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# Fulvalenes, Fulvenes, and Related Molecules: An ab Initio Study

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Ab initio calculations using conventional (HF/6-31G* and MP2/6-31G*) and density functional theory (B-LYP/6-31G*) methods have been used to determine the structures of the [*n*]fulvene and [*n*,*m*]-fulvalene ($n$, $m = 3, 5, 7$) series of molecules, with particular emphasis on heptafulvalene ($n = m = 7$: **12**). Calculations have also been performed on the parent cycloalkenes: cyclopropene, cyclopentadiene, and cycloheptatriene (**1**−**3**, respectively). All the fulvenes ($n = 3, 5, 7$: **4**−**6**, respectively) and the smaller fulvalenes ($n = 3$, $m = 3, 5, 7$: **7**−**9**, respectively, and $n = m = 5$: **10**) are found to be planar. Pentaheptafulvalene ($n = 5$, $m = 7$: **11**) adopts a very slightly nonplanar $C_s$ arrangement of the five- and seven-membered rings. Heptafulvalene (**12**) is predicted to have an *anti*-folded $C_{2h}$ structure, in accord with the X-ray crystal structure. We propose that the underlying reason for **11** and **12** adopting nonplanar conformations is the proximity of the $H_2$ and $H_{2'}$ hydrogen atoms which promotes a distortion of the rings away from planarity at the central fulvalenic C=C double bond. In the process, $\pi$-overlap is lost but this is partially regained by pyramidalization of the carbon centers in the seven-membered ring(s). The degree of folding is substantially more pronounced in **12** than in **11**. Our calculated dipole moments, $\pi$-electron distributions, bond alternation parameters, and energy comparisons indicate that the unknown smallest fulvalene, triafulvalene (**7**), is highly destabilized with localized bonding while triapentafulvalene (**8**), which is also unknown, is predicted to be stabilized and quite delocalized, consistent with Hückel $4n + 2$ considerations.

## A. Introduction

The monocyclic (poly)enes, cyclopropene (**1**), cyclopentadiene (**2**), and cycloheptatriene (**3**) (see Figure 1), may be regarded as the building blocks from which both the fulvene and fulvalene families of molecules can formally be constructed. The fulvenes, triafulvene (**4**), pentafulvene (**5**), and heptafulvene (**6**), have attracted much interest due to their unique cross-conjugated structures and questions regarding their aromatic/antiaromatic character.[1−5] The fulvalenes, triafulvalene (**7**), triapentafulvalene (**8**), triaheptafulvalene (**9**), and pentafulvalene (**10**) have also received a great deal of attention.[1,6−8] While the small fulvalenes **7**−**9** have not been synthesized, the syntheses and some chemical and physical properties of pentafulvalene (**10**), pentaheptafulvalene (**11**) and heptafulvalene (**12**) have been described.[9,10]

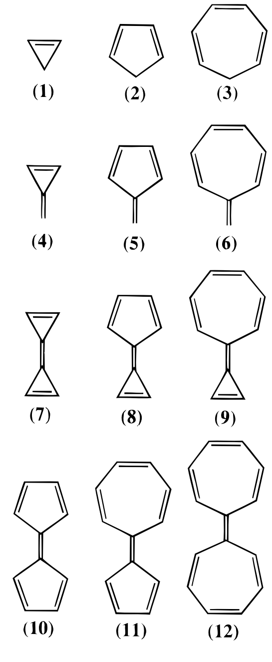

**Figure 1.** Schematic representation of the molecules investigated in this study.

Heptafulvalene (**12**)[11] is a 14$\pi$-electron symmetrical [*n*,*m*]fulvalene ($n = m = 7$). It is a permanganate-colored, fairly stable, oxygen-sensitive hydrocarbon with a melting point of 122 °C. Its resonance energy, based on heat of hydrogenation measurements, has been estimated as 117 kJ mol$^{-1}$.[12] Craig Rules[13] formally designate heptafulvalene (**12**) as "aromatic" (with a totally symmetric valence-bond wave function in the ground state) rather than "pseudoaromatic". The crystal struc-

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(1) For a recent comprehensive review on fulvenes and fulvalenes see: Neuenschwander, M. In *The Chemistry of Functional Groups. Supplement A, The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, 1989; Vol. 2, pp 1131−1268.

(2) Reviews: (a) Becker, G. Triafulvenes. *Methoden der Organischen Chemie Houben Weyl,* Georg Thieme Verlag: Stuttgart. Carbocyclische Pi-Elektronen Systeme, 1985; *5/2c*, p 476. (b) Zeller, K. P. Pentafulvenes. *Ibid*. 1985, *5/2c*, 504. (c) Asao, T.; Oda, M. Heptafulvenes. *Ibid*. 1985, *5/2c*, 769. (d) Bergmann, E. D. *Chem. Rev.* **1968**, *68*, 41.

(3) Synthesis: (a) Triafulvene: Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698. Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699. Maier, G.; Hoppe, M.; Lanz, K.; Reisenauer, P. *Tetrahedron Lett.* **1984**, *25*, 5645. (b) Pentafulvene: Kent, J. E.; Jones, A. J. *Aust. J. Chem.* **1970**, *23*, 1059. (c) Heptafulvene: Schenk, W. K.; Kyburz, R.; Neuenschwander, M. *Helv. Chim. Acta* **1975**, *58*, 1099.

(4) (a) Triafulvene: Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912. See also: Hess, B. A., Jr.; Michalska, D.; Schaad, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 1449. (b) Pentafulvene: Baron, P. A.; Brown, R. D.; Burden, F. R.; Domaille, P. J.; Kent, J. E. *J. Mol. Spectrosc.* **1972**, *43*, 401. (c) Heptafulvene: Bauder, A.; Keller, C.; Neuenschwander, M. *J. Mol. Spectrosc.* **1976**, *63*, 281.

(5) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley: New York, 1994.

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ture of **12** reveals that it adopts a nonplanar, approximately "S"-shaped conformation with a marked alternation of single and double bonds in the seven-membered rings and that it possesses a relatively long central C=C double bond (1.379 Å).[14] The chemistry of **12** is well established, and syntheses of derivatives of **12** can be found in the literature.[15] Doering took advantage of the S-shaped *anti*-folded structure of **12** in carrying out a stereospecific concerted thermal [$_{\pi}14_{a} + _{\pi}2_{s}$] cycloaddition of tetracyanoethylene to **12**.[16] The *anti* structure of **12** sets the stage ideally for an *antara* addition to the 14$\pi$-electron system, through an aromatic Möbius strip transition structure.[16]

The cause of nonplanarity in the heptafulvalene molecule has been a controversial issue.[14,17,18] Thomas and Coppens[14] have claimed that because of distortion of the internal ring bond angles the molecule is strained and that "the strain is relieved by appreciable distortions of the ring framework, some carbons being displaced by as much as 0.35 Å from the best plane through the molecule". Later, Cheng and Nyburg[17] argued that the cause of the nonplanarity in **12** is "more probably due to conflict of two pairs of hydrogen atoms within the molecule rather than the need to relieve bond angle strain within the rings". In reply, Coppens[18] concluded that although the H···H repulsions should not be ignored, steric hindrance in **12** is much less severe than in other overcrowded[19] compounds (e.g., bifluorenylidene, bianthrone, dixanthylene), and that ring strain makes a significant contribution to the deformation of the molecule.

The central carbon−carbon double bond of **12** is clearly overcrowded. In the planar $D_{2h}$ structure, the overcrowding arises from the very short distances for $H_2 \cdots H_{2'}$ (and $H_7 \cdots H_{7'}$), leading to a considerable overlap of the hydrogen van der Waals radii. Coppens[18] has predicted that the $H_2 \cdots H_{2'}$ distance in a hypothetical undistorted structure could be as little as 1.7 Å.

The associated repulsive interactions could, in principle, be relieved by structural distortions such as (a) stretching of $C_1{=}C_{1'}$, (b) distortions of the ∠CCC bond angles, particularly around $C_1$ and $C_{1'}$, (c) twisting around $C_1{=}C_{1'}$, (d) *anti*- or *syn*-folding of the cycloheptatriene rings, (e) *anti*- or *syn*-pyramidalization at $C_1$ and $C_{1'}$, or (f) some other distortions within the seven-membered rings.

Ab initio molecular orbital calculations provide an attractive means of addressing problems such as the interplay between delocalization and strain in **12** and the controversy[14,17,18] surrounding its folded structure. Application of such calculations to a broader systematic study of fulvenes and other fulvalenes would also be of interest. To this end, we have used ab initio molecular orbital theory to examine various possible structures of cyclopropene (**1**), cyclopentadiene (**2**), cycloheptatriene (**3**), triafulvene (**4**), pentafulvene (**5**), heptafulvene (**6**), triafulvalene (**7**), triapentafulvalene (**8**), triaheptafulvalene (**9**), pentafulvalene (**10**), pentaheptafulvalene (**11**), and heptafulvalene (**12**) (see Figure 1), and the results are reported in the present paper.

## B. Methods

Standard ab initio calculations[20] have been carried out using the GAUSSIAN 92/DFT series of programs.[21] Geometries for **1**−**12** were initially optimized at the HF/6-31G* level, hereinafter simply termed HF. However, it is well known[20] that bond lengths for multiple bonds are generally predicted to be too short at the HF level of theory and better agreement with experiment is usually obtained by the inclusion of electron correlation. Geometry optimizations were therefore also carried out with Møller−Plesset perturbation theory truncated at second order with the core electrons of each heavy atom held frozen (MP2-fc/6-31G*, termed MP2). Finally, further geometry optimizations were performed, for comparison purposes, using a variant of density functional theory (DFT), specifically the B-LYP/6-31G* level of theory,[22] which is termed B-LYP in later sections of this paper.

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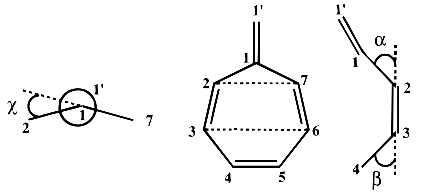
**Chart 1**



Harmonic vibrational frequencies were calculated at the appropriate levels of theory in order to confirm the nature (whether a minimum energy structure or otherwise) of all the stationary points.

## C. Results

Figures 2−8 display a selection of the calculated bond lengths and bond angles of the various conformations of the cycloalkenes, [*n*]fulvenes and [*n*,*m*]fulvalenes investigated in this study, along with a depiction of the direction and magnitude of their dipole moments (where applicable). More complete geometrical information is available in Table S1 of the Supporting Information.[23] Table S2 gives the calculated energies of the various structures of **1**−**12** and also indicates whether the structures represent minima (all real frequencies) or saddle points (one or more imaginary frequencies) on the potential surface. Unless otherwise noted, all the structures were found to be energy minima.

In those molecules for which dipolar aromatic canonical resonance structures can be drawn (**4** − **6**, **8**, **9**, and **11**), we have obtained rough estimates of the contribution of such structures, both from the calculated Mulliken $\pi$-electron distributions and from the calculated dipole moments, the latter approach assuming that the positive and negative charges are positioned at the center of mass of the respective rings and that any other contributions to the dipole moment may be neglected. The two measures are found to give very similar results. We report in this manuscript only the values obtained from the Mulliken $\pi$-electron populations, as calculated at the MP2 level.

Of particular interest in analyzing distortions associated with the nonplanar seven-membered rings in **11** and **12** are the pyramidalization angles, $\chi$, and the folding angles, $\alpha$ and $\beta$. These are shown pictorially in Chart 1. The pyramidalization angle $\chi$ at $C_1$ is defined as the dihedral angle between the planes $C_{1'}C_1C_2$ and $C_{1'}C_1C_7$ (or $\chi = 180° - \angle C_2C_1C_{1'}C_7$).[24] The atoms $C_1$ and $C_{1'}$ can be *syn*- or *anti*-pyramidalized with respect to one another. The angles $\alpha$ and $\beta$ are defined as the angles between the $C_1C_2C_7$ and $C_2C_3C_6C_7$ planes and the $C_2C_3C_6C_7$ and $C_3C_4C_5C_6$ planes, respectively.

## D. Discussion

**1. Cyclic Alkenes (1−3).** It is appropriate that we first discuss the parent cyclic alkenes **1**−**3** (Figure 2). Cyclopropene (**1**) is predicted to have a $C_{2v}$ structure at the three levels of theory used in this study in accord with the experimental structure determined by Kasai et al.[25] The geometrical parameters predicted by the B-LYP and MP2 methods are in particularly good agreement with experimental values. The experimental[25] dipole moment for **1** (0.46 D) is in reasonable agreement with our theoretical values (0.50−0.56 D).

Likewise, cyclopentadiene (**2**) is also shown to possess a planar $C_{2v}$ structure. Our calculated geometrical parameters are in good accord with those determined by Damiani et al.[26] In addition, the MP2 rotational constants agree well with Damiani's experimental values,[27] confirming that our predicted MP2 geometry is a better match to the experimental geometry than the geometries determined at HF or B-LYP. Our theoretical dipole moment values for **2** (0.30−0.46 D) are in good agreement with the experimental value (0.42 D) determined by Damiani et al.[26]

In contrast to both **1** and **2**, cycloheptatriene (**3**) is found to have a folded $C_s$ structure (**3**-$C_s$), in accord with an electron diffraction study by Traetteberg[28] and a microwave study by Butcher.[29] Traetteberg's experimental determination for the geometry of **3** remains the most complete to date. However, our predicted $C_s$ geometry shows some significant differences from it, including the internal $\angle$CCC bond angles and the degree of folding (angles $\alpha$ and $\beta$ for **3**-$C_s$ in Figure 2) predicted for the seven-membered ring. We note that our calculated values for $\alpha$ and $\beta$ ($\alpha = 49-58°$, $\beta = 24-28°$) are in the reverse order to those determined by Traetteberg[28] ($\alpha = 37°$, $\beta = 41°$) but in reasonable agreement with those determined by Butcher[29] ($\alpha = 50°$, $\beta = 29.5°$) and some earlier theoretical studies (molecular mechanics:[30a] $\alpha = 49.5°$, $\beta = 28°$; SCF/DZ:[30b] $\alpha = 50.1°$, $\beta = 26.9°$). It is also interesting to note that the X-ray crystal structure for 7,7-dimethylcycloheptatriene-3-carboxylic acid[31] shows values for these angles ($\alpha = 49.7°$, $\beta = 23.7°$) similar to those predicted by theory for **3**-$C_s$. Our predicted rotational constants[32] for **3**-$C_s$ are in reasonable agreement with those determined by Butcher.[29]

We note the large increase in the $\angle$CCC bond angle at $C_1$ in the planar $C_{2v}$ structure for **3** (about 120° in **3**-$C_{2v}$) compared with that found for **3**-$C_s$ (106−110°). We also note other major changes in the internal $\angle$CCC angles when a conformational change from $C_{2v}$ to $C_s$ symmetry takes place. All these changes can be rationalized in terms of relief of the ring strain in **3**-$C_{2v}$. Geometric and structural requirements for the ring planarization of cycloheptatriene have been elegantly described.[33] The **3**-$C_{2v}$ structure (which has one imaginary frequency) is predicted to lie between 18 (HF) and 41 (MP2) kJ mol$^{-1}$ higher in energy than **3**-$C_s$ (Table S2).

Both cyclopentadiene (**2**) and cycloheptatriene (**3**) have been classified as aromatic according to the criterion (for aromaticity) of diamagnetic susceptibility exaltation.[34] Cyclic delocalization via hyperconjugative $\pi-\sigma$ interactions has been suggested as the origin for the high exaltation values.

**2. Triafulvene (4).** Triafulvene (**4**) possesses a $C_{2v}$ structure at all the levels of theory used in this study.

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[23] Presented in the form of Gaussian archive files.

[24] See, for example, (a) Radhakrishnan T. P.; Agranat, I. *Struct. Chem.* **1991**, *2*, 107. (b) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385.

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[27] Experimental (see reference 26): $A = 8426$, $B = 8226$, $C = 4271$ MHz. HF: $A = 8572$, $B = 8268$, $C = 4319$ MHz. B-LYP: $A = 8316$, $B = 8104$, $C = 4212$ MHz. MP2: $A = 8435$, $B = 8251$, $C = 4281$ MHz.

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[32] Experimental (see Reference 29): $A = 3696$, $B = 3672$, $C = 2032$ MHz. HF: $A = 3711$, $B = 3670$, $C = 2012$ MHz. B-LYP: $A = 3626$, $B = 3607$, $C = 1975$ MHz. MP2: $A = 3712$, $B = 3707$, $C = 2060$ MHz.

[33] Ermer, O.; Klarner, F.-G.; Wette, M. *J. Am. Chem. Soc.* **1986**, *108*, 4908.

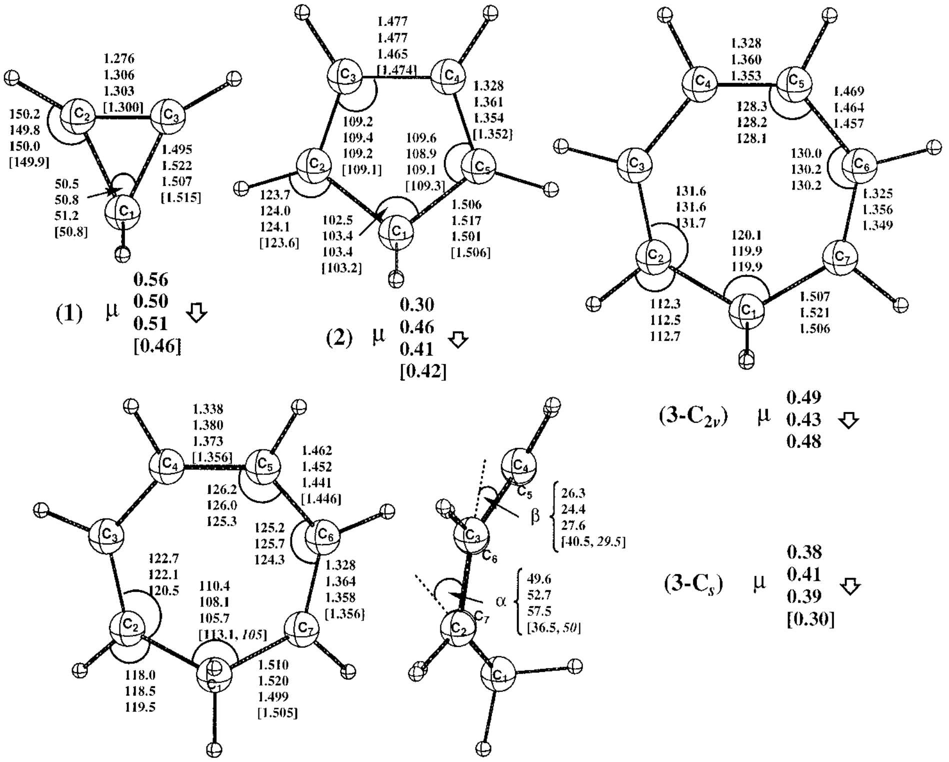


**Figure 2.** Selected geometrical parameters for cyclopropene (**1**), cyclopentadiene (**2**), and planar (**3**-$C_{2v}$) and folded (**3**-$C_s$) cycloheptatriene. Parameters are given in the following order: HF, B-LYP, MP2, and experimental (in square brackets from references 25, 26, 28, and 29, see text).

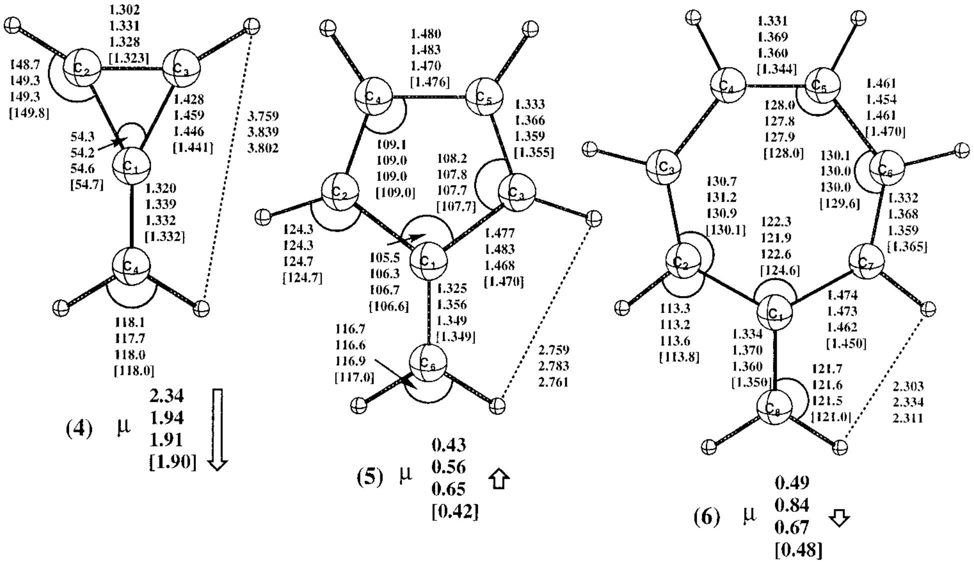
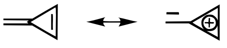


**Figure 3.** Selected geometrical parameters for triafulvene (**4**), pentafulvene (**5**), and heptafulvene (6). Parameters are given in the following order: HF, B-LYP, MP2, and experimental (in square brackets from references 4a, 4b and 4c, see text).

Comparison of the calculated geometric parameters with experimental values[4a] (Figure 3) shows good agreement, with MP2 faring best of the theoretical procedures. The endocyclic C=C bond in **4** is significantly longer than the C=C bond in **1**. The calculated dipole moment of **4** is significant (1.91–2.34 D) and compares well with the experimental dipole moment of 1.90 D determined by Nordem et al.[4a] The dipole direction, with the cyclopropenyl ring at the positive end, is in accord with the $4n + 2$ Hückel rule.[35] The contribution of the dipolar canonical form **4b** is estimated to be 19% (based on the calculated MP2 Mulliken $\pi$-electron distribution). Various theoretical methods have been previously used to study the degree of aromaticity of **4**.[36] Despite the highly polar nature of **4**, previous analyses of the experimental and calculated data have generally concluded that it is nonaromatic.[4a,37]



**(4a)** **(4b)**

**3. Pentafulvene (5).** Pentafulvene (**5**) also has a $C_{2v}$ structure at all the levels of theory used in this study.

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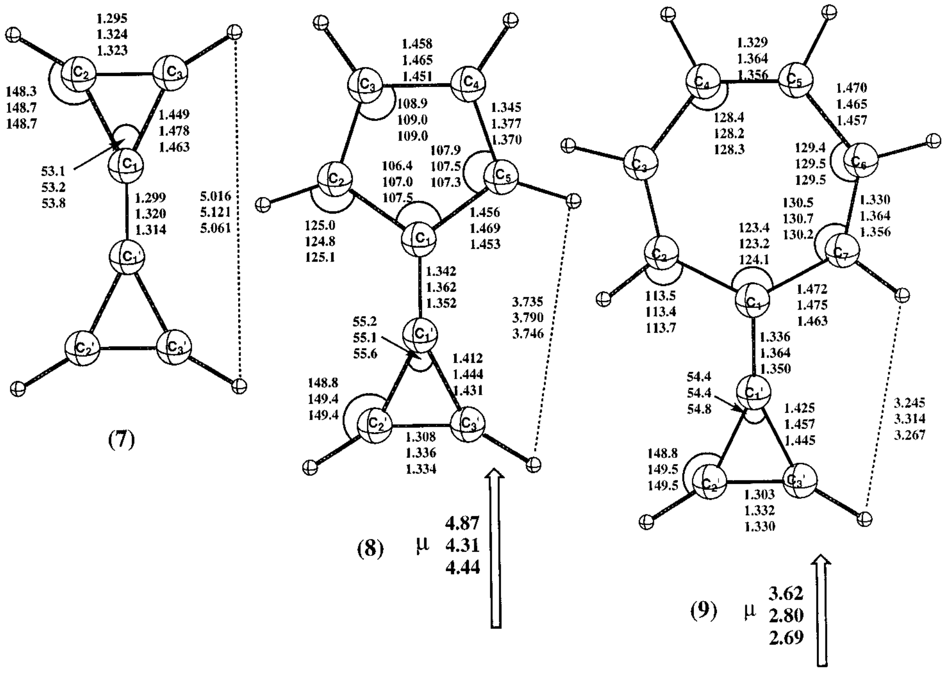
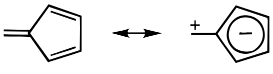
(34) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. 2, p 167.



(7) (8) (9)

**Figure 4.** Selected geometrical parameters for triafulvalene (**7**), triapentafulvalene (**8**), and triaheptafulvalene (**9**). Parameters are given in the following order: HF, B-LYP, and MP2.

There is good agreement between the theoretical and experimentally determined[4b] geometries (Figure 3), MP2 again performing best. The most noticeable differences between **5** and **2** are the substantially shorter C–C single bonds to $C_1$ and the larger internal bond angle at $C_1$, both a result of the change in hybridization at the $C_1$ center. However, the general similarity in structure between **2** and **5** suggests that both are similarly delocalized.

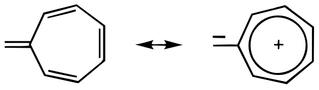


(5a) (5b)

Our calculated dipole moments for **5** of between 0.43 and 0.65 D (negative end in the cyclopentadienyl ring) are in reasonable agreement with the value determined experimentally (0.42 D) by Baron et al.[4b,38] The estimated contribution of the dipolar canonical form **5b** to the overall structure of **5** is very small (7%). Previous spectroscopic results have suggested that **5** is essentially nonaromatic in character.[1]

**4. Heptafulvene (6).** Heptafulvene (**6**) also adopts a planar $C_{2v}$ structure. Our calculated HF, MP2, and B-LYP optimized structures (Figure 3) are in good agreement with the structure reported by Bauder et al.[4c] Rotational constants obtained[4c] from a least-squares fit of the measured microwave transition frequencies also accord well with those determined by theory.[39] The internal bond angles for the seven-membered ring are quite large, the fulvenic angle being about 122–123°, while the other angles vary from 128° to 131°. It is of interest to see whether a reduction in the $\angle C_2C_1C_7$ bond angle leads to a nonplanar structure. We therefore constrained this angle at the same value as found in the $C_{2h}$ conformation of heptafulvalene, **12**-$C_{2h}$ (117.3° at the HF level) (vide infra), and optimized the remaining geometric parameters under $C_s$ symmetry. The preferred structure remains planar. We conclude, therefore, that in the absence of external influences, the cycloheptatrienylidene ring does not show a tendency to fold, even if angular strain is introduced in the seven-membered ring through a reduced bond angle at $C_1$.

Our predicted dipole moments for **6** of 0.49–0.84 D (toward the methylene group) are somewhat larger than that determined by Bauder et al.[4c] of 0.48 D. The dipole magnitude and direction are consistent with a very small contribution (5%) of **6b** to the overall structure of **6.** Previous spectroscopic results have concluded that **6** is basically nonaromatic in character.[1]



(6a) (6b)

**5. Triafulvalene (7).** Our calculated optimized structures are displayed in Figure 4. HF and B-LYP theories predict planar $D_{2h}$ structures for **7** which were confirmed as energy minima. At the MP2/6-31G* level of theory, however, the planar structure is found to be a first-order saddle point. An *anti*-folding distortion to $C_{2h}$ symmetry leads to a very small energy lowering of 0.2 kJ mol$^{-1}$. The $C_{2h}$ structure is distorted at the fulvalenic carbons by only 6° from planarity while the remaining geometrical parameters are almost identical to those calculated for the $D_{2h}$ structure. We have explored whether this prediction of a slightly nonplanar structure is

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(35) Application of the Hückel rule to odd-membered rings shows that the three- and seven-membered rings should be positively charged while the five-membered ring should be negatively charged. For the limits of applicability of the Hückel Rule, see reference 5, p 123.

(36) (a) Nakajima, T.; Katagiri, S. *Mol. Phys.* **1963**, *7*, 149. (b) Nakajima, T. *Pure Appl. Chem.* **1971**, *28*, 219. (c) Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692. (d) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371. (e) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992**, *114*, 5362.

(37) Billups, W. E.; McCord, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1332.

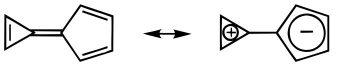
(38) See also, Replogle, E. S.; Trucks, G. W.; Staley, S. W. *J. Phys. Chem.* **1991**, *95*, 6908.

(39) Experimental (see reference 4c): $A = 3666$, $B = 2004$, $C = 1298$ MHz, HF: $A = 3695$, $B = 2028$, $C = 1309$ MHz, B-LYP: $A = 3645$, $B = 1964$, $C = 1276$ MHz, MP2: $A = 3682$, $B = 1995$, $C = 1294$ MHz.

maintained at higher levels of theory. We find that the deviation from $D_{2h}$ symmetry with the MP2 method is not affected by the inclusion of the heavy atom core electrons (MP2-full). However, increasing the basis set from 6-31G* to 6-311+G(2df,p)[40] leads to an MP2 prediction of a planar $D_{2h}$ geometry for **7**, suggesting that the MP2/6-31G* result is artificial. We conclude that triafulvalene (**7**) is planar. Considerable fulvalenic bond length compression has occurred in **7** when compared with either the fulvenic bond length in **4** or when compared with the C═C bond length in ethene. The C−C single bond lengths in **7** have also lengthened significantly compared with those found in **4** (vide infra).

**6. Triapentafulvalene (8).** HF, B-LYP, and MP2 theories predict a $C_{2v}$ structure for **8**. Our calculated optimized structures (Figure 4) show that the geometrical parameters for both rings of **8** are substantially different from those displayed in Figure 3 for **4** and **5**. In particular, the C−C single bonds of both the three- and five-membered rings have markedly decreased in length while the C═C double bonds of the five-membered ring have lengthened (as has the C═C double bond of the three-membered ring, albeit to a lesser degree). The central fulvenic C═C double bond has lengthened compared with that found in either **4** or **5** (vide infra).

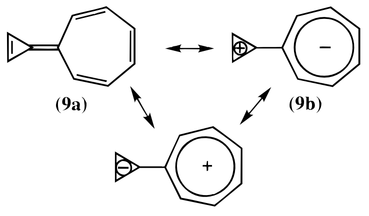
The calculated dipole moments of **8** are large, with predicted values between 4.31 and 4.87 D. An experimental value of 5.63 D has been estimated from the experimental dipole moment of 2,3,4,5-tetrachloro-2′,3′-dipropyltriapentafulvalene (7.56 D).[41] Other substituted triapentafulvalenes have similarly large dipole moments. For example, 2,3,4,5-tetraphenyl-2′,3′-dimethyltriapentafulvalene has a dipole moment of 6.0 D,[42] 2,3,4,5-tetrachloro-2′,3′-diphenyltriapentafulvalene has a dipole moment of 8.1 D,[43,44] and hexaphenyltriapentafulvalene has a dipole moment of 6.3 D.[45] The size of the dipole moment for **8** is not surprising in view of the reinforcing nature of the dipole directions of the component molecules, **4** and **5**, and reflects a 31% contribution of the aromatic cyclopropenium−cyclopentadienide structure **8b**.



**(8a)** **(8b)**

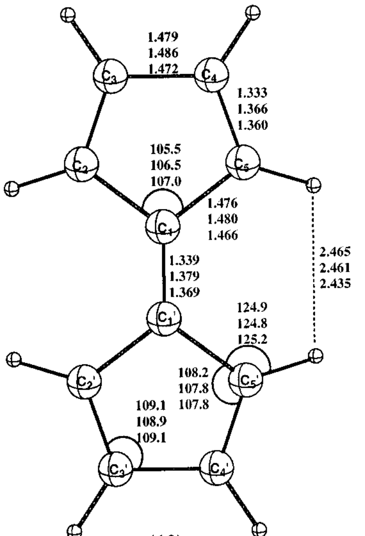
**7. Triaheptafulvalene (9).** HF, B-LYP, and MP2 theories predict a planar $C_{2v}$ structure for **9**. Our calculated optimized structures (Figure 4) show that the geometrical parameters for the three- and seven-membered rings of **9** are quite similar to those displayed in Figure 3 for **4** and **6**. The calculated dipole moments for **9** of between 2.69 and 3.62 D, although quite large, also supports the notion of a substantially lower level of interaction between the rings in **9** as compared with **8**. Two canonical dipolar forms, **9b** and **9c**, can be considered.

In each of these dipolar forms one ring has $4n + 2$ electrons while the other has $4n$ electrons. The calculated dipole direction (from the cyclopropenyl ring at the positive end to the cycloheptatrienyl ring at the negative end) suggests that **9b** is the dominant canonical structure for **9**. Assuming that the contribution of **9c** is negligible, the calculated π-electron distribution of **9** reflects a 15% contribution of **9b**.



**(9a)** **(9b)** **(9c)**

**8. Pentafulvalene (10).** This molecule, an isomer of **9**, has a planar $D_{2h}$ structure (Figure 5). In contrast to **8**, the geometrical parameters for the five-membered rings of **10** are almost identical to those observed in the isolated component molecules, **5**. The only exception is the fulvalenic C═C double bond which is found to be significantly longer than the fulvenic C═C double bond in **5**.



**(10)**

**Figure 5.** Selected geometrical parameters for pentafulvalene (**10**). Parameters are given in the following order: HF, B-LYP, and MP2.

**9. Pentaheptafulvalene (11).** A very slightly nonplanar $C_s$ structure (**11**-$C_s$) is found to be the minimum at HF and MP2 while the planar $C_{2v}$ structure (**11**-$C_{2v}$) is found to be a first-order saddle point. At the B-LYP level of theory, however, the predicted structure is the planar $C_{2v}$ form. The energy difference between **11**-$C_{2v}$ and **11**-$C_s$ is, however, very small: 0.5 kJ mol$^{-1}$ at the HF level and 0.4 kJ mol$^{-1}$ at MP2 (Table S2).

Some of the structural parameters for **11**-$C_s$ and **11**-$C_{2v}$ are displayed in Figure 6. The $H_2 \cdots H_{2'}$ intramolecular distances increase slightly in going from **11**-$C_{2v}$ (2.028−2.046 Å) to **11**-$C_s$ (2.078−2.121 Å). The degree of folding of the seven-membered ring for **11**-$C_s$ is predicted to be $\alpha = 16.5°$, $\beta = 9.8°$ (HF) and $\alpha = 14.5°$, $\beta = 7.6°$ (MP2). The $\angle C_2C_1C_7$ bond angle for **11**-$C_s$ (120.1° at HF and 120.9° at MP2) is slightly smaller than that found for **11**-$C_{2v}$ (121.1°, 121.4° and 121.7° at HF, B-LYP and MP2, respectively). The fulvalenic bond length in **11**-$C_s$ of 1.356 Å (HF) is significantly increased when calculated at MP2 (1.393 Å) and is consistent with general HF/MP2 behavior.[20] The more reliable MP2

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(40) See supporting information for energy and geometry.

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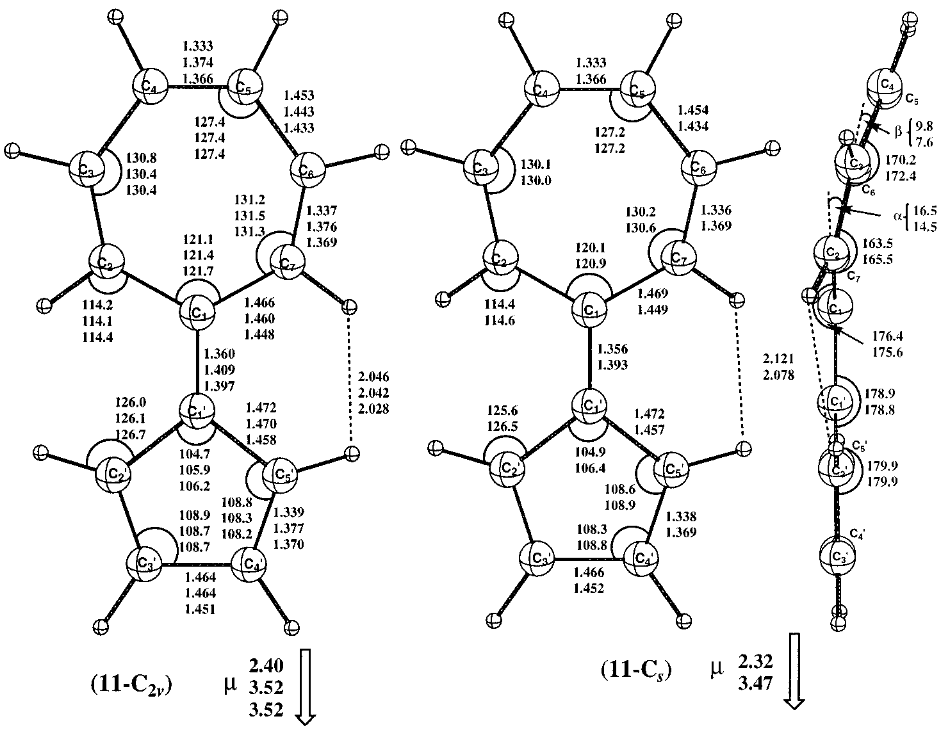
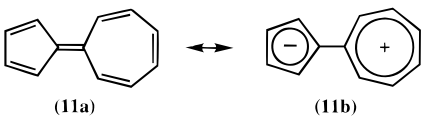


**Figure 6.** Selected geometrical parameters for planar (**11**-$C_{2v}$) and folded (**11**-$C_s$) pentaheptafulvalene. Parameters are given in the following order: HF, B-LYP, MP2 (**11**-$C_{2v}$) and HF and MP2 (**11**-$C_s$).

value of 1.393 Å indicates that pentaheptafulvalene has a very long fulvalenic C=C bond.

The dipole moments for **11**-$C_s$ calculated at the HF and MP2 levels of theory are 2.32 and 3.47 D, respectively, while B-LYP predicts a dipole moment of 3.52 D for **11**-$C_{2v}$. The direction and the relatively large magnitude of the dipole moment of **11** (towards the cyclopentadienyl ring) can be rationalized in terms of the Hückel 4n + 2 rule, the dipole directions of the components **5** and **6** reinforcing one another (cf. **8**, vide supra). The calculated $\pi$-electron distribution of **11** reflects a 22% contribution of the aromatic resonance form **11b**.


(11a) (11b)

Compared with **9**, which involves the interaction of three- and seven-membered ring components, there is a larger degree of polarization between the five- and seven-membered rings of **11** (22% in **11** vs 15% in **9**). This result is expected on the basis of Hückel 4n + 2 considerations. It is also consistent with the geometrical features of **11** and **9**, the seven-membered ring of **11** showing the greater evidence for cyclic delocalization.

**10. Heptafulvalene (12). (a) Structures and Energies. (i) $C_{2h}$ Conformation.** The *anti*-folded $C_{2h}$ structure for **12** is found to be the most stable conformation at all the levels of theory investigated in this study and frequency calculations at the HF and B-LYP level show that this structure is a true minimum. Selected structural parameters are compared with experimental values from an X-ray crystal structure[14] in Figure 7. As in previous cases, best agreement with experiment is found at the MP2 level. The experimental structure shows a slight distortion from $C_{2h}$ to $C_i$ symmetry, but this may be due to solid-state effects. There is certainly no evidence for a distortion of this type in the calculated structures. A very noticeable C−C bond length alternation is apparent in both the experimental and theoretically determined geometries, but it is less than in heptafulvene, **5**. Our calculations show that the seven-membered rings of **12**-$C_{2h}$ are considerably puckered. The degree of folding in **12**-$C_{2h}$ at the various theoretical levels are similar, with α in the range 24−33° and $\beta$ in the range 14−19°, close to the angles found in the X-ray structure[14] ($\alpha = 25°$, $\beta = 16°$). The degree of folding of the seven-membered ring of **12**-$C_{2h}$ at the MP2 level ($\alpha = 32.7°$, $\beta = 18.4°$) is more than double that found for **11**-$C_s$ ($\alpha$=14.5°, $\beta$=7.6°) while the $\angle C_2C_1C_7$ bond angle of 117.9° at MP2 for **12**-$C_{2h}$ is significantly smaller than that found in **11**-$C_s$ (120.9°). The MP2 fulvalenic $C_1{=}C_{1'}$ bond length in heptafulvalene (**12**-$C_{2h}$) of 1.378 Å is close to the experimental value (1.379 Å) and confirms that this bond is longer than typical C=C double bonds. However, it is significantly shorter than that found in **11**-$C_s$ (1.393 Å at MP2).

**(ii) $C_{2v}$ Conformation.** HF theory predicts a second stable conformation corresponding to a *syn*-folded structure with $C_{2v}$ symmetry (**12**-$C_{2v}$, Figure 7) having structural parameters around the rings similar to those found for **12**-$C_{2h}$. The major differences lie in the degree of pyramidalization at $C_1$, which is greater in **12**-$C_{2h}$ (*vide infra*), and the $H_2 \cdots H_{2'}$ distance which is much shorter in **12**-$C_{2v}$ than in **12**-$C_{2h}$. B-LYP on the other hand predicts that **12**-$C_{2v}$ is not an energy minimum and possesses two imaginary frequencies.

At the HF level, **12**-$C_{2v}$ lies about 13 kJ mol$^{-1}$ higher in energy than **12**-$C_{2h}$ and similar energy differences (13 and 16 kJ mol$^{-1}$, respectively) are predicted by B-LYP and by single-point MP2 energy calculations using the HF calculated geometry for **12**-$C_{2v}$ (cf. Table S2).

**(iii) $C_s$ Conformation.** The transition structure (**12**-$C_s$) predicted at the HF level for the interconversion of *syn*-folded (**12**-$C_{2v}$) and *anti*-folded (**12**-$C_{2h}$) conformations is displayed in Figure 8. A frequency analysis at HF shows that **12**-$C_s$ is a first-order saddle point on the HF

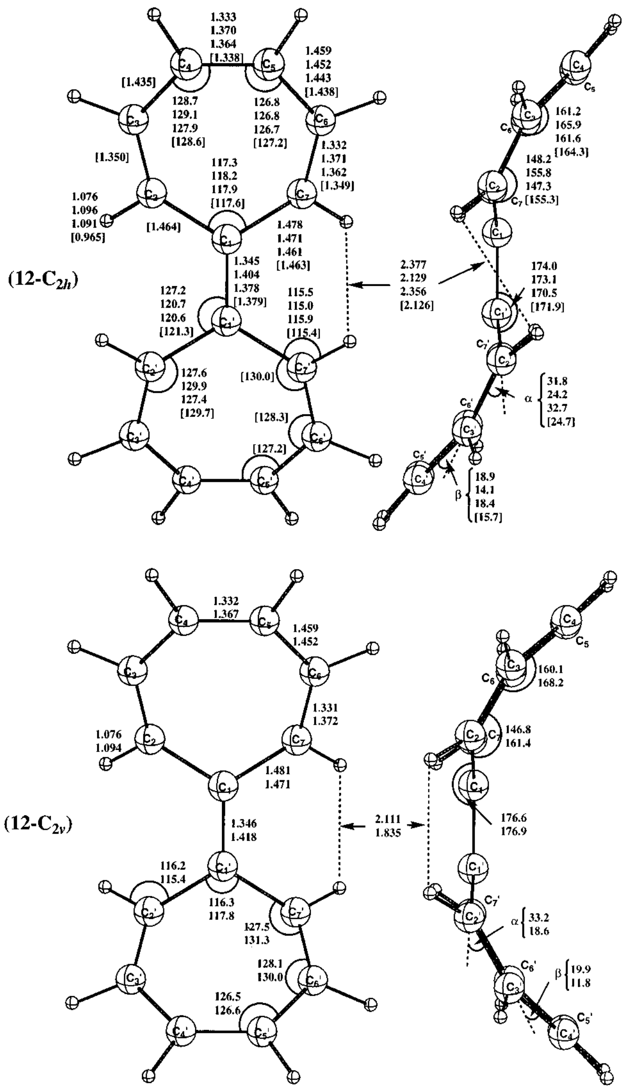


**Figure 7.** Selected geometrical parameters for *anti*-folded (**12**-$C_{2h}$) and *syn*-folded (**12**-$C_{2v}$) heptafulvalene. Parameters are given in the following order: HF, B-LYP, MP2 and experimental (in square brackets from reference 14) (**12**-$C_{2h}$) and HF and B-LYP (**12**-$C_{2v}$).

surface and somewhat resembles the $C_{2v}$ equilibrium structure (**12**-$C_{2v}$). One ring of the $C_s$ conformation is folded by about half as much ($\alpha' = 16°$, $\beta' = 10°$) as is found in the same ring in **12**-$C_{2v}$ (across lines joining $C_{2'}$-$C_{7'}$ and $C_{3'}$-$C_{6'}$), while the folding of the second ring (across lines joining $C_2-C_7$ and $C_3-C_6$) is enhanced ($\alpha = 39°$, $\beta = 23°$). The $C_s$ transition structure corresponds to a flip-flop motion (a synchronous passage of both $H_2$/$H_{2'}$ and $H_7$/$H_{7'}$), with no evidence of a twisting motion. The structure of **12** in which one seven-membered ring is planar is not a stationary point on the potential surface.

The transition structure for the *syn*−*anti* isomerization (**12**-$C_s$) is predicted to lie only 0.9 kJ mol$^{-1}$ higher in energy than the $C_{2v}$ structure when calculated at HF. However, our single-point energy calculations at MP2 (at the HF-optimized geometry for **12**-$C_s$) result in **12**-$C_s$ lying below **12**-$C_{2v}$ in energy suggesting that, as indicated also by B-LYP, **12**-$C_{2v}$ is unlikely to be a stable structure on the $C_{14}H_{12}$ surface. Indeed, optimizations at the B-LYP level starting from **12**-$C_{2v}$ but with only a $C_s$ symmetry constraint lead directly to **12**-$C_{2h}$.

**(iv) Other Conformations.** Some of the structural parameters calculated at the HF and B-LYP methods for the planar-constrained $D_{2h}$ structure (**12**-$D_{2h}$) are displayed in Figure 8. Of note is the very close contact distance between $H_2$ and $H_{2'}$ of 1.724 Å and the quite small $\angle C_2C_1C_7$ angle of about 118° predicted by the HF and B-LYP methods. **12**-$D_{2h}$ is found to be a third-order saddle point (i.e. three imaginary frequencies) at both these levels of theory. The imaginary frequencies correspond to two folding motions ($b_{2g}$ and $b_{3u}$) together with a twisting motion ($a_u$) of the seven-membered rings. Calculations at the HF level, following the $a_u$ distortion, result in a $D_2$ structure (**12**-$D_2$) which displays two imaginary frequencies ($b_2$ and $b_1$). This conformation was found to be twisted about the central fulvalenic C=C bond by about 16°, and the distance between $H_2$ and $H_{2'}$ increases slightly to 1.818 Å. An MP2 calculation on the HF-optimized structure of **12**-$D_{2h}$ yields an energy 40 kJ mol$^{-1}$ above **12**-$C_{2h}$ (Table S2).

**(b) The Role of Angular Strain.** In an attempt to shed additional light on the question of whether internal ring strain within the seven-membered rings due to small bond angles contributes to the nonplanarity of the seven-membered rings in **12**, we have performed some partial optimizations at the HF level on **12**-$C_{2h}$. In one such calculation, we constrained the $\angle C_2C_1C_7$ bond angle to be the same value as found in **6**, i.e. 122.3°. Complete optimization of all the remaining parameters resulted in a $C_{2h}$ structure not unlike that depicted for **12**-$C_{2h}$ in Figure 7, in which the folding angles α and $\beta$ as well as the degree of pyramidalization at $C_1$ had decreased only slightly. This finding, together with the fact that **6** with a tighter $\angle C_2C_1C_7$ bond angle does not promote the folding of the seven-membered ring (vide supra), tends to indicate that strain induced by small internal bond angles around the seven-membered rings in **12**-$C_{2h}$ is not responsible, in itself, for the folded conformation.

It is interesting to note that dicyclohepta[*de*,*ij*]naphthalene,[15k] a naphtholog of **12** which lacks the overcrowding around the fulvenic C=C bond, adopts essentially a planar conformation, with only a slight twist component.

**(c) The Role of Pyramidalization.** The incursion of pyramidalization into organic chemistry and its contribution to the understanding of strained situations of alkenes have been recognized[24,46] An indication of nonplanarity at the carbon centers around the seven-membered ring of the nonplanar conformations of **11** and **12** can be obtained from the pyramidalization angles $\chi$ at $C_1$, $C_2$, $C_3$, and $C_4$ listed in Table 1. The calculated values for **12**-$C_{2h}$ generally show a somewhat smaller degree of pyramidalization at the carbon centers than is found experimentally.

We have performed various modeling experiments on **12**-$C_{2h}$, **12**-$D_{2h}$ (distorting to both $C_{2h}$-like and $C_{2v}$-like structures), and the experimentally determined structure. In all cases, the $\chi(C_1)$ (and $\chi(C_{1'})$ angles were varied systematically, while keeping the geometry of the rings and $r(C_1{=}C_{1'})$ fixed. Variation of the pyramidalization angles at $C_1$ and $C_{1'}$ in this fashion particularly affects the $H_2 \cdots H_{2'}$ and $H_7 \cdots H_{7'}$ distances, the $<C_{1'}C_1C_2C_3$ and $<C_{1'}C_1C_2H_2$ torsional angles, and to some extent the $<C_{1'}C_1C_2$ bond angle. The results are displayed in Figure 9.

The first somewhat surprising result of the molecular modeling experiments is that an increase in the pyramidalization at $C_1$ and $C_{1'}$ for **12**-$C_{2h}$ actually *decreases* the nonbonding distances $H_2 \cdots H_{2'}$ and $H_7 \cdots H_{7'}$ (Figure 9a). Hence, pyramidalization at $C_1$ and $C_{1'}$ does not

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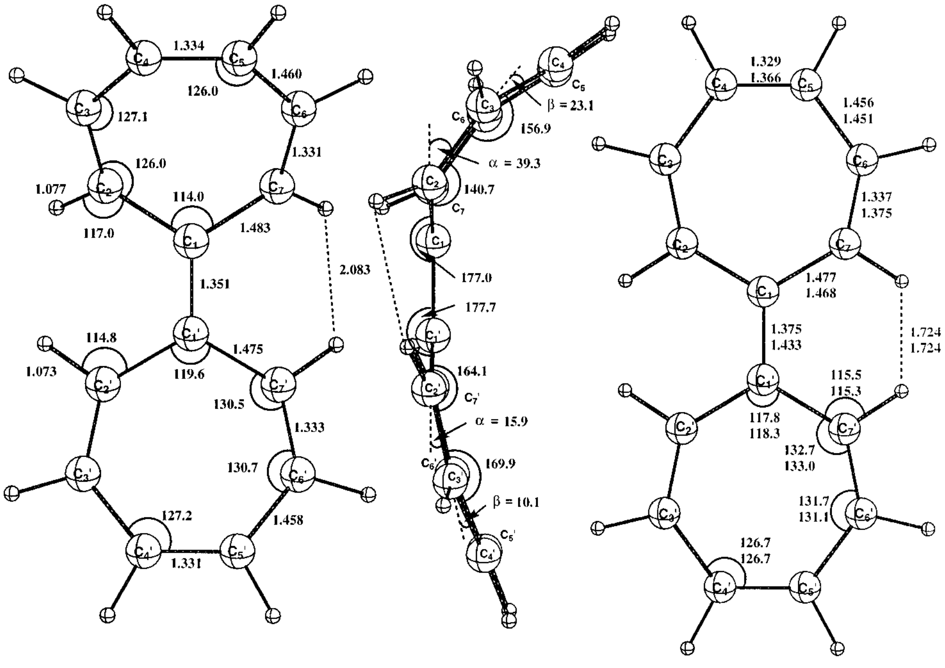

**(12-$C_s$)** **(12-$D_{2h}$)**

**Figure 8.** Selected geometrical parameters for the heptafulvalene *syn-anti* transition structure (**12**-$C_s$) and the planar $D_{2h}$ structure (**12**-$D_{2h}$). Parameters are given in the following order: HF (**12**-$C_s$) and HF and B-LYP (**12**-$D_{2h}$).

**Table 1. Pyramidalization Angles $\chi$ in the Cycloheptatrienylidene Rings for 11 and 12**

| molecule | conformation | symmetry | theory | $\chi(C_1)^a$ | $\chi(C_2)^a$ | $\chi(C_3)^a$ | $\chi(C_4)^a$ |
|---|---|---|---|---|---|---|---|
| **11**-$C_s$ | folded | $C_s$ | HF | 4.1 | 0.8 | 1.2 | 1.8 |
| | folded | $C_s$ | MP2 | 4.9 | 1.2 | 0.8 | 2.2 |
| **12**-$C_{2h}$ | *anti*-folded | $C_{2h}$ | HF | 7.3 | 0.2 | 0.8 | 3.5 |
| | *anti*-folded | $C_{2h}$ | B-LYP | 8.2 | 0.5 | 0.5 | 4.0 |
| | *anti*-folded | $C_{2h}$ | MP2 | 9.5 | 0.4 | 0.7 | 4.5 |
| | *anti*-folded | $C_i$ | exp[b] | 8.1 | 3.4 | 2.4 | 6.7 |
| | | | | | 1.0[c] | 0.1[d] | 6.2[e] |

[a] Pyramidalization angle at the specified carbon center. [b] The experimental structure shows a slight distortion from $C_{2h}$ to $C_i$, hence the pairs of $\chi$ values at $C_2$ and $C_7$, $C_3$ and $C_6$, and $C_4$ and $C_5$ are not exactly equal. From reference 14. [c] $\chi(C_7)$. [d] $\chi(C_6)$. [e] $\chi(C_5)$.

contribute toward accommodating the steric strain caused by the close intramolecular contacts between $H_2$ and $H_{2'}$. A hypothetical $C_{2h}$ structure that is planar at $C_1$ and $C_{1'}$ would actually have longer $H_2 \cdots H_{2'}$ and $H_7 \cdots H_{7'}$ distances than those observed in the X-ray structure and by calculation (2.453 Å vs 2.377 Å). In the modeling experiments that started with the $D_{2h}$ structure, we observed very little change in the $H_2 \cdots H_{2'}$ distance with variation of the pyramidalization angle around $C_1$.

However, while pyramidalization is disadvantageous with respect to the intramolecular overcrowding at $C_1$ and $C_{1'}$, it proves to be advantageous with respect to the reducing the torsional angles around the $C_1-C_2$ and $C_1-C_7$ bonds and hence the extent of $\pi$-overlap across the C$-$C single bonds in the seven-membered rings. This is shown in the plot of the $<C_{1'}C_1C_2C_3$ dihedral angle as a function of the pyramidalization angle ($\chi$) at $C_1$ (Figure 9b). A very similar result holds for the $<C_{1'}C_1C_2H_2$ dihedral angle. The twist about these bonds is smaller (i.e. the dihedral angles are closer to 0° and 180°) in the calculated and experimental structures (with pyramidalized bonding at $C_1$ and $C_{1'}$) than in a corresponding hypothetical structure with planar arrangement at the $C_1$ and $C_{1'}$ atoms. For instance, in the **12**-$C_{2h}$ conformation the torsional angle $<C_{1'}C_1C_2C_3$ is 146.4° at HF, while for a hypothetical structure with planar bonding at the $C_1$ carbon atom, the twist is 139.4°. Pyramidalization may be seen to enhance $\pi$-overlap across the single bonds by a reduction in the twist across them.

There is, however, a fine balance between the enhancement of the $\pi$-overlap across the single bonds in the seven-membered rings and the competing result of a reduction in the H$\cdots$H distance as the degree of pyramidalization increases. Our modeling experiments show that, in order to achieve perfect $\pi$-overlap (a dihedral angle of 180°), a pyramidalization angle of greater than 30° would be required at which angle the intramolecular separation of the $H_2$ and $H_{2'}$ hydrogens in **12** would be 2.078 Å (in the crude model in which all other geometric parameters are frozen).

**11. Energy Comparisons.** We have assessed the stabilities of **4**$-$**12**, relative to appropriate reference molecules, by considering a variety of idealized homodesmotic reactions (Table 2).[47] Such reactions are characterized as having (a) equal numbers of carbon atoms in their various states of hybridization in reactants and products, (b) equal numbers of carbon atoms with zero, one, two, three or four hydrogen atoms attached in reactants and products, and (c) equal numbers of each type of CC bond ($C_{sp^3}$-$C_{sp^3}$, $C_{sp^2}$-$C_{sp^3}$, $C_{sp^2}$-$C_{sp^2}$, $C_{sp^2}$=$C_{sp^2}$, etc.) in reactants and products. As a consequence, energy contributions due to changes in the hybridization of carbon atoms in reactants and products are eliminated.[47b] Homodesmotic

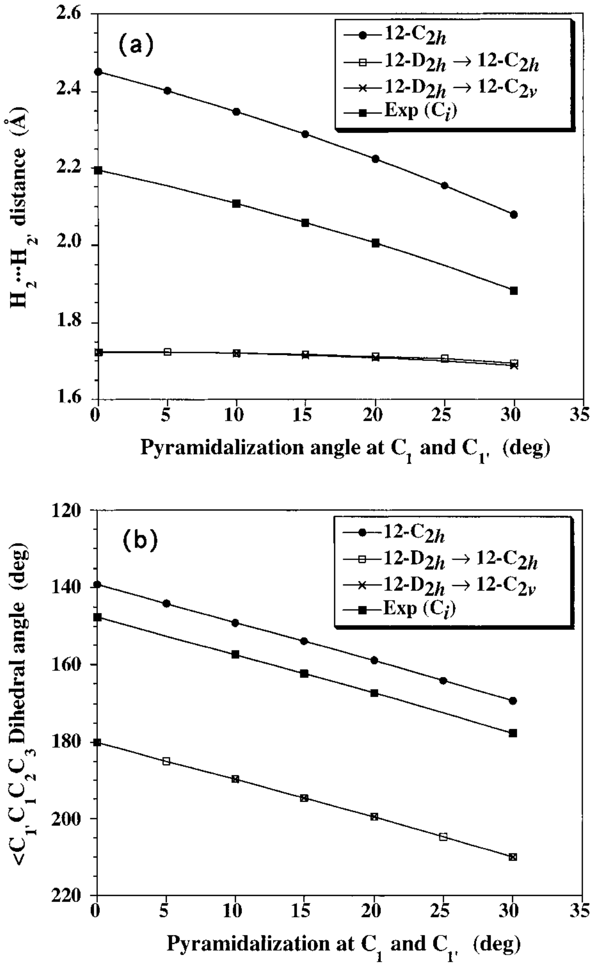

**Figure 9.** Plot of (a) the $H_2 \cdots H_{2'}$ closest-contact distance and (b) the $\angle C_{1'}C_1C_2C_3$ dihedral angle in heptafulvalene (**12**) as a function of the pyramidalization angle ($\chi$) at $C_1$.

reactions have been used in the literature to calculate the energy contributions of ring strain and cyclic conjugation.[47]

We have employed, as reference molecules, the cycloalkenes **1**–**3**, ethene, 1,1-divinylmethane (1,4-pentadiene, abbreviated in the text as DVM), 1,1-divinylethene (3-methylene-1,4-pentadiene, abbreviated as DVE), and 1,1,2,2-tetravinylethene (3,4-diethenyl-1,3,5-hexatriene, abbreviated as TVE).[48] Reaction energies in the following discussion refer to MP2 values without zero-point vibrational or temperature corrections, as listed in Table 2.

Reactions 1–3 compare the [*n*]fulvenes **4**–**6** with the cyclic alkenes **1**–**3**. The calculated energies for reactions 2 and 3 are close to zero (1.8 and −4.4 kJ mol$^{-1}$, respectively), indicating that any stabilization effects associated with cyclic delocalization in **5** and **6** are roughly balanced by the strain associated with the exocyclic double bond. On the other hand, triafulvene (**4**) is destabilized, relative to cyclopropene (**1**) by 28 kJ mol$^{-1}$, indicating a dominance of the unfavorable effect of the exocyclic double bond.

Since the [*n*]fulvenes have a constant ratio of C/H, it is also possible to compare the relative stabilities of molecules **4**–**6** using the formal isomerization reactions (a) **4** → $^{2}/_{3}$ **5**, (b) **4** → $^{1}/_{2}$ **6** and (c) **5** → $^{3}/_{4}$ **6**, for which the reaction energies are −258.2, −292.8, and −21.4 kJ mol$^{-1}$, respectively. It is clear from these reactions that **4** is highly destabilized when compared with **5** or **6**. In both the cycloalkene and fulvene series, the three-membered ring hydrocarbons (**1** and **4**) are highly strained. However, triafulvene (**4**) suffers additional steric ring strain as a result of having both an endocyclic and an exocyclic double bond associated with the three-membered ring.

Reactions 4–9 compare the fulvalenes **7**–**12** with the isolated parent cycloalkenes. Reaction 4 indicates that the fulvalenic interaction of the two three-membered rings in **7** is highly unfavorable ($\Delta E = -109.6$ kJ mol$^{-1}$) and is far beyond the destabilization expected on the basis of the formation of two triafulvene moieties from two cyclopropenes (−56 kJ mol$^{-1}$, cf. reaction 1). The fulvalenic interactions of a three- and a seven-membered ring (reaction 6) is also unfavorable ($\Delta E = -41.7$ kJ mol$^{-1}$), but the extent of destabilization of **9** is much smaller than found for **7**. In contrast, reactions 5 and 7–9 show that the fulvalenic interactions of a five-membered ring with a three-membered ($\Delta E = 1.8$ kJ mol$^{-1}$), a five-membered ($\Delta E = 8.9$ kJ mol$^{-1}$), or a seven-membered ring ($\Delta E = 19.2$ kJ mol$^{-1}$), as well as the interactions of two seven-membered rings ($\Delta E = 2.9$ kJ mol$^{-1}$) are all favorable. The slight stabilization shown by reaction 5 is remarkable in view of the expected destabilizing contribution associated with the presence of a triafulvene moiety in **8**.

Reactions 10–15 compare the fulvalenes with two isolated fulvenes. It should be noted that there is a small difference in the extent of the degree of matching of the structural elements in the homodesmotic reactions 10–15 versus reactions 1–9. All these reactions (**1**–**15**) are homoplesiotic (matching of neighboring atoms around each type of carbon atom in reactants and products by both number and type of carbon atoms) on a nearest-neighbor level.[47a] However, only reactions 1–9 are homoplesiotic at the next-nearest-neighbor level.[47a] In order to overcome this "mismatch" (at the next-nearest-neighbor level), ethene may be replaced by two molecules of DVE on the reactant side and TVE may be added to the product side in each of the reactions 10–15. This will result in a base-line shift of −5.8 kJ mol$^{-1}$ (2DVE − ethene → TVE). For example, the modified form of reaction 13 (**10** + 2DVE → 2 **5** + TVE) results in a value for $\Delta E$ of 5.4 kJ mol$^{-1}$ as compared with 11.2 kJ mol$^{-1}$ for the simpler standard reaction 13 shown in Table 2. We have chosen, however, to base our discussion uniformly on the simpler reactions 10–15.

We note the exceptionally negative energy of reaction 10, $\Delta E = -47.8$ kJ mol$^{-1}$, as compared with the energies of reactions 11–15. This is indicative of the destabilization of triafulvalene with respect to two triafulvenes. In this homodesmotic reaction the strain energy is expected to change substantially less than for reaction 4. Since triafulvene is itself destabilized (reaction 1), we can conclude that **7** is indeed a highly destabilized species. By contrast, the interaction of triafulvene and pentafulvene moieties to give **8** (reaction 11) is very favorable: $\Delta E = 33.9$ kJ mol$^{-1}$. The difference of 22.7 kJ mol$^{-1}$ between the energies of reactions 11 and 13 should also be noted. This reflects the enhanced relative stabilization

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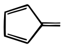
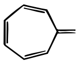
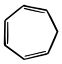
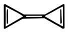
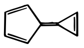
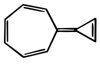
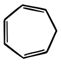
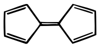
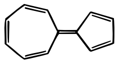
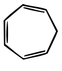
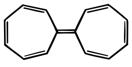
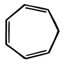
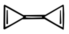
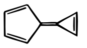
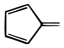
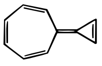
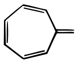
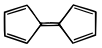
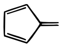
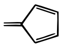
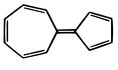
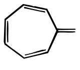
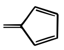
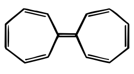
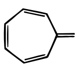
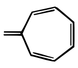
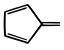
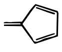
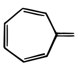
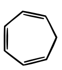
[47] (a) George, P.; Bock, C. W.; Trachtman, M. *Empirical Resonance Energies of Acyl and Carbonyl Derivatives*; VCH Publishers: New York, Chapter 6 in Molecular Structure and Energetics, Vol. 4, p 163. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317, (c) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121.

[48] Geometries and energies, calculated at the HF, B-LYP, and MP2 levels of theory, for the minimum energy conformations of DVM ($C_2$ symmetry), DVE ($C_2$ symmetry), and TVE ($D_2$ symmetry) are given in the Supporting Information.

**Table 2. Energies ($\Delta E$,[a] kJ mol$^{-1}$) for Homodesmotic Reactions Calculated at HF/6-31G*, B-LYP/6-31G*, and MP2/6-31G***

| | | | | $\Delta E$ | |
|---|---|---|---|---|---|
| Reaction | | | HF | B-LYP | MP2 |
| 1 |  + DVM | ⟶  + DVE | -6.4 | -21.1 | -28.0 |
| 2 |  + DVM | ⟶  + DVE | 9.4 | 2.8 | 1.8 |
| 3 |  + DVM | ⟶  + DVE | 13.9 | 16.6 | -4.4 |
| 4 |  + 2 DVM | ⟶ 2  + TVE | -62.3 | -83.3 | -109.6 |
| 5 |  + 2 DVM | ⟶  + TVE +  | 44.4 | 14.4 | 1.8 |
| 6 |  + 2 DVM | ⟶  + TVE +  | 17.0 | -9.8 | -41.7 |
| 7 |  + 2 DVM | ⟶ 2  + TVE | 36.3 | 17.3 | 8.9 |
| 8 |  + 2 DVM | ⟶  + TVE +  | 38.6 | 45.7 | 19.2 |
| 9 |  + 2 DVM | ⟶ 2  + TVE | 29.6 | 27.5 | 2.9 |
| 10 |  + $CH_2{=}CH_2$ | ⟶  +  | -67.3 | -51.5 | -47.8 |
| 11 |  + $CH_2{=}CH_2$ | ⟶  +  | 23.7 | 22.2 | 33.9 |
| 12 |  + $CH_2{=}CH_2$ | ⟶  +  | -8.2 | -15.7 | -3.4 |
| 13 |  + $CH_2{=}CH_2$ | ⟶  +  | -0.2 | 1.2 | 11.2 |
| 14 |  + $CH_2{=}CH_2$ | ⟶  +  | -2.4 | 15.9 | 27.7 |
| 15 |  + $CH_2{=}CH_2$ | ⟶  +  | -15.9 | -16.1 | 17.6 |
| 16 |  +  | ⟶  +  | 216.2 | 193.5 | 231.8 |
| 17 |  +  | ⟶  +  | 205.0 | 183.4 | 195.8 |

[a] $\Delta E$ = E(products) - E(reactants).

of **8** compared with **10**. Reaction 12 is slightly unfavorable, $\Delta E = -3.4$ kJ mol$^{-1}$, indicating some destabilization in **9**. Reactions 13−15 are all favorable. Of these, the highest stabilization is manifested in reaction 14, $\Delta E = 27.7$ kJ mol$^{-1}$, indicating the relative stability of pentaheptafulvalene (**11**). Interestingly, the interactions of two heptafulvenes to give **12** (reaction 15, $\Delta E = 17.6$ kJ mol$^{-1}$) is more favorable than the interaction of two pentafulvenes to give **10** (reaction 13, $\Delta E = 11.2$ kJ mol$^{-1}$), even though compound **12** is overcrowded.

A large energy difference is predicted (246 kJ mol$^{-1}$) between the two isomers, **9** and **10** (Table S2). This is consistent with reaction 16 which shows that two isolated pentafulvene molecules have a substantially lower combined energy than a heptafulvene plus a triafulvene molecule (232 kJ mol$^{-1}$). The relative destabilization of

**Table 3. Bond Alternation Parameter *ba* for the Three-, Five-, and Seven-Membered Rings in 1−12**[a]

| | | | bond alternation *ba* | | | |
|---|---|---|---|---|---|---|
| molecule | conformation | symmetry | HF | B-LYP | MP2 | exp |
| Three-Membered Rings | | | | | | |
| **1** | planar | $C_{2v}$ | 0.219 | 0.204 | 0.216 | 0.215 |
| **4** | planar | $C_{2v}$ | 0.126 | 0.128 | 0.118 | 0.118 |
| **7** | planar | $D_{2h}$ | 0.154 | 0.154 | 0.140 | |
| **8** | planar | $C_{2v}$ | 0.104 | 0.108 | 0.097 | |
| **9** | planar | $C_{2v}$ | 0.122 | 0.125 | 0.115 | |
| Five-Membered Rings | | | | | | |
| **2** | planar | $C_{2v}$ | 0.168 | 0.135 | 0.143 | 0.143 |
| **5** | planar | $C_{2v}$ | 0.145 | 0.117 | 0.110 | 0.117 |
| **8** | planar | $C_{2v}$ | 0.112 | 0.091 | 0.082 | |
| **10** | planar | $D_{2h}$ | 0.144 | 0.116 | 0.108 | |
| **11**-$C_s$ | folded | $C_s$ | 0.132 | 0.091[b] | 0.086 | |
| Seven-Membered Rings | | | | | | |
| **3**-$C_s$ | folded | $C_s$ | 0.155 | 0.117 | 0.107 | 0.120 |
| **6** | planar | $C_{2v}$ | 0.136 | 0.095 | 0.102 | 0.102 |
| **9** | planar | $C_{2v}$ | 0.141 | 0.106 | 0.104 | |
| **11**-$C_s$ | folded | $C_s$ | 0.127 | 0.076[b] | 0.074 | |
| **12**-$C_{2h}$ | *anti*-folded | $C_{2h}$ | 0.136 | 0.091 | 0.089 | 0.104 |

[a] The bond alternation parameter *ba* is defined in eq 1. [b] The preferred B-LYP structure is planar $C_{2v}$.

**9** versus **10** is probably associated with the strain in the triafulvene moiety of **9**.

To bring the stabilities of **9** and **10** into perspective, we can compare their energies with the energies of the isomers naphthalene and azulene. At the MP2 level of theory, naphthalene is more stable than azulene, **10**, and **9** by 151, 260, and 506 kJ mol$^{-1}$, respectively.[49] Thus **10** is less stable than azulene by 109 kJ mol$^{-1}$.

**12. Aspects of "Aromaticity"/"Antiaromaticity" in Fulvalenes.** The notion of "aromaticity" and the question of the aromatic/antiaromatic character of fulvenes and fulvalenes have played dominant roles in the studies of these nonbenzenoid cross-conjugated systems.[1,36e] Our calculations on the [*n*]fulvenes and [*n,m*]fulvalenes (*n*, *m* = 3, 5, 7) series can help throw light on these questions. Our analysis of the results is based on the following considerations:

**(a) Bond Alternation.** The degree of delocalization in the three-, five-, and seven-membered rings of molecules **1**−**12** may be evaluated by considering the bond alternation parameter *ba*, defined as the difference between the averaged single and double bond lengths in the ring (Table 3).

$$ba = \sum_{\text{ring}} r_{\text{single}}/n_{\text{single}} - \sum_{\text{ring}} r_{\text{double}}/n_{\text{double}} \qquad (1)$$

It is noticeable that the degree of bond alternation is generally overestimated at the Hartree−Fock level, as found previously in other conjugated systems.[51] There is much better agreement with experiment at the MP2 and B-LYP levels.

Cyclopropene (**1**), cyclopentadiene (**2**), and cycloheptatriene (**3**) have the greatest degree of bond alternation for the respective ring size. This reflects the presence of an sp$^3$ center in the ring interrupting any cyclic conjugation, and the fact that $C_{sp^2}$–$C_{sp^3}$ single bonds are longer than $C_{sp^2}$–$C_{sp^2}$ single bonds. We note that *ba* decreases in going from the planar to the folded structure of **3**, the MP2 value changing from 0.131 to 0.107. The [*n*]fulvenes, triafulvene (**4**), pentafulvene (**5**), and heptafulvene (**6**), have intermediate *ba* values. In both the cycloalkene and fulvene series, bond alternation decreases with the size of the ring.

In triafulvalene (**7**), the bond alternation *ba* is considerably greater than in triafulvene (**4**): 0.140 versus 0.118. In contrast, triapentafulvalene (**8**) has a low degree of bond alternation: 0.097 and 0.082 in the three- and five-membered rings, respectively, as compared with 0.118 and 0.110 in the component fulvenes, **4** and **5**, respectively. These bond alternation values suggest a relatively high contribution of the aromatic delocalized canonical structure, **8b**, with formally $4n + 2\pi$ electrons in each ring in **8**, in contrast to the lack of $\pi$ delocalization in **7**.

Pentaheptafulvalene (**11**) also has a low degree of bond alternation: 0.086 and 0.074 in the five- and seven-membered rings, respectively. This suggests a significant contribution of the "aromatic" dipolar canonical form **11b** with formally $4n + 2$ $\pi$-electrons in each ring. On the other hand, the rings in triaheptafulvalene (**9**) and pentafulvalene (**10**) have *ba* values close to the values for the corresponding rings in the parent fulvenes. Interestingly, however, the degree of bond alternation in heptafulvalene (**12**) is relatively low, 0.089, as compared with the component heptafulvene (**6**).

The bond alternation parameter *ba* in the [*n*]fulvenes and [*n,m*]fulvalenes does not take into consideration the exocyclic C═C double bonds, which may also bear relevance to the questions of delocalization and aromaticity. It is interesting to note that the central fulvalenic C═C bonds are generally longer than the fulvenic double bonds. A notable exception is in **7**, where significant fulvalenic bond length compression has occurred when compared with the fulvenic double bond in **4** (1.314 Å *vs* 1.332 Å). The most pronounced elongation appears in **11**-$C_s$ (1.393 Å *vs* 1.349 Å in **5** and 1.360 Å in **6**). This elongation is consistent with the contribution of the canonical dipolar form **11b**. In **8**, however, the lengthening of the central fulvalenic double bond is less pronounced (1.352 Å *vs* 1.332 Å in **4** and 1.349 Å in **5**).

**(b) Energy Comparisons.** The energy comparisons, as outlined in section 11, indicate that triafulvalene (**7**) is highly destabilized, as compared with two triafulvenes (**4**). The enhanced destabilization of **7** may be attributed to "antiaromaticity".[5] In contrast, triapentafulvalene (**8**) is stabilized, as compared with its components, **4** and **5**. A similar stabilization effect is shown by pentaheptafulvalene (**11**) (as compared with **5** and **6**). These stabilizations may be attributed to "aromaticity". Pentafulvalene (**10**) and heptafulvalene (**12**) show some stabilization compared with their component fulvalenes, while triaheptafulvalene (**9**) is destabilized.

**(c) Dipole Moments.**[52] The calculated $\pi$-electron distributions as well as the sign and magnitude of the dipole moment in triapentafulvalene (**8**) indicate a significant contribution of the aromatic dipolar structure **8b**, in accord with the Hückel rule. A smaller effect is shown by pentaheptafulvalene (**11**). In this context, it is interesting to note that the cyclopropenylidene ring is more effective than the cycloheptatrienylidene ring in serving as the aromatic cation component in dipolar structures.

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(49) Experimental[50] and theoretical (MP2) energy differences between naphthalene and azulene at 298 K are 139 and 143 kJ mol$^{-1}$, respectively.

(50) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(51) See, for example, Szalay, P. G.; Karpfen, A.; Lischka, H. *J. Chem. Phys.* **1987**, *87*, 3530.

(52) For a discussion on the significance of the dipole moments of the triapentafulvalenes from the point of view of the "aromaticity", see: Agranat, I. In *MTP Int. Rev. Sci.*, Organic Chemistry, Series One, Vol. 3, Aromatic Compounds; Zollinger, H., Ed.; Butterworths: London, 1973; p 139.

## E. Conclusions

Our calculations indicate that a cycloheptatrienylidene ring containing an exocyclic C═C double bond is intrinsically planar as found in **6** and also in **9**. However, it is distorted from planarity if steric effects become important, as found to a very slight extent in **11** and to a greater extent in **12**. We submit that the primary cause for the nonplanarity of **12**, leading to the *anti*-folded conformation exhibited by **12**-$C_{2h}$, is the intramolecular overcrowding due to the $H_2\cdots H_{2'}$ and $H_7\cdots H_{7'}$ close contacts. Ring strain is not found to be a major contributor to the nonplanarity of **12**. We also find that it is the folding of the rings rather than the pyramidalization at the central C═C double bond that enables the strained hydrogens to avoid one another. The stabilizing role of the pyramidalization at $C_1$ and $C_{1'}$ may be attributed to the resulting more effective $\pi$-overlap in the seven-membered rings.

Our analysis of the calculated $\pi$-electron distributions, dipole moments, bond alternations, and energy comparisons leads to the conclusion that the hitherto unknown smallest fulvalene **7** is highly localized and destabilized ("antiaromatic") while **8**, which is also unknown, is predicted to be relatively delocalized and stabilized ("aromatic").

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**Supporting Information Available:** More detailed geometrical information in the form of Gaussian archive files for **1**−**12** and reference molecules DVM, DVE, TVE, naphthalene, and azulene (Table S1), calculated (HF/6-31G*, B-LYP/6-31G*, and MP2/6-31G*) total energies and relative energies for all these molecules (Table S2), structural parameters associated with the cycoheptatrienylidene ring pertaining to possible overcrowding in **6**, **9**, **11,** and **12** (Table S3), and dihedral angles around the (nonplanar) seven-membered rings in **3**, **11**, and **12** (Table S4) (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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