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Carbene Rearrangements Unsurpassed: Details of the C_7H_6 Potential Energy Surface Revealed

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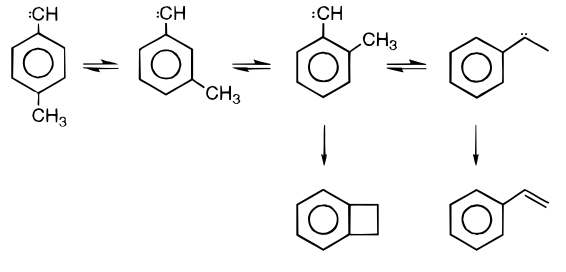
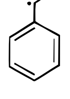
The rearrangement of phenylcarbene (**1**) to 1,2,4,6-cycloheptatetraene (**3**) has been studied theoretically, using SCF, CASSCF, CASPT2N, DFT (B3LYP), CISD, CCSD, and CCSD(T) methods in conjunction with the 6-31G*, 6-311+G*, 6-311G(2d,p), cc-pVDZ, and DZd basis sets. Stationary points were characterized by vibrational frequency analyses at CASSCF(8,8)/6-31G* and B3LYP/6-31G*. Phenylcarbene (**1**) has a triplet ground state ($^3A''$) with a singlet−triplet separation (ΔE_{ST}) of 3−5 kcal mol^{-1}. In agreement with experiment, chiral **3** is the lowest lying structure on this part of the C_7H_6 potential energy surface. Bicyclo[4.1.0]hepta-2,4,6-triene (**2**) is an intermediate in the rearrangement of **1** into **3**, but it is unlikely to be observable experimentally due to a barrier height of only 1−2 kcal mol^{-1}. The enantiomers of **3** interconvert via the $^1A_2$ state of cycloheptatrienylidene (**4**) with an activation energy of 20 kcal mol^{-1}. The "aromatic" $^1A_1$ state, previously believed to be the lowest singlet state of **4**, is roughly 10 kcal mol^{-1} higher in energy than the $^1A_2$ state, and, in violation of Hund's rule, $^3A_2$ is also calculated to lie above $^1A_2$ in energy. Thus, even if $^3A_2$ were populated, it is likely to undergo rapid intersystem crossing to $^1A_2$. We suggest $^3B_1$-**4** is the metastable triplet observed by EPR.

Introduction

Multistep isomerizations of arylcarbenes result in remarkable rearrangements.[2] A spectacular example is afforded by *p*-tolylcarbene. As indicated below, the final products, benzocyclobutene and styrene, arise after a series of ring expansion-ring contraction steps which interconvert the *para, meta, ortho,* and *ipso* carbenes:[3]



Experimental studies of the simplest arylcarbene, phenylmethylene (**1**), have led to the spectroscopic characterization of triplet **1** ($^3A''$-**1**) in low-temperature matrices.[4] The triplet state of **1** is believed to be the ground state, but the singlet−triplet separation has *not* been measured precisely.[5,6] Chapman and co-workers have characterized (spectroscopically) the photochemical rearrangement product of **1**, 1,2,4,6-cycloheptatetraene (**3**).[4b,c] Pyrolytic routes[7] also led to **3**, which appears to be the most stable isomer in this region of the C_7H_6 potential surface.[2] The proposed[3a] intermediacy of bicyclo[4.1.0]-hepta-2,4,6-triene (**2**) in the rearrangement of **1** to **3** is consistent with all available experimental data, but **2** has so far eluded detection by both direct and indirect means. Benzannelated derivatives of **2** have been trapped chemically[8] and observed directly,[9] suggesting that **2** may also be an energy minimum on the C_7H_6 singlet potential energy surface.



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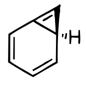

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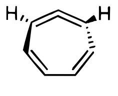

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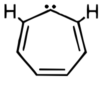

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Previous theoretical studies on the ring expansion of **1** have employed either semiempirical methods[10] or *ab initio* calculations[11] that were performed at levels of theory which are relatively low by current standards.

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(2) This topic has been reviewed extensively; see, *inter alia* (a) Wentrup, C. *Top. Curr. Chem.* **1976**, *62,* 173. (b) Jones, W. M. *Acc. Chem. Res.* **1977**, *10,* 353. (c) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, A. E., Eds.; Academic: New York, 1977; Vol. 1, Chapter 3. (d) Wentrup, C. In *Reactive Intermediates*; Ambramovich, R., Ed.; Plenum: New York, 1980; Vol. 1, Chapter 4. (e) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; pp 220, 242. (f) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Wiley: New York, 1985; Vol. 3, p 91. (g) Jones, W. M. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 3. (h) Wentrup, C. In *Methoden der Organischen Chemie* (Houben-Weyl); Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E19b, p 824 ff.

(3) (a) Vander Stouw, G. G.; Shechter, H. *Diss. Abstr.* **1965**, *25,* 6974. Vander Stouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94,* 1655. (b) Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92,* 4739. (c) Hedaya, E. Kent, M. E. *J. Am. Chem. Soc.* **1971**, *93,* 3283. (d) Mayor, C.; Wentrup, C. *J. Am. Chem. Soc.* **1975**, *97,* 7467. (e) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M. *Tetrahedron* **1985**, *41,* 1479. (f) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110,* 501.

(4) (a) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84,* 4990. (b) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104,* 1779. (c) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109,* 2456.

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During the course of this work, we became aware of two similar independent studies on the same subject.[12,13] All studies found **3** to be considerably more stable than **4**. The most extensive previous computational investigations of the C_7H_6 singlet potential energy surface is the 1977 MINDO/3 study of Dewar and Landman,[10b] which located the bicyclo[4.1.0]heptatriene intermediate **2**, as well as the transition structures connecting **1** with **2** (**TS1**) and **2** with **3** (**TS2**). While the qualitative features of the potential energy surface (PES) still seem quite reasonable, the authors pointed out possible uncertainties in their quantitative results, such as the stability of the bicyclic cyclopropene **2**, due to the MINDO/3 underestimation of the strain in three-membered rings.

The nature and the role of cycloheptatrienylidene (**4**, tropylidene) is of long-standing interest and controversy in C_7H_6 chemistry.[2c] Numerous experimental studies[7,8a,10d,14,15] have failed to clarify the relationship between **3** and **4**. A metastable triplet state of **4** has been observed by EPR,[15] but the ground state of **4** has not been established. Furthermore, the exact nature of the observed triplet state ($^3B_1$ or $^3A_2$) is still open.

The previous computational investigations of **4** have not been conclusive. Singlet **4** has been predicted to be either a potential energy minimum,[11b] or a transition state for the racemization of **3**.[10c] Both a singlet[11] and a triplet[10c] ground state of **4** have been proposed.

Clearly, the time has come for a comprehensive high level *ab initio* investigation to answer the many open questions concerning the C_7H_6 singlet potential energy surfaces (PES).[13] Based on both single and multiconfigurational reference wave functions, we have now computed important parts of the C_7H_6 PES and address the following key issues:

1. What is the singlet−triplet energy separation in phenylcarbene (**1**)? How well do different theoretical methods reproduce the singlet−triplet energy splitting in methylene, and can they be expected to perform equally well for **1**?

2. Is bicyclo[4.1.0]heptatriene (**2**) an intermediate in the rearrangement of **1** to **3** on the singlet PES? If so, how high are the barriers to formation of **2** from singlet **1** and to rearrangement of **2** to **3**? Should **2** be experimentally observable?

3. What is the ground state of cycloheptatrienylidene (**4**)? What are the relative energies of the many low-lying electronic states of **4**? Is the lowest singlet state of **4** an energy minimum or a transition structure for the racemization of **3**? What is the barrier to racemization of **3**?

4. What are the magnitudes of the diamagnetic ring currents in the closed-shell singlet states of **1**−**4** and in the transition state(s) connecting **1** with **3**? In particular, do the six π electrons in the closed-shell cycloheptatrienylidene singlet state of **4** result in aromaticity?

Computational Methods

Geometries of all stationary points were optimized using analytical energy gradients of self-consistent-field,[16] density functional theory (DFT),[17] complete active space SCF (CASSCF),[18] and configuration interaction (CI)[19] calculations. Single-point energies were further evaluated using CASPT2N,[20] coupled cluster with all single and double substitutions (CCSD),[21] and CCSD calculations with the effects of connected triple excitations included perturbatively [CCSD(T)].[22] For the DFT computations, Becke's three-parameter exchange-correlation functional[23] including the nonlocal gradient corrections described by Lee−Yang−Parr (LYP)[24] was used, as implemented in the Gaussian 94 program package.[25] Residual cartesian and internal coordinate gradients for the stationary points were always less than 10^{-5} atomic

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(5) (a) For reviews on arylcarbene spin states, see Trozzolo, A. M.; Wasserman, E. In *Carbenes*, Moss, R. A.; Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. 2, Chapter 5. (b) Platz, M. S. In *Kinetics and Spectroscopy of Carbenes and Diradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; Chapter 6. (c) Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311. (d) Savino, T. G.; Kanakarajan, K.; Platz, M. S. *J. Org. Chem.* **1986**, *51*, 1305.

(6) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.

(7) (a) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1967**, *89*, 3069. (b) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391. (c) Joines, R. C.; Turner, A. B.; Jones, W. M. *J. Am. Chem. Soc.* **1969**, *91*, 7754. (d) Schissel, P.; Kent, M. E.; McAdoo, D. J.; Hedaya, E. *J. Am. Chem. Soc.* **1970**, *92*, 2147.

(8) (a) Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218. (b) Billups, W. E.; Lin, L. P.; Chow, W. Y. *J. Am. Chem. Soc.* **1974**, *96*, 4026. (c) Billups, W. E.; Reed, L. E. *Tetrahedron Lett.* **1977**, 2239. (d) Billups, W. E.; Reed. L. E.; Casserly, E. W.; Lin, L. P. *J. Org. Chem.* **1981**, *46*, 1326. (e) Mykytka, J. P.; Jones, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 5933. (f) Halton, B.; Officer, D. L. *Tetrahedron Lett.* **1981**, *22*, 3687.

(9) (a) West, P. R.; Mooring, A. M.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem.* **1986**, *51*, 1316. (b) Albrecht, S. W.; McMahon, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 855.

(10) (a) Tyner, R. L.; Jones, W. M.; Ohrn, Y.; Sabin, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 3765. (b) Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6179. (c) Waali, E. E. *J. Am. Chem. Soc.* **1981**, *103*, 3604. (d) Balci, M.; Winchester, W. R.; Jones, W. M.. *J. Org. Chem.* **1982**, *47*, 5180. (e) Kassaee, M. Z.; Nimlos, M. R.; Downie, K. E.; Waali, E. E. *Tetrahedron* **1985**, *41*, 1579. (f) Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J. *Tetrahedron* **1985**, *41*, 1601.

(11) (a) Radom, L.; Schaefer, H. F.; Vincent, M. A. *Nouv. J. Chem.* **1980**, *4*, 411. (b) Janssen, C. L.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 5030.

(12) All three research groups have exchanged computational results and drafts of the manuscripts describing them. Although they describe different computational methods, which seem to give somewhat different orderings of the electronic states of **4**, the relative energies of the lowest singlet states of **1**−**4**, computed by all three groups, are quite similar. This agreement suggests that the portion of the C_7H_6 singlet potential surface on which **1**−**4** lie has been accurately described by all three of the different sets of calculations.

(13) (a) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. (b) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022.

(14) (a) Wentrup, C.; Wilczek, K. *Helv. Chim. Acta* **1970**, *53*, 1459. (b) Waali, E. E.; Jones, W. M. *J. Am. Chem. Soc.* **1973**, *95*, 8114. (c) Mayor, C.; Jones, W. M. *Tetrahedron Lett.* **1977**, 3855. (d) Waali, E. E.; Lewis, J. M.; Lee, D. E.; Allen, E. W.; Chappell, A. K. *J. Org. Chem.* **1977**, *42*, 3460. (e) Hackenberger, A.; Dürr, H. *Tetrahedron Lett.* **1979**, 4541. (f) Kirmse, W.; Loosen, K.; Sluma, H.-D. *J. Am. Chem. Soc.* **1981**, *103*, 5935. (g) Harris, J. W.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *104*, 7329. (h) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1986**, *108*, 1713. (i) Chateauneuf, J. E.; Horn, K. A.; Savino, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 539.

(15) Kuzaj, M.; Lüerssen, H.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 480; *Angew. Chem.* **1986**, *98*, 476.

(16) Pulay, P. In *Modern Theoretical Chemistry;* Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 4, p 153.

(17) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(18) (a) Roos, B. O. *Int. J. Quantum Chem. Symp.* **1980**, *14*, 175. (b) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 339.

(19) (a) Brooks, B. R.; Laidig, W. D.; Saxe, P.; Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *72*, 4625. (b) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *85*, 963.

(20) (a) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483. (b) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(21) Scheiner, A. C.; Scuseria, G. E.; Lee, T. J.; Rice, J. E.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 5391.

(22) Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *176*, 27.

(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(25) 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.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., *Gaussian 94, Revision B.3*, Gaussian, Inc., Pittsburgh PA, 1995.

units. CASSCF harmonic vibrational frequencies were evaluated via finite differences of analytical gradients.[26]

With the exception of the CISD calculations, all geometry optimizations were performed using the 6-31G* basis set.[27] A double-ζ (DZd) basis set, derived from Dunning's C(9s5p/4s2p) and H(4s/2s) basis sets[28,29] with one set of six-component *d* polarization functions on all carbon atoms [a_d(C) = 0.75] was employed for the CISD optimizations. Three further basis sets were utilized for single point energy evaluations: a standard 6-311+G* basis set,[30] the 6-311G(2d,p) basis set,[31] and Dunning's correlation-consistent polarized valence double-zeta basis set (cc-pVDZ).[32]

A preliminary RHF/6-31G* exploration of the reaction coordinate for ring expansion of **1** was performed by stepping θ, the C1−C7−C6 angle (for numbering see Figures 1 and 2) in **3**, from the RHF/6-31G* optimized value ($\theta = 112.8°$) down to $\theta = 30°$, which is close to the corresponding angle in **1**. At each value of θ the geometry of the rest of the molecule was optimized. In this manner we located an energy maximum near $\theta = 85°$ (**TS2**), a minimum near $\theta = 65°$ (**2**), and another maximum near $\theta = 50°$ (**TS1**), before reaching singlet **1**. Subsequent full geometry optimizations near these extrema resulted in structures for the bicyclic cyclopropene intermediate (**2**) and the two transition states (**TS1** and **TS2**). The RHF geometries were then reoptimized with the CASSCF method.[18]

In the CAS computations, an eight-electron, eight-orbital active space, hereafter designated (8,8), was used for all species. The (8,8) active space for **1** consisted of the seven conjugated π/π^* orbitals plus the in-plane nonbonding orbital on the carbene carbon. For **3**, the eight π/π^* orbitals of the four double bonds were employed. The active space for the two transition states (**TS1** and **TS2**) consisted of six orbitals that were mainly π/π^* in character, plus a σ/σ^* pair for the partially formed/broken C−C single bond. For **4**, the seven π/π^* MOs plus the in-plane nonbonding orbital on the carbene carbon comprised the active space.

The choice of active space for **2** was somewhat problematic. In order to maintain consistency in the size of the active space over the entire singlet potential surface, CASSCF(8,8) calculations were required. Six orbitals, primarily π in character, were chosen easily. However, the decision of which σ/σ^* pair to choose—the pair corresponding to the C−C bond between the bridgehead carbons or that corresponding to the external C−C single bond of the cyclopropene ring—seemed somewhat arbitrary. Since both bonds were about the same length (1.50 Å) at the RHF/6-31G* level, it was not obvious which set of σ/σ^* orbitals should be placed in the active space for correlation.

Upon inspection of the HF orbitals, however, it was relatively straightforward to locate the σ/σ^* MO pair corresponding to the external bond. Therefore, this bond was chosen for inclusion in the active space since its orientation causes its orbitals to mix considerably with the π orbitals of the six-membered ring.

In order to determine the consequences of this somewhat arbitrary choice, CASSCF(6,6) calculations on **2** were also performed using an active space that consisted of just the six MOs which were primarily π/π^* in character. These CASSCF(6,6) calculations led to an optimized geometry for **2** with a somewhat shorter external C−C bond length than the geometry optimized with the (8,8) active space. However, the relative energies of the CASSCF(6,6) and CASSCF(8,8)/6-31G* geometries were the same to within 0.1 kcal mol^{-1}, when dynamic electron correlation for both CASSCF wave functions was included by CASPT2N single-point energy calculations, using the 6-31G*, cc-pVDZ, and 6-311G(2d,p) basis sets.

In order to assess the aromatic/antiaromatic character of the various cyclic π-systems, we computed (at RHF/6-31G* using the GIAO approach)[35] the absolute magnetic shieldings, termed the "nucleus independent chemical shifts" (NICS), at selected points in space as a function of the electron density.[33,34] NICS are taken negative to conform with chemical convention. The geometrical center of the ring's heavy atoms served as the most easily defined reference point.

These isotropic chemical shifts yield information about ring currents and aromatic properties of molecules. Following the convention, aromatic molecules have negative isotropic NICS, while antiaromatic molecules have positive values. The absolute magnitude of a negative NICS is approximately proportional to the aromatic stabilization energy.[34]

In this study we used the following programs: Gaussian 94[25] for HF, DFT, and CASSCF calculations, MOLCAS[36] for CASPT2N,[37] and PSI 2.0.8[40] for CISD, CCSD, and CCSD(T) calculations. Unless noted otherwise, "CASPT2N" energies are those computed at the CASPT2N(8,8)/cc-pVDZ//CASSCF(8,8)/6-31G* + ZPVE level, and "B3LYP" energies are those computed at the B3LYP/6-311+G*//B3LYP/6-31G* + ZPVE level of theory, where ZPVE are the zero-point vibrational energies.

Results and Discussion

Phenylcarbenes (^{1}A′-**1** and ^{3}A″-**1**, Figure 1). The geometries of singlet and triplet **1** are very similar at CASSCF/6-31G* (first entry), B3LYP/6-31G* (second

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[26] Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *S13*, 225.

[27] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[28] Huzinaga, S. *J. Chem. Phys.* **1965**, *42***,** 1293.

[29] Dunning, T. H. *J. Chem. Phys.* **1970**, *53***,** 2823.

[30] (a) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

[31] Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

[32] Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

[33] The shifts were computed using the GIAO-algorithm, as implemented in the Gaussian 94 program package[25] (see also ref 34).

[34] Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[35] Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

[36] Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O., *MOLCAS*-3, University of Lund, Sweden.

[37] Since the CASPT2N method—occasionally denoted "CASPT2−0"—sometimes overestimates the stability of open-shell systems relative to closed-shell systems, we also performed these calculations with the CASPT2-g1 procedure.[38,39] However, the CASPT2-g1/6-31G* relative energies for **1**−**4** differ very little from the CASPT2N values; so we report only the CASPT2N results.

[38] Andersson, K. *Theor. Chim. Acta* **1995**, *91*, 31.

[39] We thank M. Fülscher for supplying us with the modified version of MOLCAS.

[40] PSI2.0.8: Janssen, C. L.; Seidl, E. T.; Scuseria, G. E.; Hamilton, T. P.; Yamaguchi, Y.; Remington, R. B.; Xie, Y.; Vacek, G.; Sherrill, C. D.; Crawford, T. D.; Fermann, J. T.; Allen, W. D.; Brooks, B. R.; Fitzgerald, G. B.; Fox, D. J.; Gaw, J. F.; Handy, N. C.; Laidig, W. D.; Lee, T. J.; Pitzer, R. M.; Rice, J. E.; Saxe, P.; Scheiner, A. C.; Schaefer, H. F., PSITECH, Inc., Watkinsville, GA, 30677, 1994.

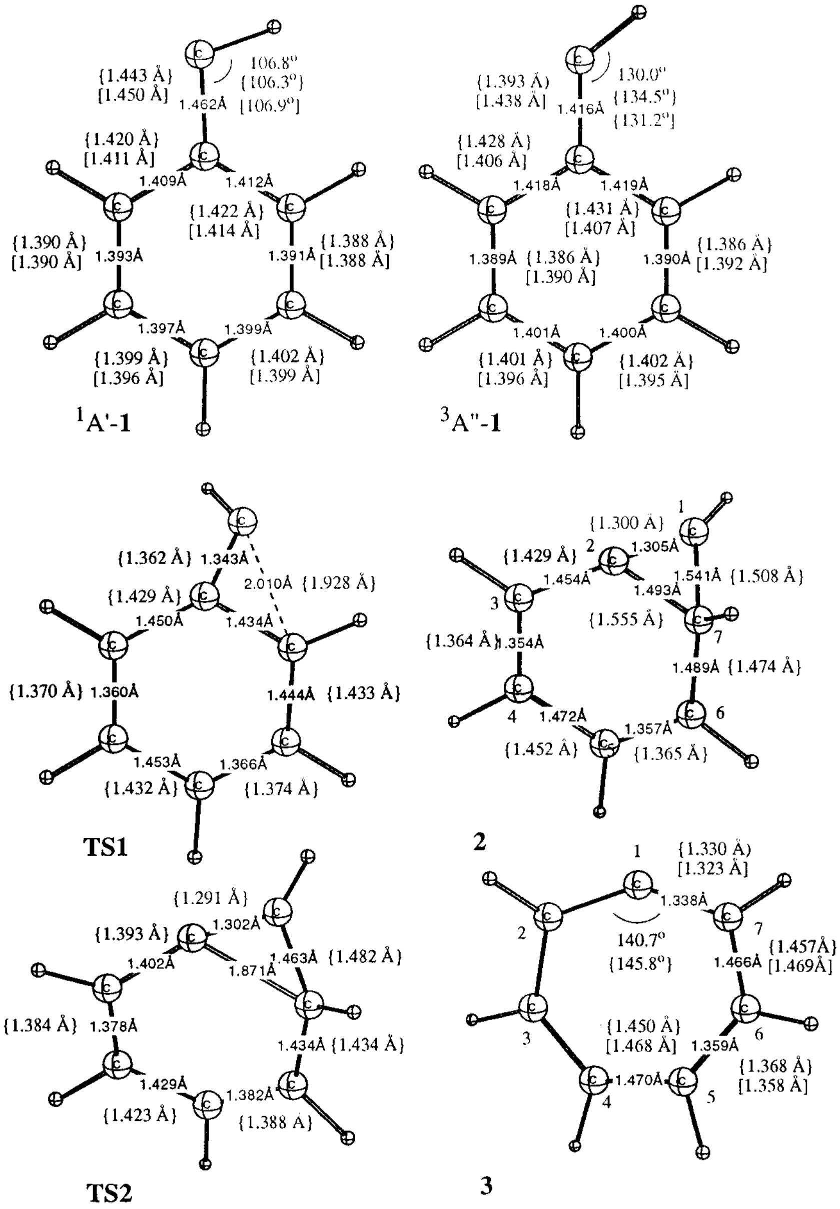

Figure 1. CASSCF(8,8)/6-31G* (in bonds), B3LYP/6-31G* (in curly brackets), and CISD/DZd (in square brackets) optimized structures of phenylcarbene (**1**), bicyclo[4.1.0]hepta-2,4,6-triene (**2**), cycloheptatetraene (**3**), and their interconnecting transition structures (**TS1** and **TS2**). Bond lengths in angstroms, angles in degrees.

entry), and CISD/DZd (third entry): while ^{1}A′-**1** has a small angle (106.8°; 106.3°; 106.9°) at the carbene carbon and a long exocyclic C−C bond (1.462 Å; 1.443 Å; 1.450 Å), ^{3}A″-**1** has a larger angle (130.0°; 134.5°; 131.2°) at the carbene carbon and a shorter exocyclic C−C bond (1.416 Å; 1.393 Å; 1.438 Å).

Singlet−triplet energy differences (ΔE_{ST}) in carbenes are often difficult to compute reliably.[41] SCF (UHF or ROHF for $^3B_1$-CH_2 and RHF for $^1A_1$-CH_2) and MPn (n = 2−4) treatments all fail to reproduce even approximately the experimental ΔE_{ST} in methylene.[42] This failure is due to the improper single configuration description of the singlet, when a two-configuration reference wave function is needed.[41] This deficiency is remedied by explicit correlation of the lone pair of the singlet at CASSCF(2,2).

While the CAS levels reproduce the experimental ΔE_{ST} for methylene quite well (error: 1.1 kcal mol^{-1} at CASSCF/cc-pVTZ//CASSCF/6-31G*, Table 1), they overestimate the ΔE_{ST} for phenylcarbene. Singlet phenylcarbene, with a vacant p-orbital, is stabilized more than the triplet, with its half-filled MO, by phenyl conjugation. As a consequence, the ΔE_{ST} of phenylcarbene is smaller than that of methylene.

Inclusion of dynamic electron correlation by CASPT2N leads to an increase of ΔE_{ST} in methylene and in **1** by 3−4 kcal mol^{-1} over the CASSSCF values. The CASPT2-g1 procedure[38] gives ΔE_{ST} of methylene closer to experiment than the CASPT2N; however, CASSCF still performs better. Both CASPT2 methods overestimate the stabilization of the triplet relative to the singlet by inclusion of dynamic electron correlation.

The stabilizing effect of a phenyl group on singlet methylene, expressed as the difference between ΔE_{ST} between methylene and phenylcarbene ($\Delta\Delta E_{ST}$) also is

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[41] Review: Shavitt, I. *Tetrahedron* **1985**, *41*, 1531.

[42] (a) 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. (b) Leopold, D. G.; Murray, K. K.; Miller, A. E. S.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849. (c) Bunker, P. R.; Sears, T. J. *J. Chem. Phys.* **1986**, *85*, 4866. (d) Bunker, P. R.; Jensen, P.; Kraemer, W. P.; Beardsworth, R. *J. Chem. Phys.* **1986**, *85*, 3724.

Table 1. ΔE_{ST} of CH_2 and 1 and $\Delta\Delta E_{ST}$ for the Isodesmic Comparison ($^3CH_2 + {}^1C_6H_5CH \rightarrow {}^1CH_2 + {}^3C_6H_5CH$) at Various Levels of Theory (in kcal mol^{-1} including ΔZPVE[a]). Optimization at the Level Given Unless Otherwise Noted

level	ΔE_{ST} of CH_2	ΔE_{ST} of **1**	$\Delta\Delta E_{ST}$
(U)HF/6-31G*	30.5	–	–
R(O)HF/6-31G*	27.2	17.4	9.8
(U)MP2/6-31G*	20.5	–	–
RMP2/6-31G*	20.1	–	–
(U)MP3/6-31G*//(U)MP2/6-31G*	18.0	–	–
(U)MP4SDTQ/6-31G*// (U)MP2/6-31G*	16.7	–	–
CASSCF(2,2)/6-31G* [b,c]	14.0	13.3	0.7
CASSCF(2,2)/cc-pVDZ[b,c]	11.6	9.5	2.1
CASSCF(2,2)/6-311G(2d,p)[b,c]	10.7	8.5	2.2
CASSCF(2,2)/cc-pVTZ[b,c]	10.2	–	–
CASPT2N(2,2)/6-31G* [b,d]	17.4	14.1	3.3
CASPT2N(2,2)/cc-pVDZ[b,d]	15.0	13.0	2.0
CASPT2N(2,2)/6-311G(2d,p)[b,d]	14.7	12.5	2.2
CASPT2N(2,2)/cc-pVTZ[b,d]	14.3	–	–
CASPT2-g1(2,2)/6-31G* [b,d]	15.4	–	–
CASPT2-g1(2,2)/cc-pVDZ[b,d]	12.7	–	–
CASPT2-g1(2,2)/6-311G(2d,p)[b,d]	12.1	–	–
CASPT2-g1(2,2)/cc-pVTZ[b,d]	11.4	–	–
(U)B3LYP/6-31G*	13.3	7.4	5.9
(U)B3LYP/6-311+G*// (U)B3LYP/6-31G*	11.4	5.0	6.4
CISD/DZd[e]	13.3	10.2	3.1
CISD+Q/DZd[e]	12.9	7.8	5.1
CCSD/DZd//CISD/DZd[e]	13.5	7.7	5.8
CCSD(T)/DZd//CISD/DZd[e]	12.9	6.2	6.7
experiment	9.1[f]	2−5[g]	4−7

[a] ZPVE differences at the respective optimization level, unless noted otherwise. [b] Singlet geometry optimized at CASSCF(2,2)/6-31G*; triplet at ROHF/6-31G*. [c] Single point energies calculated using CASSCF for singlet, ROHF for triplet. [d] Single point energies were calculated using CASPT2 for both singlet and triplet. [e] Including ΔZPVE at B3LYP/6-31G*. [f] 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. [g] The ΔE_{ST} for phenylcarbene of 2−5 kcal mol^{-1}: Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487 and literature cited therein.

summarized in Table 1. Systematic computational inadequacies, such as errors introduced by using finite basis sets, should at least partially cancel in $\Delta\Delta E_{ST}$. While all methods reproduce the correct sign of $\Delta\Delta E_{ST}$, the CASSCF and CASPT2N values are the smallest. CASPT2N probably overestimes the delocalization energy of triplet **1**, as it does in the allyl and benzyl radicals.[43] Although the ΔE_{ST} in phenylcarbene is not known precisely, the B3LYP, configuration interaction, and coupled cluster results lie within the experimental estimates.[6]

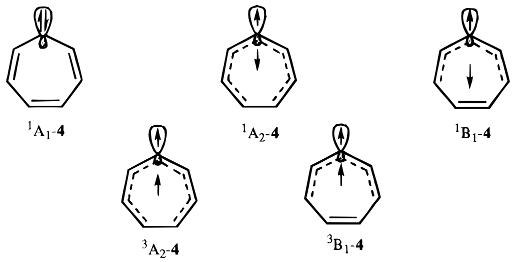
Our best estimate for ΔE_{ST} of **1** is 2.4 kcal mol^{-1}, derived by subtracting $\Delta\Delta E_{ST}$ [CCSD(T)/DZd/CISD/DZd + ZPVE(B3LYP/6-31G*)] from the experimental value of $\Delta E_{ST} = 9.1$ kcal/mol in methylene. For comparison, the same procedure gives a ΔE_{ST} of **1** of 2.7 kcal mol^{-1} at B3LYP/6-311+G*//B3LYP/6-31G* + ZPVE.

Bicyclo[4.1.0]hepta-2,4,6-triene (2). Although **2** has been postulated to be an intermediate in arylcarbene rearrangements,[2] **2** has never been observed. The relative energy difference between **2** and ^{1}A′-**1** is small; CASPT2N favors **2** by 2.9 kcal mol^{-1}, while **1** is 2.5 kcal mol^{-1} more stable than **2** at B3LYP.

The activation barrier for formation of **2** from ^{1}A′-**1** (*via* **TS1**, CAS: 13.2 kcal mol^{-1}; B3LYP: 14.9 kcal mol^{-1}) is much larger than the 1.5 kcal mol^{-1} (CASPT2N) [1.1 kcal mol^{-1} (B3LYP)] barrier (*via* **TS2**) for **2** rearranging into **3**. The latter very low barrier is easily understood in terms of it being a Woodward−Hoffmann allowed, disrotatory opening of a cyclohexadiene ring and relief of ring strain in **2**, providing a driving force. Thus, **2** is not stable kinetically and its observation is unlikely.

1,2,4,6-Cycloheptatetraene (3). In agreement with experimental observations[7] and previous computational studies,[10,11] **3** is the most stable product derived from phenylcarbene (**1**) or tropylidene (**4**) precursors. However, due to the large strain imposed on the allenic moiety by its incorporation in a seven-membered ring,[44] **3** has been found experimentally to be highly reactive. The dihedral angle of about 50° between the bonds from the terminal allenic carbons to C-3 and C-6 (Figure 1) differs markedly from the dihedral angle of 90° in an unstrained allene; and, in addition, the C−C−C bond angle at the central carbon deviates by about 40° from linearity. Nevertheless, the allenic double bonds are slightly shorter than the non-allenic double bonds. Although the strongly alternating C−C bond lengths in **3** suggest little delocalization, our calculations indicate that there is a diamagnetic ring current in **3**, albeit of a smaller magnitude than in the six-electron π system of the $^1A_1$ state of planar cycloheptatrienylidene (**4**).

2,4,6-Cycloheptatrienylidene (4). Despite a considerable number of experimental[7,14,15] and theoretical[10,11] investigations, the role of cycloheptatrienylidene (**4**) in C_7H_6 chemistry is still unclear. One reason for this confusion is perhaps the large number of low-lying spin states available to this intriguing carbene. We have considered five different spin states for planar, C_{2v}-symmetric **4**: three singlets ($^1A_1$, $^1A_2$, and $^1B_1$) and two triplets ($^3B_1$ and $^3A_2$). This is the first report on the energies of all possible spin states at a *uniform* level (CASPT2N(8,8)/cc-pVDZ//CASSCF(8,8)/6-31G*; Figure 2; Tables 2 and 3). For ease in the following discussion, the eight active orbitals for **4** are depicted in Figure 3.



Triplet States. The two triplet states of **4** are close in energy, depending upon the level of theory. At the CASSCF level, the $^3B_1$ state is 2−3 kcal mol^{-1} below the $^3A_2$ state; the latter has one imaginary vibrational frequency.

Following the imaginary mode of $^3A_2$-**4** leads, via some intermediate geometries of C_s symmetry, to the $^3B_1$ state. This process is related to pseudorotation in the Jahn−Teller-distorted cycloheptatrienyl radical.[45] However, in **4** the in-plane radical center at C-1 lifts the degeneracy between both the seven minima and the seven maxima that exist on the potential surface for pseudorotation of the cycloheptatrienyl radical. Consequently, there seems to be only one energy maximum ($^3A_2$) and only one energy minimum ($^3B_1$) on the PES of **4**.

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(43) Hrovat, D. A.; Borden, W. T. *J. Phys. Chem.* **1994**, *98*, 10460.

(44) Strained cyclic allenes, including **3**, have been reviewed: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(45) For an excellent discussion of pseudorotation in Jahn-Teller distorted molecules see Liehr, A. *J. Phys. Chem.* **1963**, *67*, 389.

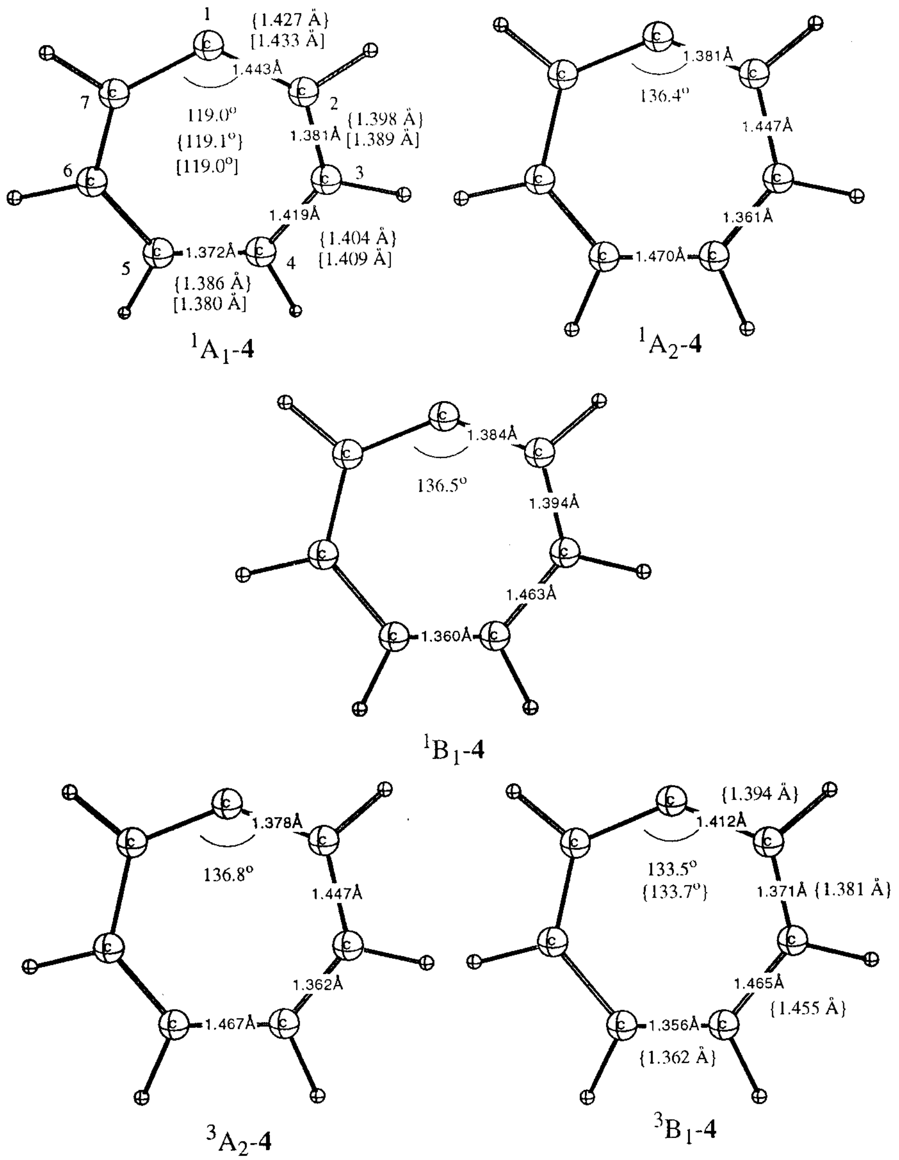

Figure 2. CASSCF(8,8)/6-31G* (in bonds), B3LYP/6-31G* (in curly brackets), and CISD/DZd (in square brackets) optimized structures of the five C_{2v} symmetric cycloheptatrienylidene (**4**) states. Bond lengths in angstroms, angles in degrees.

Table 2. Absolute SCF and CASSCF Energies (in au) of C_7H_6 Isomers

species	R(O)HF/ 6-31G*	CAS(8,8)/ 6-31G*	CAS(8,8)/ cc-pVDZ//[a]	CAS(8,8)/ 6-311G (2d,p)//[a]	CASPT2N/ 6-31G* (ref wt %)//[a]	CASPT2N/ cc-pVDZ (ref wt %)//[a]	CASPT2N/ 6-311G(2d,p)//[a]	B3LYP/ 6-31G*	B3LYP/ 6-311+G*// B3LYP/ 6-31G*
3A″-**1**	−268.47590	−268.55494	−268.57547	−268.61941	−269.36231 (78.8)	−269.39486 (77.4)	−269.66390 (75.9)	−270.22927	−270.28912
1A′-**1**	−268.44864	−268.53807	−268.56141	−268.60705	−269.34083 (79.2)	−269.37535 (77.8)	−269.64510 (76.4)	−270.21797	−290.28154
TS1	−268.40288	−268.50537	−268.52750	−268.57343	−269.32073 (78.7)	−269.35273 (77.4)	–	−270.19457	−270.25702
2	−268.42684	−268.53373	−268.55351	−268.59889	−269.35245 (78.7)	−269.38061 (77.5)	–	−270.21790	−270.27810
2 (6,6)[b]	–	−268.51083[b]	–	–	−269.35203[b] (78.1)	−269.37976[b] (76.9)	–	–	–
TS2	−268.41078	−268.52181	−268.54222	−268.58750	−269.34670 (78.4)	−269.37637 (77.1)	–	−270.21446	−270.27524
3	−268.44773	−268.56640	−268.58687	−268.63232	−269.37403 (78.9)	−269.40401 (77.6)	−269.67494 (76.2)	−270.24237	−270.30437
$^1A_2$-**4**	–	−268.53007	−268.55017	−268.59406	−269.33827 (78.6)	−269.37044 (77.2)	−269.63981 (75.7)	–	–
$^1A_1$-**4**	−268.42407	−268.51705	−268.53945	−268.58496	−269.32508 (78.9)	−269.35838 (77.5)	−269.62833 (76.1)	−270.20784	−270.27205
$^3B_1$-**4**	−268.43562	−268.52971	−268.54999	−268.59382	−269.33453 (78.7)	−269.36682 (77.3)	−269.63572 (75.8)	−270.20663	−270.26774
$^3A_2$-**4**	−268.43178	−268.52357	−268.54395	−268.58779	−269.33394 (78.5)	−269.36646 (77.1)	−269.63610 (75.6)	–	–
$^1B_1$-**4**	–	−268.49839	−268.51946	−268.56332	−269.31111 (78.4)	−269.34437 (77.0)	not converged	–	–

[a] Energies calculated at the CASSCF(8,8)/6-31G* optimized geometries. [b] Calculated at the CASSCF(6,6)/6-31G* optimized geometry, and using a CASSCF(6,6)/6-31G* reference wavefunction.

At CASPT2N the electronic energies of the $^3A_2$ and $^3B_1$ states are within 0.2−0.4 kcal mol^{-1}, depending on the basis set. Since the topology of the PES for $^3A_2$-**4** and $^3B_1$-**4** obviously changes on going from CASSCF to CASPT2N, it is inappropriate to apply the CASSCF ΔZPVE correction to the CASPT2N energies. Thus, it is not at all clear at the CASPT2N level which triplet state actually is the lower in energy.

The change in the relative energies of $^3A_2$ and $^3B_1$ on going from CASSCF to CASPT2N can be attributed to the more delocalized $^3A_2$ vs $^3B_1$ wavefunction. The bond lengths in Figure 2 suggest that the $^3A_2$ state resembles

Table 3. Relative SCF and CASSCF Energies (kcal mol^{-1}) of C_7H_6 Isomers; Relative Energies in kcal mol^{-1} Including ZPVE Corrections

species	R(O)HF 6-31G*	ΔZPVE[b] (NI)	CAS(8,8)/ 6-31G*	ΔZPVE[b] (NI)	CAS(8,8)/ cc-pVDZ[a]	CAS(8,8)/ 6-311G(2d,p)[a]	CASPT2N/ 6-31G*[a]	CASPT2N/ cc-pVDZ[a]	CASPT2N/ 6-311G(2d,p)[a]	B3LYP/ 6-31G*	ΔZPVE[b] (NI)	B3LYP 6-311+G*[c]
3A″-**1**	0.0	68.8 (0)	6.3	−0.9 (0)	6.3	7.2	6.5	4.8	6.0	7.1	−1.1 (0)	8.5
1A′-**1**	17.4	+0.3 (0)	17.6	−0.2 (0)	15.8	15.7	20.6	17.8	18.5	14.5	−0.8 (0)	13.5
TS1	45.7	−0.1 (1)	37.1	−1.2 (1)	36.1	35.8	32.2	31.0	–	28.7	−1.3 (1)	28.4
2	31.9	+1.1 (0)	20.7	+0.2 (0)	21.1	21.2	13.7	14.9	–	14.9	−0.5 (0)	16.0
TS2	40.8	−0.1 (1)	27.1	−0.9 (1)	27.1	27.2	16.2	16.4	–	16.3	−1.2 (1)	17.1
3	19.1	+1.4 (0)	0.0	68.2 (0)	0.0	0.0	0.0	0.0	0.0	0.0	65.2 (0)	0.0
$^1A_2$-**4**	–	–	21.3	−1.5 (1)	21.5	22.5	20.9	19.6	20.5	–	–	–
$^1A_1$-**4**	32.5	+1.3 (0)	31.6	+0.6 (0)	30.4	30.3	31.3	29.2	29.8	21.1	−0.6 (1)	19.7
$^3B_1$-**4**	25.3	+0.7 (0)	22.1	−0.9 (0)	22.2	23.3	23.9	22.4	23.7	19.2	−3.0 (1)	20.0
$^3A_2$-**4**	27.7	−1.6 (1)	24.5	−2.4 (1)	24.5	25.5	22.8	21.2	22.0	–	–	–
$^1B_1$-**4**	–	–	38.5	−4.2 (3)	38.1	39.1	35.3	33.2	not converged	–	–	–

[a] Energies calculated at the CASSCF(8,8)/6-31G* optimized geometries. HF relative energies are corrected for differences in (unscaled) HF zero point vibrational energies (ZPVE). All other relative energies include corrections for (unscaled) CASSCF(8,8)/6-31G* ZPVE. [b] Difference in ZPVE (unscaled), relative to $^3A''$-**1** for HF calculations, and relative to **3** for all other calculations. NI = number of imaginary vibrational frequencies. [c] Energies calculated at the B3LYP/6-31G* optimized geometries.

Table 4. Absolute Energies (in au) of the Triplet and Singlet States of Phenylcarbene (1)[a] and ΔE_{ST} (kcal/mol), after Correction for the Zero Point Energy Difference[b]

	CISD/DZd	CISD+Q/DZd	CCSD/DZd// CISD/DZd	CCSD(T)/DZd// CISD/DZd
$^3A''$	−269.20056	−269.32256	−269.37988	−269.41687
$^1A'$	−269.18483	−269.31063	−269.36815	−269.40751
3	−269.19549	−269.32694	−269.39022	−269.43220
ΔE_{ST}	10.2	7.8	7.7	6.2

[a] Based on RHF wavefunctions. [b] Including ZPVE at B3LYP/6-31G*.

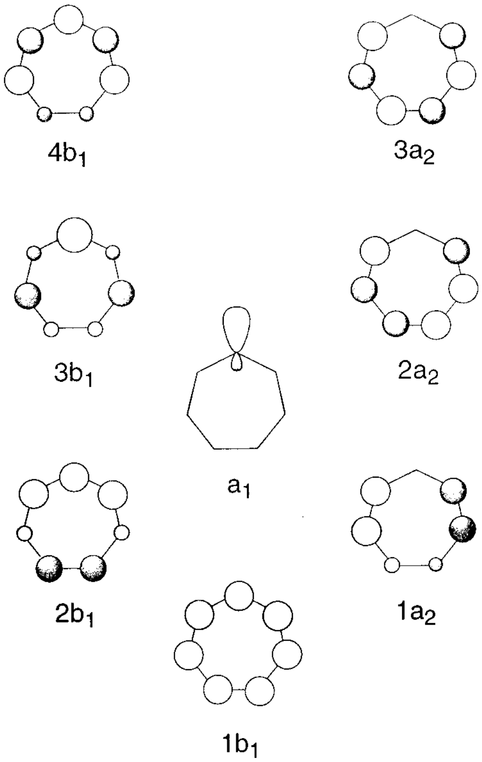

Figure 3. Schematic diagram of the π, π^*, and carbenic molecular orbitals of planar C_{2v} cycloheptatrienylidene (**4**). The vertical positions of the MOs correspond roughly to their relative energies.

a heptatrienyl radical, whereas the $^3B_1$ state rather corresponds to a pentadienyl radical, whose terminal atoms interact only weakly with the connecting C−C double bond. Inclusion of dynamic correlation is more important for the more delocalized wavefunctions, resulting in selective stabilization.[46]

However, it seems quite likely that CASPT2N overestimates the effect of dynamic electron correlation on selectively stabilizing $^3A_2$ (see also discussion of Table 1 above).[43] Therefore, we conjecture that the lowest triplet is probably $^3B_1$, which most likely also is the metastable species observed by EPR.[15,47] This conclusion is based not just on the relative energies of $^3A_2$ and $^3B_1$ at the CASSCF and CASPT2N levels but also on the relative energies of the corresponding singlet states.

Singlet States. In contrast to the very small energy difference between the two triplet states of **4**, we find substantial energy gaps between the three lowest lying singlet states of **4**. At the CASPT2N/6-311G(2d,p) level, the open-shell $^1A_2$ state is 9.3 kcal mol^{-1} lower in energy than the closed-shell $^1A_1$ state, and it is also 20.1 kcal mol^{-1} below the open-shell $^1B_1$ state. The $^1A_2$ state is slightly lower (by 1.5 and 3.2 kcal mol^{-1}) than the two triplets, making $^1A_2$ the ground state of **4**.

The CASSCF(8,8)/6-31G* vibrational analysis reveals one imaginary frequency for the $^1A_2$ state, corresponding to an out-of-plane a_2 vibration, which leads to the cyclic allene (**3**). Thus, $^1A_2$-**4** is a transition state for the enantiomerization (racemization) of **3**. The enantiomerization of allene is also suggested to occur via a C_{2v}-symmetric $^1A_2$ transition state.[48]

$^1A_2$-**4** is 20.5 kcal mol^{-1} higher in energy than **3**. This is approximately half of the racemization barrier of allene.[48,49] This barrier height in **3** is reasonable if one considers that the dihedral angle between the bonds from the terminal allenic carbons to C-3 and C-6 in **3** (Figure 1) is approximately half-way to coplanarity, compared to the dihedral angle of 90° in allene.

Previous theoretical investigations of planar singlet **4** have dealt only with the closed-shell $^1A_1$ state.[10,11] Some groups have predicted $^1A_1$ to be a minimum on the potential surface,[11b] while others have found it to be a transition state for enantiomerization of **3**.[10c,e] Our CASSCF(8,8)/6-31G* vibrational analysis shows no imaginary frequencies for $^1A_1$, indicating that it is a potential

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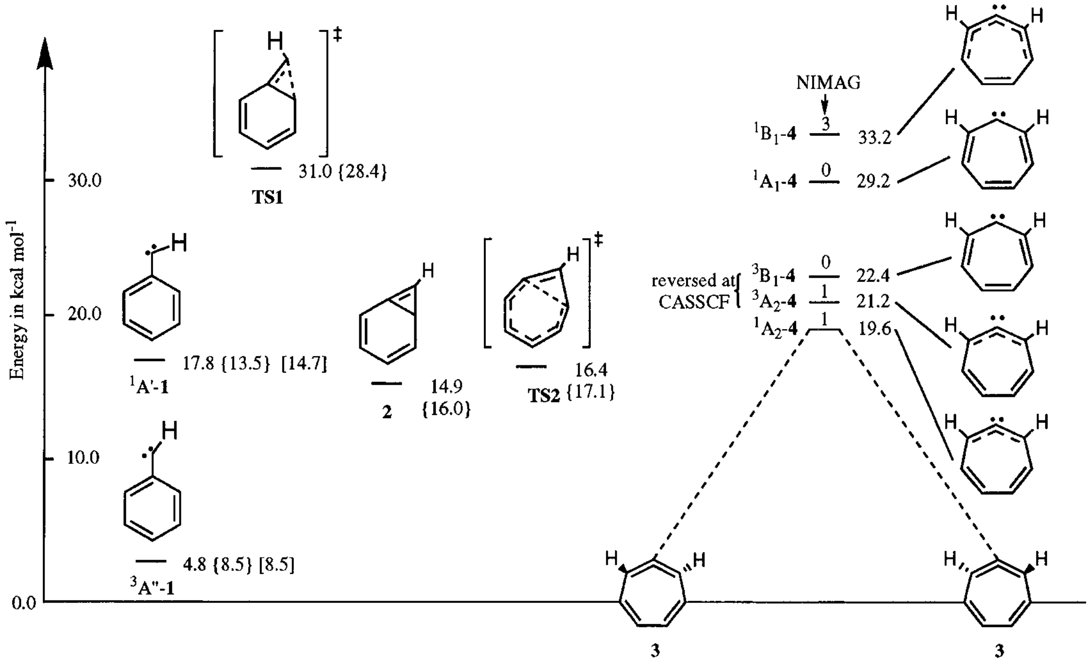
(46) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

(47) The other reported observation of triplet cycloheptatrienylidene by EPR[14h] has since been found to be in error: McMahon, R. J. Personal communication, 1996.

(48) (a) Dykstra, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 2060. (b) Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103. (c) Staemmler, V. *Theor. Chim. Acta* **1977**, *45*, 89. (d) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479. (e) Staemmler, V.; Jaquet, R. In *Energy Storage and Redistribution in Molecules*; J. Hinze, Ed.; Plenum: New York, 1983; pp 261−273. (f) Rauk, A.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1985**, *107*, 3780. (g) Pedash, Y. F.; Ivanov, V. V.; Luzanov, A. V. *Theor. Exp. Chem.* **1992**, *28*, 114. *Teor. Eksp. Khim.* **1992**, *28*, 130.

(49) (a) Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48. (b) Brudzynski, R. J.; Hudson, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 4963. (c) Bettinger, H. I.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. I. *J. Phys. Chem.* **1996**, in press.

Scheme 1 Schematic Presentation of the Relative Energies of the C_7H_6 Isomers and the Electronic States, Considered in the Present Work, at CASPT2N/cc-pVDZ//CASSCF(8,8)/6-31G* + ZPVE, {B3LYP/6-311+G*// B3LYP/6-31G* + ZPVE}, and [CCSD(T)/DZd//CISD/DZd + ZPVE(B3LYP/6-31G*)] in kcal/mol. (NIMAG = number of imaginary frequencies. As discussed in the text, better estimates of ΔE_{ST} in 1 can be obtained by subtracting $\Delta\Delta E_{ST}$ in Table 2 from the experimental value of ΔE_{ST} = 9.1 kcal/mol in CH_2.[42] This gives values for 1 of ΔE_{ST} = 7.1, {2.7}, and [2.4] kcal/mol.)



minimum at this level of theory, but our B3LYP/6-31G* calculations identify it as a transition state. In fact, inspection of the CASSCF results shows that the lowest vibrational frequency for $^1A_1$ is only 59 cm^{-1} and corresponds to the a_2 mode leading to **3**. Thus, it is quite possible that $^1A_1$ is, like $^1A_2$, a transition state for enantiomerization of **3**.[50] Nevertheless, our finding that $^1A_1$ is substantially higher than $^1A_2$ in energy indicates that the $^1A_2$ transition state provides the lowest energy pathway for enantiomerization of **3**. The $^1B_1$ state of **4** is much higher in energy than either of the other two singlet states. The $^1B_1$ state is destabilized by strong Coulomb repulsion, which results from both of the singly occupied orbitals (a_1 and $3b_1$ in Figure 3) having large coefficients on the carbene carbon atom. The nondisjoint nature of these two MOs results in the occupying electrons simultaneously appearing in the regions of space where both of these orbitals have electron density; this creates high-energy ionic terms in the wavefunction for the $^1B_1$ state.[51] This does not occur in the $^3B_1$ state, since the Pauli principle prevents the parallel-spin electrons in the a_1 and $3b_1$ MOs to appear in the same region of space simultaneously.

Electron repulsion in the $^1A_2$ state is much smaller than in $^1B_1$, since the two singly occupied MOs in $^1A_2$ (a_1 and $2a_2$ in Figure 3) are disjoint. Since these two MOs have no atoms in common, the two electrons in these MOs, unlike those in the a_1 and $3b_1$ MOs in $^1B_1$, do not appear in the same region of space, even though they have antiparallel spins. Consequently, the Coulomb repulsion energy between these two electrons in $^1A_2$ is small compared to that in $^1B_1$.

The Coulomb repulsion energy between the two electrons in a_1 and $2a_2$ is also small, compared to that between the two electrons that occupy the a_1 hybrid orbital at the carbene center in $^1A_1$. Thus, despite the $^1A_1$ state's having two electrons in the low-lying a_1 hybrid orbital and an aromatic π system with six electrons, the open-shell $^1A_2$ state is significantly lower in energy. In addition, as pointed out by Matzinger *et al.*,[13a] the larger bond angle at the carbene carbon, which is preferred when the a_1 hybrid orbital is singly occupied (as in $^1A_2$), is more easily accommodated in the planar seven-membered ring of **4** than is the smaller bond angle that is favored when a_1 is doubly occupied (as in $^1A_1$). This effect also acts to stabilize the $^1A_2$ state of **4**, relative to the $^1A_1$ state.

Hund's Rule Violation. $^1A_2$-**4** is lower in energy than $^3A_2$-**4** at all levels of theory, constituting a formal violation of Hund's rule, which states that a triplet state should be lower in energy than the singlet state that has the same configuration.[52] The violation predicted for **4**[53] can be understood qualitatively on the basis of spin polarization in open-shell singlet and triplet states[51] and its effect on the Coulomb repulsion energy between the π electrons and the single electron that occupies the a_1 hybrid orbital in both $^1A_2$ and $^3A_2$.

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(50) At the equilibrium geometry of $^1A_2$, $^1A_1$ is an excited state and *vice versa*. Thus, the equilibrium geometries of $^1A_2$ and $^1A_1$ both lie on the lowest singlet potential surface. An a_2 distortion of **4** from planarity allows $^1A_2$ and $^1A_1$ to mix and connects the equilibrium geometries of these two states of **4** to the geometry of **3**. At some geometries of **4**, intermediate between the equilibrium geometries of $^1A_2$ and $^1A_1$, these two states must have the same energy. At these geometries there is an "accidental" Jahn-Teller effect, so that energy lowering caused by mixing of $^1A_2$ and $^1A_1$ is linear, rather than quadratic in the a_2 distortion coordinate.

(51) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 1. Borden, W. T. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195.

(52) Hund, F. *Linienspektren und periodisches System der Elemente*; Springer-Verlag: Berlin, 1927; p 124 ff. Hund, F. *Z. Phys.* **1925**, *33*, 345. Hund, F. *Z. Phys.* **1928**, *51*, 759.

(53) For other examples of violations of Hund's rule in organic molecules, see: Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.

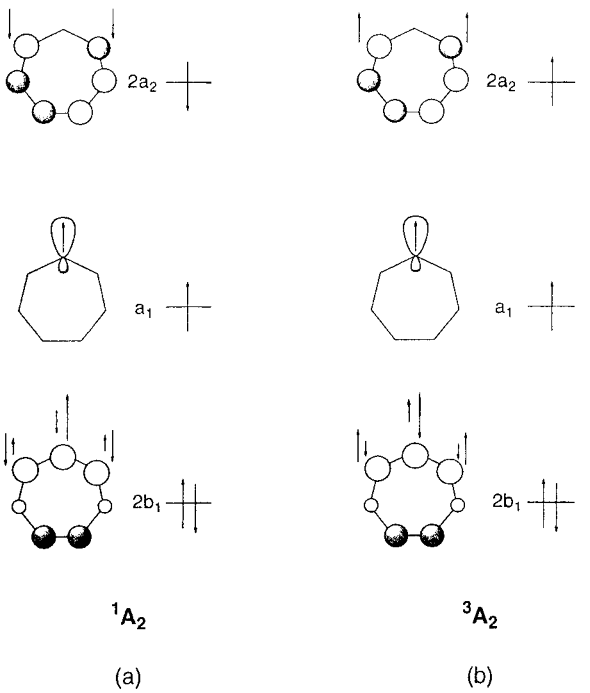

Figure 4. Schematic diagram showing spin polarization in two spin states of C_{2v} cycloheptatrienylidene (**4**). Only the spin polarization in the top half of the molecule is shown. (a) $^1A_2$-state; (b) $^3A_2$-state.

The unpaired electron in the $2a_2$ π orbital in both states results in polarization of the spins in the doubly occupied π orbitals, as shown schematically for $2b_1$ in Figure 4. In both the $^1A_2$ and $^3A_2$ states the single electron in $2a_2$ causes the electron of opposite spin in $2b_1$ to localize to the carbon where $2a_2$ has a node. This type of localization keeps these two electrons of opposite spin from simultaneously appearing in the same region of space.

As shown in Figure 4a, dynamic spin polarization in $^1A_2$ results in excess electron spin in the p-π orbital of the carbenic carbon that is parallel to the spin of the electron in the a_1 hybrid orbital at this carbon. In the $^3A_2$ state spin polarization results in excess electron spin in the p-π orbital of the carbenic carbon that is antiparallel to that of the electron in the a_1 orbital. Since electrons of the same spin in the a_1 and $2b_1$ orbitals are prevented by the Pauli exclusion principle from appearing simultaneously in the same region of space, but those of opposite spin are not, spin polarization leads to a lower Coulomb repulsion energy in $^1A_2$ than in $^3A_2$. This is what causes $^1A_2$ to lie below $^3A_2$ at both CASSCF and CASPT2N.

This violation of Hund's rule makes it unlikely that $^3A_2$-**4** is the state that has been observed by EPR.[15,47] Since $^1A_2$ lies lower in energy than $^3A_2$ and both states have nearly the same equilibrium geometry, intersystem crossing of $^3A_2$ to the lower energy $^1A_2$ state would be likely to depopulate $^3A_2$ so rapidly that $^3A_2$ would not be observable by EPR.

In contrast, $^3B_1$-**4** is much lower in energy than $^1B_1$-**4**. Although $^1A_2$-**4** lies slightly below the equilibrium geometry of $^3B_1$ in energy, the difference between the singly occupied π MOs causes these two states to have very different geometries (Figure 2). Consequently, at the CASSCF/6-31G* equilibrium geometry of $^3B_1$, its CASSCF/cc-pVDZ and CASPT2N/cc-pVDZ energies are, respectively, 20.0 kcal mol^{-1} and 14.0 kcal mol^{-1} below those of $^1A_2$, when the calculations on $^1A_2$ are performed at the equilibrium geometry of $^3B_1$.[54] Thus, at the equilibrium geometry of $^3B_1$, this triplet state lies lower than any singlet state; and its metastability at this geometry[55] suggests that it is the triplet state of **4** that has been detected by EPR.

Ring Currents and Aromaticity. Only ring currents in closed-shell singlets can be computed reliably using the NICS method (see Computational Methods). The closed-shell singlet states in **1**−**4** all exhibit diamagnetic ring currents, which are indicative of aromatic character. In particular, the $^1A_1$ state of **4** with a nucleus independent chemical shift (NICS) of −8.9 reveals a substantial diamagnetic ring current. But even nonplanar **3** has an NICS of −7.4. For comparison, the six π electron Hückel-aromatic tropylium cation has an NICS of −8.2.[34]

Singlet phenylcarbene ($^1A'$-**1**, NICS = −8.2) is somewhat less aromatic than benzene (NICS = −11.5).[34] The bicyclic intermediate (**2**), formed from **1**, shows strong aromaticity in the three-membered ring (NICS = −33.5), but almost no ring current in the six-membered ring (NICS = −4.4). For comparison, the NICS of cyclopropene and 1,3-cyclohexadiene are −29.6 and +3.6, respectively.

Although the NICS value of the three-membered ring remains almost constant (NICS = −32.5 in **TS2**) on going from **2** to **TS2**, the NICS of the six-membered ring increases (NICS = −15.6 in **TS2**). This increase in the diamagnetic ring current in the six-membered ring is consistent with the aromatic character expected for the Woodward−Hoffmann allowed, disrotatory opening of the cyclohexadiene ring in **2**. In contrast, in **TS1**, the transition state for addition of the carbene center in **1** to the benzene ring, a NICS value of −7.3 indicates that the aromaticity of phenylcarbene (NICS = −8.2) decreases slightly.

Conclusions

Nonwithstanding minor quantitative differences, the results of this study are in overall agreement[12] with an independent recent study on the same subject based on CCSD(T) methods[13a] and another one which employed the G2(SVP, MP2) model.[13b] In particular we found the following:

(a) Phenylcarbene (**1**) has a triplet ground state ($^3A''$) with a 4−6 kcal mol^{-1} smaller singlet−triplet separation than methylene. The ΔE_{ST} for **1** is 3−5 kcal mol^{-1} (various methods), in good agreement with experimental estimates.[6] CASPT2N underestimates the phenyl stabilization in of the singlet state **1**, probably due to overestimating the delocalization energy of the triplet.

(b) Bicyclo[4.1.0]hepta-2,4,6-triene (**2**) is an intermediate in the rearrangement of **1** to **3**, but the direct observation of **2** seems unlikely. Although **2** is an energy minimum, the barrier for ring opening to **3** via **TS2** is small, and the reaction is exothermic. Moreover, although the rearrangement of **1** to **2** is close to thermoneutral, the transition state (**TS1**) connecting these two

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[54] Calculated energies of $^1A_2$-**4** at the CASSCF(8,8)/6-31G* optimized geometry of $^3B_1$-**4** (hartrees): CASSCF(8,8)/6-31G* −268.49785; CASSCF(8,8)/cc-pVDZ −268.51816; CASPT2N/6-31G* −269.31144; CASPT2N/cc-pVDZ −269.34446.

[55] Since $^3A_2$ lies above $^1A_2$, pseudorotation of $^3B_1$ to $^3A_2$, followed by intersystem crossing and vibrational relaxation, would provide a low energy pathway for the lowest triplet state of **4** to reach the equilibrium geometry of **3**.

intermediates lies well above both. Thus, upon formation from **1**, **2** should have more than enough internal energy to undergo ring opening to **3**.

(c) In agreement with experiment, 1,2,4,6-cycloheptatetraene (**3**) is the lowest-lying structure on this part of the singlet C_7H_6 potential energy surface. The enantiomers of **3** are interconverted via the $^1A_2$ state of cycloheptatrienylidene (**4**) with a barrier of about 20 kcal mol^{-1}. The aromatic $^1A_1$ state, previously believed to be the lowest singlet state of **4**, lies well above the $^1A_2$ state.

The two triplet states of **4**, $^3A_2$ and $^3B_1$, have rather similar relative energies. However, we suggest that $^3B_1$ is the triplet state of **4** that has been observed by EPR, because, in violation of Hund's rule, $^3A_2$ lies slightly above $^1A_2$ in energy. Hence, intersystem crossing of $^3A_2$ to $^1A_2$ is expected to occur readily; so $^3A_2$ is unlikely to live long enough to be detectable in a standard EPR experiment.

$^3B_1$ is also higher in energy than $^1A_2$. However, the large differences between the equilibrium geometries of these two states results in $^3B_1$ being lower in energy than $^1A_2$, when the calculations on both states are performed at the equilibrium geometry of $^3B_1$. Metastable $^3B_1$-**4** is suggested to have been the triplet species detected by EPR.

(d) All closed shell monocyclic structures examined exhibit some degree of aromaticity which is, however, less than that of benzene, but still considerably higher than that of the corresponding nonconjugated hydrocarbons. As expected, the transition state (**TS2**) for the Woodward−Hoffmann allowed electrocyclic ring opening of **2** is highly aromatic.

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