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The C_7H_6 Potential Energy Surface Revisited: Relative Energies and IR Assignment

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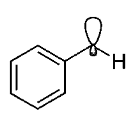
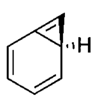
Abstract: The geometries and force fields of phenylcarbene (**PC**) and cycloheptatrienylidene (**CHT**) in their singlet and triplet electronic states as well as of cycloheptatetraene (**CHTE**) and bicyclo[4.1.0]heptatriene (**BCT**) and the transition states for the formation and decay of the latter were evaluated by various methods. Relative single point energies were calculated at the CCSD(T)/cc-pVDZ//BLYP/6-31G* level. Finally, the effects of extending the basis set to triple-ζ quality were estimated by (R)MP2 calculations and carried over proportionally to CCSD(T). These calculations show that **CHTE** which has a strongly distorted allenic structure is the most stable species on that part of the $C(CH)_6$ surface which was examined in the present study, followed by planar **^{3}PC**. The strained **BCT** is found to be nearly degenerate in energy with **^{1}PC**, but the high activation energy for its formation from **^{1}PC** together with the low activation energy for ring-opening to **CHTE** suggests that this species cannot persist under the experimental conditions employed for production of **CHTE**. In analogy to the case of cyclopentadienylidene, **CHT** exists in the form of a closed shell singlet ($^1A_1$) and two related pairs of open shell singlet and triplet states ($^{1,3}A_2$ and $^{1,3}B_1$) which correspond to the Jahn−Teller distorted structures of the cycloheptatrienyl radical. The relative energies and the nature of the different **CHT** stationary points depend on the method of calculation, but it appears that the decrease in electron repulsion lowers the $^1A_2$ state slightly below the $^1A_1$ state so that the open shell species serves as a planar transition state for enantiomerization of **CHTE** with an estimated activation energy of ~20 kcal/mol. The two triplets are very close in energy with the higher lying being either a transition state or a shallow minimum. The $^1B_1$ state is an excited state of the open-shell singlet. The calculated IR spectra of the three most stable isomers were compared to those published previously by Chapman et al. whereby the assignment of the photoproduct of UV photolysis of phenyldiazomethane to **CHTE** was confirmed. A full study of the force fields of **PC** and **CHTE** is under way.

Introduction

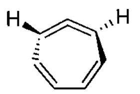
Arylcarbenes undergo remarkably complex skeletal rearrangements.[1−4] Despite 30 years of study, several aspects of these rearrangement mechanisms remain the subject of debate and uncertainty. In the case of phenylcarbene itself, ring expansion to cyclohepta-1,2,4,6-tetraene is well established.[5] Uncertainty persists concerning the involvement of bicyclo-[4.1.0]hepta-2,4,6-triene in this process.[6] Cycloheptatrienylidene remains an enigma. The C_7H_6 energy surface represents a difficult challenge for theoreticians because of both the size of the molecules and the fact that several of the important species are open-shell carbenes. Given recent advances in computational power and methodology, *reliable* ab initio calculations can now be performed on open-shell organic species of moderate size. In this report, we describe computational studies concerning key isomers on the C_7H_6 energy surface. Computed IR spectra for cycloheptatetraene, bicyclo[4.1.0]hepta-2,4,6-triene, and their monodeuterio analogs confirm key aspects of Chapman's spectroscopic characterization of cycloheptatetraene.[7] Detailed studies of the potential energy surface provide a framework for interpreting the known experimental data and provide important insight into the interconversion mechanisms of these highly reactive C_7H_6 intermediates.



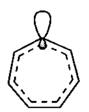
^{1,3}PC



BCT



CHTE



^{1,3}CHT

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Background

In the late 1960's, several groups independently demonstrated the rearrangement of *phenylcarbene* (**PC**) to a ring-expanded intermediate.[8] Wentrup's data established the reversibility of the ring-expansion process. At the time, two indirect pieces of evidence suggested that the ring-expanded intermediate was cycloheptatrienylidene (**CHT**): (i) heptafulvalene, the formal dimer of **CHT**, was the major isolable product obtained upon decomposition of phenylcarbene precursors,[8−10] and (ii) **^{1}CHT** was expected to be an unusually stable carbene because of its "aromatic" π-electron system (see below).[9] Untch later suggested that the ring-expanded intermediate might also exist as cycloheptatetraene (**CHTE**), a twisted and bent allene.[11] Semiempirical[12−14] and ab initio[15] calculations supported this suggestion. Dewar and Landman's MINDO/3 calculations predicted that the ring expansion of **PC** to **CHTE** occurs via a **BCT** intermediate on the singlet surface, but proceeds without intervention of an intermediate on the triplet surface.[13]

Chapman provided compelling spectroscopic and mechanistic evidence for *cycloheptatetraene* (**CHTE**) intermediates in the ring expansion of phenylcarbene,[7] halophenylcarbenes,[7b,16] and tolylcarbenes[17] using matrix-isolation techniques. Interestingly, he did not obtain evidence for either **BCT** or **^{1}CHT** to occur as intermediates in any of these cases, although the benzannelated analogs of these two intermediates are clearly involved in the chemistry of the naphthylcarbenes.[2,3,18,19] Trapping studies further support the involvement of **CHTE**.[20,21] The currently accepted mechanism for the interconversion of simple phenylcarbenes involves the (reversible) ring-expansion of a carbene to a cycloheptatetraene. The intimate details of this reaction—whether it occurs as a direct process or via an undetected **BCT** intermediate—are not well-understood.[3,22,23]

Questions concerning the structure of *cycloheptatrienylidene* (**CHT**) and its role in arylcarbene rearrangements remain unresolved. Most π-substituted carbenes (aryl carbenes, vinyl carbenes, acetylenic carbenes) possess triplet ground states unless the carbene carbon bears a heteroatom substituent or is constrained to a 3- or 4-membered ring.[24] However, **CHT** represents an unusual case. The closed-shell singlet state, **^{1}CHT**, will experience stabilization by virtue of its aromatic tropylium ion character.[9b,12−15,25] Whether this stabilization is sufficient to cause the singlet state to fall below the triplet state (or even below an open-shell singlet state, see below) remains an open question. In 1986, Wentrup[26] and Chapman[27] independently reported ESR spectra attributed to **^{3}CHT**, but unfortunately, the two spectra clearly arise from different species. This discrepancy has not yet been resolved and therefore **^{3}CHT** remains elusive. On the theoretical side, Radom et al. pointed out in their first ab initio study on C_7H_6 that **^{3}CHT** can exist in two distinct states ($^3A_2$ and $^3B_1$) which arise by formal excitation of the single π-electron. These states were found to be nearly degenerate at their respective equilibrium geometries.[15]

At that time, Radom et al. refrained from making any prediction of the S/T gap in **CHT**, but it can be gathered from their data that the closed-shell singlet was found to be more stable than the triplet by 4.6 kcal/mol at the 4-31G level. The most recent ab initio SCF calculations, dating from 1987, confirmed this by predicting a S/T energy separation of ∼5 kcal/mol[25] while a vibrational analysis indicated that both singlet and triplet **CHT** exist as true energy minima. However, previous MNDO calculations had predicted that **^{1}CHT** represents the transition state for interconversion of the enantiomeric **CHTE**'s.[14] The trapping studies of Kirmse seem to suggest that the ab initio prediction is correct, i.e. that **^{1}CHT** exists as a discrete intermediate,[28] but the issue was never settled on the theoretical side. Finally, both **CHT** and **CHTE** form isolable transition metal complexes.[28c]

A question which has never been addressed to date concerns the possible role of the *open-shell* singlet states which correspond to the A_2 and B_1 triplets found by Radom et al.[15,29] In related cyclopentadienylidene the open-shell $^1A_2$ state is far more stable than the closed-shell singlet state ($^1A_1$).[30] This is due in part to the antiaromaticity of the π-system in $^1A_1$ of cyclopen-

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tadienylidene, and in part to the effect of removing an electron from the lone pair in $^1A_1$, where it suffers strong repulsion, and its promotion into a π-MO which is essentially disjoint from the latter. Although the π-system of $^1A_1$-**CHT** is aromatic, it remains to be examined whether this gain outweighs both (a) the destabilizing effect of widening the angle at the carbenic carbon from the equilibrium value of ca. 105° in the closed-shell singlet carbenes to the 119° which prevails in $^1A_1$ and (b) the decreased electron repulsion on going from the closed-shell $^1A_1$ to the open-shell $^1A_2$ state.

Triplet phenylcarbene (**^{3}PC**) has been characterized by ESR,[7,31] UV/vis,[7] IR,[7] and fluorescence[32] spectroscopy. ESR spectroscopy establishes a triplet ground state. Higuchi estimated the bond angle at the triplet carbene center of **^{3}PC** as 155° using an empirical relationship between the bond angle and the ratio of the zero-field splitting parameters, D/E.[33] In most instances, **PC** displays singlet reactivity[34] which implies that the singlet and triplet states are in rapid equilibrium, and that the singlet−triplet separation is small (<5 kcal/mol).[34,35] Several computational studies were dedicated to the structure and energetics of **PC**,[13,15,36−39] although only a single study addressed the reaction coordinate for ring expansion.[13] Calculated estimates for the S/T splitting vary widely depending on the level of theory; the most recent value is 4.3 kcal/mol from density functional theory.[38]

The present work was undertaken with the aim of clarifying some of the above-mentioned unresolved issues by carrying out a comprehensive study of the $C(CH)_6$ potential energy surface. Recent developments in the area of quantum chemistry and the rapid development of computational hardware make it possible nowadays to carry out ab initio calculations at a level which is likely to yield reliable predictions on systems of this size, thus warranting a fresh look at the fascinating and still partially confusing chemistry and spectroscopy of C_7H_6 from the theoretical side.

Methods

Initially, we optimized all geometries at the (U)HF and (U)MP2 level,[40] but it turned out that spin contamination caused problems in the open-shell species (especially at the UMP2 level). This rendered comparison with the closed-shell isomers very difficult. Therefore, and in view of gratifying recent experiences in our and other laboratories,[41] we turned to density functional methods for geometry optimizations and force field calculations. In particular, we tried combinations of Becke's gradient corrected exchange functionals (both the original[42a] and the new hybrid 3-parameter one[42b]) with the correlation functional of Lee, Yang, and Parr[43a] (combinations usually denoted as BLYP or B3LYP, respectively[43b]). A rapidly increasing body of recent evidence shows that these give excellent agreement with experiment and/or higher level calculations for geometries and harmonic frequencies[41] if used with the 6-31G*[41e,f,h] or similar double-ζ basis sets.[41g]

In order to get reliable estimates for the relative energies of the different isomers, we carried out single-point CCSD(T) calculations[44] with Dunning's correlation-consistent polarized valence double-ζ (cc-pVDZ) basis set[45] which gave 128 basis functions for C_7H_6. Thereby the BLYP geometries invariably gave CCSD(T) energies which were lower by 0.6−1.5 kcal/mol than either the HF, B3LYP, or MP2 geometries for the closed-shell species. In spite of the fact that B3LYP is usually considered slightly superior to BLYP,[41d−g] we conclude that the BLYP geometries are closer to those one would obtain by CCSD(T) (if geometry optimizations would not be too costly at this level for C_7H_6). Therefore, the relative energies of all stationary points were finally based on geometries evaluated by the BLYP/6-31G* method. This has the additional advantage that vibrational frequencies can be used in a first approximation without scaling,[46] which is done for some of the C_7H_6 isomers in the present work. Unscaled BLYP/6-31G* frequencies were also used to compute some of the thermodynamic parameters such as zero-point vibrational energies and vibrational entropies, which are needed to convert relative energies into thermochemically meaningful quantities.

As with all methods for recovering correlation energy which are based on some form of perturbation theory, the CCSD(T) method[44] can only be expected to work reliably if the zero-order reference wave function is a reasonable approximation to the final correlated one. In particular, one must ascertain that a single-determinant reference gives a qualitatively correct description of the electronic structure of the system under investigation, i.e. that strong nondynamic correlation effects which require multideterminantal reference wave functions are absent. Two methods were used to check this: First, we carried out single-point CASSCF calculations (including all π-electrons in all π-MOs plus the unpaired σ-electron in the case of **^{3}CHT**) to see if any excited configurations would contribute significantly to the reference determinant. Second, we inspected the T_1 diagnostic for the CCSD wave function[47] which measures the degree of reorganization of the

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[44] The CCSD(T) acronym stands for coupled-cluster calculations accounting for all single and double substitutions (see e.g.: Bartlett, R. J. *J. Phys. Chem*. **1989**, *93*, 1697 and references cited therein) supplemented by a quasiperturbative account for triple excitations (Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett*. **1989**, *157*, 479). Extensive applications have shown that this method consistently yields results very close to those obtained by full configuration interaction (cf.: Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995).

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[46] A recent systematic study[41e] has shown that due to a fortuitious cancellation of errors, unscaled BLYP frequencies show no *systematic* deviation from observed ones (in a SQM scheme, the optimal scaling factors for most BLYP valence force constants are in the range 1.00 ± 0.07, i.e. those for frequencies are 1.00 ± 0.035) whereas B3LYP frequencies are systematically too high. Note, however, that upon proper scaling, B3LYP valence force constants give better ultimate agreement with experiment.[41e]

wave function in going from HF to CCSD due to inadequacies of the HF reference determinant. With the exception of the open-shell singlet states of **CHT** (see below), all species considered in this study passed both of the above tests in that (i) no single excited configuration contributed by more than 1.2% to the reference in CASSCF and (ii) the coupled cluster T_1 diagnostic was below 0.02 in all cases. Thus, we are confident that our theoretical approach is valid.

As mentioned above, the open-shell singlet states of **CHT**[29] called for special attention, because these require a two-determinant reference for a correct description of the spin coupling. In order to avoid inconsistencies due to the use of different methods for geometry optimization, we assumed that the geometries of the A_2 and B_1 singlets are the same as those of the corresponding triplets—probably a reasonable assumption in view of the analogous case of cyclopentadienylidene where $^1A_2$ and $^3A_2$ were found to have nearly identical geometries.[30b] Thus, we took the BLYP geometries of the triplets to carry out two-determinant CCSD calculations for the open-shell singlets according to the procedure recently proposed by Balková and Bartlett.[48] As the quasiperturbative triples correction is presently not available for this method, the energies of the open-shell singlets of **CHT** can only be compared at the CCSD level and are therefore associated with a slightly larger uncertainty.

As it was impossible to carry out a full set of CCSD(T) calculations with a basis set of triple-ζ quality, the effect of enlarging the basis set was examined at the MP2 level using Dunning's cc-pVTZ basis[45] (294 basis functions for C_7H_6). For the triplets we relied on a restricted open-shell MP2 method[49] because UMP2 and "projected" UMP2 energies were found to be in serious disagreement with the CCSD(T) results due to spin contamination. The effects of extending the basis set from double-ζ (DZ) to triple-ζ (TZ) quality at the CCSD(T) level were estimated by the following formula:[50]

$$E^{\mathrm{CCSD(T)}}_{\mathrm{estim}}(\mathrm{TZ}) = E(\mathrm{HF/TZ}) + \frac{E^{\mathrm{MP2}}_{\mathrm{corr}}(\mathrm{TZ})}{E^{\mathrm{MP2}}_{\mathrm{corr}}(\mathrm{DZ})}E^{\mathrm{CCSD(T)}}_{\mathrm{corr}}(\mathrm{DZ}) \qquad (1)$$

where $E(\mathrm{HF/TZ})$ is the Hartree−Fock energy (ROHF for triplets), E_{corr} are the correlation energies obtained by the MP2 or CCSD(T) methods with the DZ or TZ basis set, and $E^{\mathrm{CCSD(T)}}_{\mathrm{estim}}(\mathrm{TZ})$ are the estimated energies at the CCSD(T)/cc-pVTZ level which, after correction for relative zero-point energies at the BLYP/6-31G* level, are listed in Figure 3 and will serve as a basis for our discussion.

The Hartree−Fock-, MP2-, density functional-, CASSCF-, and UCCSD(T) calculations were carried out with the Gaussian program package in its G92-DFT or G94 incarnation[51] whereas MOLPRO[52] was used for partially spin restricted CCSD(T) calculations based on an ROHF reference wave function (RCCSD(T)[53]). The energies of the triplets relative to the closed-shell singlets varied by <0.5 kcal/mol when UCCSD(T) was used instead of RCCSD(T). The two-determinant CCSD calculations were done with the latest version of the ACES II program.[54]

The IR spectrum of **CHTE** shown in Figure 4 for reference purposes was obtained by bleaching phenyldiazomethane in an Ar matrix (1:1000 v/v) at >280 nm which yields mainly **CHTE** along with a small amount of benzoic acid and some other, unidentified side product.[62] A full account of the vibrational structure of **^{3}PC** and **CHTE**, including also some deuterated derivatives and scaled quantum mechanical force fields, is in preparation.

Results

The structures and the most important geometrical parameters[40] of all stationary points on the C_7H_6 potential energy surface that were investigated in this work are depicted schematically in Figure 1. Figure 2 shows the optimized geometries of **CHTE**, **BCT**, and the two transition states as ball-and-stick models for a better appreciation of the out-of-plane distortions which prevail in these molecules. Table 1 lists the relative energies of these species at the BLYP geometries as obtained by the different ab initio procedures described above. Also shown are the zero-point vibrational energies used to evaluate $\Delta H(0\ \mathrm{K})$ as well as the $S°$ values. A schematic summary of the relative enthalpies is given in Figure 3. Finally, Figure 4 shows the IR spectrum of **CHTE** in juxtaposition to the BLYP predictions for **CHTE** and **BCT** while Table 2 lists the corresponding frequencies.

Discussion

Phenylcarbene (PC). The geometries of singlet and triplet **PC** present no surprises. The main difference between the two spin states is the angle at the carbenic center, in accord with qualitative expectations and observations on CH_2 and alkylcarbenes.[55] Conversely, the geometry of the phenyl ring is only slightly affected by the spin state of the carbene which is in agreement with the fact that the highest π-MO of **PC** is essentially nonbonding (and hence it does not matter whether it is singly occupied or not) and that the sp^n hybrid carrying the second single electron in **^{3}PC** or the lone pair in **^{1}PC** extends only slightly into the σ-frame of the phenyl ring.[56] In accord with this and with indirect experimental data,[34,35] the calculated S/T gap for **PC** is ~4 kcal/mol. This value is smaller than in CH_2, but larger than in dialkyl carbenes where the singlet falls below the triplet due to preferential stabilization of the former by hyperconjugation.[55]

Cycloheptatetraene (CHTE). This is clearly the most stable species on that part of the $C(CH)_6$ surface covered by the present study, and its structure is in agreement with that proposed on the basis of earlier calculations.[12−15] In particular, the bond length alternation, the strong nonplanar distortion, and the widening of the apical angle to 145.8° testify to the bent allene character of this species. The marked deviation of the allenic moiety from linearity may lead to admixture of biradicaloid resonance structures, which could explain the high reactivity of this compound[20,21] as well as the relatively long-wavelength onset (near 400 nm) of its UV absorption.[7] Finally, the

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(47) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.

(48) Balková, A.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *193*, 364.

(49) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130.

(50) This scheme corresponds to a linear *multiplicative* scaling of the CCSD(T) correlation energy in the spirit of the SAC method of Truhlar (see: Rossi, I.; Truhlar, D. G. *Chem. Phys. Lett.* **1995**, *234*, 64 and references cited therein) whereby the scaling factor is defined as the ratio of the correlation energies at the MP2 level, the assumption being that this will be the same at the CCSD(T) level (the ratio is around 1.2 for the molecules of this study). Very similar results were obtained by an *additive* scaling in the spirit of the G2/MP2 method (Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293), i.e.: $E^{\mathrm{CCSD(T)}}_{\mathrm{estim}}(\mathrm{TZ}) = E^{\mathrm{CCSD(T)}}(\mathrm{DZ}) + [E^{\mathrm{MP2}}(\mathrm{TZ}) - E^{\mathrm{MP2}}(\mathrm{DZ})]$.

(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Comperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, M. C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(52) MOLPRO 94: Werner, H.-J.; Knowles, P. J. with contributions from Almlöf, J.; Amos, R. D.; Deegan, M. J. O.; Elbert, S. T.; Hampel, C.; Meyer, W.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.

(53) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.

(54) ACES II Release 2.0. For a description of this program package, see: Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 879.

(55) See for example: (a) Matzinger, S.; Fülscher, M. P. *J. Phys. Chem.* **1995**, *99*, 10747. (b) Richards, C. A.; Kim, S.-J.; Yamaguchi, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 10104.

(56) It is interesting to note that the same is not true at the UMP2 level, where heavy spin contamination in **^{3}PC** ($\langle S^2\rangle = 2.35$) leads to a pronounced distortion of the phenyl ring.

Table 1. Relative Energies (in kcal/mol) of C_7H_6 Isomers by Different Quantum Chemical Methods[a]

species	state	**HF/DZ**[b]	**MP2/DZ**[c]	**MP2/TZ**[c]	**BLYP/6-31G*** [d]	**CCSD/DZ**[e]	**CCSD(T)/DZ**[e]	**CCSD(T)/TZ** (est.)[f]	**ZPE/$S°$** [g]
CHTE	^1A	−268.464772	−269.384105	−269.638110	−270.120753	−269.428629	−269.475563	−269.748484	63.14/73.16
^{3}PC	$^3A''$	−16.27	11.21	13.99	12.68 (0)	8.19	11.63	14.10	−0.87/+4.27
^{1}PC	$^1A'$	−3.06	18.23	19.51	18.22 (0)	13.99	16.26	16.69	−1.00/+4.02
TS1	A	24.79	31.82	34.58	30.57 (1)	31.52	31.93	31.54	−1.34/+0.18
BCT	A	14.80	12.41	11.63	17.43 (0)	14.48	15.58	15.45	−0.66/+1.55
TS2	A	20.95	13.46	12.29	18.04 (1)	18.82	18.74	18.74	−1.21/+0.33
^{1}CHT[h]	$^1A_2$	10.36				21.22			−1.86/+1.26[h]
^{1}CHT	$^1A_1$	13.11	24.99	25.90	22.30 (2)[i]	25.25	25.83	26.69	−0.96/−2.53
^{3}CHT	$^3B_1$	8.17	28.32	30.34	24.97 (1)	25.20	27.91	29.55	−2.46/+3.69
^{3}CHT	$^3A_2$	8.61	27.85	29.14	23.29 (0)	25.92	28.04	29.04	−1.86/+3.44
^{1}CHT[h]	$^1B_1$	23.83				40.92			−2.46/+1.51[h]

[a] Calculations with Dunning's cc-pVDZ (double-ζ, **DZ**) or the cc-pVTZ (triple-ζ, **TZ**) basis set at the BLYP/6-31G* geometries (except for open−shell singlets); absolute energies in Hartrees are given for **CHTE** which serves as the reference. [b] RHF for closed-shell species, ROHF for triplets, TCSCF for open-shell singlets. [c] Restricted MP2 for triplets. [d] Number in parentheses indicates the number of imaginary frequencies on this energy surface. [e] Evaluated on the basis of an ROHF reference wave function for triplets,[53] 2-determinant ROHF for open shell singlets.[48] [f] Estimated by formula 1 in the text. [g] Relative zero-point energies (ZPE) in kcal/mol and relative entropies ($S°$) in cal/(K·mol) from BLYP/6-31G* calculations; absolute values are given for **CHTE** which serves as a reference. [h] Geometries and ZPE assumed to be identical to those of the triplets of the same symmetry. $S°$ taken as that of the corresponding triplet minus the contribution R ln(3) = 2.18 kcal/mol due to the electronic degeneracy of the latter. [i] For discussion see text.

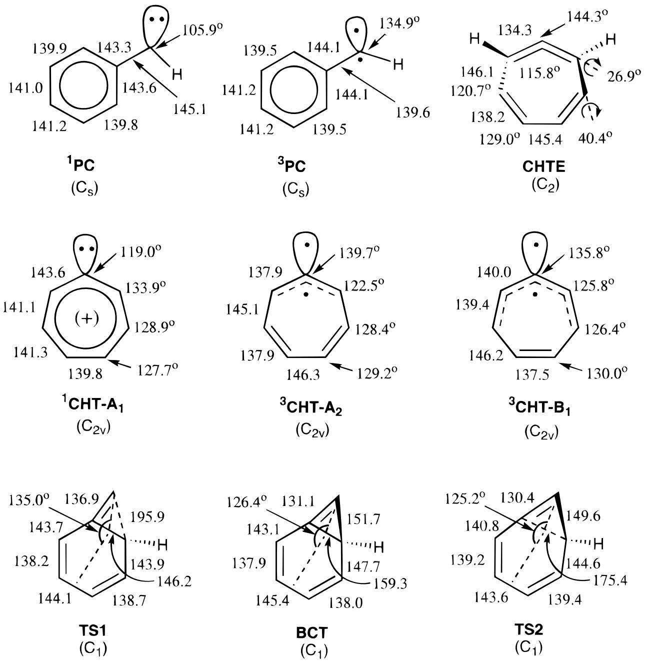

Figure 1. Important geometrical parameters of C_7H_6 structures investigated in the present study (BLYP/6-31G* optimized).

calculated IR spectrum of **CHTE** agrees very well with that observed by Chapman et al.[7] (see below).

Bicyclo[4.1.0]hepta-2,4,6-triene (BCT). This strained bicyclic intermediate is found to be slightly lower in energy than **^{1}PC**, hence its formation from the latter is not inconceivable on energetic grounds. However, the disposition of transition states for its formation from **^{1}PC** (**TS1** in Figures 1 and 2, 14.5 kcal/mol above **^{1}PC**) and its decay to **CHTE** (**TS2** in Figures 1 and 2, 2.7 kcal/mol above **BCT**) suggest that it may not persist under conditions which allow its production from **PC**. Even if **BCT** could be generated via some other, low-energy pathway, it would be difficult to stabilize it in its shallow potential well.[57] Thus, our calculations lead us to conclude that **BCT** is unlikely to have been observed in any study to date. In agreement with this conclusion, the IR spectrum computed for **BCT** (cf. Figure 4) bears no resemblance to the spectrum observed upon photolysis of **PC**.

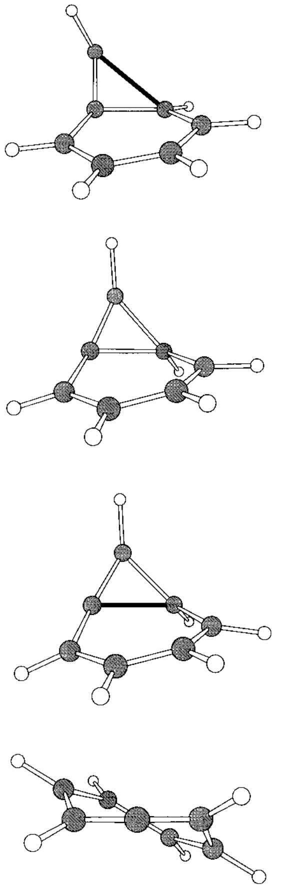

Figure 2. Ball-and-stick models of the nonplanar C_7H_6 species in Figure 1.

Triplet Cycloheptatrienylidene (^{3}CHT). This enigmatic species may be described as an (iso-π-electronic) cycloheptatrienyl radical where one of the C−H bonds has been homolytically cleaved.[13] Therefore the degeneracy of the cycloheptatrienyl radical ground state in D_{7h} symmetry is broken, and **^{3}CHT** is no longer subject to a first-order Jahn−Teller (JT) effect. However, the vibronic coupling which drives Jahn−Teller distortion in cycloheptatrienyl radical is also operative in **^{3}CHT** and causes it to exist in the form of two geometrically distinct states of C_{2v} symmetry, $^3A_2$ and $^3B_1$, as pointed out

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(57) The energies of **TS1** and **TS2** relative to **BCT** depend rather strongly on the geometries of the former, in particular the lengths of the bonds which are formed or broken. Although the BLYP geometries for **TS1** and **TS2** gave the lowest CCSD(T) energies, as in the case of the minima, this does not prove that BLYP is a reliable method for calculating geometries of such transition states. Therefore, their relative energies are associated with a bit more uncertainty, but we believe that this does not affect the general conclusions.

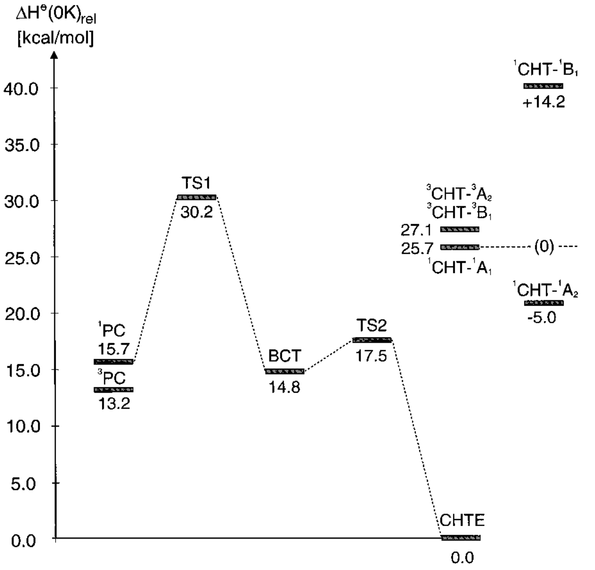

Figure 3. Schematic representation of the relative enthalpies of the C_7H_6 species, based on estimated CCSD(T)/cc-pVTZ energies and BLYP/6-31G* zero-point energies. The open-shell **CHT** singlets on the right-most side were calculated at the TC-CCSD/cc-pVDZ level and are drawn relative to the closed-shell singlet ($^1A_1$) state calculated at the same level (their energies cannot be directly compared to those of the other species in the figure).

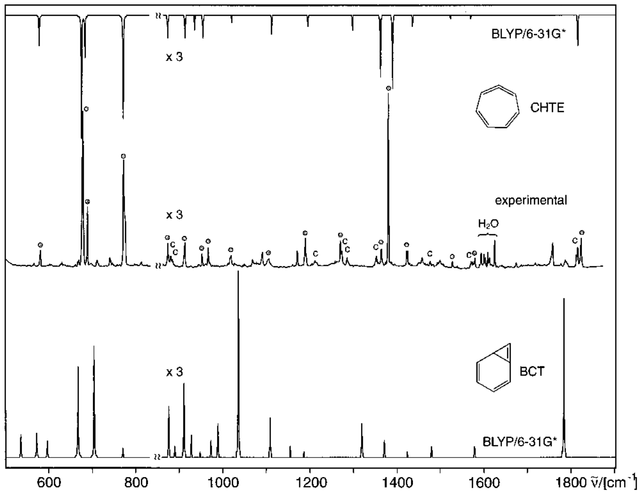

Figure 4. IR spectrum obtained after complete bleaching of phenyldiazomethane at >280 nm and calculated spectra for **CHTE** and **BCT**. The bands which are marked with a dot (fundamentals of **CHTE**) or with a "c" (combination bands) grow concertedly upon stepwise photolysis whereas unmarked IR bands belong to an unidentified side product which arises at a different rate.[62]

first by Radom et al.[15] The first of these resembles a butadiene bridged by an allyl radical whereas the second shows a bond length alternation pattern in better agreement with the usually depicted cycloheptatriene structure (cf. Figure 2). The two triplet states are so close in energy that their ordering depends critically on the method of calculation.

In the cycloheptatrienyl radical the corresponding pair of states may interconvert through a process of pseudorotation along the bottom of the JT well (one of them being an energy minimum, the other a transition state). This pathway is not available to ^{3}**CHT** because its σ-radical center cannot be interchanged with other centers in the ring. Thus, one might expect that in ^{3}**CHT** both states correspond to minima on the potential energy surface. At the SCF levels (ROHF and UHF), this expectation is confirmed, but at levels including dynamic correlation (UMP2, BLYP) one finds that the $^3B_1$ state is a saddle point. This is surprising because the substantial vertical energy gaps between the $^3A_2$ and $^3B_1$ states at their respective C_{2v} optimized geometries (cf. Figure 5) suggest an activated adiabatic interconversion.

Table 2. Calculated and Experimental Frequencies of **CHTE**[a]

	calcd (BLYP)		exptl (IR)	
symmetry	freq (cm^{-1})	rel intensity	freq (cm^{-1})	intensity
B	284	3.8		
A	294	7.3		
B	378	4.5		
A	403	27.2		
B	475	1.2		
A	577	25.7	581	w
B	675	100.0	679	s
A	682	33.8	689	s
B	771	84.7	772	s
A	800	0.4		
A	834	0.3		
B	872	6.7	874	m
A	913	6.7	913	m
B	934	3.8	952	w
A	953	6.8	967	w
A	1011	0.2		
B	1019	1.8	1019	w
A	1112	4.8	1104	w
B	1194	3.2	1189	m
A	1221	0.2		
B	1297	4.7	1270	m
A	1361	17.4	1364	w
B	1389	20.2	1380	s
A	1435	3.0	1423	w
A	1522	0.9	1527	w
B	1569	1.3	1579	w
B	1813	8.5	1823	m

[a] The BLYP force field predicts furthermore five C−H stretching fundamentals between 3046 and 3084 cm^{-1} which can be associated with a group of IR bands between 3012 and 3057 cm^{-1}, but no attempt was made to assign those individually.

In order to shed light on this point we followed the nuclear displacement corresponding to the imaginary frequency of the $^3B_1$ state by doing an IRC calculation[58] on the BLYP potential energy surface. This led smoothly to $^3A_2$ via intermediary structures which exhibit rather pronounced distortion to C_s symmetry. Such distortions are necessary to allow for strong mixing of $^3B_1$ with $^3A_2$ which results in an entirely downhill path connecting the former to the latter. In Figure 5 we depict the change of the singly occupied π-HOMO for some of the points along the reaction coordinate. This shows how mixing between the two states sets in early upon distortion toward C_s. As the reaction proceeds, this leads to the disappearance of the AO coefficient which must change sign in order to reach the $^3A_2$ state upon return to C_{2v} symmetry.

Whatever the exact disposition of stationary points on the triplet **CHT** surface, it contains two distinct structures of very similar energy. These structures either interconvert rapidly or one serves as the transition state for the automerization of the other. A question which is not addressed presently and which could be a worthwhile target for future calculations concerns possible pathways for rearrangement of ^{3}**CHT** to more stable species, in particular ^{3}**PC**. These could possibly furnish predictions with regard to the persistence of the yet elusive ^{3}**CHT**.

Singlet Cycloheptatrienylidene (^{1}CHT). In addition to a pair of open-shell states ($^1A_2$ and $^1B_1$) corresponding to the above two triplets (see below), ^{1}**CHT** can form a *closed-shell*

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[58] IRC = intrinsic reaction coordinate. Thereby the valley leading from a saddle point down to a minimum is followed. See: Gonzales, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523 and references cited therein.

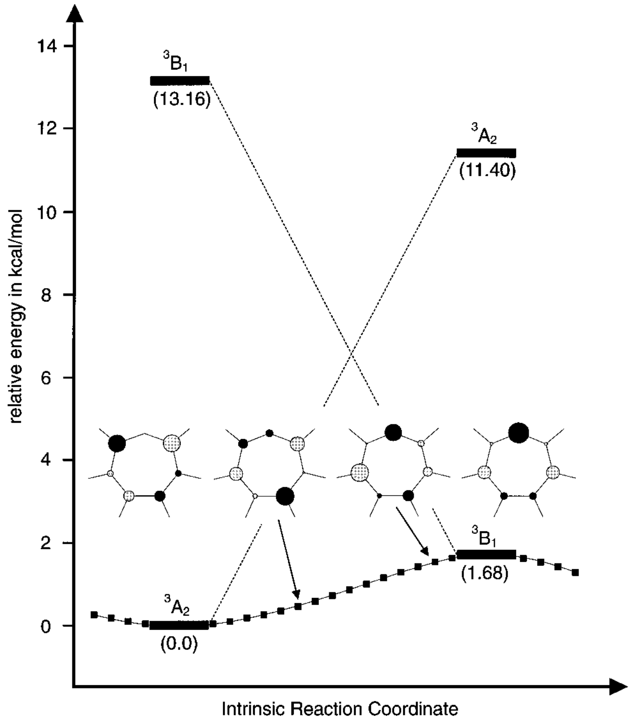

Figure 5. Correlation diagram for the $^3B_1$ and $^3A_2$ states of **CHT** and change of the two singly occupied MO's along the intrinsic reaction coordinate (IRC) connecting the two at the BLYP/6-31G* level (each dot corresponds to a point on the IRC; MO's are shown for the 1st, 7th, 15th, and last points.

singlet state ($^1A_1$) in which the carbene sp^n hybrid orbital is doubly occupied. In the case of **CHT** this state enjoys the energetic advantage of containing a 6π aromatic system analogous to tropylium cation. However, this advantage is at least partially offset by the additional repulsion of the two electrons confined to a strongly localized lone pair MO. In the related case of cyclopentadienylidene (which has, however, an antiaromatic 4π-system) this effect pushes the closed-shell $^1A_1$ state far above the open-shell $^1A_2$ state where the two electrons experience much less repulsion because they reside in essentially disjoint MO's.[59] We therefore examined which effects win out in the present case of **CHT**.

First, we note that at the BLYP/6-31G* level the $^1A_1$ state corresponds to a second-order saddle point (two imaginary frequencies). One of them (a_2, -1314 cm^{-1}) corresponds to the out-of-plane deformation leading to **CHTE**, while the other (b_1, -228 cm^{-1}) leads to a C_s-folding of the ring analogous to that found in $^1A_1$ cyclopentadienylidene.[30] However, following this b_1 mode leads to practically no energy lowering. Furthermore, as the frequency of this mode is positive at the B3LYP and the MP2 levels, we may disregard this particular feature found only at the BLYP level and note simply that the energy surface is very flat for folding the seven-membered ring along a b_1 coordinate.

As outlined in the Methods section, the relative energy of the two *open-shell* singlet states ($^1A_2$ and $^1B_1$)[29] could unfortunately not be computed at the same level of theory as employed with the other species due to the inherent two-determinantal nature of open-shell singlet wave functions which prohibits (i) a BLYP geometry optimization and (ii) CCSD(T) single-point calculations. With regard to (i), we assumed that the geometries and the zero-point energies of the singlets are identical to those of the corresponding triplets. With regard to (ii), we can only compare the energies of the $^1A_2$ and $^1B_1$ states to that of the others at this and the CCSD level, i.e. must allow for a somewhat larger uncertainty due to the lack of triples corrections to the 2-determinant CCSD energies. Under these premises, it appears that the electron repulsion wins out even in the present case of an aromatic π-system, i.e. the $^1A_2$ state lies more than 4 kcal/mol below the $^1A_1$ state, a difference which is enhanced by 0.9 kcal/mol on a ΔH scale. (The $^1B_1$ state where the singly occupied π-MO has a large coefficient at the carbenic center, and which can hence not profit fully from the loss in electron repulsion, lies at much higher energy.[59b])

However, in assessing this result, one must also consider that the seven-membered ring imposes a widening at the carbenic angle from the equilibrium value of ~102° for closed-shell singlet carbenes whereas the deviation from the equilibrium angle of ~134° for the open-shell triplet (and, hence, also the corresponding singlet) is much smaller and associated with an almost negligible energy penalty due to the flatness of the corresponding potential energy surface. An estimate for the effect of this distortion can be obtained by taking the energy difference of the $^1A_1$ CH_2 at its equilibrium angle vs 119° (i.e. the angle prevailing in **CHT**-$^1A_1$). At the CCSD(T) level employed in this study this amounts to 4.35 kcal/mol, which is commensurate with the $^1A_1$/$^1A_2$ energy difference in **CHT**. Therefore, in the final analysis, it may be the effect of the geometric distortion which pushes the open-shell below the closed-shell singlet in **CHT** whereas the aromatic stabilization and the difference in electron repulsion nearly cancel.

This raises the question whether the $^1A_2$ takes over the role of the transition state for enantiomerization of **CHTE** from the $^1A_1$ state (which we find to be a saddle point of the proper nature,[60] in agreement with the earlier MNDO results of Waali[14]). A full clarification of this point would require the calculation of second derivatives at a correlated level of two-determinant theory for $^1A_2$ **CHT** which is currently impossible. However, as the $^1A_1$ and the $^1A_2$ state have the same symmetry in the C_2 subgroup to which the product **CHTE** belongs, both correlate adiabatically with the ground state of the latter and hence nothing speaks against the $^1A_2$ state serving as a lower-energy transition state. If this applies in reality, then the activation enthalpy for the enantiomerization of **CHTE** is predicted to be ~20 kcal/mol by the present calculations.

The IR Spectrum of Cycloheptatetraene. Our computed IR spectra for **CHTE** and **BCT** (BLYP/6-31G* geometries) provide confirmation of the original structural assignments by Chapman et al.[7] The authors found that photolysis of PhCH produces IR absorptions at 1824/1816 cm^{-1}, i.e. at frequencies which lie midway between what would be expected for a strained allene (e.g. 1,2-cyclohexadiene, 1886 cm^{-1})[61] and a substituted cyclopropene (e.g. 1,3,3-trimethylcyclopropene, 1768 cm^{-1}).[7] Thus, an unambiguous distinction between **CHTE** and **BCT** could not be achieved solely on the basis of this frequency.

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(59) (a) The same feature is also responsible for $^1A_2$ lying *below* the $^3A_2$ state, in apparent violation of Hund's rule (for a lucid discussion of this aspect, see: Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109 and references cited therein). (b) At the two-determinant CCSD level employed in this work, the lowest open-shell singlet state of CH_2 ($^1B_1$) lies 1.68 eV above the closed shell singlet ($^1A_1$), in excellent accord with higher-level MRCI calculations.

(60) This is only true at correlated levels of theory such as MP2 or BLYP. At the SCF level, **CHT**-$^1A_1$ is a shallow minimum with a low frequency of b_1 distortion leading to a low-lying transition state for decay to **CHTE**.

(61) Wentrup, C.; Gross, G.; Maquestiau, A.; Flammang, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 542−543.

(62) Next to the bands which we assign to **CHTE** the spectrum in Figure 4 contains a small amount of a side product of the photolysis of phenyldiazomethane. This arises probably by reaction of the initially formed **^{3}PC** with traces of $^3O_2$ which are very difficult to eliminate completely from Ar matrices.[7] Indeed, the peaks at 1757 and 712 cm^{-1} coincide with those of matrix-isolated benzoic acid, as found by Sander (Sander, W. *Angew. Chem.* **1985**, *97*, 964; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 988).

Photolysis of the isotopomer, PhCD, produced IR absorptions at 1820/1811 cm^{-1}. The isotopic shift of -4 cm^{-1} was deemed consistent with the allenic structure of **CHTE** and inconsistent with the cyclopropenic structure of **BCT**. The present results leave no doubt that the original assignment[7] is correct as the entire calculated IR spectrum for **CHTE** is in excellent agreement with the experimental one obtained presently following the same procedure as that used by Chapman et al. (cf. Figure 4).[62] Conversely, the calculated spectrum of **BCT** displays no similarities to the observed one.

The present results also confirm the validity of the earlier argument concerning the isotopic shifts expected for **CHTE** and **BCT**. Thus, the allenic vibrations computed for **CHTE** (1813 cm^{-1}) and **CHTE**-*1-d* (1804 cm^{-1}) reflect an isotopic shift of -9 cm^{-1}. In contrast, the cyclopropenic vibrations computed for **BCT** (1783 cm^{-1}) and **BCT**-*7-d* (1738 cm^{-1}) reflect an isotopic shift of -45 cm^{-1}. These results are important not only in confirming the structural assignment of cycloheptatetraenes obtained upon photolysis of simple phenylcarbenes[7,16,17] but also in confirming the structural assignment of benzobicyclo[4.1.0]hepta-2,4,6-trienes (obtained upon photolysis of naphthylcarbenes).[18] Finally, the computed IR spectra of **CHTE**-*1-d*, **CHTE**-*4-d*, and **CHTE**-*5-d* display very good agreement with Chapman's experimental IR spectra.[7] (Comparisons of computed and experimental spectra are available in supporting information.) Hence, our results confirm beyond any doubt that the photoproduct of ^{3}**PC** is indeed **CHTE**.

Remark about Different Computational Models

Table 1 shows that the different quantum chemical procedures used in the present study give, at least in part, rather widely varying predictions with regard to the C_7H_6 species. In particular, the simple Hartree–Fock model is entirely inadequate, even if one takes the appropriate 2-determinant modifications for the open-shell singlet species, indicating that dynamic correlation plays a crucial role in shaping this potential energy surface. If we take the final CCSD(T) energies as a reference, then MP2 calculations already give a qualitatively correct account of the picture, provided they are based on *restricted* (ROHF) wave functions. What is not reported in Table 1 is that UHF and UMP2 give absurd results for the triplets, even if quintet contributions are projected out of the UHF wave function before MP2 (cf. supporting information). Therefore, UHF/UMP2 calculations should only be trusted when the deviations from the correct $\langle S^2 \rangle$ expectation value are insignificant.

When passing to the coupled cluster level, we note that the perturbative triples corrections are most important in the open-shell species. On the other hand, calculations on **PC** and **CHT** have shown that on the CCSD(T) level, the choice of a reference function (ROHF vs UHF) makes little difference,[53] as pointed out recently by Stanton.[63]

The most encouraging result of the present study is that the very economical BLYP method comes surprisingly close to the CCSD(T) predictions[64] and that the corresponding geometries invariably give the lowest CCSD(T) energies. Unfortunately, it is impossible to calculate open-shell singlets by this method, but this is perhaps a specific problem of the present work. On the other hand, the corresponding force fields permit a direct comparison between calculated and observed IR spectra with no need for elaborate scaling procedures (although these do of course improve the agreement with experiment).[41h,54] Thus, it appears that computational chemists have a new tool in their hands which permits them to reliably make reasonably accurate predictions of relative energies and geometries at moderate cost even in those difficult cases where closed-shell singlets are compared to open-shell triplets.

Conclusions

Quantum chemical calculations at the CCSD(T)/cc-pVDZ//BLYP/6-31G* level corrected systematically for basis set extension effects and zero-point energies show that cycloheptatetraene (**CHTE**) is the most stable species among the $C(CH)_6$ isomers investigated by us. Planar triplet phenylcarbene (^{3}**PC**) lies 13.2 kcal/mol higher in energy, followed by the presumed bicyclo[4.1.0]hepta-2,4,6-triene intermediate (**BCT**), which is nearly at the same energy as ^{1}**PC** (14.9 vs 15.7 kcal/mol relative to **CHTE**), but is only marginally resistant toward ring opening to **CHTE** ($\Delta H^{\ddagger} = 2.7$ kcal/mol). Various states of the elusive cycloheptatrienylidene (**CHT**) lie >20 kcal/mol above **CHTE**, but somewhat surprisingly, the most stable of those is an *open-shell* singlet state ($^{1}A_2$) which lies ~5 kcal/mol below the closed-shell $^{1}A_1$ state, in spite of the latter's aromatic 6π-system. Presumably, the $^{1}A_2$ state of **CHT** takes the role of the lowest energy transition state for enantiomerization of **CHTE**. Slightly above the closed-shell singlet we find two triplet states ($^{3}A_2$ and $^{3}B_1$) which correspond to two Jahn-Teller distorted structures of the iso-π-electronic cycloheptatrienyl radical. They lie very close in energy, and IRC calculations indicate that they interconvert rapidly via C_2 distorted structures.

Comparison of the BLYP/6-31G* calculated IR spectra of **CHTE** and **BCT** with that obtained experimentally by photolysis of ^{3}**PC** (or directly from phenyldiazomethane) shows unambiguously that the original assignment of this spectrum to **CHTE** had been correct. This conclusion is also supported by the good agreement between calculated and observed isotopic shifts for single D substitution in **CHTE**.

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Supporting Information Available: Comparison of computed and experimental IR spectra for **CHTE** and monodeuterated isotopomers; computed IR spectra for **BCT** and **BCT**-*7-d*; figures showing the (U)HF, (U)MP2, and B3LYP geometries of all C_7H_6 stationary points; and a table with the corresponding relative energies (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(63) Stanton, J. F. *J. Chem. Phys.* **1994**, *101*, 371.

(64) The same is true of the B3LYP method, although the corresponding geometries give slightly higher *total* CCSD(T) energies. However, the relative energies are very similar to those obtained by BLYP.