by a less favorable enthalpy of activation for ring closure, given the distortions observed in (NP)Mo(CO)$_4$. It is evident that both kinetics and structural studies such as these for other chelating systems will be required before relationships between reactivity and substrate structure can be elucidated. In the (chelate)M(CO)$_4$ complexes thus far investigated structurally, only one of the two major distortions observed, diminuition of the N–Mo–P angle from its expected value of 90°, is also noted in (NP)Mo(CO)$_4$. It will be important to investigate systems for which the other major distortion, an unsymmetrical angular distribution of ligands in the equatorial plane containing the non-carbonyl substituents,[9] is also present.

Supplementary Material Available: Atomic coordinates and thermal parameters for (NP)Mo(CO)$_4$ (Table IIA) and for (NP)Cr(CO)$_4$ (Table IIB) and least-squares planes through groups of atoms and their deviations from the planes (Table V) (3 pages). Ordering information is given on any current masthead page.

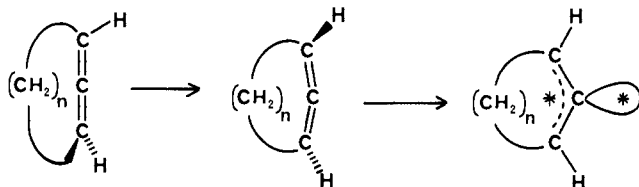# Small-Ring Cyclic Cumulenes: Theoretical Studies of the Structure and Barrier to Inversion in Cyclic Allenes

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Contribution from the Departments of Chemistry, Iowa State University, Ames Laboratory, U.S. Department of Energy, Ames, Iowa 50011, and North Dakota State University, Fargo, North Dakota 58105. Received June 11, 1984

Abstract: Results of ab initio SCF, MCSCF, and Möller–Plesset calculations on 1,2-cyclopentadiene and 1,2-cyclohexadiene are described. 1,2-Cyclohexadiene is calculated to prefer a chiral allenic structure, with a barrier to inversion of ca. 15 kcal/mol. 1,2-Cyclopentadiene is predicted to have an inversion barrier of 2–5 kcal/mol, with a chiral equilibrium geometry. MCSCF calculations on planar allene (C_{2v}) show that the open-shell singlet ($^1A_2$) should be below the triplet ($^3A_2$), owing to differences in correlation energy. Semiempirical (MNDO) calculations on four- to nine-membered ring allenes and on bicyclo[3.2.1]-octa-2,3,6-triene are reported.

Introduction

One primary goal of experimentalists and theoreticians has been to explore structural limitations of hydrocarbons. Allenes are an important class of unsaturated hydrocarbons which contain two cumulated double bonds in an orthogonal geometry. Ring constraints bend and twist the normally linear, perpendicular allene and will engender substantial strain and resultant kinetic reactivity.[2] One fundamental question is the influence of ring size on the barrier to π-bond rotation. In cyclic allenes, this is most accurately described as an inversion barrier, since rotation interconverts enantiomers. Equally fundamental questions are at what point π-bonding will yield to ring strain, affording a planar allene, and what is the electronic nature of planar allene? Such
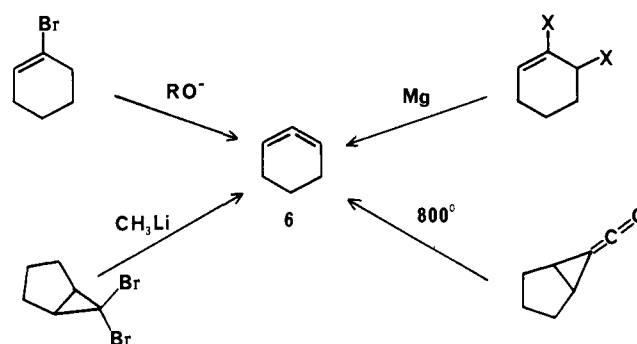

4, n = 1   7, n = 4
5, n = 2   8, n = 5
6, n = 3   9, n = 6

Scheme I

questions have proven difficult to answer unambiguously through experiment;[2] thus, theory should be an important adjunct in their resolution.

It is well known experimentally that allene kinetic stability decreases rapidly with smaller ring size, presumably because reaction is accompanied by substantial strain relief. 1,2-Cyclononadiene (**9**) is a distillable liquid,[2] while 1,2-cyclooctadiene (**8**) rapidly dimerizes at ambient temperature.[3] Its ^{1}H NMR spectrum proved measurable at -60 °C.[4] 1,2-Cycloheptadiene (**7**) and a number of derivatives have been chemically trapped,

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(2) Reviews: (a) Greenberg, J.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978. (b) Hopf, H. In "The Chemistry of Ketenes, Allenes, and Related Compounds", Part 2; Patai, S., Ed.; Wiley: New York, 1980; Chapter 20, p 779.

(3) (a) Marquis, E. T.; Gardner, P. *Tetrahedron Lett.* **1966**, 2793. (b) Wittig, G.; Dorsch, H. L.; Menske-Schüler, J. *Justus Liebigs Ann. Chem.* **1968**, *711*, 55. (c) Reese, C. B.; Shaw, A. *J. Chem. Soc., Chem. Commun.* **1972**, 787.

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but not directly observed; however, it seems generally believed that **7** possesses a chiral structure.[2,4-6]

Considerable controversy has arisen over the structure of 1,2-cyclohexadiene (**6**).[2,5,7-9] This archetypal strained allene has been generated by diverse routes (Scheme I) and trapped through [2 + 2] and [2 + 4] cycloadducts, dimerization, and by reaction with nucleophiles.[5,7,8] Structures proposed to date consist of chiral (**6**), zwitterionic (**6-Z$_1$** and **6-Z$_2$**) and triplet or singlet biradical (**6-^{1}D** or **6-^{3}D**) allene moieties. The latter four differ only in spin and electronic configuration.

Moore and Moser originally proposed singlet structure **6-Z$_1$**.[8]
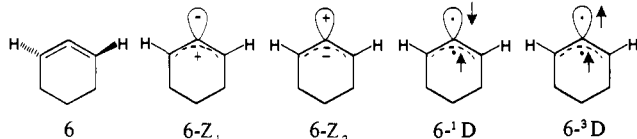
This idea later received support from INDO calculations by Dillon and Underwood, although these authors noted that the triplet might be lower energy.[9] Extensive mechanistic studies by Bottini[7] led to argument for dimerization through **6-^{1}D**, and nucleophilic trapping at C-2 through **6-Z$_2$**. The recognition that, among these many possibilities, only **6** is inherently chiral led Balci and Jones to perform some elegant experiments in which optically active 1,2-cyclohexadiene was successfully trapped with diphenylisobenzofuran.[5] Racemization proved to be competitive with trapping at 80 °C, which suggests a low barrier for this process. Our related work on allene excited states and cyclic allene photochemistry led us to examine this problem theoretically, and, in a preliminary communication, we have reported that chiral **6** should indeed correspond to the equilibrium structure for 1,2-cyclohexadiene.[10] More recently, Wentrup has trapped pyrolytically generated 1,2-cyclohexadiene in an argon matrix at 11 K.[11] Its infrared spectrum showed a characteristic absorption at 1886 cm^{-1}, which is shifted only ca. 70 cm^{-1} from that of a normal allene.

Smaller cyclic allenes have received far less attention. Solution-phase experiments which might have yielded 1,2-cyclopentadiene (**5**) instead gave evidence for the isomeric alkyne.[12] Matrix isolation attempts are in progress.[13] We are aware of no reported attempts to generate 1,2-cyclobutadiene (**4**) although there are several related theoretical studies. A bicyclo[1.1.0]butane structure (**10**) was considered by Hehre and Pople,[14a] while Dewar calculated the energetics of this and a related planar structure.[14b]
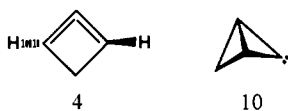

The only previous theoretical study devoted to simple small-ring allenes was a series of model INDO calculations on allene, reported in 1974 by Dillon and Underwood.[9] Unfortunately, their inability to calculate the singlet open-shell diradical state (1^1A_2) resulted

in a conclusion that the planar singlet is zwitterionic (**13**). This
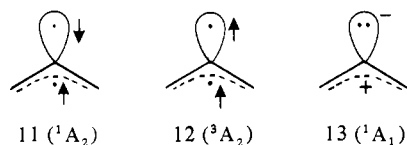

led to the prediction that singlet cyclopentadiene and cyclohexadiene would be zwitterionic, but that the triplet (**12**) would be of lower energy and might represent the true ground state. Subsequent calculations show that **13** is an excited state of **11**;[15,16] thus, arguments for singlet zwitterionic ground states of planar allene are incorrect. The order of $^1A_2$ (**11**) and $^3A_2$ (**12**) has not been reliably determined; results for this are described below.

Cycloheptatetraene (**14a**) and its isomer cycloheptatrienylidene (**14b**) have been the subject of semiempirical[17] and ab initio[18] theoretical studies, which have led to the conclusion that **14a** is of lower energy. Experiments by Jones[19] and by Chapman[20] appear to confirm this.
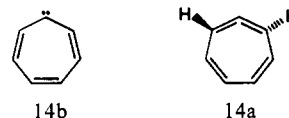
Molecular mechanics also has been applied to chiral cyclic allenes; geometries for 1,2-cyclooctadiene (**8**)[23] and 1,2-cyclononadiene (**9**)[24] have been reported. One X-ray structure for a crystalline derivative of **9** yielded an allenic bending angle of 168.4°.[21]

In one very recent report, a 1,2-dioxacyclohexa-3,4-diene (**15'**)
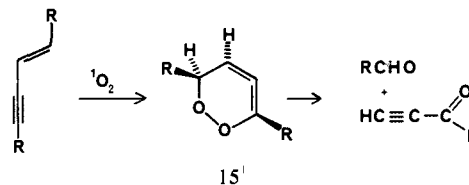
was postulated as an intermediate in singlet oxygen addition to but-1-en-3-ynes. A chiral equilibrium geometry and inversion barrier of 27.9 kcal/mol were predicted by ab initio calculations on the parent structure (R = H).[22] The computational methodology for the planar allenic structure was not described.[22]

We present here full details of our previously communicated[10] ab initio studies on 1,2-cyclohexadiene, in addition to results of similar calculations on 1,2-cyclopentadiene, and semiempirical (MNDO) calculations on cyclic allenes with four to nine carbons.

Computational Methods

Ab initio calculations were performed with a modified version of GAMESS[25] or with GAUSSIAN 80.[26] Semiempirical studies employed a standard version of MNDO.[27]

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Table I. Ab Initio Computational Results for 1,2-Cyclopentadiene

basis set	computational method	state energies (hartrees)[a]			
		$5(1^1A)^b$	$5\text{-}^1D(^1A_2)^c$	$5\text{-}^3D(^3A_2)^c$	$5\text{-}^1Z_1(^1A_1)^d$
STO-3G	RHF/ROHF[e]	-190.31037 (0.0)	-190.36874 (-36.6)	-190.37294 (-39.3)	
3-21G	RHF/ROHF[e]	-191.58548 (0.0)	-191.62131 (-22.5)	-191.62488 (-24.7)	-191.56213 (14.7)
3-21G & STO-3G	RHF/ROHF[e]	-191.11159 (0.0)	-191.14984 (-24.0)	-191.15332 (-26.2)	-191.08564 (16.3)
3-21G + pol	RHF/ROHF[e]	-191.69779 (0.0)	-191.72666 (-18.1)		-191.67802 (12.4)
3-21G & STO-3G	UHF		-191.18672 ($s^2 = 1.26$)	-191.16713 ($s^2 = 2.11$)	
3-21G & STO-3G	RMP2/UMP2[f]	-191.49527 (0.0)	-191.49614 (-0.5) ($s^2 = 1.19$)	-191.49090 (2.74) ($s^2 = 2.08$)	
3-21G & STO-3G	RMP3/UMP3[f]	-191.52958 (0.0)	-191.53639 (-4.3) ($s^2 = 1.19$)	-191.53105 (-0.92) ($s^2 = 2.08$)	
3-21G & STO-3G	FORS[g]	-191.19929 (0.0)	-191.20093 (-1.03)		

[a] Relative energies for comparable species are given in kcal/mol. [b] All calculations at STO-3G/RHF geometry in C_2. [c] STO-3G/ROHF geometry. [d] At geometry for ^1D state. [e] RHF or ROHF for closed- or open-shell species. [f] Second- or third-order Möller–Plesset calculation with RHF or UHF wave functions. [g] 12- or 8-configuration MCSCF.

Table II. Ab Initio Computational Results for 1,2-Cyclohexadiene[a-g]

basis set	computational method	state energies (hartrees)[a]			
		$6(1^1A)^b$	$6\text{-}^1D(^1A)^c$	$6\text{-}^3D(^3A)^c$	$6\text{-}^1Z_1(1^1A)^d$
STO-3G	RHF/ROHF[e]	-228.95597 (0.0)	-228.96296 (-4.4)		-228.79919 (98.4)
3-21G	RHF/ROHF[e]	-230.46297 (0.0)	-230.45734 (3.5)		
3-21G & STO-3G	RHF/ROHF[e]	-229.74931 (0.0)	-229.74613 (2.0)	-229.74941 (-0.06)	
3-21G + pol	RHF/ROHF[e]	-230.56712 (0.0)	-230.56095 (3.9)		-230.49076 (47.9)
3-21G & STO-3G	UHF		-229.78341 ($s^2 = 1.26$)	-229.76355 ($s^2 = 2.11$)	
	RMP2/UMP2[f]	-230.18044 (0.0)	-230.14565 (21.8) ($s^2 = 1.18$)	-230.14006 (25.3) ($s^2 = 2.07$)	
	FORS[g]	-229.81769 (0.0)	-229.79679 (13.1)		

[a-g] See corresponding footnotes in Table I.

Geometries for C_5 and C_6 allenes were initially optimized with MNDO, then further optimized with STO-3G RHF or ROHF (restricted closed or open-shell Hartree–Fock) methods, within appropriate (C_s or C_2) symmetry constraints. Improved SCF energetics were determined with a split-valence 3-21G basis,[28] and with the same basis augmented by a full set of polarization (d) functions ($\alpha = 0.8$)[29] on the three allenic carbons (3-21G + pol). Wave functions for 5 and 6 in these calculations comprised 75 or 88 contracted basis functions, respectively.

Both FORS-MCSCF (full-optimized reaction space multiconfiguration self-consistent field)[30] and Möller–Plesset perturbation theory[31] were used to account for the anticipated large difference in correlation energies for closed- and open-shell species. In the FORS approach, as developed by Ruedenberg and co-workers,[30] correlation energy changes along a reaction coordinate are accounted for by MCSCF calculation within a restricted configuration space. For allene racemization, this requires all configurations (maximum of 20) generated by distributing the four π electrons among the π MO's and the sp hybrid at C-2.

No FORS rotational barriers have been reported; thus it was necessary to establish whether this approach reliably models the rotational barrier in allene. FORS calculations on allene (D_{2d}) and the singlet planar C_{2v} species 11, which corresponds to the rotational barrier,[15,16] were carried out with the 3-21G basis and the π and sp hybrid orbital space described above. Both allene and 11 were calculated at their STO-3G RHF or ROHF optimized geometries, with resultant 3-21G FORS energies of -115.273 96 and -115.200 16 hartrees, respectively. This affords a rota-

tional barrier of 46.3 kcal/mol, which is slightly lower than the best previous values of 50.1,[15a] 49,[15b] 52,[15c] and 53[15d] kcal/mol.

The MNDO rotational barrier in allene (SCF level) is calculated to be 31.2 kcal/mol at a nearly linear geometry. Thus both the predicted barrier and geometry differ substantially from previous values.[15] This may in part be due to neglect of differential correlation energies.

Möller–Plesset (MP) corrections to second or third order were based on RHF (closed-shell) or UHF (unrestricted open-shell) wave functions.[31] These should be most reliable for the triplet states, which were found to have little contribution from higher spin states. By contrast, the singlet UHF wave functions were heavily contaminated by higher states (especially the very close triplet), and we regard the resultant singlet energies as unreliable.

For both MCSCF and MP calculations on cyclic allenes, molecular size precluded use of a full split-valence basis. Therefore, a 3-21G basis was used for the allenic carbons and hydrogens, with an STO-3G basis for the $-(CH_2)_n-$ linkage ($n = 2$ or 3). This combined basis, denoted 3-21G & STO-3G, yielded (vide infra) SCF energy differences which were comparable to the full 3-21G basis.

Electronic Structure of Planar Allene

The two lowest electronic states in planar allene are the $^1A_2$ and $^3A_2$ biradicals, which correspond to structures 11 and 12, shown above. At the SCF level, $^3A_2$ lies 2–3 kcal/mol below $^1A_2$. This small splitting is due to different spatial localizations of the singly occupied MO's. Krogh-Jespersen[15d] has suggested that the planar singlet might lie below the triplet because of correlation energy differences; however, no comparable direct calculations on these states have been reported.

To unambiguously establish the state order, geometries and energetics were determined at the 3-21G FORS MCSCF level. The two geometries proved to be nearly identical, with bending angles of 134.88° ($^3A_2$) and 134.29° ($^1A_2$). Energies (hartrees) and relative energies (kcal/mol) are as follows: $^1A_2$, -115.204 84 (0.0); $^3A_2$, -115.197 059 (4.9). We conclude that correlation energy

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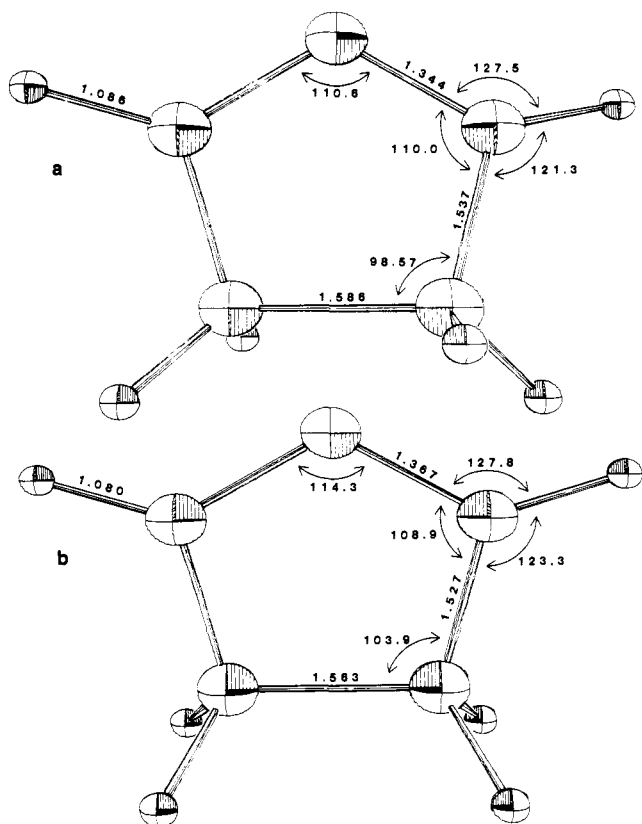
Figure 1. (a) STO-3G geometry for **5**. (b) STO-3G geometry for **5-^{1}D**.

lowers the singlet more than the triplet; thus $^1A_2$ should be the ground state for planar allene.

Results of Ab Initio Calculations on Cyclic Allenes

Energies for 1,2-cyclohexadiene and 1,2-cyclopentadiene which are derived from various levels of calculation are summarized in Tables I and II. STO-3G SCF geometries for 1,2-cyclopentadiene are given in Figure 1; results for 1,2-cyclohexadiene were described previously.[10] In chiral **5** and **6** the allenic hydrogens are bent out of the plane defined by the allenic carbons 20.9 or 30.4°, respectively. Triplet ROHF geometries proved nearly identical with those for the open-shell singlets.

Beginning with the smaller homologue, 1,2-cyclopentadiene, we find that SCF energies strongly favor the planar diradical structures **5-^{1}D** or **5-^{3}D**, with a small singlet–triplet splitting. Improvements in the allene basis set to 3-21G or 3-21G + pol diminish the **5–5-^{1}D** gap to only 18 kcal/mol. Inclusion of
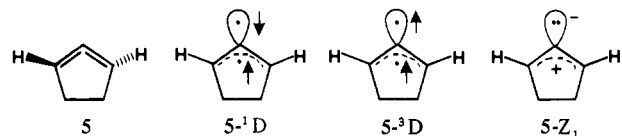
correlation energy through MCSCF or MP calculations further diminishes the predicted energy difference. If we assume that SCF energy differences between 3-21G & STO-3G, and 3-21G + pol basis sets (5.9 kcal/mol) can be carried over to correlated wave functions, this leads to a "corrected" FORS-MCSCF difference of 4.9 kcal/mol, favoring the chiral structure.

Interpretation of the MP results is more problematic owing to the aforementioned contamination from higher spin states in the singlet UHF wave function. At the 3-21G & STO-3G MP 3 level, the planar diradical is favored by 4.3 kcal/mol. Inclusion of a 5.9 kcal/mol basis set improvement "correction", as above for MCSCF, yields a **5–5-^{1}D** difference of 1.6 kcal/mol, favoring **5**. This number would increase somewhat with a pure singlet wave function.

MP3 calculations predict the singlet to be below the triplet by 3.35 kcal/mol.

Either calculation leads to the remarkable prediction that *1,2-cyclopentadiene may exist as a chiral allenic structure, with a low barrier (2–5 kcal/mol) for racemization.* This energy difference is certainly within the expected accuracy of our computational methods. However, further improvements in geometry optimization, basis set, or correlation corrections would be expected to afford greater relative stabilization for the chiral structure **5**, with its unusual π bonding and hybridization, thus reinforcing the above conclusion. Whatever the geometry, the ground state probably will be singlet rather than triplet. Ring opening or some other type of rearrangement also seems possible for this highly strained structure.

For 1,2-cyclohexadiene, the predictions are clearer and in good qualitative agreement with experiment.[5] SCF energy differences show a small preference for the chiral structure. Inclusion of correlation through FORS calculation increases this to 13.1, and addition of a small "correction" for basis set improvement yields 15.0 kcal/mol.

Second-order Möller–Plesset calculations predict a larger inversion barrier for **6**. Appending a 1.9-kcal/mol correction to the calculated value yields a prediction of 23.7 kcal/mol for the inversion barrier. Use of a pure singlet wave function would increase this slightly.

No experimental value for this barrier is available; however, the facile racemization at 80 °C, which was observed by Balci and Jones,[5] is consistent with 15–30 kcal/mol. Our preference is that the MCSCF value may be more accurate than that from MP2, especially since MP3 calculations (omitted here because of time constraints) would probably partially reverse the MP2 predictions.

In comparing racemization barriers for **5** and **6**, the relative effects of correlation energy and polarization functions are of interest. In the six ring, it is the greater correlation energy possessed by the chiral form with its one additional electron pair which is dominant, with polarization functions contributing only ca. 2 kcal/mol to the predicted barrier. Both contributors to stability of the chiral form increase in the five-membered ring, with its more unusual bonding and hybridization. The FORS correlation energy difference between closed- and open-shell singlets is 23 kcal/mol, while d orbitals yield an additional 6-kcal/mol relative stabilization for the chiral form. These effects combine to reverse the large SCF preference for the open-shell form, producing the small 2–5 kcal/mol final estimate for the racemization barrier. Thus, as has been observed in many other cases, d orbitals on carbon prove critical in quantitative estimates for increasingly unusual bonding situations.

Although we have performed no ab initio calculations on 1,2-cyclobutadiene (**4**), extrapolation from the present results supports a planar ground-state singlet. Closure to a carbenic structure (**10**) also seems possible.

Results of MNDO Calculations

For large molecules, the MNDO method provides a computationally efficient means of geometry optimization.[27] However, its quantitative accuracy often is difficult to predict for anything but molecular ground states. Salient geometric parameters and heats of formation for the series of cyclic allenes **4–9** and planar biradical structures **4-^{1}D** to **6-^{1}D** are summarized in Table III. In general, MNDO and ab initio SCF results are in reasonable qualitative agreement.

The MNDO SCF barrier to inversion for 1,2-cyclohexadiene (1.5 kcal/mol) is quite close to that at the 3-21G level (3.5 kcal/mol). Inclusion of limited CI (2 × 2) slightly increases this to 5.7 kcal/mol. For cyclopentadiene, MNDO favors the planar biradical, although the CI energy difference is only 3.3 kcal/mol. Thus, MNDO seems to perform reasonably well on this difficult problem, but the rotational barrier is consistently too small. A similar result was obtained for parent allene (vide supra).

Geometries for the series of chiral allenes **4–9** clearly show the effects of ring constraint. The C_1–C_2–C_3 angle in 1,2-cyclononadiene is predicted to be 170.4°, in good agreement with the X-ray structure reported for a crystalline derivative,[21] and with

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Table III. MNDO Results for Cyclic Allenes

| species	ΔH_f (kcal/mol) SCF	ΔH_f (kcal/mol) CI	C_1–C_2–C_3 (deg)	out-of-plane hydrogen bending[a] (deg)
4	156.9 (0.0)[b]	166.2 (0.0)	93.0	0.7
4-^{1}D	134.4 (−22.5)	134.4 (−31.8)	99.5	0.0
4-^{3}D	132.4 (−24.5)		99.5	0.0
5	104.3 (0.0)	93.5 (0.0)	121.0	13.0 (20.9)[a]
5-^{1}D	90.2 (−14.1)	90.2 (−3.3)	119.9	0.0
5-^{3}D	89.0 (−15.3)		119.9	0.0
6	67.7 (0.0)	63.5 (0.0)	138.46	22.9 (30.4)[a]
6-^{1}D	69.2 (1.5)	69.2 (5.7)	135.36	0.0
6-^{3}D	68.5 (0.8)		135.36	0.0
7	44.2		153.4	27.6
8	32.7		161.5	31.0
9	29.2		170.4	33.7
15	122.9	117.4	111.7	
allene			180.0	45.0

[a] Defined as the angle made by the C–H bond with the plane defined by C_1–C_2–C_3. Corresponding ab initio values are given in parentheses. [b] Relative energies (kcal/mol).

a molecular mechanics calculation of Anet and Yavari (171°).[23] The allenic hydrogens are bent only 34° out of plane; in allene this would be 45°. Predicted vertical ionization potentials are 9.55 and 10.1 eV, while experimental values of 8.87 and 9.35 eV have been reported.[32] Bending in 1,2-cyclononadiene may critically influence the mechanism by which it photorearranges to a bicyclic cyclopropene.[33]
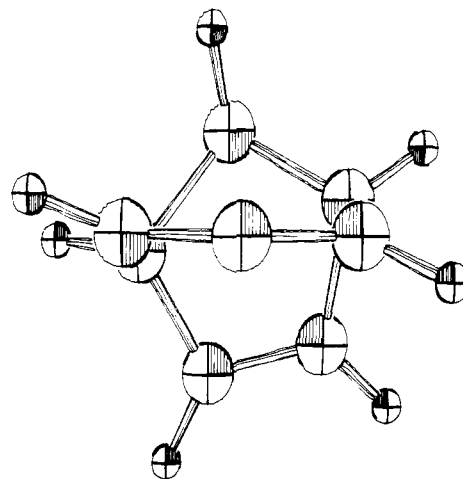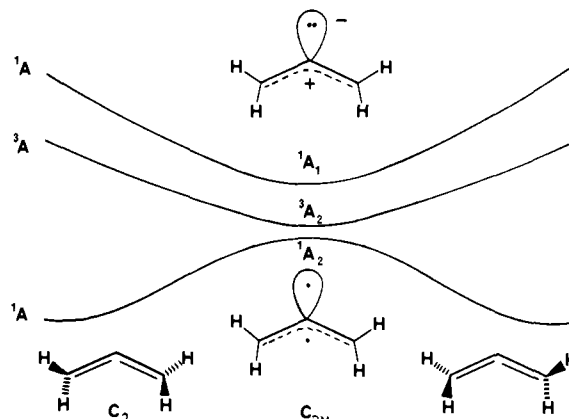
In smaller homologue **8**, MNDO values for C_1–C_2–C_3 bending and hydrogen out-of-plane bending are 161.5 and 31°, respectively. Molecular mechanics calculations on **8** by Yavari predicted two nearly degenerate conformational minima with C_1–C_2–C_3 angles of 160°.[24] Cycloheptadiene (**7**) continues observed trends.

For smaller homologues **4–6**, geometries change in a predictable fashion. MNDO geometries for **5** and **6** are less twisted out of plane than those from STO-3G calculations. Remarkably, even 1,2-cyclobutadiene maintains a C_2 structure, with the allenic hydrogens twisted 0.5° out of plane. However, this is substantially higher in energy than the singlet or triplet diradical structures. Further ab initio studies will be necessary to determine the accurate energetics of **4** relative to cyclopropylidene isomer **10** and other isomers.[14]

Bicyclo[3.2.1]octa-2,3,6-triene (**15**), another strained cyclic allene, was originally prepared by Bergman and Rajadbyaksha in 1970, and was observed to undergo facile rearrangement to **18**.[34] Two additional routes to **15** have been reported.[35]
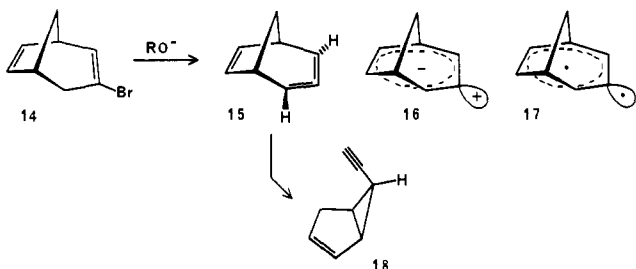
Bergman suggested a symmetrical zwitterionic structure **16**, which might be considered homoaromatic; however, we believe that diradical **17** might be more appropriate for the planar allenic structure.[36] Subsequent experiments by Balci and Jones[37] sup-

(32) Brogli, F.; Crandall, J. K.; Heilbroner, E.; Kloster-Jensen, E.; Sojka, S. A. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 455.
(33) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 2492.
(34) Bergman, R. G.; Rajadbyaksha, V. J. *J. Am. Chem. Soc.* **1970**, *92*, 2163.
(35) (a) Klumpp, G. W.; van Dijk, P. M. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 381. (b) Freeman, P. K.; Swenson, K. E. *J. Org. Chem.* **1982**, *47*, 2033. (c) A benzannelated derivative which does not rearrange has recently been described: Balci, M.; Harmandar, M. *Tetrahedron Lett.* **1984**, *25*, 237.

Figure 2. MNDO optimized structure for bicyclo[3.2.1]octatriene (**15**).

Figure 3. State correlation for racemization in a C_2 allene.

ported a chiral structure, since optically active cycloadducts were isolated when **15** was generated through elimination with a chiral base. In the absence of trapping agent, optically active **18** was isolated.

The MNDO structure for chiral bicyclo[3.2.1]octa-2,3,6-triene (ΔH_f = 122.8 kcal/mol) is shown in Figure 2. Geometry optimization for the planar biradical structure **17** did not converge satisfactorily, but the best MNDO energy was slightly below that of **15**. Ab initio calculations undoubtedly would reverse this order, which is not in agreement with experiment.[37] In the present context the chiral structure **15** seems unremarkable. The allene is strongly bent and twisted, with the attached cyclopentene ring appropriately skewed. The inversion barrier probably is quite small, but this may not compete with rearrangement to **18**, with its attendant strain relief.

Interpretive Discussion

Figure 3 shows a state correlation for a simple $C_2 \rightarrow C_{2v}$ twisting motion in allene, similar to those occurring during racemization of a bent cyclic allene. Correlations are derived from the present work and from more detailed ab initio CI calculations on allene excited-state potential surfaces.[16] Relative energetics will vary substantially with ring size. This will depend upon synergistic

(36) The bicyclo[3.2.1]octadienyl anion is quite analogous to species **16**. Although this may be considered homoaromatic, two recent theoretical studies show no evidence for significant homoconjugative stabilization [Grutzner, J. B.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1372. Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. V. R. *Ibid.* **1981**, *103*, 1375.]. This conclusion has been challenged by a third theoretical study [Brown, J. M.; Elliot, R. J.; Richards, W. G. *J. Chem. Soc., Perkin Trans. 2* **1982**, 485], and by a recent report on the ^{13}C NMR spectrum of the anion, [Christl, M.; Leininger, H.; Brückner, D. *J. Am. Chem. Soc.* **1983**, *105*, 4843.]. Nevertheless, stabilization from homoaromaticity should not overcome the degree of charge separation engendered by structure **16**.
(37) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1981**, *103*, 2874.

effects of allene strain, due to in-plane bending and diminished π-bonding, and strain in the $-(CH_2)_n-$ linkage.

For moderate to large ring sizes (>6 carbons), the C_2 chiral structures are global minima, with racemization occurring through a bent planar diradical. The allene triplet also should have a minimum at this geometry, with a small singlet–triplet gap[15,38] and a nearly identical geometry. However, as noted above, the singlet is predicted to lie below the triplet.

A second excited singlet minimum is predicted to occur for the lowest closed-shell state, which corresponds to a zwitterion.[9,15] This is of higher energy than the open-shell singlet because of one additional electron intrapair repulsion.

Our calculations permit a quantitative estimate of the strain inherent in allenes **5** and **6**. Previous calculations by Pople and co-workers show that allenes should racemize through a C_{2v} biradical species, with a bending angle of ca. 130°.[15] The in-plane bending potential is relatively soft.[16] Thus, for **5** and **6**, the racemization transition states **5**-^{1}D and **6**-^{1}D, with bending angles 123 and 127°, respectively, should be essentially unstrained. Roth has measured an experimental racemization barrier of 46.2 kcal/mol in 2,3-pentadiene, another disubstituted allene.[39] Combining this value with our predicted MCSCF inversion barriers (4.9 and 15.0 kcal/mol) yields strain estimates of 41.3 and 31.2 kcal/mol, respectively, for **5** and **6**. Dimerization or other reactions would be accompanied by substantial strain release.

Conclusions
One of the lessons which has been learned during the past several decades is the degree to which hydrocarbons may be structurally distorted and yet remain thermodynamically stable (if reactive) molecules.[2a] Cyclic allenes further demonstrate the remarkable tenacity of π-bonding. Thus, while a chiral allenic structure for 1,2-cyclohexadiene may have seemed only remotely possible, experiment and theory now have converged on this remarkable conclusion. For the smaller homologue, 1,2-cyclopentadiene, our calculations slightly favor a chiral structure, but the energy difference is within reasonable estimates for computational error bounds, and confirmation must await the results of careful experimentation.

We are continuing to explore other strained cyclic allene structures, as well as cyclic butatrienes, the next homologous cumulene. The smallest isolable cyclic butatriene probably is 1,2,3-cyclononatriene, which we have recently prepared for the first time.[40]

(38) Pasto, D. J.; Haley, M.; Chipman, D. M. *J. Am. Chem. Soc.* **1978,** *100,* 5272.
(39) Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974,** *107,* 48.

(40) Angus, R. O. Jr.; Johnson, R. P. *J. Org. Chem.* **1984,** *49,* 2880.

Structural and Energetic Features of Fully Substituted Silylenes, Disilenes, and Silylsilylenes (SiX$_2$, X$_2$SiSiX$_2$, and XSiSiX$_3$; X = Li, CH$_3$, and F)

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Abstract: Ab initio molecular orbital calculations with basis sets of split valence plus polarization function quality (6-31G*) have been carried out on some fully substituted silylenes, disilenes, and silylsilylenes (SiX$_2$, X$_2$SiSiX$_2$, and XSiSiX$_3$; X = Li, CH$_3$, and F). The silylenes SiH$_2$, Si(CH$_3$)$_2$, and SiF$_2$ are all strongly bent in both their singlet ground and triplet excited states, but SiLi$_2$ has a triplet ground state with a linear geometry and a bent singlet excited state. Singlet–triplet separations are calculated (CISD/6-31G*//6-31G*) in SiH$_2$, Si(CH$_3$)$_2$, SiF$_2$, and SiLi$_2$ as 17.6, 22.9, 74.0, and −10.3 kcal/mol, respectively. The Si$_2$(CH$_3$)$_4$ isomers resemble the analogous Si$_2$H$_4$ species with respect to structural and energetic features. Thus, the singlet disilenes and silylsilylenes are almost isoenergetic, the disilene dissociation energies toward two simple silylenes are comparable, and both disilenes feature very flat potential energy surfaces for bending of the geminal groups in a mutual trans fashion or twisting around the SiSi bond. In contrast, no closed shell singlet minimum could be located for F$_2$SiSiF$_2$ corresponding to a disilene; a minimum for a diradical-like triplet ·F$_2$SiSiF$_2$· species was obtained, but this structure is considerably less stable ($\approx$25 kcal/mol; HF/6-31G*//6-31G$^+$) than the singlet silylsilylene, :FSiSiF$_3$. For the model Si$_2$Li$_4$ species, there is no minimum corresponding to a conventional disilene or a silylsilylene. A distorted, planar structure with two bridging Li atoms (LiSiLi$_2$SiLi, C_{2h} symmetry) has been located as the global minimum for singlet Si$_2$Li$_4$.

I. Introduction
There is at present considerable interest in molecules featuring trivalent or divalent silicon.[1] Experimental determinations of physical parameters for these generally short-lived, reactive silicon species are difficult to obtain and hence largely nonexistent. Such systems are, however, amenable to accurate theoretical investigations, and it is desirable to explore the possibility and opportunity to obtain reliable information in this manner. This paper presents results from ab initio molecular orbital calculations on fully substituted silylenes, disilenes, and silylsilylenes (SiX$_2$, X$_2$SiSiX$_2$, and XSiSiX$_3$; X = Li, CH$_3$, and F) with the aim to assess structural and energetic substituent effects on the parent systems

(1) Review: Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979,** *79,* 529. Gaspar, P. P. "Reactive Intermediates"; Moss, R. A., Jones, M., Jr., Eds.; Wiley, New York, 1985; Vol. 3, Chapter 9.