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Tetra-*tert*-butylethylene: An Elusive Molecule with a Highly Twisted Double Bond. Can It Be Made by Carbene Dimerization?

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Abstract: A theoretical evaluation of tetra-*tert*-butylethylene (**1**) at the BLYP/DZd level confirms that it should be a stable molecule with a singlet ground state. The synthesis of **1** from two molecules of di-*tert*-butylcarbene (**6**) is unlikely. Although the formation of singlet **1** from the triplet ^{3}B ground state of **6** (singlet **6** is only 1−3 kcal/mol higher in energy) is highly exothermic ($\Delta H = -73.7$ kcal/mol), the barrier $\Delta G^{\ddagger} = 25$ kcal/mol (298 K, 1 atm, BLYP/DZd) for the dimerization is too large to compete with the barrier for intramolecular carbene insertion. The barrier for singlet **6** to yield 1,1-dimethyl-2-*tert*-butylcyclopropane (**12**) is only 5 kcal/mol. The CC double bond in singlet **1** is twisted by 45°, and the strain energy is ∼93 kcal/mol in agreement with molecular mechanics results. Triplet **1** has a nearly perfectly perpendicular conformation at the central CC bond (87° torsional angle), but it is still strained by 42 kcal/mol and is 12 kcal/mol higher in energy than singlet **1**. Alkyl substitution decreases the S−T separation of carbenes due to the greater hyperconjugative stabilization of the singlet than the triplet.

Introduction

The ultimate sterically crowded alkene,[2] tetra-*tert*-butylethylene (**1**) remains elusive despite numerous synthetic attempts.[10−16,18−30] While McMurry coupling of ketones[3] yields tetraisopropylethylene,[4,5] tetraneopentylethylene,[6] and 1,2-di-*tert*-butyl-1,2-diethylethylene,[7,8] di-*tert*-butylketone does not give **1**.[9] Instead, the carbonyl group is reduced to the secondary alcohol by low-valent titanium reagents.[9] Coupling of dibromodi-*tert*-butylmethane with magnesium resulted in tetra-*tert*-butylethane instead of **1**.[10] Di-*tert*-butylcarbene, formed via low-temperature photolysis of di-*tert*-butyldiazomethane or by its decomposition on metal surfaces, did not dimerize to **1**.[11,12] Barton's extrusion method, which employs pyrolysis of a 1,3,4-Δ^3-selenadiazoline or the sulfur analog to generate olefins, also failed to give **1**,[13−16] even through di-*tert*-butyldiisopropylethylene (**2**), tetra-(1-methylcyclopropyl)ethylene (**3**), *syn*-2,2′-bisfenchylidene (**4**), and *anti*-bisfenchylidene (**5**) could be prepared successfully.[17−20] However, **4** and **5** are less sterically hindered than **1**, since the substituent groups are "tied back". Krebs et al.,[21−23] Guziec et al.,[24−27] and Garratt et al.[28] have explored the strategy of using "tied back" precursors of **1**, which were than to be "untied" (i.e., by ring opening) once the central

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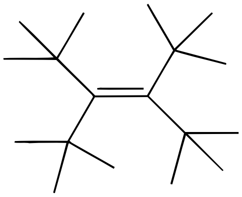

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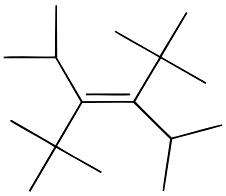

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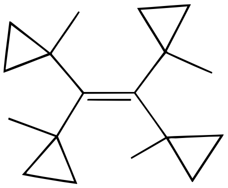

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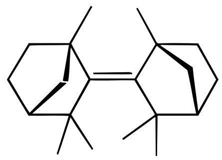

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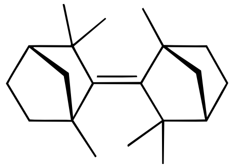

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double bond had been formed. This approach has not succeeded either. Krebs et al. were able to prepare tetra-(2-formyl-2-propyl)ethene, in which the double bond is twisted by 28.6°,[22,29] but the complete reduction of the aldehyde groups to give **1** was not achieved.[30]

In view of these synthetic failures, **1** has been the subject of several theoretical studies. Early force field computations predicted **1** to have a 75° torsional angle at the central "double bond".[31] More recent MM1 and MM2 results gave double bond torsions of 44° (MM2)[32] and 45° (MM1).[33,34] Favini et al. found a second minimum with a torsional angle of only 13° using the Schleyer−Andose−Mislow force field.[35] All these molecular mechanics results predict **1** to have a strain energy in the 90−105 kcal/mol range.

Force field methods are based on Taylor series expansions to mimic energy potentials for bond stretching, angle bending, torsional bending, and various cross terms.[36] In the simplest treatment, the series is broken off after the quadratic term, which gives the harmonic approximation. The coefficients are derived either from a fit to experimental data or from *ab initio* computations. Highly strained and distorted systems like **1** are inherently difficult to treat since they may be well outside the range where empirically derived parameters can be expected to be reliable. Moreover, parameters have only been derived for the electronic ground state, which is a singlet for "normal" organic molecules and for radicals. Hence, while the singlet electronic state of **1** can be explored with the use of molecular mechanics, neither the triplet surface nor processes that involve bond breaking or intermediates like carbenes (or those with considerable diradical character) are appropriate for such investigations.

Therefore, we used *ab initio* methods and density functional theory to study tetra-*tert*-butylethylene (**1**) and to address the following questions: (1) Is singlet **1** or triplet **1** the ground state? What is the singlet−triplet energy separation? To what extent are both geometries distorted from "standard" values? (2) What are the strain energies of singlet **1** and triplet **1**? (3) To what extent do theoretical evaluations of the singlet surface of **1** at various *ab initio* and density functional levels agree with the force field results? (4) Can two molecules of di-*tert*-butylcarbene (**6**) dimerize to form **1**? What is $\Delta G^{\ddagger}$ and what is the structure of the transition state for the dimerization? (5) Does **6** have a singlet or a triplet ground state? What is the singlet−triplet splitting and how does it compare with that of other alkylcarbenes? What factors stabilize the singlet and the triplet electronic states of alkylcarbenes and determine the singlet−triplet separation? (6) Why have attempts to synthesize **1** from the di-*tert*-butylcarbene led to 1-*tert*-butyl-2,2′-dimethylcyclopropane instead?

Methods and Computational Details

The *ab initio* and density functional (DFT) geometry optimizations as well as analytic and finite difference second-derivative computations at the restricted Hartree−Fock (RHF),[37] restricted open shell Hartree−Fock (ROHF),[38] Becke−Lee−Yang−Parr (BLYP-DFT), and Becke3LYP-DFT levels[39] were carried out with CADPAC 5.2[40] (RHF, ROHF, BLYP) and Gaussian92[41] (RHF, ROHF, Becke3LYP). For the CISD, single points PSI 2.0.8 was employed.[42] The standard Gaussian STO-3G and 6-31G* basis sets[43] and the double-ζ (DZ) C(9s5p/4s2p), H(4s/2s) and the triple-ζ (TZ) C(11s6p/5s3p), H(5s/3s) basis sets of Huzinaga[44] in Dunning's contractions[45,46] were employed. The DZ basis was appended with a set of six Cartesian d polarization functions on carbon (orbital exponent $\alpha_d = 0.80$) (DZd basis set). The TZ basis was augmented with two sets of five spherical d polarization functions on carbon (orbital exponents $\alpha_{d1} = 1.50$, $\alpha_{d2} = 0.375$) and two sets of p polarization functions on hydrogen (orbital exponents $\alpha_{p1} = 1.50$, $\alpha_{p2} = 0.375$) (TZ2P basis set). The nature of all stationary points was characterized with analytic (RHF/STO-3G, RHF/DZd, ROHF/STO-3G, ROHF/DZd, or Becke3LYP/DZd) or finite difference second derivatives (ROHF/DZd).

Results and Discussion

Tetra-*tert*-butylethylene. The major effect of strain in singlet **1** is the torsional angle of 45° at the central double bond as well as the lengthening of the $C(sp^2)-C(sp^2)$ and $C(sp^2)-C(sp^3)$ bonds. While triplet **1** does have a torsional angle at the central CC bond near the 90° ideal, the $C(sp^2)-C(sp^3)$ and $C(sp^2)-C(sp^3)$ bonds are also lengthened.

Geometry of Singlet 1. Figures 1 and 2 show that some of the structural parameters of singlet **1** (D_2 symmetry) deviate strongly from these found in unstrained hydrocarbons.[47] The

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Table 1. C(sp^2)−C(sp^2) and C(sp^2)−C(sp^3) Bond Lengths of Singlet **1** at the RHF/STO-3G, RHF/DZd, and BLYP/DZd Levels and Bond Lengthening Compared to Tetramethylethylene (**10**) (C(sp^2)−C(sp^2) Bond) and to *tert*-Butylethylene (**11**) (C(sp^2)−C(sp^3) Bond)

	C(sp^2)−C(sp^2) bond lengths, Å			C(sp^2)−C(sp^3) bond lengths, Å		
level of theory	**1**	**10**	Δ, **1** − **10**	**1**	**11**	Δ, **1** − **11**
RHF/STO-3G	1.360	1.321	0.039	1.600	1.537	0.063
RHF/DZd	1.372	1.334	0.038	1.596	1.518	0.078
BLYP/DZd	1.408	1.367	0.041	1.610	1.531	0.079

Table 2. C(sp^2)−C(sp^2) and C(sp^2)−C(sp^3) Bond Lengths of Triplet **1** at ROHF/STO-3G, ROHF/DZd, and BLYP/DZd and Bond Lengthening Compared to Triplet Tetramethylethylene (**10**) (C(sp^2)−C(sp^2) Bond) and Triplet *tert*-Butylethylene (**11**) (C(sp^2)−C(sp^3) Bond)

	C(sp^2)−C(sp^2) bond lengths, Å			C(sp^2)−C(sp^3) bond lengths, Å		
level of theory	**1**	**10**	Δ, **1** − **10**	**1**	**11**	Δ, **1** − **11**
ROHF/STO-3G	1.533	1.511	0.022	1.579	1.536	0.043
ROHF/DZd	1.520	1.491	0.029	1.573	1.522	0.051
BLYP/DZd	1.510	1.485	0.025	1.587	1.536	0.051

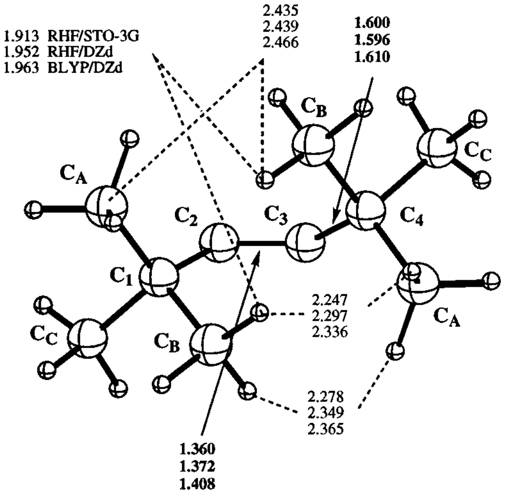

Figure 1. Side-on view of the front-half of singlet **1** (D_2 symmetry). The back half of the molecule has been omitted for clarity. All bond lengths are given in angstroms.

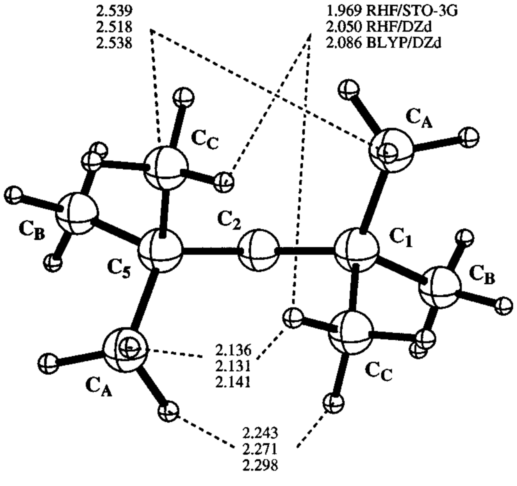

Figure 2. End-on view of the front-half of singlet **1** (D_2 symmetry). The back half of the molecule has been omitted for clarity. All bond lengths are in angstroms.

torsional angles around the central CC double bond are 43.9° at RHF/STO-3G, 46.2° at RHF/DZd, and 47.6° at BLYP/DZd).[48] These agree qualitatively with two of the molecular mechanics results, MM1 (45°)[34] and MM2 (44°).[32] The central CC "double" bond length, 1.360 Å (RHF/STO-3G), 1.372 Å (RHF/DZd), and 1.408 Å (BLYP/DZd),[49] is elongated by ~0.04 Å relative to the corresponding distances in tetramethylethylene (**10**), computed at the same levels (Table 1). The C(sp^2)−C(sp^3) bond lengthening ~0.07 Å as compared to the C(sp^2)−C(sp^3) bond in *tert*-butylethylene (**11**) is even more pronounced: 1.600 Å (RHF/STO-3G), 1.596 Å (RHF/DZd), and 1.610 Å (BLYP/DZd) (Table 1). For bis[1,3-bis(dicyanomethylene)indan-2-ylidene], which has a torsional angle of 49.9°, the experimentally determined CC "double" bond length is 1.402 Å, in good agreement with our DFT results.[50]

The structure of singlet **1** is dominated by the hydrogen−hydrogen repulsions between adjacent *tert*-butyl groups. These are responsible not only for the CC double bond twisting of ~45° but also for the "locked" conformations of the *tert*-butyl groups, which minimize the vicinal and geminal steric interactions. The methyl groups in the optimized singlet **1** are rotated so that the closest hydrogen−hydrogen interaction between geminal butyl groups as well as between vicinal butyl groups is ~2.0 Å (Figures 1 and 2). The repulsions of the *tert*-butyl groups result in pairwise parallel arrangements of C$_A$ and C$_B$ on both C$_1$ and C$_4$ (Figure 1), as well as C$_A$ and C$_C$ on both C$_1$ and C$_5$ (Figure 2).

The methyl group at C$_A$ interacts both with the geminal and with the vicinal *tert*-butyl groups. The methyl group at C$_B$ interacts only with the vicinal, and the methyl group at C$_C$ only with the geminal butyl group. Consequently, C$_B$ and C$_C$ are forced together, C$_B$−C$_1$−C$_C$ is only ~102° while C$_A$−C$_1$−C$_B$ is 108° and C$_A$−C$_1$−C$_B$ is 107°.

Geometry of Triplet 1. Figures 3−5 show that triplet **1**,[47] although less distorted than singlet **1**, is highly strained as well. The two halves of the triplet are twisted by ~87°, only 3° from the ideal value of 90° for the triplet ethylene minimum (Table 3). However, the central CC bond lengths, 1.533 Å at ROHF/STO-3G, 1.520 Å at ROHF/DZd, and 1.510 Å at BLYP/DZd, exceed the corresponding CC bond lengths in triplet tetramethylethylene by ~0.03 Å (Table 2) at all levels. The C(sp^2)−C(sp^3) bond lengths, 1.579 Å at ROHF/STO-3G, 1.573 Å at ROHF/DZd, and 1.587 Å at BLYP/DZd (Table 2), also are elongated by ~0.05 Å as compared to the C(sp^2)−C(sp^3) length in triplet *tert*-butylethylene (**11**). Indeed, as shown in Figures 3−5, the optimized structure for triplet **1** has several short, repulsive hydrogen−hydrogen distances.

Singlet−Triplet Splitting of 1. To ensure that a single-reference treatment was appropriate, a CISD/DZP single-point

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(48) We were unable to locate a minimum for **1** that employs *trans*-bending to reduce the strain.

(49) At ROHF/DZd, the CC double bond length in ethylene is 1.325 Å compared to 1.351 Å at BLYP/DZd. Hence, at ROHF/DZd, the computed values for the strained CC double bond are expected to be slightly too small, while the CC bond lengths that are obtained at BLYP/DZd will be somewhat too large.

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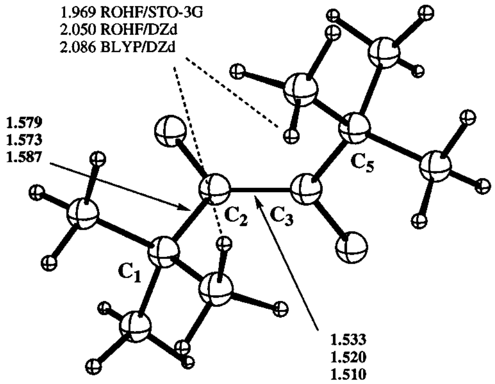

Figure 3. Top view of the upper-half of triplet **1** (D_2 symmetry). The bottom half of the molecule (with the exception of the central *tert*-butyl carbon atoms) has been omitted for clarity. All bond lengths are in angstroms and all angles in degrees.

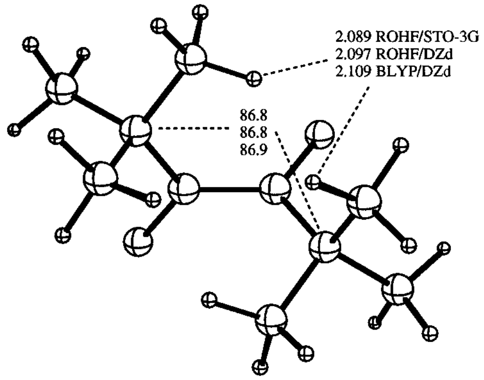

Figure 4. Side-on view of the front-half of triplet **1** (D_2 symmetry). The back half of the molecule has been omitted for clarity. All bond lengths are in angstroms and all angles are in degrees.

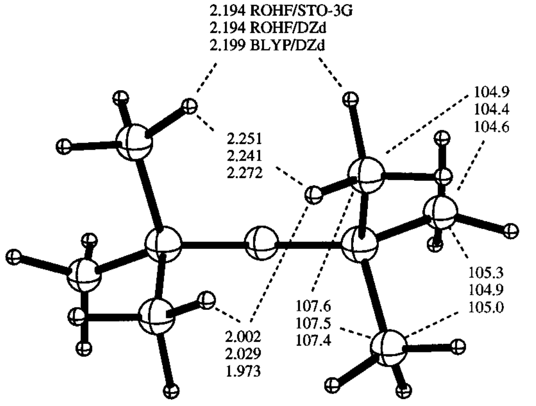

Figure 5. End-on view of the front-half of triplet **1** (D_2 symmetry). The back half of the molecule has been omitted for clarity. All bond lengths are in angstroms and all angles in degrees.

calculation employing natural orbitals was performed for both fully optimized ethylene (D_{2h}) and a D_2-constrained ethylene model with a CC bond length and torsional angle identical to that in **1** (BLYP/DZd). The coefficients for the reference configuration are 0.950 for D_{2h} ethylene and 0.946 for twisted ethylene. The configuration with the highest contribution is in both cases that with an empty π and a doubly occupied π^* orbital. Its coefficients are −0.143 (D_2) and −0.119 (D_{2h}). All other configurations are much less important. From these numbers we conclude that a single-determinant treatment is appropriate.

The singlet−triplet splitting of **1** is 12.6 kcal/mol at BLYP/DZd.[51] The quality of the BLYP/DZd results was evaluated by comparison of literature data for ethylene. Table 3 shows that the singlet−triplet splitting for ethylene computed at BLYP/DZd (64.8 kcal/mol) is close to the 68.5 kcal/mol obtained at UMP2/6-311+G* (Table 3).[52] The singlet−triplet splitting in ethylene is only ~1 kcal/mol smaller than the barrier for rotation around the CC bond,[53] which has been determined experimentally to be 65.9 kcal/mol.[8,54] Hence, the singlet−triplet splitting at BLYP/DZd agrees well with experimental data and BLYP/DZd should also give reliable results for **1**.

Table 3. Comparison of BLYP/DZd, UMP2/6-311+G*, and CIS/6-311+G* Results for Triplet Ethylene[a]

	BLYP/ DZd	UMP2/ 6-311+G*[b]	CIS/ 6-311+G*[b]
r(CC)	1.464	1.459	1.461
r(CH)	1.100	1.084	1.076
H−C−H	116.3	117.0	117.2
C−C−H	121.9	121.5	121.4
H−C−C−H	90.0	90.0	84.7
Δ(S−T)[c], kcal/mol	64.8	68.5	50.0

[a] Bond lengths in angstroms; bond angles in degrees. [b] Results from ref 52. [c] Computed energy difference between the ground state singlet and the lowest triplet excited state.

Strain Energies of Singlet and Triplet 1. Much distortion is needed to achieve the ~45° torsional angle of the "double bond" in singlet **1**. While there are five unfavorable HH interactions between geminal *tert*-butyl groups in the optimized geometries both in the singlet and in the triplet (Figures 2 and 5), triplet **1** has only *three* short HH distances across the double bond (two with the "*cis*" *tert*-butyl group (Figure 4) and one with the "*trans*" *tert*-butyl group (Figure 3), compared to *five* for the singlet.

Indeed, the strain energies computed at BLYP/DZd by means of homodesmotic eq 1 are "only" 42 kcal/mol for triplet **1**, but

$$(t\text{-Bu})_2CC(t\text{-Bu})_2\ (S/T) + 4CH_3CH_3 \rightarrow (Me)_2CC(Me)_2\ (S/T) + 4CMe_4 \quad (1)$$

89 kcal/mol for singlet **1**. However, singlet **1** is still lower in energy than triplet **1**.

Since the reference olefin, singlet tetramethylethylene, is strained by 4 kcal/mol due to the repulsions of the *cis* and geminal methyl groups,[31] the strain energy of singlet **1** derived with eq 1 is ~4 kcal/mol too small. The corrected value of 93 kcal/mol for the strain energy of singlet **1** agrees with the results from the various molecular mechanics force fields which range from 90 to 105 kcal/mol. This agreement also demonstrates the reasonable performance of these force fields for such strained and distorted systems.

Synthesis of 1 from Carbene Precursors: Dimerization versus C−H Insertion. The dimerization of two di-*tert*-butylcarbenes **6** is one of the seemingly promising routes to **1**. But even though Δ$G°$ (298 K, 1 atm) for the formation of **1** from two molecules of singlet **6** is −52 kcal/mol (Table 4), attempts to synthesize **1** from **6** by low-temperature photolysis of di-*tert*-butyldiazomethane yielded the C−H insertion product,

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(51) (a) See ref 43. (b) The stability of the triplet electronic state is overestimated at the ROHF level because the triplet has one less doubly occupied MO than the singlet. Since electron correlation is neglected, the HF level gives a nonrealistically low energy for the triplet as compared to the singlet.

(52) Wiberg, K. B.; Hadad, C. M.; Foresman, J. B.; Chupka, W. A. *J. Phys. Chem.* **1992**, *96*, 10756.

(53) (a) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1985; Vol. III. (b) Doering, W. v. E.; Roth, W. R.; Lenoir, D.; Boese, R. *Chem. Ber.* **1989**, *122*, 1263.

(54) An older value of 63.5 kcal/mol is given by: Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

Table 4. Absolute Energies (hartree) for 1,1-Dimethyl-2-*tert*-butylcyclopropane (**12**), the Transition State for Intramolecular Carbene Insertion (**6**−**12**), the Singlet Carbene, the Transition State for Carbene Dimerization, and **1** at the RHF/STO-3G, RHF/DZd, and BLYP/DZd Levels of Theory[a]

level of theory	**12**	TS **6**−**12**	**6** (S)	TS **6**−**1**	**1** (S)
RHF/STO-3G					
abs energy	−347.14396	−346.97204	−347.02505	−694.02673	−694.18868
energy rel to **6**	−74.62	33.26	0.00	14.66	86.96
ΔG rel to **6**	−72.14	32.52	0.00	34.13	−59.10
RHF/DZd					
abs energy	−351.30517	−351.17680	−351.20947	−702.37348	−702.50385
energy rel to **6**	−60.05	20.50	0.00	28.53	−53.29
ΔG rel to **6**	−57.57	19.76	0.00	48.00	−25.42
BLYP/DZd					
abs energy	−353.55529	−353.44495	−353.45483	−706.90143	−707.03687
energy rel to **6**	−63.04	6.20	0.00	5.16	−79.83
ΔG rel to **6**	−60.56	5.45	0.00	24.63	−51.97

[a] Relative energies and ΔG^a (kcal/mol) are reported with respect to singlet **6**. [b] The thermal data for **11**, TS **6**−**12**, and **1** were obtained at the HF/DZd level. For TS **6**−**1**, HF/STO-3G thermal data were used and compared to thermal data of **6** computed at the same level.

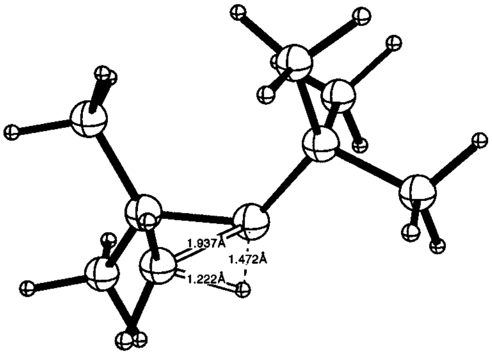

Figure 6. Transition state for the intramolecular C−H insertion which converts **6** into a cyclopropane derivative (**11**). In accordance with the Hammond postulate, the transition state for this highly exothermic reaction lies very early on the reaction coordinate. The migrating hydrogen atom is still almost entirely on the methyl group, and the C−H bond has only been elongated by 0.12 Å.

1,1-dimethyl-2-*tert*-butylcyclopropane (**12**), instead.[11,12] While **6** has a triplet ground state that is 1−3 kcal/mol lower in energy than singlet **6**, intramolecular rearrangements of carbenes proceed mostly via the singlet state.[55] Consequently, we have limited our theoretical evaluation to reaction pathways that start from singlet **6**. $\Delta G^‡$ (298 K, and 1 atm) for the intramolecular C−H insertion of singlet **6** that leads to **12** is only 5.5 kcal/mol. The TS for this insertion (TS **6**−**12**) resembles the carbene more than the cyclopropane products, in accord with the Hammond postulate (Figure 6). The C−H bond of the migrating hydrogen atom is only slightly elongated to 1.222 Å, and the hydrogen distance to the carbenoid carbon is still 1.472 Å. For *tert*-butylcarbene, $\Delta H^‡$ for the C−H insertion has been computed to be only 0.8 kcal/mol (QCISD(T)/6-31G(d)//MP2/6-31(d)).[56] This decrease in the barrier height is due to the even more TS-like structure of the singlet carbene (compare Figure 8).

Alternatively, two molecules of singlet **6** could dimerize to singlet **1**, or two molecules of triplet **6** could combine to give either triplet **1** or singlet **1**.[57] The experimentally observed products of the intramolecular rearrangement of triplet **6** suggest that most of the triplet is first converted to singlet **6**, which then undergoes the intramolecular carbene reactions. We have therefore limited our theoretical investigation to the dimerization of singlet **6**. The TS for this dimerization (TS **6**−**1**, C_1 symmetry, Figure 7) is dominated by the repulsion of the *tert*-butyl groups and the bonding interaction of the doubly occupied sp^2 orbital of singlet **6** with the empty p orbital of the other molecule of **6**. Figure 7 shows that the axis of the doubly occupied sp^2 orbital of di-*tert*-butylcarbene **A** is nearly parallel to the line of approach ($\phi = 31°$), while the angle of the axis of the doubly occupied sp^2 orbital of **B** with the line of approach (ψ) is still 46°.[58] The two fragments are twisted by ~60° in TS **6**−**1**. Consequently, formation of the π bond has hardly begun.

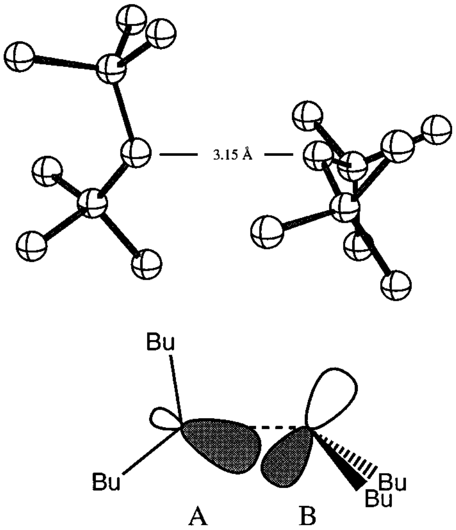

Figure 7. Transition state for the dimerization of two molecules of **6**. The upper part shows the carbon skeleton of the TS (the hydrogens are omitted for clarity). The lower part depicts the important interaction between the sp^2 orbital of carbene **A** with the empty p orbital of carbene **B** leading to the σ bond in **1**.

Even in the most favorable cases, dimerization of carbenes is seldom observed. Although $\Delta G°$ (298 K, 1 atm) for the formation for the $^1A_1$ ground state of **1** from two molecules of singlet **6** is −52 kcal/mol (Table 4), dimerization of **6** is relatively unfavorable. The steric crowding in TS **6**−**1** leads to a $\Delta G^‡$ of 25 kcal/mol (298 K, 1 atm),[59] but this cannot compete with the $\Delta G^‡$ of only 5.5 kcal/mol (298 K, 1 atm) for intramolecular hydrogen insertion to form the cyclopropane product.[59] Furthermore, in contrast to the carbene dimerization, intramolecular hydrogen insertion is a unimolecular reaction and low concentrations of **6** will not affect its rate. Since dimer-

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(55) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84.

(56) Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 3685.

(57) Pauncz, R. *Spin Eigenfunctions*; Plenum Press: New York, 1979; pp 1−7.

(58) Only the central six carbon atoms of the transition state are shown. The rest of the molecule has been omitted for reasons of clarity.

(59) With respect to singlet **6**.

Table 5. Becke3LYP/TZ2P values for the Singlet−Triplet Splitting (S−T) in Di-*tert*-butylcarbene, Methylcarbene, *tert*-Butylcarbene, and Dimethylcarbene and Estimated Values for the Singlet−Triplet Splitting[a]

Molecule	S−T, calcd	with ZPVE[c]	$Stab_S - Stab_T$	S−T, method I	S−T, method II
methylene	11.84	11.32	0.0	9.05	9.05
t-Bu-C-t-Bu (**6**)	5.43	5.16	6.40	2.89	2.65
BLYP/DZd	3.05	2.78	8.83	0.47[d]	0.22
Me-CH (**7**)	4.86	4.53	6.98	2.26	2.07
t-Bu-CH (**8**)	1.66	2.10	10.17	−0.17	−1.12
Me−C−Me (**9**)[e]	0.46	−0.20	11.38	−2.47	−2.33

[a] Obtained by (a) subtracting the known difference between the experimental and the computed (Becke3LYP/TZ2P) S−T for methylene from the computed S−T values of **6**−**9** (method I), or (b) subtracting the theoretically derived difference between the stabilization of the singlet and of the triplet of **6**−**9** from the experimental value for S−T in methylene (method II).[b]

[b] For the BLYP optimizations of the triplet, the restricted open-shell method was used, while Becke3LYP defaults to a UHF wave function for triplets, which could cause the difference between the BLYP and the Becke3LYP results.

[c] For the ZPVE correction, unscaled vibrational frequencies at Becke3LYP/6-31G* were employed.

[d] At BLYP the calculated S−T for methylene (including ZPVE computed at Becke3LYP/6-31G*) is 11.36 kcal/mol.

[e] The best theoretical value obtained at CCSD(T)/TZ2P+f is −1.4 kcal/mol.[62]

ization of **6** cannot compete with C−H insertion, synthesis of **1** by carbene dimerization is highly unlikely.

Singlet−Triplet Splitting of 6. The possible dimerization pathways that lead from **6** to **1** are determined by the singlet or triplet nature of **6** and by the singlet−triplet splitting (S−T). Experimentally, **6** is known to have a triplet ground state, but the S−T separation has not been measured.[11] At Becke3LYP/TZ2P, triplet **6** is 5.2 kcal/mol more stable than singlet **6**. The experimental S−T of methylene is 9.05 ± 0.06 kcal/mol,[61] while at Becke3LYP/TZ2P the singlet−triplet splitting for methylene is 11.32 kcal/mol,[61] ~2.3 kcal/mol more than the experimental result. If we assume the computed singlet−triplet splitting of **6** to be overestimated by the same amount, our corrected value for the S−T in **6** is 2.9 kcal/mol (method I, Table 5).

Radom, Hehre, Schleyer, and Pople have employed an alternative method to evaluate ΔE(S−T). Isodesmic eq 2 was

$$\mathrm{CHR\ (S/T)} + \mathrm{CH_4} \rightarrow \mathrm{CH_2\ (S/T)} + \mathrm{CH_3{-}R} \qquad (2)$$

$$\mathrm{CR_2\ (S/T)} + \mathrm{CH_4} \rightarrow \mathrm{CH_2\ (S/T)} + 2\mathrm{CH_2R_2} \qquad (3)$$

used to assess the stabilizing effect of substituents, R, on the singlet ($Stab_S$) and on the triplet ($Stab_T$) at modest computational levels.[43] The results from eq 2 or 3 together with the experimental singlet−triplet splitting of methylene (see above), allow reasonable predictions for the singlet−triplet splitting of **6** (eq 4, method II). At Becke3LYP/TZ2P the S−T of **6**

$$\Delta_{R_1R_2} = \Delta_{\mathrm{methylene}}\ (9.05\ \mathrm{kcal/mol}) - [\mathrm{Stab_S} - \mathrm{Stab_T}] \qquad (4)$$

estimated with eq 4 is 2.7 kcal/mol (Table 5).

To evaluate the factors that stabilize singlets and triplets we computed the singlet and triplet stabilization of **6**, $CH-CH_3$ (**7**), $CH-C(CH_3)_3$ (**8**), and CH_3-C-CH_3 (**9**)[62] and their ΔE(S−T) values at Becke3LYP/TZ2P (eqs 2 and 3, Table 5) at Becke3LYP/TZ2P.

Singlet carbenes are isoelectronic with carbocations, and the same effects that stabilize carbocations also will stabilize singlet carbenes. Triplet carbenes have a singly occupied p orbital as is the case for radicals. While both carbocations and radicals are stabilized by hyperconjugation, the magnitude is much less for the radicals.[43] This is exactly what we find for the dialkylcarbenes in this study. Compared to methylene, both the singlet and the triplet are stabilized by the alkyl substituent(s), but the magnitude of the effect for the singlets is about twice as large for the triplets.[63]

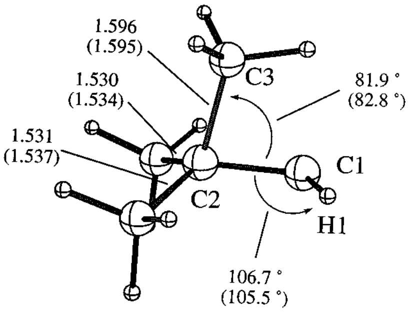
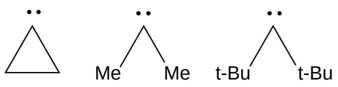


Figure 8. Geometry distortions in singlet **8** at the Becke3LYP/TZ2P and Becke3LYP/6-31G* (values in parentheses) levels of theory (bond lengths in angstroms). The C1−C2−C3 bond angle has decreased to 81.9 from 109.45° for a tetrahedral carbon. At the same time, the C2−C3 bond is elongated to 1.596 Å.

The hyperconjugation between the empty p orbital and the alkyl substituent(s) is most pronounced for singlet *tert*-butylcarbene (**8**, Figure 8). The *tert*-butyl group stabilizes singlet **8** by 17.8 kcal/mol relative to singlet methylene! The C2−C3 bond in singlet **8** is elongated by ~0.065 Å to 1.596 Å at Becke3LYP/TZ2P and $\angle_{C1-C2-C3}$ (Figure 8), which is a measure of the amount of hyperconjugation, has decreased from the ideal tetrahedral value of 109 to 82° in agreement with the MP2/6-31G* value of 79.8°.[56]

The steric repulsion between the two *tert*-butyl groups in **6** (C_2 symmetry) widens the CCC bond angle and influences the singlet−triplet splitting. The effect of the CCC bond angle is shown by the computed singlet−triplet separations of cyclopropylidene, **6** and **9** (Becke3LYP/TZ2P).



		9	**6**
S–T (kcal/mol)	-12.9	-0.2	5.16
$\angle C\ddot{C}C$			
singlet	59.7°	113.5°	125.1°
triplet	69.1°	133.9°	141.9°

Figure 9 shows the relative energies of singlet and triplet methylene for various HCH angles. Under the assumption that the change in energy as a function of the bond angle at the carbene center is the same for all molecules in our study, the

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(60) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251.

(61) Including ZPVE computed at Becke3LYP/6-31G*.

(62) For a more detailed discussion of CH_3-C-CH_3, see: Richards, C. A., Jr.; Kim, S.-J.; Yamaguchi, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 10104.

(63) Detailed tables are provided in the Supporting Information.

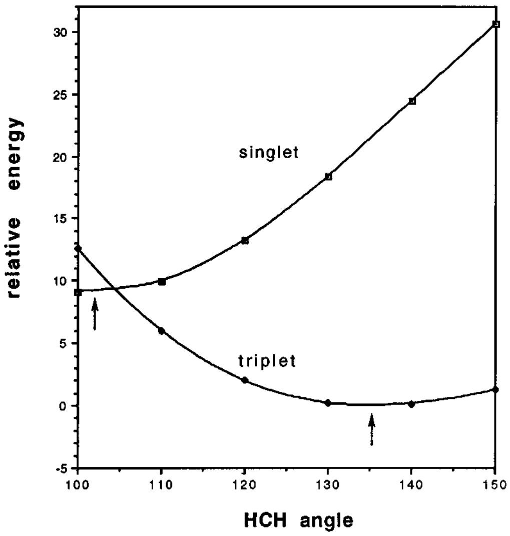

Figure 9. Change in the relative energy of singlet and triplet methylene with respect to ∠$_{HCH}$ at Becke3LYP/TZ2P (kilocalories per mole and degree). The ∠$_{HCH}$ angles of the fully optimized structures are indicated by the arrows.

CCC bond angle of 125° at the carbene center of singlet **6** should raise its energy by 7.2 kcal/mol with respect to a hypothetical singlet **6** with a CCC bond angle of 102°. Consequently, the additional stabilization that is obtained by the second *tert*-butyl group in singlet **6** is only 8.8 kcal/mol, while singlet **8** is stabilized by 17.8 kcal/mol by the first *tert*-butyl group.

The CCC bond angle at the carbene center of triplet **6** is 142°, only 7° more than the HCH angle in triplet methylene. In addition, the energy changes very little for HCH angles between 120 and 150°. Consequently, the second *tert*-butyl group stabilizes triplet **6** by an additional 12.5 kcal/mol! The diminished magnitude of the stabilizing effect of the second *tert*-butyl group in singlet **6** and the large stabilization of triplet **6** by the second *tert*-butyl group cause **6** to be a ground state triplet, whereas **8** should be a ground state singlet.[64]

Our findings contradict the conclusion of Khodabandeh and Carter that the smaller singlet−triplet gap in CH_3CH (**7**) as compared to methylene is due to destabilization of the triplet rather than to the greater stabilization of the singlet.[65] We conclude that the bond angle at the carbene center and hyperconjugation dominate the stability of simple alkylcarbenes. The ideal value for the bond angle at the carbene center in singlet methylene is only 102°. Sterically demanding substituents, like the *tert*-butyl groups in **6**, force a widening of this bond angle. This increases the p character of the doubly occupied "sp^2" orbital and destabilizes the singlet. Triplet methylene has an ideal bond angle at the carbene center of ~134° and structures with even larger angles are only slightly higher in energy (compare Figure 9). Alkyl substitution stabilizes both the singlet and the triplet states through hyperconjugation. The stabilization of the triplet is only half that of the singlet, because the p orbital is already singly occupied in the triplet. Hyperconjugatively stabilized carbenes with normal carbene bond angles will be ground state singlets, while those with little hyperconjugation or strongly widened bond angles at the carbene center will favor the triplet state.

Conclusions

We predict tetra-*tert*-butylethylene (**1**) to be a stable molecule with an S_0 ground state, D_2 symmetry, a 45° double bond torsion, and a strain energy near 93 kcal/mol. Di-*tert*-butylcarbene, from which **1** could conceivably be formed through dimerization, has a triplet ground state and a singlet−triplet splitting of ~1 kcal/mol. The smaller singlet−triplet splitting compared to methylene (S−T = 9 kcal/mol) is due to the larger stabilization of the singlet by the alkyl substituents rather than to destabilization of the triplet. Although the dimerization of two molecules of singlet **6** to give **1** is exothermic by 52 kcal/mol (BLYP/DZd), this reaction is not likely, because the competing intramolecular CH carbene insertion in the *tert*-butyl groups (to form **12**) is preferred kinetically. Triplet **1** (D_2 symmetry) is 12 kcal/mol higher in energy (BLYP/DZd) than singlet **1** with an 87° torsional angle at the central CC bond.

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Supporting Information Available: Table with absolute and relative energies for triplet and singlet **1** and **6**, important angles for singlet **1**, absolute energies needed to evaluate the strain energy of singlet and triplet **1**, relative singlet and triplet stabilization of methyl carbene, dimethylcarbene, *tert*-butylcarbene, and di-*tert*-butylcarbene, Cartesian coordinates of **1**, TS **6**−**1** and TS **6**−**12**, and absolute energies of singlet and triplet **6**−**9** at Becke3LYP/TZ2P (9 pages). Ordering information is given on any current masthead page.

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[64] However, on the basis of method I, Armstrong et al.[54] compute triplet **8** to be 1−2 kcal/mol lower than singlet **8** at QCISD(T)/6-31+G(2d,p)//MP2/6-31G(d).

[65] Khodabandeh, S.; Carter, E. A. *J. Phys. Chem.* **1993**, *97*, 4360.