Ab Initio Studies of Benzocyclopropenone, Benzocyclopropenone-Containing [2.2]paracyclophane, Its Benzyne Derivative, and the Bridged Benzobarrelene Formed by Intramolecular [4 + 2]Cycloaddition

Charles U. Pittman, Jr.,* Svein Saebo, and Hanying Xu

Department of Chemistry, Mississippi State University, Mississippi 39762
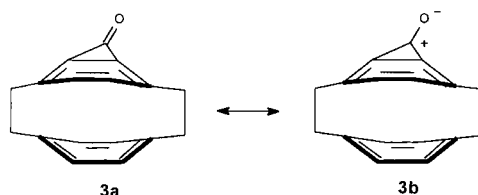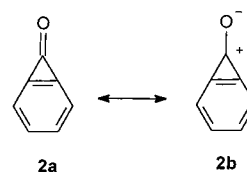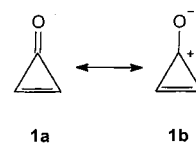
cpittman@ra.msstate.edu

Received May 22, 2000

Ab initio calculations were carried out on cyclopropenone, **1**, benzocyclopropenone, **2**, the benzocyclopropenone-containing [2.2]paracyclophane derivative tetracyclo[8.3.2.^{4,7}0^{11,13}]heptadeca-1(13),4,6,10,14,16-hexaen-12-one, **3**, its decarbonylation product tricyclo[8.2.2.2^{4,7}]hexadeca-1(12), 4,6,10,13-pentaen-15-yne, **5**, a benzyne intermediate, and the bridged benzobarrelene derivative, pentacyclo[5.5.2.2.^{1,4}0.^{4,14}0^{10,13}]hexadeca-2,7,9,13,15-pentaene, **6**. These calculations suggest that benzocyclopropenone-containing [2.2]paracyclophane, **3**, and highly strained bridged benzobarrelene, **6**, could exist as stable species. Both aryl rings of the benzocyclopropenone derivative **3** are predicted to be distorted from planarity. This distortion relieves some angle strain present in planar benzocyclopropenone due to the presence of the annulated three-membered ring. Calculations on benzobarrelene, **8**, and [2.2]paracyclophane, **4**, were performed for comparison to gain a better understanding of the strain borne in bridged benzobarrelene **6**. The activation barrier for the intramolecular [4 + 2] cycloaddition of **5** to give **6** was estimated at 18.8 kcal/mol while that for the corresponding [2 + 2] cycloaddition, giving the less stable **9**, was 54.5 kcal/mol. The [2 + 2] cycloaddition's transition state was twisted in a manner reminiscent of the conservation of orbital symmetry prediction for an unstrained system.

Introduction

Benzocyclopropenone, **2**, (IUPAC name: bicyclo[4.1.0]-hepta-1,3,5-triene-7-one) has been reported to be an active intermediate in the photochemical reaction of lithium 3-*p*-tolylsulfonylamino-1,2,3-benzotriazin-4(3*H*)-one[1] and in the room-temperature oxidation of 3-amino-1,2,3-benzotriazin-4-one by lead tetraacetate.[2] While the successful isolation of benzocyclopropenone or its derivatives has never been reported, benzocyclopropenone was trapped as a stable guest in a hemicarcerand.[3] This implies that benzocyclopropenone is thermodynamically stable but is extremely reactive. The low-temperature ^{1}H and ^{13}C NMR spectra of a mixture of compounds containing benzocyclopropenone, prepared from the photochemical decarbonylation of benzocyclobutene-1,2-dione in an argon matrix at 193 K have been reported.[4] The IR and UV–vis spectra of benzocyclopropenone, prepared in an argon matrix at 12 K, were also claimed on the basis that the experimental data were in agreement with the calculated harmonic vibrational frequencies reported by Schaefer's group using the HF/DZ+P method.[5] In sharp contrast, cyclopropenone, **1**, was synthesized by Breslow[6]

and shown to have fairly high chemical stability. At 25 °C, cyclopropenone has a 1-week half-life in aqueous solution.[6]

What causes this appreciable difference in stabilities of benzocyclopropenone, **2**, and cyclopropenone, **1**? Is the stability difference due to the difference in magnitude of the positive charge on the carbonyl carbon in cyclopropenone versus that in benzocyclopropenone or is it due to the difference in strain between these two molecules? If it is due to the difference in strain, can the benzocy-

(1) Ao, M.; Burgess, E. H.; Schauer, A. L.; Taylor, E. A. *Chem. Commun.* **1969,** *5,* 220 and references therein.

(2) Adamson, J.; Forster, D. L.; Gilchrist, T. L.; Rees, C. W. *Chem. Commun.* **1969,** *5,* 221.

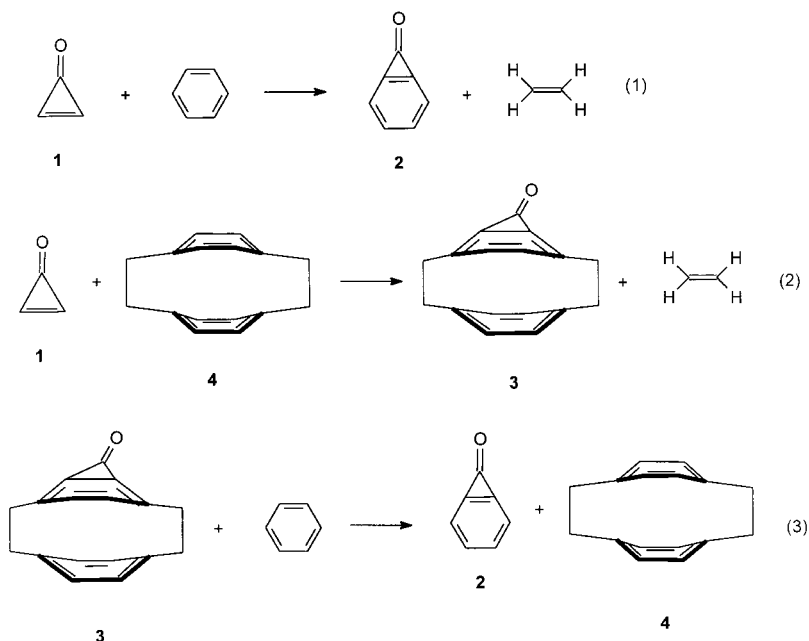(3) Warmuth, R. *Angew. Chem., Int. Ed. Engl.* **1997,** *36*(12), 1347.

(4) Simon, J. G. G.; Schweig, A. *Chem. Phys. Lett.* **1993,** *201*(1−4), 377.

(5) Simon, J. G. G.; Schweig, A.; Xie, Y.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1992,** *200*(6), 631.

(6) Breslow, R.; Ryan, G. *J. Am. Chem. Soc.* **1967,** *89*(12), 3073.

Chart 1

(1)

1   **2**

(2)

1   **4**   **3**

(3)

3   **2**   **4**

clopropenone relieve a portion of this strain by distorting the planarity of its benzene ring? Some aromatic resonance stabilization would be lost but small distortions would minimize this effect. Such distortion from planarity of a benzene ring is known to occur within [2.2]-paracyclophane.[7] Will including the benzocyclopropenone moiety in a benzocyclopropenone-containing [2.2]paracyclophane provide some relief of angle strain present at the annulated three-membered ring?

To help answer these questions, cyclopropenone **1**, benzocyclopropenone **2** and its [2.2]paracyclophane derivative **3** (IUPAC name: tetracyclo[8.3.2.$^{4,7}0^{11,13}$]heptadeca-1(13),4,6,10,14,16-hexaen-12-one) were investigated by ab initio calculations. The isodesmic eqs 1−3 were also calculated to evaluate the relative angle strains present in the three-membered ring of **1**, **2** and **3** (Chart 1).

Another purpose of these calculations was to help evaluate a possible route to synthesize the highly strained bridged benzobarrelene, **6**, via the benzyne derivative, **5**, formed from decarbonylation of the benzocyclopropenone-containing [2.2]paracyclophane, **3**. Benzocyclopropenone is known to generate a benzyne intermediate upon photolysis.[8] Therefore, benzocyclopropenone-containing [2.2]paracyclophane **3** might be expected to produce its benzyne derivative, **5**, upon photolysis and **5** might provide **6** via a transannular [4 + 2]cycloaddition. Such cycloaddition reactions of benzyne and aryl rings are well documented.[9−13] Furthermore, transannular intramolecular addition of the benzyne moiety to the benzene ring within [3.3]paracyclophanes have been reported to give bridged benzobarrelenes.[14] However, the

intramolecular benzyne addition of tricyclo[8.2.2.2^{4,7}]-hexadeca-1(12), 4,6,10,13-pentaen-15-yne, **5**, to generate **6** has never been reported. This reaction is of interest because considerably more strain should be incurred upon generating bridged benzobarrelene **6**, with bridges containing only two carbons each, than was encountered in the analogous reaction reported with three carbon bridges present.[14] The calculations described here suggest benzocyclopropenone-containing [2.2]paracyclophane, **3**, may serve as a precursor to the synthesis of the highly strained bridged benzobarrelene, pentacyclo[5.5.2.2.^{1,4}-0.$^{4,14}0^{10,13}$]hexadeca-2,7,9,13,15-pentaene, **6**, through benzyne intermediate **5** and calculations predict a reasonably low energy energy barrier between **5** and **6**. Intermediate **5** should form **6** via a transition state of C_s symmetry. This highly strained bridged benzobarrelene, **6**, should be isolable (Chart 2).

Computational Details

All structures were completely optimized at the Hartree−Fock and B3-LYP[15,16] levels of theory using the 6-31G(d,p)[17,18] basis set. For all optimized structures harmonic vibrational frequencies were calculated at the same level, mainly to characterize the stationary points as minima or transition states. Even though the B3-LYP approach does include some electron correlation, the molecules studied here are highly strained and a better treatment of electron correlation would be desirable. Cyclopropenone, **1**, and benzocyclopropenone, **2**, were therefore completely optimized at the MP2 level[19−21] using 6-311G(d,p)[22] basis set.

The results in Table 1 show only small differences between the MP2, HF, and B3-LYP results. Therefore, at the MP2/6-311G(d,p) level, the energy differences of isodesmic eqs 1−3 were only calculated as single-point

(7) Boekelheide, V. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, Heidelberg, 1983; Vol. 113, pp 109 and 120−121 and references therein.

(8) Simon, J. G. G.; Muenzel, N.; Schweig, A. *Chem. Phys. Lett.* **1990**, *170*(2−3), 187.

(9) Friedman, L. *J. Am. Chem. Soc.* **1967**, *89*(12), 3071.

(10) Stiles, M.; Burckhardt, H.; Freund, G. *J. Org. Chem.* **1967**, *32*, 3718.

(11) Friedman, L.; Lindow, F. *J. Am. Chem. Soc.* **1968**, *90*, 2329.

(12) Brewer, J. P. N.; Heaney, H. *Tetrahedron Lett.* **1965**, 4709.

(13) Brewer, J. P. N.; Eckhard, I. F.; Heaney, H.; Marples, B. A. *J. Chem. Soc. C* **1968**, 664.

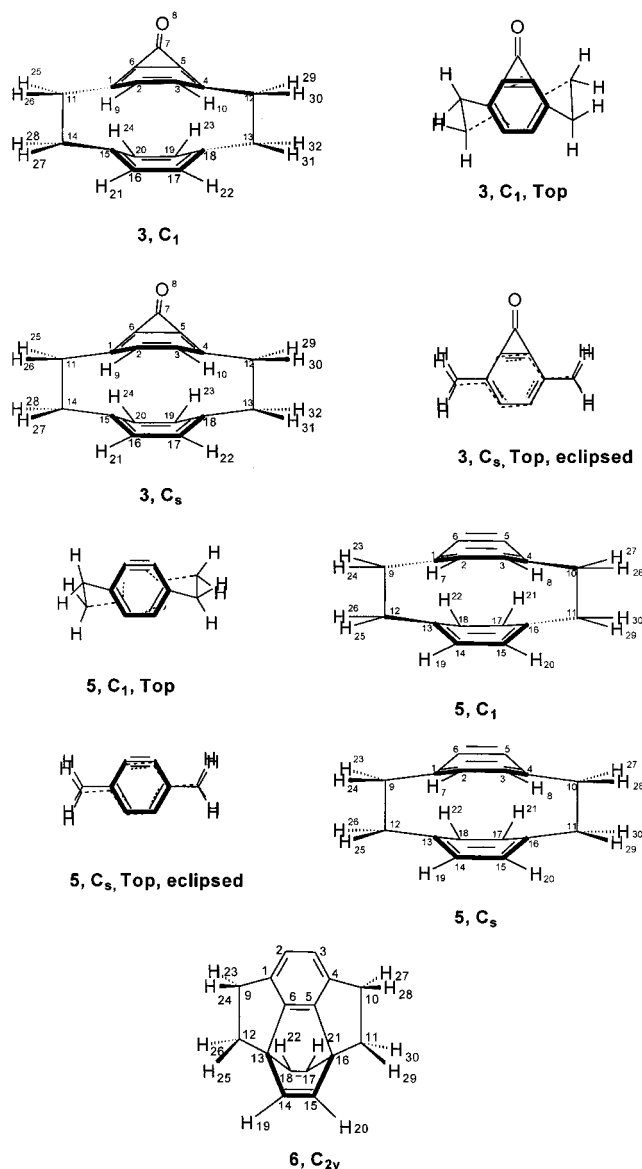(14) Longone, D. T.; Gladysz, J. A. *Tetrahedron Lett.* **1976**, 4559.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

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

(17) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(18) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

Chart 2

3, C₁

3, C₁, Top

3, Cₛ

3, Cₛ, Top, eclipsed

5, C₁, Top

5, C₁

5, Cₛ, Top, eclipsed

5, Cₛ

6, C₂ᵥ

amounts of positive charge to the β-ring carbons consistent with 2π aromatic-like stabilization. This kind of stabilization was used to explain the stability of cyclopropenone in aqueous solution at room temperature.[6] The same type of stabilization exists but to different extents in **2b** and **3b**. One might predict that the resonance hybrid **1b** would contribute more than **2b**. The benzene ring aromaticity in benzocyclopropenone, **2**, tends to localize the carbon−carbon π-bond within the 6π aromatic system. Thus, π-delocalization within the three-membered, cyclopropenyl ring portion of benzocyclopropenone should actually be reduced relative to such delocalization in cyclopropenone, leading to less aromatic stabilization of the fused cyclopropenone moiety in benzocyclopropenone versus that in cyclopropenone. This effect is known as the "Mills−Nixon" effect[25] or more descriptively as "strain-induced bond localization".[26] It has been a topic of considerable debate since 1930.[25,27,28]

If the carbonyl carbon of benzocyclopropenone, **2**, held more positive charge than the carbonyl carbon in cyclopropenone, **1**, then nucleophiles may react faster with **2** accounting, in part, for its higher reactivity. However, the ab initio calculations suggest that the carbonyl carbon of cyclopropenone bears more positive charge than that of benzocyclopropenone. Thus one might expect, on this basis alone, that cyclopropenone would be more reactive toward nucleophiles than benzocyclopropenone. This reasoning does not agree with the known relative reactivities. Cyclopropenone is stable in water, a nucleophile, for one week at room temperature[6] while benzocyclopropenone has never been successfully isolated. Clearly, other factors must be operative.

A key candidate to explain this difference in reactivities is the relative strain from bond angle distortions (Baeyer strain) in **1** versus **2**. The $H_2C_3C_5$ bond angle in cyclopropenone can be adjusted to minimize angle strain whereas the $C_1C_6C_7$ bond angle in benzocyclopropenone is restricted due to the presence of the benzene ring. Changes in this $C_1C_6C_7$ bond angle which lower the angle strain within the three-membered ring, will cause an increase in strain within the benzene ring. Thus, benzocyclopropenone cannot relieve this angle strain as well as cyclopropenone can. Consequently, the angle strain (Baeyer strain) is greater in benzocyclopropenone than that in cyclopropenone, constituting a contribution to the

calculations on the B3-LYP/6-31G(d,p)-optimized structures.

Throughout this paper, bond lengths are given in Angstroms, bond angles in degrees, dihedral angles in degrees, dipole moments in Debyes, atomic charges in electrostatic units, total energies in Hartrees, and relative energies in kcal/mol.

All calculations were carried out using the Gaussian 94[23] and Gaussian 98[24] suite of programs on Silicon Graphics and Cray computers available at the Mississippi Center for Supercomputing Research.

Results and Discussion

Cyclopropenone, **1**, is stabilized by resonance hybrid **1b** which illustrates the delocalization of significant

(19) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(20) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.
(21) Bartlett, R. J.; Silver, D. M. *Int. J. Quantum Chem. Symp.* **1975**, *9*, 183.
(22) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(23) Gaussian 94, Revision E.3: 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.; Gompert, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.
(24) Gaussian 98, Revision A.7, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. A.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gompert, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzales, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.
(25) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.
(26) Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1721.
(27) Stanger, A. *J. Am. Chem. Soc.* **1998**, *120*, 12034.

Table 1. Optimized Geometrical Parameters, Total Energies, and Some Physical Properties of 1–9, Transition State 1 (TS1), and Transition State 2 (TS2) at Different Levels with Different Basis Sets

	RHF/6-31G(d,p)	B3LYP/6-31G(d,p)	MP2/6-311G(d,p)
compound **1**, C_{2v}	minimum	minimum	minimum
C_3-C_4	1.3279	1.3462	1.3577
$\angle H_2C_3C_4$	145.2	144.1	143.5
$\angle H_2C_3C_5$	152.9	153.8	154.5
$\angle H_4C_3C_5$	61.9	62.1	62.0
C_3-C_5	1.4119	1.4362	1.4446
atomic charge on carbonyl carbon	0.5	0.3	0.4
dipole moment	4.6973	4.0054	4.7300
total energy	−189.5380111	−190.6454513	−190.1671077
compound **2**, C_{2v}	minimum	minimum	minimum
C_5-C_6	1.3542	1.3893	1.4019
C_1-C_6	1.4044	1.4002	1.3997
atomic charge on carbonyl carbon	0.5	0.2	0.3
$\angle C_1C_6C_7$	174.5	175.4	175.5
$\angle C_5C_6C_7$	61.6	61.3	61.2
dipole moment	5.6588	4.9285	5.6608
total energy	−342.1772444	−344.2840907	−343.3769410
compound **3**, C_1	minimum	minimum	
C_5-C_6	1.3593	1.3958	
C_1-C_6	1.4064	1.4039	
C_4-C_5	1.4062	1.4037	
C_1-C_{15}	2.8298	2.8277	
C_4-C_{18}	2.8286	2.8266	
C_2-C_{16}	3.2050	3.2005	
$C_{11}-C_{14}$	1.5935	1.6068	
$\angle C_1C_6C_7$	164.8	164.7	
$\angle C_1C_6C_5$	124.1	123.6	
$\angle C_5C_6C_7$	61.5	61.1	
Dihedral $C_6C_1C_2C_3$	−17.6	−17.8	
dihedral $C_{20}C_{15}C_{16}C_{17}$	14.2	13.6	
dipole moment	5.3422	4.6510	
total energy	−726.6622637	−731.3609758	
compound **3**, C_s	transition state	transition state	
C_5-C_6	1.3587	1.3958	
C_1-C_6	1.4070	1.4042	
C_1-C_{15}	2.8233	2.8223	
C_2-C_{16}	3.1957	3.1936	
$C_{11}-C_{14}$	1.5982	1.6090	
$\angle C_1C_6C_7$	165.3	164.9	
dihedral $C_6C_1C_2C_3$	−17.3	−17.5	
dihedral $C_{20}C_{15}C_{16}C_{17}$	14.2	13.7	
dipole moment	5.3446	4.6566	
total energy	−726.6621151	−731.3609077	

	RHF/6-31G(d,p)	B3LYP/6-31G(d,p)
compound **5**, C_1,	minimum	minimum
C_5-C_6	1.2236	1.2507
C_4-C_{16}	2.8372	2.8319
$C_{10}-C_{11}$	1.5884	1.6089
C_1-C_{13}	2.8391	2.8314
$C_{14}-C_{15}$	1.3822	1.3927
C_9-C_{12}	1.5940	1.6033
$C_{17}-C_{18}$	1.3859	1.3951
dihedral $C_3C_4C_5C_6$	−16.4	−15.5
dihedral $C_{15}C_{16}C_{17}C_{18}$	14.5	14.1
dipole moment	1.2985	1.1733
total energy	−613.8758156	−617.9899802
compound **6**, C_{2v},	minimum	minimum
C_5-C_6	1.3454	1.3501
C_5-C_{16}	1.4853	1.4936
C_6-C_{13}	1.4853	1.4936
$C_{10}-C_{11}$	1.5903	1.5975
C_9-C_{12}	1.5903	1.5975
$C_{17}-C_{18}$	1.3245	1.3408
$C_{14}-C_{15}$	1.3245	1.3408
dihedral $C_3C_4C_5C_6$	0	0
dihedral $C_{15}C_{16}C_{17}C_{18}$	54.3	54.1
dipole moment	0.5574	0.5538
total energy	−613.9819004	−618.0681244
compound **4**, D_{2h}		minimum
C_1-C_{15}		2.8268
C_1-C_{11}		1.5139
$C_{11}-C_{14}$		1.6134
C_2-C_{16}		3.1488

Table 1 (Continued)

	RHF/6-31G(d,p)	B3LYP/6-31G(d,p)
dihedral $C_6C_1C_2C_3$		-14.8
dipole moment		0
total energy		-619.3237765
compound **8**, C_{2v}		minimum
C_6-C_{13}		1.5363
$C_{14}-C_{15}$		1.3325
$\angle C_6C_{13}H_{12}$		112.6
$\angle C_6C_{13}C_{14}$		105.1
dipole moment		0.5984
total energy		-463.2557893
compound **9**, C_1,		minimum
C_5-C_6		1.3969
$C_{17}-C_{18}$		1.5771
C_6-C_{18}		1.5245
C_5-C_{17}		1.5245
$C_{13}-C_{14}$		1.3491
$C_{13}-C_{18}$		1.5081
C_5-C_{16}		2.3478
C_1-C_6		1.3825
C_3-C_4		1.4127
dipole moment		0.8435
total energy		-618.0475623

	RHF/6-31G(d,p)	B3LYP/6-31G(d,p)
transition state 1 (**TS1**)		
C_5-C_6		1.2723
C_6-C_{13}		2.2228
C_5-C_{16}		2.2233
C_5-C_{17}		2.7170
C_6-C_{18}		2.7168
$C_{17}-C_{18}$		1.3847
dihedral angle $C_5C_6C_{13}C_{16}$		0.01
dihedral angle $C_5C_6C_{18}C_{17}$		0.02
dipole moment		1.2606
total energy		-617.960041
transition State 2 (**TS2**)		
C_5-C_6		1.3497
C_6-C_{13}		2.6306
C_5-C_{16}		2.5802
C_5-C_{17}		2.1526
C_6-C_{18}		2.1327
$C_{17}-C_{18}$		1.4544
dihedral angle $C_5C_6C_{13}C_{16}$		-12.5
dihedral angle $C_5C_6C_{18}C_{17}$		-15.2
dipole moment		2.3566
dotal energy		-617.9031574

relative stabilities of cyclopropenone versus benzocyclopropenone.

1, C_{2v}   **2, C_{2v}**
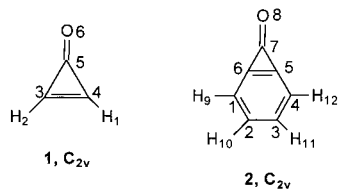
In benzocyclopropenone-containing [2.2]paracyclophane, **3**, the presence of the two carbon bridges exerts a force to distort the aromatic ring from planarity. How much can this distortion help in releasing some angle strain in the benzocyclopropenone moiety? RHF/6-31G-(d,p) and B3LYP/6-31G(d,p) calculations predict the aryl ring annulated to the three-membered ring is significantly distorted from planarity. This distortion is illustrated by the size of the $C_6C_1C_2C_3$ dihedral angle (Chart 2 gives numbering system) found to be 17.6° at RHF/6-31G(d,p) and 17.8° at B3LYP/6-31G(d,p) theory levels, respectively (Table 1). The $C_8C_7C_6C_5$ dihedral angle is 179.8° at the RHF/6-31G(d,p) level and 179.5° at the B3LYP/6-31G(d,p) level, confirming that the car-

bonyl oxygen atom is essentially in the three-membered ring's plane. The dihedral angle between the C_5C_6 and the C_2C_3 bonds is close to zero. The shape of the aryl ring fused to the three-membered ring in **3** is distorted into a boatlike geometry allowing the $C_1C_6C_7$ angle to vary, thereby lowering angle strain in the three-membered ring.

The other benzene ring in **3** is also distorted into a boatlike geometry. This is illustrated by the almost parallel $C_{16}C_{17}$ and $C_{19}C_{20}$ bonds (the dihedral angles were about 0.3° over the range of levels used). The $C_{20}C_{15}C_{16}C_{17}$ dihedral angles were 13.6 and 14.4° at B3-LYP and RHF levels, respectively. The boatlike distortions of the two aryl rings in **3** are very similar according to the values of the $C_6C_1C_2C_3$ and $C_{20}C_{15}C_{16}C_{17}$ dihedral angles. This distortion enables the $C_1C_6C_7$ bond angle (from 164.7 to 165.5°, Table 1) to adjust so that the angle strain can be lowered. Hence, this distortion from planarity appears to decrease the strain of the benzocyclopropenone moiety in **3**, relative to that in **2**.

To evaluate the relative angle strains present in the three-membered rings of **1**, **2** and **3**, the reaction energies

(28) Eckert-Maksic, M.; Glasovac, Z.; Maksic, Z. B. *J. Organomet. Chem.* **1998**, *571*(1), 65.

Table 2. the Energy Differences (kcal/mol) of the Isodesmic Eqs 1−3 at RHF/6-31G(d,p), B3-LYP/6-31G(d,p) Levels and Single-Point Calculations at the MP2/6-311G(d,p) Level

	RHF/6-31G(d,p)	B3-LYP/6-31G(d,p)	MP2/6-311G(d,p)[a]
1	22.5	16.2	15.0
2	14.0	9.1	6.3
3	8.5	7.1	8.7

[a] Single-point calculations of B3-LYP/6-31G(d,p)-optimized structures at the MP2/6-311G(d,p) level.

were calculated for the three isodesmic reactions shown in eqs 1−3 (Table 2). The energy differences for eq 1 suggests that cyclopropenone, **1**, bears about 16 kcal/mol less strain than benzocyclopropenone, **2**. This is consistent with the higher chemical reactivity of **2**. The energy differences for eq 2 show that benzocyclopropenone-containing [2.2]paracyclophane, **3**, is about 9 kcal/mol more strained than cyclopropenone, **1**. The energy differences in reaction 3 illustrate **3** is less strained than benzocyclopropenone by about 7 kcal/mol. Thus, the Baeyer strain in the three-membered ring of **3** is predicted to be 7−9 kcal/mol smaller than that in **2**.

For the benzocyclopropenone-containing [2.2]paracyclophane, **3**, our calculations predicted two equivalent minima without symmetry (e.g., C_1). Furthermore, the C_s geometry of **3** is a transition state between these two C_1 minima. However, the energy barrier is so small at both levels of theory (0.04kcal/mol and 0.09kcal/mol) that this system is best described as having a shallow energy well where C_1 vs C_s symmetry is indistinguishable (energy barrier is lower than the zero point vibrational energy). It should be noted that the structure of [2.2]-paracyclophane, **4**, has been shown to have D_{2h} symmetry by X-ray crystallography.[7]

Photolysis of **3** is expected to generate a benzyne moiety via loss of CO. This benzyne derivative **5** exists as a metastable high energy discrete energy minimum species with C_1 symmetry (Table 1). Like **3**, both the benzyne and benzene rings of **5** are distorted into boatlike structures. This is illustrated by the magnitudes of the $C_3C_4C_5C_6$ and $C_{15}C_{16}C_{17}C_{18}$ dihedral angles (Chart 2) which are around 15° (see Table 1). The bond length C_5C_6 is short (1.22 to1.25 Å, Table 1) indicating triple bond character in the C-5 to C-6 bond.

There is a transition state of C_s symmetry between two C_1 forms on its potential energy surface of **5** but the energy barrier between the equivalent energy C_1 forms is negligible (0.06kcal/mol) as was the case with **3**.

When benzyne **5** undergoes transannular [4 + 2]-cycloaddition to its other benzene ring, the bridged benzobarrelene, **6**, should form. This highly strained molecule, **6**, is predicted to have a stable C_{2v} minimum energy structure lying significantly below **5** (by 64 and 49kcal/mol at the RHF and B3-LYP methods, respectively) on the potential energy surface. In **6**, the C_5C_{16} bond length is 1.49 Å (B3LYP/6-31G(d,p) level) which is about 0.03 Å shorter than either the C_7C_8 bond length or the C_1C_2 bond length in tribromobenzobarrelene **7** determined by X-ray crystallography.[29] In parent benzobarrelene, **8**, the C_5C_{16} bond length was calculated to be 1.54 Å (B3LYP/6-31G(d,p) level). This considerable bond shortening in **6** versus **8** might be caused by strain
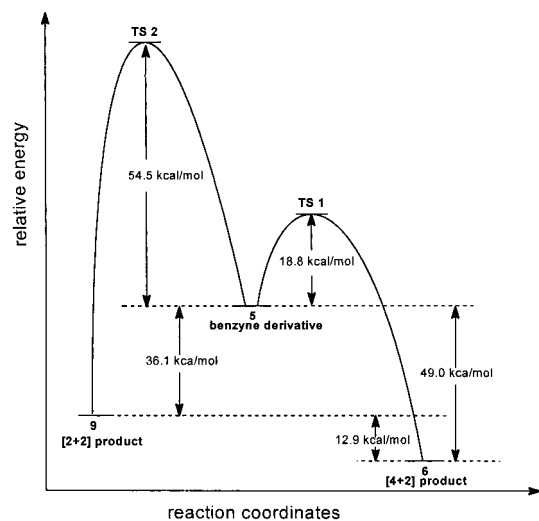
(29) Balci, M.; Cakmak, O.; Hokelek, T. *Tetrahedron* **1992**, *48*(15), 3163.

Figure 1. Energy diagram for the conversion of benzyne derivative **5** to its respective [4 + 2] and [2 + 2] cycloaddition products **6** and **9** (calculated at the B3-LYP/6-31G(d,p) level).

induced by the two two-carbon bridges. The $C_6C_{13}C_{12}$ bond angle of **6** is significantly compressed to about 100°. In **8**, the corresponding $C_6C_{13}H_{12}$ bond angle is a much larger 112.6° (B3LYP/6-31G(d,p) level). The angle compressions in **6** are induced by the strain caused by the two two-carbon bridges. Furthermore, in [2.2]paracyclophane, **4**, the bridging $C_{12}C_{13}$ bond length is calculated to be very long 1.613 Å. In **6**, the corresponding bridging-(C_9C_{12} bond length), while still long, is predicted to be 1.598 Å (both at B3LYP/6-31G(d,p) level). This bond shortening of the bridges in **6** versus those in **4** is in agreement with the C_5C_{16} bond shortening and the $C_6C_{13}C_{12}$ bond angle compression in **6** which are induced by the strain caused by the two −CH₂CH₂- bridges in **6**. However, in **3** and **5**, the bridging carbon carbon distances are 1.607 Å and 1.608 Å, respectively. These distances are very close that in [2.2]paracyclophane 1.613 Å.

4, D$_{2h}$, [2.2]paracyclophane

7

8, C$_{2v}$, benzobarrelene
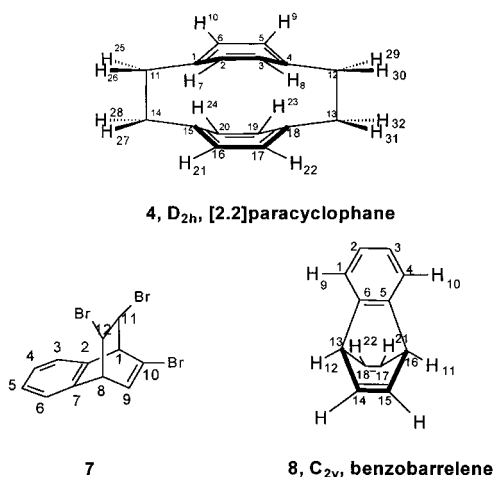
Intramolecular benzyne addition is thermodynamically favorable and it should pass through a transition state with a structure more like **5** (Hammond postulate) than that of **6**. A similar transannular benzyne addition in the much less strained [3.3]paracyclophane has been experimentally observed.[14] The transition state (**TS1**, Figure 1) between **5** and **6** was found to be 18.8 kcal/mol above

5 indicating this [4 + 2] cycloaddition would be kinetically feasible. Furthermore, the geometry of this transition state is only minutely distorted from C_{2v} symmetry due to forces generated in the two-carbon bridges. This tiny distortion is illustrated by the small, 0.01°, dihedral angle between the C_5C_6 bond and the $C_{13}C_{16}$ axis. The synthesis of highly strained bridged benzobarrelenes in the highly strained [2.2]paracyclophane series is predicted to be possible.

As **5** rotates toward the geometry of **TS1**, carbon atoms C_5 and C_6 pass fairly close to C_{17} and C_{18}, respectively. In this distorted and strained system could a [2 + 2] (e.g., or [2 + 6]) cycloaddition occur? To answer this question the structure of the [2 + 2] product, **9**, was optimized-(B3-LYP/6-31G(d,p) level) and found to be 12.9 kcal/mol less stable than **6**. Furthermore, the energy barrier going from **5** to **9** (e.g., **TS2**) was 54.4 kcal/mol (Figure 1). This transition state was also highly twisted away from an approximate C_{2v} symmetry. This is illustrated by the large C_5C_6 to $C_{18}C_{17}$ dihedral angle of 15.2°. This distortion is in a direction moving toward a suprafacial-antarafacial reaction geometry. Thus, conservation of orbital symmetry considerations, which predict the thermal [2 + 2] (or [2 + 6]) cycloaddition must avoid a suprafacial suprafacial mode, appear to be manifest and a huge activation energy (54.4 kcal/mol) is required to go from **5** to **9**. The Hammond Postulate predicts the structure of **TS1** should be closer to **5** (vs **6**) than **TS2** is to **5** (vs **9**). This was reflected in the calculated (B3-LYP/6-31G(d,p)) transition state structures. For example the "benzyne", C_5C_6 bond lengths in **5**, **TS1**, and **TS2** were 1.252, 1.272, and 1.350 Å, respectively. Thus, this bond lengthening is greater in the higher energy **TS2**.

Conclusions

Ab Initio calculations at RHF/6-31G(d,p), B3LYP/6-31G(d,p), and MP2/6-311G(d,p) levels of theory (Table 1) predict that both the benzocyclopropenone- containing-[2.2]paracyclophane, **3**, and highly strained bridged benzobarrelene, **6**, can exist as stable molecules. The angle strain in the benzocyclopropenone moiety of **3** is predicted to be reduced by the distortion from planarity of the aryl
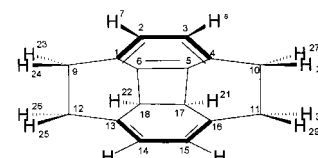
9, [2+2] product
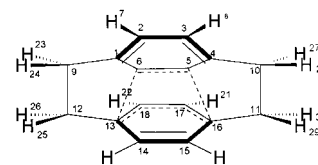
TS 1
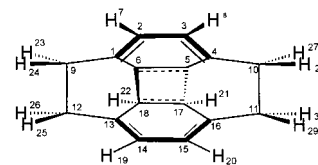
TS 2

ring induced by the strain caused by the two two-carbon bridges. Highly strained bridged benzobarrelene, **6**, might be prepared from photolysis of the [2.2]paracyclophane derivative, **3**, via the benzyne intermediate, **5**. While photolysis of benzocyclopropenone is known to eject carbon monoxide and form benzyne,[8] the photolysis of highly strained **3** may lead to other reactions such as homolysis of the CH_2-CH_2 bond in one of the bridges in **3**. At present, only experiments can resolve this question. However, [2.2]paracyclophane bridge cleavage only occurred at about 300 nm or below.[7] CO loss from benzocyclopropenone, **2**, occurs on photolysis at 334−335 nm.[8] Thus, photolysis of **3** at wavelengths longer than 300 nm should generate **5**.

JO0007884