correlation-energy corrections are necessary to give final results that are relatively correct at the level of basis set used. However, these correlation-energy corrections are applied to geometry-optimized structures which at times also have an artifactual character. The next level of treatment would be to optimize at the UHF-MP2 level which is technically possible but financially prohibitive, or at the MCSCF level. The latter methodology [14] is coming into more general use but cannot yet be used blindly as a black box since there remains the question of the optimum-choice configurations within which geometry optimizations can be effected at a reasonable cost. The MCSCF approach avoids the problem of spin contamination of UHF functions. As can be seen in the appropriate tables, the UMP2 treatments did not significantly reduce the contamination levels. Although these are not computed at the UMP3 levels, there is no theoretical reason to believe that they would be significantly improved. Therefore, one is still dealing with final UMP3 functions which have varying

and unknown degrees of (principally) quintet contamination. The most optimistic expectation is that UHF-optimized structures will be close to any obtained at the MCSCF level which span a reasonably large configurational space and that the UMP3 energies are within several kilocalories per mole of what one could obtain at the UMP4 level. With respect to using RHF- or Nesbet open-shell-optimized structures, it seems to us that intrinsic HF instabilities will be encountered in the situations in which the structures can be described as having allyl-like moieties. Results obtained using these methods should automatically be considered as suspect.

Acknowledgment

This study was initiated during a workshop on the "sudden polarization effect" held at the European Centre for Atomic and Molecular Calculations (Orsay, France) in July, 1979. We thank both Professor L. Salem and the Director Carl Moser for their sponsorship of this workshop. We also thank Professor J. Koutecky and Professor V. Bonacic-Kouteck for their comments during the workshop on the relative merits of the Nesbet and UHF operators.

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