The Triplet Potential Energy Surface of *s-trans*-2,4-Hexadiene. A Comparison of Theory and Experiment

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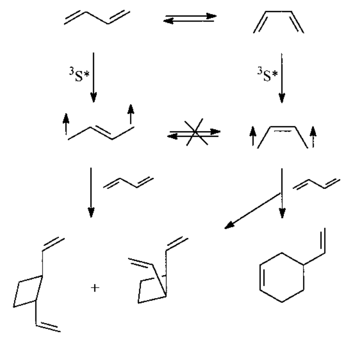
The mechanism of *s-trans*-2,4-hexadiene triplet interconversion has been explored using the B3LYP method with 6-31+G(d,p) and cc-pVTZ basis sets. Nine stationary points are located on the T_1 surface and five on the S_0 surface of *s-trans*-2,4-hexadiene. The results are consistent with experimental observations that indicate that the triplet-state photoisomerization of the 2,4-hexadiene involves the interconversion of allylmethylene triplet intermediates. Furthermore, this equilibration is predicted to proceed via readily accessible planar triplet intermediates which are nearly isoenergetic. The accessibility of planar triplet intermediates is consistent with triplet excitation transfer steps between the diene isomers that are responsible for the observed quantum chain process in the photoisomerization of the 2,4-hexadienes.

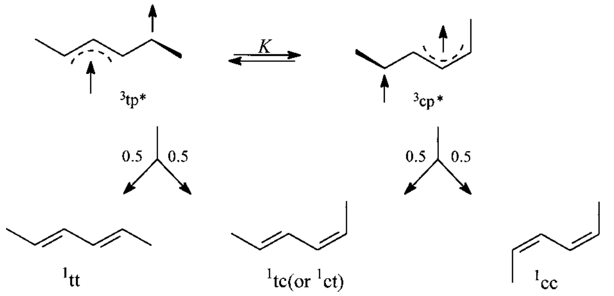
Introduction

1,3-Butadiene is the prototypical example of a molecule with conjugated double bonds which, by virtue of facile rotation about the essential single bond, exists in the ground state as an equilibrium mixture of s-cis and s-trans conformers.[1] An early success of Hückel molecular orbital theory was the prediction that reversal of single/double bond character upon electronic excitation would convert the freely interconverting ground-state conformers into noninterconverting excited isomers. The different photochemical reactivity of such conformers was recognized by Havinga, who attributed the excitation wavelength dependence of photoproduct distributions of trienes in the vitamin D field to preferential excitation of ground-state conformers to nonequilibrating excited rotamers (the NEER principle).[2,3] Hammond and co-workers provided an unambiguous demonstration of the validity of the NEER principle by showing that it accounted for the dependence of 1,3-diene photodimer distributions obtained by triplet sensitization on the triplet energy of the sensitizer[4] (Scheme 1).

SCHEME 1



SCHEME 2



The equilibrium geometries of 1,3-diene triplets were probed in studies of the triplet-sensitized photoisomerization of the 2,4-hexadienes (2,4-HDs).[5] Hammond and co-workers reasoned that a 1,4-biradical geometry with both ends twisted would require both bonds to isomerize, whereas, an allylmethylene geometry, with only one end twisted might lead to the isomerization of only one of the bonds.[6] The formation of common triplet intermediates from the trans,trans (tt), cis,trans (ct), and cis,cis (cc) isomers of hexadiene, leading to two-bond isomerization, was established by Saltiel and co-workers,[7] who also demonstrated that 1,3-diene photoisomerization adheres to the NEER principle as the energy of the triplet energy donor is varied.[8] The fact that the diene triplets maintain geometric integrity about the 2,3 bond, but undergo facile rotation about the 1,2 and 3,4 bonds, could be explained if the common triplet adopted the 1,4-biradical geometry, or if twisting at one end gave trans,-twisted (tp) and cis,twisted (cp) allylmethylene triplets in rapid equilibrium. A study of the benzophenone-sensitized photoisomerization of the 2,4-hexadienes (selective for s-trans geometries) over a wide temperature range in hydrocarbon media established equilibrating allylmethylene triplets as the correct interpretation (Scheme 2).[9] An excellent fit of the observations down to 159 K was obtained with $\Delta H = 0.333$ kcal/mol for the ^{3}tp* to ^{3}pc* equilibrium. Allylmethylene triplet equilibration was inhibited only at lower temperatures and more so in hydrocarbons that form harder glasses. An upper limit of 3.45 kcal/mol was obtained for the Arrhenius activation energy in the ^{3}tp* to ^{3}pc* direction. Saltiel's demonstration that 1,3-

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diene triplets transfer triplet excitation to ground-state 1,3-diene molecules, thus participating as the chain carriers in a quantum chain photoisomerization process, implied that planar triplet geometries are sufficiently close in energy to be readily accessible from the relaxed triplets.[10] The energy difference between allylmethylene and planar 2,4-hexadiene triplets, ~3.3 kcal/mol (an estimated value based on the inefficiency of the diene/diene triplet excitation transfer process),[10] rendered planar triplets viable intermediates in ^{3}tp*/^{3}pc* equilibration.[5]

This rich experimental detail has provided the landscape for the evaluation of theoretical predictions concerning the structure and energy of 1,3-diene triplets. The allylmethylene geometry for relaxed 1,3-diene triplets was predicted by early low-level molecular orbital calculations.[11] However, the reliability of the prediction and especially the pathway for allylmethylene triplet interconversion remained in question. A recent important contribution provided a critical comparison of the application of different theoretical approaches to the calculation of the triplet-state potential energy surfaces of 1,3-butadiene and 1,3,5-hexatriene. It was shown that energies obtained by use of density functional theory (DFT) methods are in good agreement with energies predicted by CASSCF, CASPT2, and spin-projected UMP4(SDTQ) calculations and with experiment.[12] The encouraging conclusion was that the less CPU-costly DFT-based methods can be used effectively to address some of the remaining mechanistic questions concerning the dynamics of 1,3-diene triplets.

We use the DFT approach in this article to explore the triplet energy surface of the *s-trans*-2,4-hexadienes. We specifically address the questions: In allylmethylene vs 1,4-biradicaloid, what is the relative energy and the structure of a 1,4-biradicaloid-type triplet? What is the pathway for ^{3}tp*/^{3}pc* equilibration? Is there simultaneous rotation at both ends of the diene moiety, or are planar triplets involved as intermediates or transition states (TS) in the process?

Computational Details

Calculations were performed with the Gaussian98 program package.[13] The Becke three-parameter hybrid functional,[14a,15a] in combination with the Lee−Yang−Parr correlation functional,[14b] denoted B3LYP,[15b] was used in these DFT calculations. Geometry optimizations[16] were performed with the 6-31+G(d,p) and the cc-pVTZ basis sets.[13,17] Stationary points on S_0 and T_1 potential energy surfaces were characterized further with calculations of vibrational frequencies for both the B3LYP/6-31+G(d,p) and the B3LYP/cc-pVTZ levels. No scaling factors were used for zero-point energy (ZPE) corrections or for any other calculated thermochemical values. Global energy minima on the triplet surface were refined with the use of Gaussian-2 (G2) theory.[18] Calculated bond lengths and bond angles are given in Angstroms and degrees, respectively. The reader should consult Scheme 2 for the symbols used to designate 1,3-diene geometries. The corresponding symbol for the 1,4-biradicaloid triplet (both ends twisted 90°) is ^{3}pp*.

Results and Discussion

Energetics. Calculated energies for stationary points of 2,4-HD in S_0 and T_1 are given in Table 1 relative to the ^{1}tt global energy minimum in S_0. All levels of theory used in this work predict that the global energy minimum in T_1 is close to the postulated ideal *trans*-allyl twisted methylene geometry, ^{3}tp (Table 2). Also in accord with experimental data[9] is a predicted geometry close to that expected for ^{3}cp for the next higher energy minimum. However, the predicted 1.0 kcal/mol ^{3}tp-to-^{3}cp energy gap is somewhat larger than the experimental value of 0.33 kcal/mol.[5] Much better agreement between prediction and experiment is obtained at the more advanced G2 level of theory, which gives 0.50 kcal/mol for the energy difference between the isomeric allylmethylene triplets (Table S2 in Supplementary Information). Not unexpectedly, because G2 calculations have been calibrated only for S_0, the G2 value for the ^{1}tt-^{3}tp energy gap, 59.2 kcal/mol, is 4−5 kcal/mol higher than the calculated values in Table 1.

TABLE 1: Relative Energies of Triplet (T_1) and Singlet (S_0) Stationary Points for 2,4-Hexadiene Based on B3LYP/cc-pVTZ and B3LYP/6-31+G(d,p) Calculations[a]

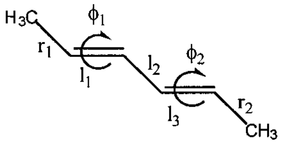
	cc-pVTZ			6-31+G(d,p)		
	E_{rel}	$(E+ZPE)_{rel}$	G_{rel}	E_{rel}	$(E+ZPE)_{rel}$	G_{rel}
triplet state, T_1						
^{3}cc*	58.20	54.94	53.09	57.06	53.86	52.07
TS_1(cc-cp)	58.41	55.16	54.22	57.29	54.06	53.13
^{3}pc*	55.34	52.39	50.47	54.21	51.26	49.00
TS_2(tc-cp)	58.23	54.77	53.54	57.05	53.64	52.46
^{3}tc*	58.18	54.73	52.44	57.01	53.62	51.43
TS_3(tc-tp)	58.32	54.85	53.49	57.19	53.76	52.48
^{3}tp*	54.34	51.34	49.89	53.17	50.20	48.77
TS_4(tt-tp)	58.31	54.67	53.23	57.14	53.54	52.16
^{3}tt*	58.30	54.73	52.19	57.13	53.59	51.06
singlet state, S_0						
^{1}cc	2.88	3.19	2.79	2.85	3.15	2.74
^{1}cp-TS	54.86	51.33	50.39	53.71	50.21	49.21
^{1}ct	1.37	1.55	1.40	1.36	1.54	1.37
^{1}tp-TS	53.84	50.28	49.84	52.65	49.13	48.68
^{1}tt	0	0	0	0	0	0

[a] All energies are expressed in kcal/mol relative to the ^{1}tt global minimum in S_0. See Table S1 in Supporting Information for absolute values.

Shallow energy minima are located for the T_1 geometries (E_{rel}) of the relaxed planar triplets ^{3}tt, ^{3}tc, and ^{3}cc (58.2, 58.2, and 58.3 kcal/mol, respectively, at the B3LYP/cc-pVTZ level) which are in good agreement with 58.7 kcal/mol, the value obtained from the S_0-to-T_1 absorption spectrum of 2,4-hexadiene (isomer not specified) in chloroform in the presence of a high pressure of molecular oxygen.[19] Inclusion of ZPE vibrational corrections and entropy contributions to the electronic energy lowers the energy separation between the T_1 and S_0 surfaces. However, it also predicts a significant entropy difference between the isomeric allylmethylene triplets, in contradiction to strong experimental evidence indicating that difference to be zero.[9] ZPE and entropy values were calculated at 298.15 K by using the rigid rotor and harmonic oscillator approximations. The reliability of these values is questionable, and we prefer to rely on the "uncorrected" electronic energy values, which are in much better agreement with the experimental value for the $S_0 - T_1$ energy gap. This agreement is especially satisfactory when one considers that we have avoided the more time-demanding, detailed calculations that were performed at the highest levels of theory on planar and twisted 1,3-butadiene triplets.[12]

We have located nine stationary points on the T_1 surface, four of which are rotational transition states for the interconversion of ^{3}tp* and ^{3}cp* via the three planar triplet intermediates, ^{3}tt*, ^{3}tc*, and ^{3}cc*. Pertinent geometrical parameters are given in Table 2. No stationary point was found in the proximity of the two-"double" bond-twisted 1,4-biradicaloid structure (^{3}pp*). Geometry optimization for a triplet with fixed 90° dihedral angles around both "double" bonds resulted in a structure corresponding to a prohibitively high energy of 17.3 kcal/mol relative to the global ^{3}tp* minimum (B3LYP/6-31+G(d,p) (see Supplementary Information). This energy difference is in

TABLE 2: Geometric Parameters for T_1 and S_0 Energy Minima and Transition States (TSs)[a]



	ϕ_1[b] (deg)	ϕ_2[b] (deg)	r_1 (Å)	r_2 (Å)	l_1 (Å)	l_2 (Å)	l_3 (Å)
triplet state, T_1							
^{3}cc*	0	0	1.4839	1.4839	1.4521	1.3523	1.4521
	0	*0*	*1.4902*	*1.4902*	*1.4583*	*1.3637*	*1.4583*
TS$_1$(cc-cp)	24	−4	1.4840	1.4868	1.4641	1.3583	1.4312
	24	*−4*	*1.4904*	*1.4931*	*1.4705*	*1.3669*	*1.4381*
^{3}cp*[c]	0	−98	1.4919	1.4928	1.3842	1.3870	1.4622
	0	*−98*	*1.4979*	*1.4990*	*1.3927*	*1.3949*	*1.4691*
	(0)	(−100)	(1.4964)	(1.4952)	(1.3838)	(1.3748)	(1.4671)
TS$_2$(tc-cp)	153	3	1.4846	1.4855	1.4600	1.3556	1.4380
	153	*3*	*1.4909*	*1.4918*	*1.4665*	*1.3644*	*1.4442*
^{3}tc*	170	3	1.4843	1.4836	1.4526	1.3541	1.4489
	168	*3*	*1.4906*	*1.4901*	*1.4596*	*1.3628*	*1.4545*
TS$_3$(tc-tp)	−171	−18	1.4859	1.4829	1.4342	1.3562	1.4630
	−171	*−19*	*1.4923*	*1.4895*	*1.4404*	*1.3650*	*1.4694*
^{3}tp*[c]	180	97	1.4905	1.4931	1.3803	1.3875	1.4612
	180	*97*	*1.4965*	*1.4993*	*1.3884*	*1.3955*	*1.4677*
	(*180*)	(*99*)	(*1.4921*)	(*1.4954*)	(*1.3752*)	(*1.3811*)	(*1.4661*)
TS$_4$(tt-tp)	−170	161	1.4850	1.4842	1.4432	1.3534	1.4567
	−170	*160*	*1.4915*	*1.4907*	*1.4497*	*1.3621*	*1.4628*
^{3}tt*	−168	168	1.4845	1.4845	1.4504	1.3526	1.4504
	−180	*180*	*1.4906*	*1.4906*	*1.4582*	*1.3612*	*1.4582*
singlet state, S_0							
^{1}cc	0	0	1.4965	1.4965	1.3407	1.4519	1.3407
	0	*0*	*1.5021*	*1.5021*	*1.3450*	*1.4576*	*1.3450*
^{1}cp-TS	0	96	1.4921	1.4936	1.3830	1.3888	1.4612
	0	*96*	*1.4980*	*1.4999*	*1.3912*	*1.3970*	*1.4679*
^{1}tc	180	0	1.4944	1.4968	1.3374	1.4515	1.3396
	180	*0*	*1.5001*	*1.5024*	*1.3465*	*1.4574*	*1.3488*
^{1}tp-TS	180	96	1.4906	1.4939	1.3792	1.3894	1.4600
	180	*96*	*1.4966*	*1.5001*	*1.3873*	*1.3974*	*1.4666*
^{1}tt	−180	180	1.4948	1.4948	1.3367	1.4519	1.3367
	−180	180	*1.5003*	*1.5003*	*1.3458*	*1.4565*	*1.3458*
	(*−180*)	(*180*)	(*1.4955*)	(*1.4955*)	(*1.3451*)	(*1.4525*)	(*1.3451*)

[a] B3LYP/cc-pVTZ optimized values are given by plain numerals, values obtained with the 6-31+G(d,p) basis set are in *italics*, and values obtained at the MP2/6-31G (d) level of theory are in parentheses. [b] Dihedral angles $C_1C_2C_3C_4$ and $C_3C_4C_5C_6$ are given by ϕ_1 and ϕ_2, respectively. [c] Dihedral angles HC_2C_3H and HC_4C_5H are 0° and −85° for ^{3}cp*, 180° and 85° for ^{3}tp*.

satisfactory agreement with results from an electron spin resonance kinetics study of the syn/anti interconversion of the α-deuterioallyl radicals that gives 15.7 ± 1.0 kcal/mol as the allyl rotational barrier.[20] Loss of the stabilization energy of the allyl moiety, 13.5 ± 1.0 kcal/mol,[21] accounts for most of the calculated energy increase in the ^{3}tp* → ^{3}pp* conversion. Similar optimization with dihedral angles fixed at 45° at each end of the diene moiety resulted in a structure whose energy is 7.7 kcal/mol higher than the energy of ^{3}tp* on the T_1 surface (Table S1 in Supplementary Information), indicating that simultaneous rotation at both ends of the diene does not lead to a viable transition state for allylmethylene triplet equilibration. The optimum pathway for ^{3}tp* and ^{3}cp* interconversion is predicted to involve the three isomeric planar triplets (Figure 1), consistent with experimental observations on the triplet-sensitized cis−trans photoisomerization of the 2,4-HDs. At the B3LYP/cc-pVTZ level of theory, energy barriers for this interconversion do not exceed 4 kcal/mol (Table 3). Mulliken population analysis[22] indicates that conversions of planar triplets to allylmethylene triplets are accompanied by pronounced enhancements of spin and electron density in the methylene and allyl segments of the molecule (Table 4). Localization of the spins on the two methylene ends of the 1,4-biradicaloid structure occurs at the expense of the allyl radical stabilization energy, accounting for its predicted higher energy. The hypothetical ^{3}tp* and ^{3}cp* interconversion pathway that involves simultaneous rotation at the C_2C_3 and C_4C_5 bonds of 2,4-HD retains partial conjugation in the entire diene moiety throughout the process and, although it provides an energetically more advantageous process than a 1,4-biradicaloid transition state, is still too high in energy to compete with the planar triplet intermediates.

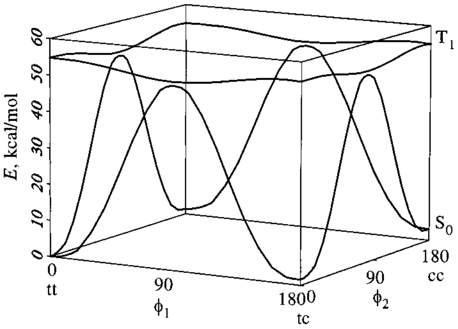


Figure 1. Calculated S_0 and T_1 potential energy curves for *s-trans*-2,4-hexadiene obtained at the B3LYP/cc-pVTZ level of theory.

According to the calculations, the isomeric 2,4-HD planar triplets lie only 3−4 kcal/mol above the allylmethylene triplets and are thus energetically accessible. This accounts for the functioning of 1,3-dienes as nonvertical donors of triplet excitation.[4,10,23] Clearly, the condition of substantially different

TABLE 3: Calculated Activation Parameters for Discrete Isomerization Steps on the T_1 Surface of 2,4HD[a]

	$\Delta E^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (e.u.)	$\Delta G(T)^\ddagger$ (kcal/mol)
^{3}cc*→TS$_1$(cc-cp)	0.21 (0.23)	−5.01 (−4.78)	1.13 (1.06)
^{3}cp*→TS$_1$(cc-cp)	3.07 (3.08)	−4.63 (−5.84)	3.75 (4.13)
^{3}cp*→TS$_2$(tc-cp)	2.89 (2.84)	−3.36 (−4.79)	3.07 (3.46)
^{3}tc*→TS$_2$(tc-cp)	0.04 (0.04)	−5.48 (−5.29)	1.10 (1.03)
^{3}tc*→TS$_3$(tc-tp)	0.14 (0.18)	−4.99 (−4.87)	1.05 (1.05)
^{3}tp*→TS$_3$(tc-tp)	3.98 (4.02)	−1.07 (−1.27)	3.61 (3.70)
^{3}tp*→TS$_4$(tt-tp)	3.97 (3.97)	−0.53 (−0.69)	3.34 (3.39)
^{3}tt*→TS$_4$(tt-tp)	0.01 (0.01)	−5.5 (−5.69)	1.04 (1.10)

[a] Entries are B3LYP/cc-pVTZ-optimized values, 298.15 K; values obtained with the 6-31+G(d,p) basis set are given in parentheses.

TABLE 4: Mulliken Charge and Spin Densities for ^{3}tt* and ^{3}tp*[a]

	^{3}tt*		^{3}tp*	
	charge	spin density	charge	spin density
C1	0.0145	−0.045	0.0316	−0.031
C2	−0.0186	0.835	−0.0544	0.940
C3	0.0041	0.164	0.0023	0.556
C4	0.0041	0.164	0.0165	−0.172
C5	−0.0186	0.835	−0.0088	0.582
C6	0.0145	−0.045	0.0127	−0.03

[a] Charges include attached hydrogen atoms; twisting in ^{3}tp* is at the C_2C_3 bond.

equilibrium geometries in S_0 and T_1 is fulfilled in 1,3-dienes. Just as nonvertical triplet excitation requires torsional excursions toward nonplanar ground-state geometries in conjugated acceptors, the process requires torsional excursions toward planar triplet-state geometries in conjugated donors. Whereas the nonvertical triplet-energy acceptor seeks to minimize its effective $S_0 - T_1$ energy gap to accommodate an energy-deficient donor, the nonvertical triplet-energy donor seeks to maximize its effective $S_0 - T_1$ energy gap to meet the energy demand of the acceptor.

Energy minima for 2,4-HD in S_0, located at the planar geometries, are predicted to increase in energy by about 1.4 kcal/mol for each *cis* double bond (Table 1). This increment agrees well with 1.3 ± 0.5 kcal/mol, the experimental enthalpy difference between *cis*- and *trans*-1,3-pentadiene.[24] Transition states for the interconversion of the ground-state isomers are at allylmethylene geometries that are nearly isoenergetic with the minima on the T_1 surface (Table 1). They are in excellent agreement with 53 ± 2 kcal/mol, the activation energy for the thermal isomerization of *cis*-1,3-pentadiene in the gas phase.[25]

Calculated Geometries. Use of the two basis sets, 6-31+G(d,p) and cc-pVTZ, leads to nearly identical geometries for analogous intermediates and transition states in S_0 and T_1 (see Figure 2 for geometries corresponding to the lowest energy minima). Bond lengths are predicted to be systematically longer by 0.006−0.011 Å with the use of the 6-31+G(d,p) basis set, corresponding to less than 1% deviation between the two sets of calculations (Table 2). Furthermore, the MP2/6-31G(d) bond length values for ^{1}tt, ^{3}tp*, and ^{3}cp* from the G2 calculations are bracketed by the two sets of B3LYP values. Expectations based on simple Hückel MO considerations are largely fulfilled. Planar triplets display the expected reversal of single/double bond character in the diene moiety, consistent with the adherence of 1,3-diene triplets to Havinga's NEER principle. The three 2,4-HD isomers are predicted to be strictly planar in S_0 based on ϕ_1 and ϕ_2 dihedral angles (Table 2). The same holds for the analogous relaxed triplet intermediates, with the exception of ^{3}tt* for which optimization with the cc-pVTZ basis set results in some distortion (12° for ϕ_1 and ϕ_2 dihedral angles) from planarity. If correct, this would be a departure from expectation because it seems unlikely that the planar structures of the isomeric triplets with cis orientations about former double bonds would occupy energy minima on the triplet energy surface, whereas the planar all-trans isomer would not. We emphasize here that, based on the energies of the TSs for relaxation to the allylmethylene triplets, the T_1 surface is very flat in the regions of planar triplets, rendering energy minima at planar geometries extremely shallow. Energy relaxations that can be attributed to bond-length reversal in T_1 were estimated by calculation of triplet electronic energies for geometries corresponding to the predicted optimum geometries of the 2,4-HD isomers in S_0. Energies obtained at the B3LYP/cc-pVTZ level of theory are 75.07, 75.99, and 76.48 kcal/mol for *tt*-, *ct*-, and *cc*-2,4-HD in T_1, respectively, all relative to *tt*-2,4-HD in S_0. Corresponding estimates for Franck−Condon S_0–T_1 transitions for the three isomers in the same order, 75.07, 74.62, and 73.60 kcal/mol, seem reasonable. Relaxation from the Franck−Condon triplet states to the planar geometries with optimum bond lengths affords stabilizations in the 17−18 kcal/mol range.

Allyl units are clearly defined in the allylmethylene structures, ^{3}tp* and ^{3}cp* intermediates in T_1, and ^{1}tp and ^{1}cp TSs in S_0, as planar moieties with reasonable predicted bond lengths. Furthermore tp and cp energies and geometries in S_0 are nearly identical to the corresponding energies and geometries in T_1. The calculated expectation values of the total spin operator are 2.03 for ^{3}tp* and ^{3}cp* (sufficiently close to the expected $<\hat{S}^2> = 2$ for pure triplets) and are 1.03 for ^{1}tp and ^{1}cp TSs in S_0. (The spin annihilation procedure incorporated in the UB3LYP calculations decreases the latter values to 0.27.) The deviation from $<\hat{S}^2> = 0$ reveals that the DFT calculations have not yielded results for pure singlet biradicals. A spin-projection procedure[26] could be applied to correct DFT results, but the correction is negligible when, at the optimized geometries, the UB3LYP energies of the triplet ($<\hat{S}^2> = 2$) and "singlet" ($<\hat{S}^2> = 1$) biradicals are close to each other as in the 2,4-HD.[27] Accordingly, only unprojected energies are reported in Tables 1 and S1.

The prediction of small deviations from orthogonality between allyl and methylene units in the twisted species is somewhat unexpected. Dihedral angles describing the relative orientation of the planar allyl units and the allyl and methylene units deviate uniformly from 90° by 6−8° [6° for S_0, 7−8° for T_1, the latter deviation increasing by 2° for the MP2/6-31G(d) geometries] with excellent agreement between predictions for the two B3LYP basis sets. The calculated spin−orbit coupling is nearly zero at the ideal perpendicular geometry of the ethylene triplet state, but increases dramatically with modest torsional and, to a lesser degree, pyramidalization distortions from that geometry.[28,29] It follows that small deviations from strict orthogonality at the twisted double bond of the equilibrium triplet geometry may have a controlling influence on 1,3-diene triplet lifetimes.

Conclusions

The calculations presented in this work are consistent with experimental data and lead to the following conclusions on the mechanism of cis−trans photoisomerization via the *s-trans*-2,4-hexadiene triplet state:

- Allylmethylene geometries are global minima on the T_1 surface, with the ^{3}cp* structure slightly higher in energy than ^{3}tp* (0.5 kcal/mol according to G2 calculations, 0.33 kcal/mol experimental[9]). Similar in structure and energy are ^{1}cp and ^{1}tp on the singlet ground-state surface, the biradicaloid transition-state structures for double-bond C=C rotation in S_0.

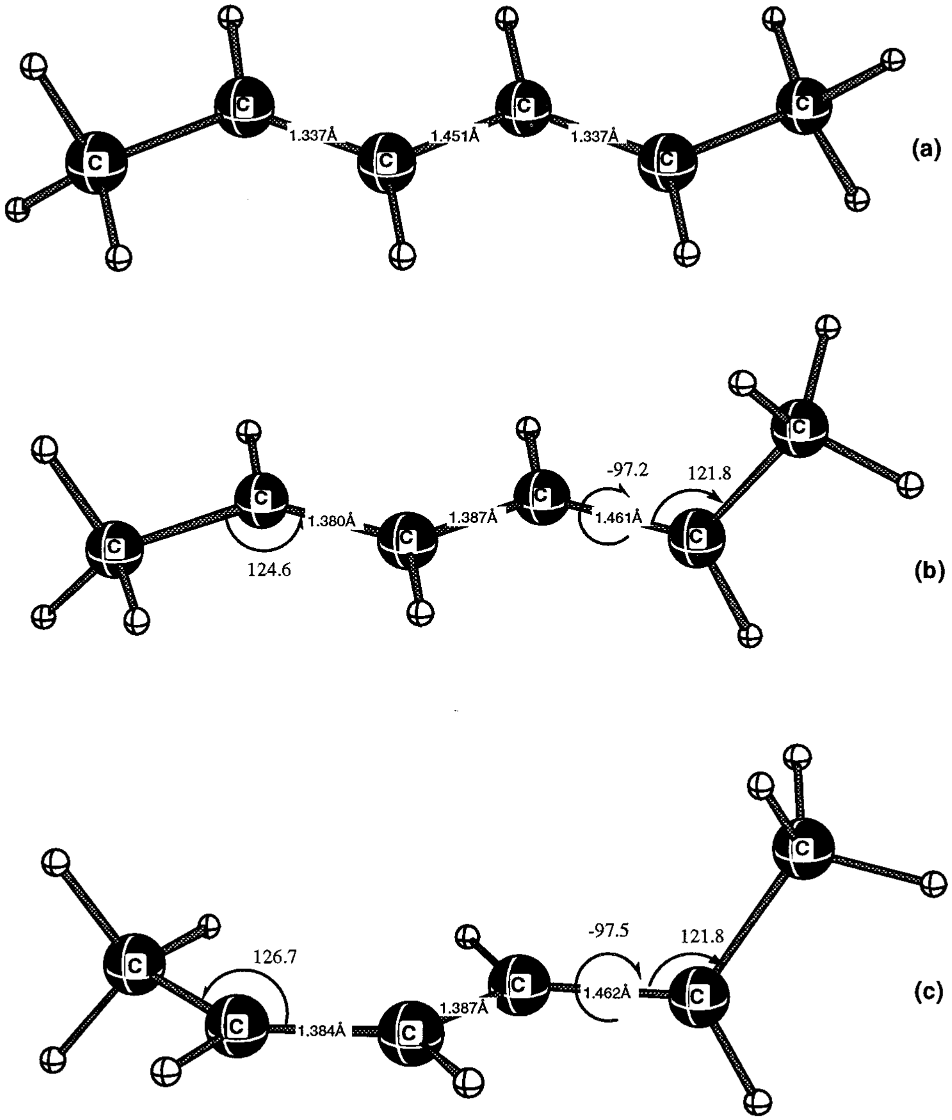


Figure 2. Calculated B3LYP/cc-pVTZ geometries of (a) ^{1}tt ($E_{tot} = -234.72260$ au), the global ground-state energy minimum and two views each of the allylmethylene triplets (b) ^{3}tp* ($E_{tot} = -234.63600$ au) and (c) ^{3}cp* ($E_{tot} = -234.63441$ au).

- Interconversion of ^{3}tp* and ^{3}cp* occurs by a two-step mechanism through a planar intermediate, ^{3}tc*.
- The other two planar triplets, ^{3}cc* and ^{3}tt*, are similarly energetically accessible from ^{3}cp* and ^{3}tp*, respectively. The three planar triplets are probable chain carriers in the quantum chain mechanism for the sensitized 2,4-HD cis−trans photoisomerization.
- The ^{3}pp* structure is too high energy to be of mechanistic importance.

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Supporting Information Available: Table S1 (total energies, dipole moments, and related thermochemical data of stationary point structures on S_0 and T_1 surfaces calculated at the B3LYP/6-31+G(d,p) and B3LYP/cc-pVTZ levels). Table S2 (intermediate and final data for G2 energy calculations for ^{3}tp* and ^{3}cp*). This material is available free of charge via the Internet at http://pubs.acs.org.

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