Fullerenes vs Fulleroids: Understanding Their Relative Energies

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Abstract: Both force-field (MMPI) and AM1 (restricted and unrestricted HF) calculations are herein used to investigate the underlying reasons for the fullerene–fulleroid structural dichotomies observed in carbene, silylene, nitrene, and oxygen adducts of C_{60}. Via the investigation of a series of model systems, it is demonstrated that curvature actually favors the open, fulleroid structure; this effect of curvature on the norcaradiene–cycloheptatriene equilibrium is general. Strategies for the creation of 6,6-bridged fulleroids are suggested.

Introduction

Despite the dizzying pace of developments in fullerene chemistry,[1–3] some fundamental aspects of their properties remain incompletely understood. For some time, it has been apparent that addition of a carbene unit to C_{60} might result in an enlarged fullerene[4] (a fulleroid). Indeed this occurs when the carbene (or a formal nitrene[5]) is added across the 5,6-junction. However, addition across the 6,6-junction produces a closed methanofullerene. Similarly, oxidation of C_{60} gives a 6,6-fused epoxide[6] (oxidofullerene), and diphenylsilene addition, a 6,6-fused silafullerene.[7] For the former case, MNDO calculations[8] placed the 5,6-bridged $C_{60}O$ 6 kcal/mol *below* the 6,6-fused one, while in the latter case, AM1 calculations[7] indicated the 6,6-fused isomer to be the global $C_{60}Si(Ph)_2$ minimum by 10.7 kcal/mol over the 5,6-bridged silafulleroid; AM1 also calculated[7] 6,6-fused $C_{60}C(Ph)_2$ to be more stable than the 5,6-fulleroid, but by only 1.2 kcal/mol. How can these relative energies and structures be understood? Haddon[9] has emphasized the importance of the effects induced by the curved shape of buckyballs. The induced strain in responsible for an *apparent* decrease in aromaticity. But does the curved shape have anything to do with the fullerene–fulleroid valence isomerization energetics? To gain insight into this question, we now report the results of MMPI, RHF/AM1,[10] and UHF/AM1 calculations on a series of model compounds.[11]

Theoretical Methodology

All calculations were performed on a DX486-50 PC machine. The MMPI calculations were done using PCMODEL-386 from Serena Software. The AM1 calculations were performed using the version implemented in HYPERCHEM; several cases were also checked with AM1 as implemented in GAUSSIAN 92W-DFT. The *ab initio* calculations were carried out using the GAUSSIAN 92W-DFT program.[12]

Results and Discussion

Calibration of the Calculational Methodology. To investigate a series of reasonable models for fullerenes, the molecular size is such that high-level *ab initio* calculations (these would have to include some correlation correction, at least via density functional theory, at the 6-31G* basis set level) would be quite time consuming. In line with many others,[11] we made use of

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(11) While many semiempirical and *ab initio* calculations have appeared on fullerenes themselves [including predictions for those with small rings (Gao, Y.-D.; Herndon, W. C. *J. Am. Chem. Soc.* **1993**, *115*, 8459) and some interesting rearrangement processes (Murry, R. L.; Strout, D. L.; Odom, G. K.; Scuseria, G. E. *Nature* **1993**, *366*, 665)], and fullerene MM3 calculations have been touted as comparable to minimal correlation corrected *ab initio* results (Murry, R. L.; Colt, J. R.; Scuseria, G. E. *J. Phys. Chem.* **1993**, *97*, 4954), and univalent atom addition patterns to C_{60} have been extensively investigated theoretically (Matsuzawa, N.; Fukunaga, T.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 10747. Matsuzawa, N.; Dixon, D. A.; Krusic, P. J. *J. Phys. Chem.* **1992**, *96*, 8317. Matsuzawa, N.; Dixon, D. A.; Fukunaga, T. *J. Phys. Chem.* **1992**, *96*, 7594. Henderson, C. C.; Cahill, P. A. *Chem. Phys. Lett.* **1992**, *198*, 570. Dixon, D. A.; Matsuzawa, N.; Fukunaga, T.; Tebbe, F. N. *J. Phys. Chem.* **1992**, *96*, 6107. Dunlap, B. I.; Brenner, D. W.; Mintmire, J. W.; Mowrey, R. C.; White, C. T. *J. Phys. Chem.* **1991**, 95, 5763), the only theoretical considerations of polyvalent atom additions are the aforementioned[7,8] additions to C_{60}; our model approach has apparently not been employed.

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Table 1. Cycloheptatriene (CHT)−Norcaradiene (NCD) Energy Differences Calculated at Various Levels of Semiempirical and *Ab Initio* Theory

method	E_{rel} (cycloheptatriene), kcal/mol (ΔH_f, kcal/mol) or [E, au]	E_{rel} (norcaradiene), kcal/mol (ΔH_f, kcal/mol) or [E, au]
experiment	0 (44.6)[13]	5.0,[a] 6.2[b]
RHF/MMPI//RHF/MMPI	0 (42.57)	7.8 (50.38)
RHF/AM1//RHF/AM1	0 (38.14)	13.3 (50.86)
UHF/AM1//UHF/AM1	0 (37.55)	12.1 (49.62)
RHF/STO-3G//RHF/STO-3G[c]	0 [−266.4067787]	−8.0 [−266.4195052]
RHF/6-31G//RHF/STO-3G	0 [−269.5818711]	10.3 [−269.5654330]
RHF/6-31G*//RHF/STO-3G[c]	0 [−269.6810170]	5.7 [−269.672018]
RHF/6-31G*//RHF/6-31G*	0 [−269.6823297]	5.9 [−269.6729495]
RMP2/6-31G*//RHF/6-31G*	0 [−270.5663915]	3.0 [−270.5616776]
BLYP/STO-3G//RHF/STO-3G	0 [−268.0175917]	0.5 [−268.0168036]
BLYP/6-31G*//RHF/STO-3G	0 [−271.3597527]	7.4 [−271.3480077]
BLYP/6-31G*//RHF/6-31G*	0 [−271.3610723]	8.4 [−271.3477166]
Becke3LYP/STO-3G//RHF/STO-3G	0 [−268.1877697]	−2.5 [−268.1917745]
Becke3LYP/6-31G*//RHF/STO-3G	0 [−271.5045925]	5.4 [−271.4959115]
Becke3LYP/STO-3G//Becke3LYP/STO-3G	0 [−268.1945495]	−2.5 [−268.1984709]
Becke3LYP/6-31G*//Becke3LYP/STO-3G	0 [−271.5066884]	6.6 [−271.4962397]
Becke3LYP/6-31G*//RHF/6-31G*	0 [−271.5064663]	6.3 [−271.4964399]

[a] An average value from several experiments.[14] [b] A value gleaned from the work of Anet and Miura, quoted in ref 15a. [c] These methods have already been applied to CHT and NCD with the same results (see ref 15).

Table 2. Energies[a] of Some "Calibration Compounds" via Various Theoretical Methods

	theoretical method							expt	
	MMPI		RAM1		UAM1		*ab initio*		
compd	ΔH_f [$r_{1,6}$, Å]	E_{rel}	ΔH_f [$r_{1,6}$, Å]	E_{rel}	ΔH_f [$r_{1,6}$, Å]	E_{rel}	E_{rel}	ΔH_f [$r_{1,6}$, Å]	E_{rel}
1o	72.94 [2.222]	(0)	80.84 [2.302]	(0)	77.50[c] [2.287]	(0)	(0)[d,e]	77.1[14] [2.235][19]	(0)[19]
1c	84.74 [1.514]	11.8	87.88 [1.567]	7.0[b]	83.48 [1.545]	6.0	5.5[d,e]		5.7 ± 2[20]
2o	68.53 [2.229]	(0)	86.13 [2.257]	(0)	77.96 [2.246]	(0)	(0)[f]		(0)[21]
2c	72.25 [1.516]	3.7	82.20 [1.536]	−3.9	74.15 [1.535]	−3.8	−20.3[f]		≈0.2[21]
3o	36.46 [2.161]	(0)	46.33 [2.235]	(0)	44.66 [2.241]	(0)	(0)[d,g]		
3c	43.08 [1.502]	6.6	45.86 [1.547]	−0.5	42.64 [1.524]	−2.0	−9.4[d,g]	45.5[14] [1.564][h]	
4o	59.88 [2.205]	(0)	67.95 [2.284]	(0)	58.55 [2.303]	(0)		**4o** more stable[22]	
4c	75.94 [1.511]	16.1	72.32 [1.565]	4.4	71.51 [1.563]	13.0			
5o	76.91 [2.154]	(0)	90.79[i] [2.237]	(0)	81.04 [2.254]	(0)		**5o** more stable[22]	
5c	96.24 [1.493]	19.3	87.26[i] [1.545]	−3.5[i]	86.56 [1.544]	5.5			
6o	115.72[j] [2.079]	(0)	130.38 [2.227]	(0)	121.06 [2.247]	(0)		**6c** more stable[22]	
6c	125.42[j] [1.481]	9.7[j]	123.55 [1.536]	−6.8	117.35 [1.529]	−3.7			
7o	48.13 [2.193]	(0)	59.41 [2.239]	(0)	50.14 [2.261]	(0)		**7o** more stable;[23] r_{C1-C6} = 2.22 Å (X-ray)[23b]	
7c	59.43 [1.510]	11.3	68.13 [1.547]	8.7	68.12 [1.547]	18.0			
8o	67.41 [2.278]	(0)	62.47 [2.341]	(0)	54.19 [2.360]	(0)		**8o** more stable[24]	
8c	83.67 [1.467]	16.3	76.81 [1.590]	14.3	75.96 [1.586]	21.8			
9o			135.01 [2.425]	(0)	127.14 [2.448]	(0)			
9c			150.21 [1.601]	15.2	149.03 [1.595]	21.9			

[a] In kcal/mol. [b] This value has been previously reported.[25] [c] UMNDO gives ΔH_f(**1o**) = 63.8 kcal/mol[26] an obvious overcorrection, as dis-cussed by the authors. [d] E(**1o**) = −422.135, E(**1c**) = −422.127, E(**3o**) = −385.598, E(**3c**) = −385.613. [e] RHF/6-31G//RHF/6-31G results.[27] [f] RHF/STO-3G//RHF-STO-3G results "corrected" to the RHF/4-31G level.[28] [g] RHF/6-31G*//RHF/STO-3G results (at the RHF/6-31G//RHF/STO-3G level, the norcaradiene tautomer is only 5.8 kcal/mol below the triene). [h] Value for the 1,6 bond in [4.3.1]propella-2,4-dien-8-one.[29] The $r_{1,10}$ distance for this compound is 1.506 Å, while the corresponding RAM1 value for **3c** is 1.510 Å. [i] At the RAM1/CI level, **5c** is calculated to be only 0.3 kcal/mol below **5o**. [j] If the 5-membered ring π bond is also "π atom labeled", the ΔH_f's are 107.62 (**6o**) and 115.56 kcal/mol (**6c**) and $\Delta\Delta H_f$ = 7.9 kcal/mol.

force-field calculations corrected for conjugation and the semiempirical program, AM1, at both the restricted and unrestricted Hartree−Fock levels. Although the molecules under consideration are all closed shell species, it is not improper to utilize a UHF approach, especially for large aromatic species. How well do these methods do in comparison to experiment or *ab initio* methods? As an initial calibration for the type of problem addressed here [basically the norcaradiene (NCD)−cycloheptatriene (CHT) equilibrium], we investigated the parent equilibrium problem at various levels of theory (Table 1). Compared to the experimental ΔH_f[13] and CHT−NCD energy gap,[14] the MMPI method does fortuitously well (see, however, below), while the AM1 methods clearly favor the CHT structure too much (even limited RHF/AM1/CI improves the value to only 11.6 kcal/mol). As has been reported before,[15] at the *ab initio* level, a minimal basis set overly favors the cyclopropane structure, while a split basis overcorrects the problem; the polarized basis set, even at the minimal basis set geometry, gives a quite good value and has to be rated as the best result for the computational time invested. It is seen that MP2 correction and the BLYP density functional method[16] are unsatisfactory, while the hybrid Becke3LYP density functional theory method[17] gives quite good results when a polarized basis set is used.

A few other "calibration compounds" were investigated, and

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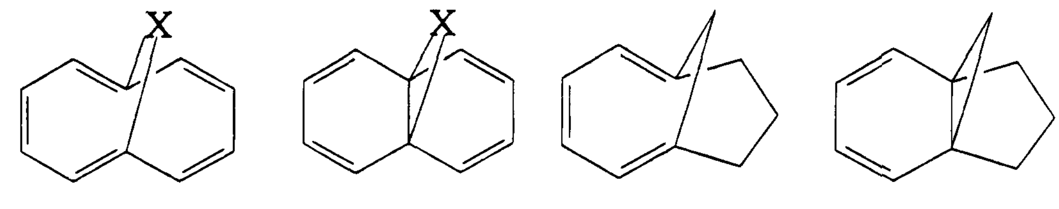
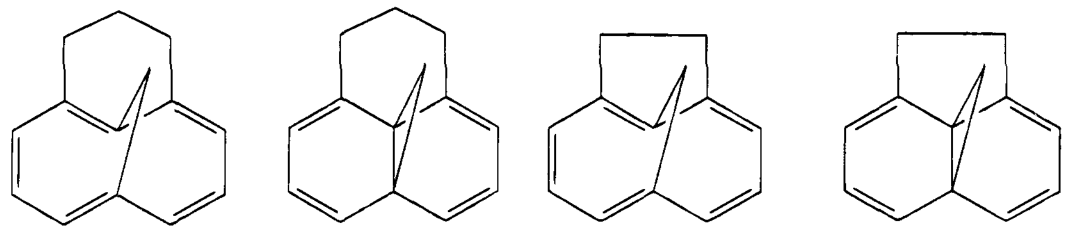
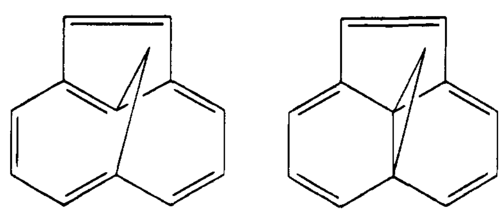
Chart 1



1o, X = CH_2 **1c** **3o** **3c**
2o, X = CMe_2 **2c**
7o, X = O **7c**
8o, X = C=O **8c**
9o, X = BCN **9c**



4o **4c** **5o** **5c**



6o **6c**

the results are given in Table 2. The initial success of MMPI is largely reversed in these cases, with the direction and/or the magnitude of the equilibrium mispredicted; also the 1,6-bond lengths seem generally too short. Both RAM1 and UAM1 give reasonably good values for the energies. For most cases, UAM1 has a greater effect on the annulenic energy, and this can be significant, for example, in the case of **5**, where only UAM1 gives the correct energy ordering. On the other hand, the energetic advantage of **7o** over **7c** seems overestimated by UAM1. UAM1 has the advantage that the annulenic ring structures are all C_{2v}, which, at the *ab initio* level, is not the case without at least a split basis set; RAM1 minimizes these structures to C_s symmetry. In the two cases where the heats of formation from RAM1 and UAM1 may be compared with experiment, the results are split, with RAM1 doing better for the [4.3.1] system and UAM1 preeminent for **1o**. All in all, the *trends* observed for a series of compounds are very reliable, although the absolute values for the energy differences may not be, especially if those differences are small. For example, as one progresses through the series **4–6**, one sees a steady decrease in the $r_{1,6}$ distances (all theoretical methods); at the same time, the relative stability of the closed form increases. For most of the cases presented herein, we give the results for MMPI, RAM1, and UAM1 calculations; for some of the larger substituted cases, UAM1 calculations were not carried out due to the unreasonably long computational times required.

Effect of Benzo Fusion and Bridging on the Annulene–Bis(norcaradiene) Equilibrium. As expected from a consideration of resonance structures, either the open (**10o** over **10c**) or closed (**11c** over **11o**) forms may be favored by appropriate placement of two fused benzene rings around **1**. The detailed numerical results are inconsistent, however, for the MMPI calculations, since the value attributable to the extra benzenoid ring of **10o** is worth 15 kcal/mol, while for **11c** it is worth 22.5 kcal/mol (i.e., **11c** should be 12 kcal/mol above **11o** without consideration of the benzenoid ring question but is actually 10.5 kcal/mol below **11c**). The results for both RAM1 and UAM1 are internally consistent; the former gives a value of 15 kcal/mol for the extra benzenoid ring, while the latter sets that value at only 5 kcal/mol (Table 3). Like RAM1, UAM1 shows the 10-membered ring of **10o** to be "localized" (1.36 and 1.45 Å

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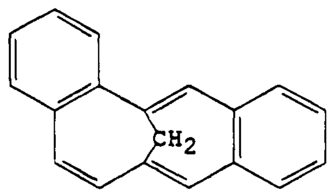
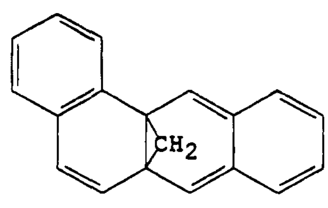
Table 3. Calculated Parameters for Benzannelated and Bridged Model Compounds

compd	theoretical method					
	MMPI		RAM1		UAM1	
	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}
10o	93.84 [2.219]	(0)	106.08 [2.301]	(0)	101.32 [2.283]	(0)
10c	121.00 [1.515]	27.2	128.05 [1.563]	22.0	112.32 [1.535]	11.0
11o	110.70 [2.240]	16.9	121.22 [2.272]	15.1	104.15 [2.286]	2.8
11c	100.34 [1.519]	6.5	112.56 [1.554]	6.5	103.02 [1.534]	1.7
12o(5/6)	80.74 [2.114]	(0)	86.10 [2.195]	(0)	76.53 [2.188]	(0)
12c(5/6)	95.34 [1.498]	14.6	95.56 [1.558]	9.5	79.66 [1.526]	3.1
12o(6/6)	83.48 [2.101]	2.7	103.70 [2.080]	17.6	83.81 [2.178]	7.3
12c(6/6)	113.38 [1.473]	32.6	91.14 [1.522]	5.0	79.51 [1.507]	3.0

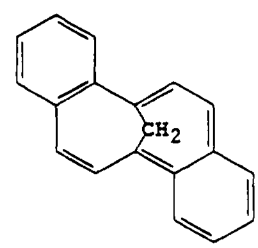
Chart 2



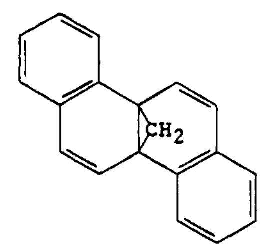
10o



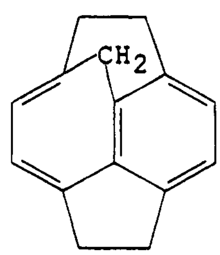
10c



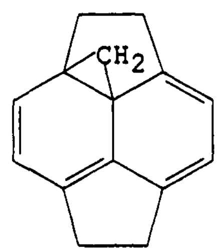
11o



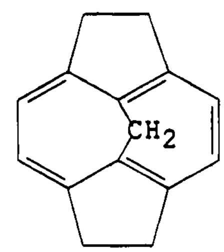
11c



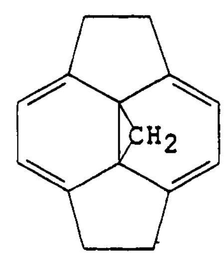
12o(5/6)



12c(5/6)



12o(6/6)



12c(6/6)

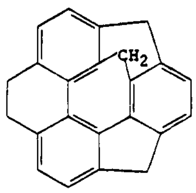
around the bridgehead carbons) in order to have two "benzene" rings, while the UAM1 (but not RAM1) structure for **11o** is "delocalized" but twisted.

As for model compounds **12**, AM1 (see Table 3) indicates that bridging the positions around both bridgehead carbons of **1** favors the bis(norcaradiene) structure [**12c(6/6)** over **12o(6/6**]. The results also show that the 5,6-bridged structure [**12o(5/6)**] is more stable than the corresponding 6,6-open [**12o(6/6)**] or 6,6-fused [**12c(6/6)**] ones in this essentially "flat" case. It is noteworthy that UAM1 lowers the energy of the 5,6-fused form relative to the 5,6-bridged one, whereas the opposite is generally true for the 6,6-isomers; also, the 6,6-bridged is lowered relative to the 5,6-bridged isomer. Once again, the MMPI results are spotty, with **12c(6/6)** calculated to be much less stable than **12o(6/6)**.

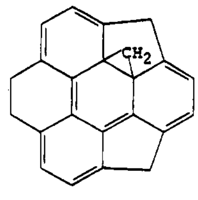
Effect of Curvature on the Annulene–Bis(norcaradiene) Equilibrium. More enlightening regarding the fullerenes are the calculated energies and structures for the series **13–15**. As a measure of curvature, Table 4 includes the calculated pyramidalization angles[9a,b] of the to-be-bridged carbons in the precursor alkenes (*i.e.*, the "parent" aromatic compounds). Curvature increases on going from **13** to **15**, with **15** pyramidalized to about the same extent as C_{60}. The results show that the stability of the 5,6-bridged structure, relative to the 6,6-fused one, *increases with increasing curvature* (the 5,6-closed structure was not an AM1 minimum for any of these cases). Furthermore, as judged from the distances between the bridgehead carbons for each homologous series ($r_{1,6}$ in Table 4), *increased curvature pulls the bridgehead carbons apart*. Thus, for the relatively flat **13**, as for **12**, the 6,6-fused structure is much more stable (AM1), but a crossover occurs with increasing curvature (at **14** for UAM1 and at **15** for RAM1), whereby the 6,6-bridged structure becomes more stable than the fused one. Although MMPI places the 6,6-bridged below the 6,6-fused structure for all these cases, the *trend* is the same as seen with AM1. Additionally, the apparent instability of the 5,6-fused structures is quantified by MMPI.

Equally dramatic effects are seen for **16–19**, where these tetrabenzo compounds are reasonable models for $C_{60}CH_2$ adducts. The curvature of each 6,6-fused adduct is shown by superimposition upon C_{60}. The 5,6-bridged adduct is *less stable* than the 6,6-fused one for the two cases (**16** and **17**) in which the adducts are less curved than C_{60}. But for **18** and (by implication) **19**, which are more curved than C_{60}, the relative stablities of the two reverse (RAM1; the trend is in the same direction as with UAM1, but the reversal only occurs for **19**). In fact, now the 6,6-open structures are more stable than the 6,6-fused structures. All the 6,6-bridged tetrabenzo compounds have close to or exact C_{2v} symmetry. They have highly bond-alternant benzene rings, with short benzo fusion bonds (1.38–1.39 Å) and long bridgehead to benzene ring bonds of about 1.43 Å; i.e., there is no partial *o*-quinodimethane structure. This seems to be an example of the Mills–Nixon effect[18] and makes the structures appear to be bis(norcaradiene)-like with a very long bridgehead–bridgehead bond. This might also be interpreted in terms of diradical character in these molecules, which might explain the large decrease in ΔH_f calculated on switching from RAM1 to UAM1. However, it is noteworthy that this switch results in a 69 kcal/mol decrease in ΔH_f for **18c(6/6)a**,

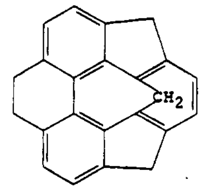
Chart 3



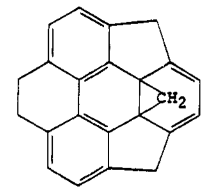
13o(5/6)



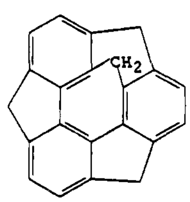
13c(5/6)



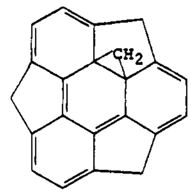
13o(6/6)



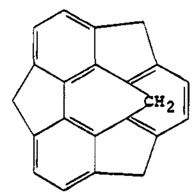
13c(6/6)



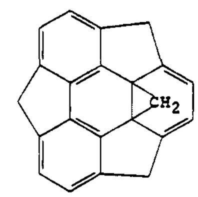
14o(5/6)



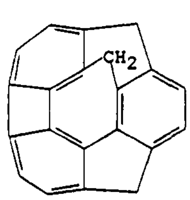
14c(5/6)



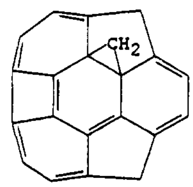
14o(6/6)



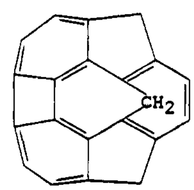
14c(6/6)



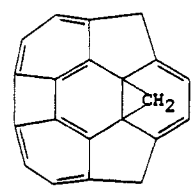
15o(5/6)



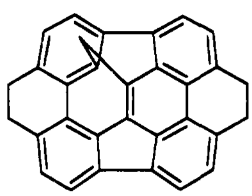
15c(5/6)



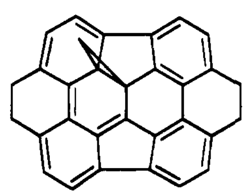
15o(6/6)



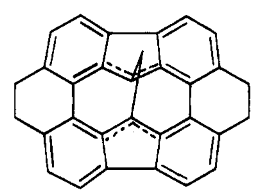
15c(6/6)



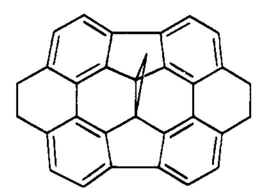
16o(5/6)



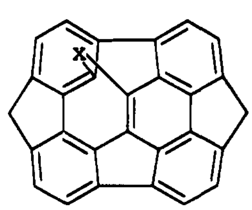
16c(5/6)



16o(6/6)

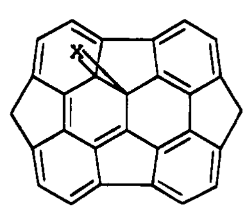


16c(6/6)



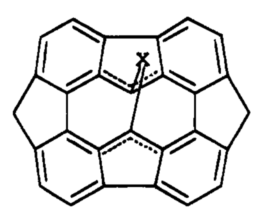
17o(5/6)

a, X = CH_2
b, X = CMe_2



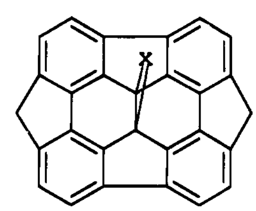
17c(5/6)

c, X = O
d, X = C=O



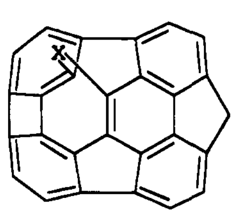
17o(6/6)

e, X = BCN
f, X = $CtBu_2$



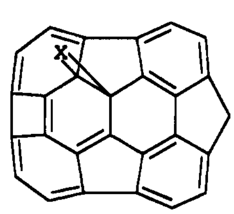
17c(6/6)

g, X = CPh_2



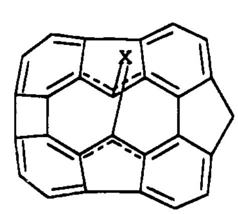
18o(5/6)

a, X = CH_2
b, X = CMe_2
c, X = O



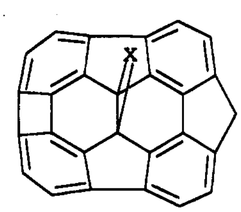
18c(5/6)

d, X = C=O
e, X = BCN



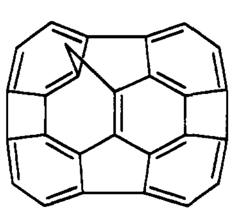
18o(6/6)

g, X = CPh_2
h, X = NH

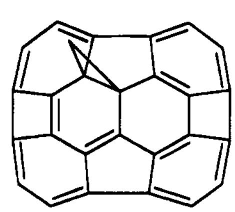


18c(6/6)

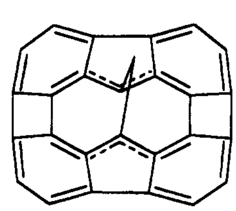
i, X = SiH_2
j, X = $SiPh_2$



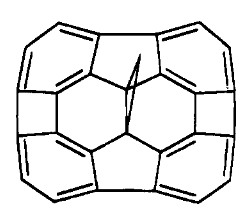
19o(5/6)



19c(5/6)



19o(6/6)

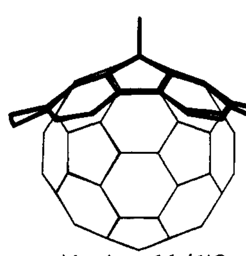


19c(6/6)

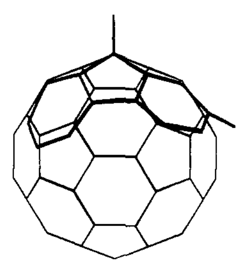
Table 4. Calculated Parameters for Some Curved Fullerene Model Compounds

	theoretical method					
	MMPI		RAM1		UAMI	
compd[a]	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}
13o(5/6)	121.86 [2.150]	(0)	142.49 [2.194]	(0)	120.30 [2.192]	(0)
13c(5/6)	183.02 [1.506]	61.2	*b*		*b*	
13o(6/6)	133.87 [2.115]	12.0	160.75 [2.105]	18.3	130.36 [2.155]	10.1
13c(6/6)	143.16 [1.479]	21.3	144.71 [1.518]	2.2	122.74 [1.503]	2.4
14o(5/6)	145.68 [2.187]	(0)	175.26 [2.205]	(0)	145.69 [2.205]	(0)
14c(5/6)	208.08 [1.518]	62.4	*b*		*b*	
14o(6/6)	154.20 [2.195]	8.5	187.28 [2.186]	12.0	151.24 [2.206]	5.6
14c(6/6)	169.94 [1.498]	24.3	182.46 [1.547]	7.2	153.13 [1.526]	7.4
15o(5/6)	221.99 [2.246]	(0)	267.91 [2.235]	(0)	222.21 [2.241]	(0)
15c(5/6)	288.09 [1.523]	66.1	*b*		*b*	
15o(6/6)	225.07 [2.257]	3.1	276.90 [2.256]	9.0	225.60 [2.261]	3.4
15c(6/6)	250.61 [1.509]	28.6	287.78 [1.599]	19.9	241.53 [1.570]	19.3
16o(5/6)	182.57 [2.092]	(0)	215.08 [2.185]	(0)	181.16 [2.212]	(0)
16c(5/6)	222.68 [1.511]	40.1	*b*		*b*	
16o(6/6)	202.00 [2.114]	19.4	*b*		213.59 [2.134]	32.4
16c(6/6)	188.85 [1.483]	6.3	207.19 [1.529]	−7.9	171.65 [1.504]	−9.5
17o(5/6)a	237.25 [2.208]	(0)	286.10 [2.197]	(0)	274.07 [2.219]	(0)
17c(5/6)a	275.14 [1.526]	37.9	*b*		*b*	
17o(6/6)a	250.66 [2.262]	13.4	*b*		268.64 [2.237]	−5.4
17c(6/6)a	241.82 [1.517]	4.6	279.56 [1.565]	−6.5	267.73 [1.560]	−6.3
18o(5/6)a	316.09 [2.259]	(0)	377.08 [2.227]	(0)	316.34 [2.241]	(0)
18c(5/6)a	362.24 [1.531]	46.2	*b*		*b*	
18o(6/6)a	329.09 [2.315]	13.0	380.97 [2.183]	3.9	309.69 [2.285]	−6.7
18c(6/6)a	323.45 [1.526]	7.4	382.63 [1.614]	5.6	313.60 [1.568]	−2.7
19o(5/6)	404.40 [2.269]	(0)	484.07 [2.235]	(0)	455.42 [2.259]	(0)
19c(5/6)	453.07 [1.535]	48.7	*b*		*b*	
19o(6/6)	403.78 [2.350]	−0.6	471.87 [2.252]	−12.2	435.37 [2.346]	−20.1
19c(6/6)	403.72 [1.536]	−0.7	*b*		*b*	

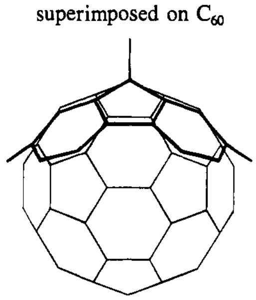
[a] Calculated pyramidalization angles for the "to-be-bridged" carbons of the precursor alkenes as a measure of curvature. **13**: 8.13° (carbons bridged in the 6,6-isomer), 6.77° (additional carbon bridged in the 5,6-isomer). **14**: 9.84°. **15**: 11.09°, 12.03°. **16**: 11.30°, 8.49°. **17**: 12.27°, 10.52°. **18**: 12.91°, 12.78°. **19**: 13.39°, 12.14°. C_{60}: 11.64°. [b] Structure not an AM1 minimum.



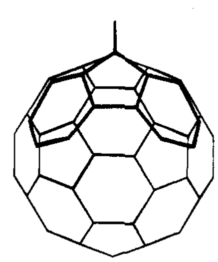
side view, **16c(6/6)** superimposed on C_{60}



side view, **18c(6/6)a**, superimposed on C_{60}



side view, **17c(6/6)a**, superimposed on C_{60}



side view, **19o(6/6)**, superimposed on C_{60}

a completely "closed-shell" molecule, compared to the slightly greater 71 kcal/mol decrease for **18o(6/6)a**. Similar comments apply to the **13(6/6)**−**15(6/6)** series.

Bridge Substituent Effects on the Fullerene−Fulleroid Equilibrium. With the understanding that increased curvature favors the 5,6- and 6,6-bridged over the 6,6-fused structure (probably due to the decreasing importance of aromatic stabilization with increased curvature, together with the fact that two of the aromatic rings in the 5,6-bridged structure are of the less stable "metacyclophane" type, and the less strained nature of open structures), we investigated the effects of substitution on **17** and **18** (Tables 5 and 6). The structural framework of **18** approximates C_{60} more closely than does that of **17**. For example the $\Delta\Delta H_f$ between the 5,6-bridged and 6,6-fused derivative for X = CPh_2 is 0.4 kcal/mol (compared to 1.2 kcal/mol for $C_{60}CPh_2$[7] and 13.7 kcal/mol for **17**; RAM1); for X = O, the difference is −9.7 kcal/mol (RAM1) or −7.2 kcal/mol (UAM1) [compared to −6.0 kcal/mol for $C_{60}O$—but by MNDO[8]—and 0.6 kcal.mol (RAM1) or 0.2 kcal/mol (UAM1) for **17**]; for X = $SiPh_2$, the RAM1 difference is 5.3 kcal/mol (compared to 10.7 kcal/mol for $C_{60}SiPh_2$[7]).

In all cases, RAM1 indicates that the more curved **18** favors the 5,6-open structure more than does C_{60}. This is (partially) corrected by UAM1, which anyhow favors the annulenic valence isomers. While MMPI never favors the annulenic 6,6-bridged structure, AM1 often does; for UAM1, that structure is favored over the 6,6-fused one for every equilibrium investigated. Of note is the dramatic stabilization of the fused isomers afforded by bulky groups, particularly *tert*-butyl. Apparently anomalous are the UAM1 results for **18(6/6)c** (X = O), where the bridged form is calculated to enjoy an 8.6 kcal/mol advantage over the fused isomer. Given the known preference for the fused isomer, this is too large a misprediction. However, the calculated distances between the bridgehead carbons ($r_{1,6}$ in the tables) are not consistent with the enhanced relative stability for the bridged form. Thus the $r_{1,6}$'s *increase* as the bridged form becomes relatively more stable (UAM1: **18o(6/6)b**, 2.274 Å; **a**, 2.285 Å; **d**, 2.305 Å; **e**, 2.395 Å; *but for c, 2.212* Å. RAM1: **b**, 2.144 Å; **c**, 2.130 Å; **a**, 2.183 Å; **d**, 2.218 Å; **e**, 2.286 Å), except for the X = O case. Here, RAM1 slightly underestimates the bond length and the UAM1 distance is significantly off, suggesting that the relative stability of the bridged form has been mispredicted (as is the oxepin structure relative to benzene oxide—data not shown).

Table 5. Calculated Substituent Effects on Model Fullerene Monoadducts of Structure **17**

	theoretical method					
	MMPI		RAM1		UAM1	
compd	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}
17o(5/6)b X = CMe_2	224.78 [2.207]	(0)	283.41 [2.183]	(0)	271.02 [2.206]	(0)
17c(5/6)b X = CMe_2	261.92 [1.529]	37.1	*a*		*a*	
17o(6/6)b X = CMe_2	236.96 [2.260]	12.2	*a*		264.82 [2.221]	−6.2
17c(6/6)b X = CMe_2	228.21 [1.520]	3.4	271.21 [1.559]	−12.2	259.29 [1.553]	−11.7
17o(5/6)c X = O	213.23 [2.164]	(0)	268.40 [2.141]	(0)	257.17 [2.162]	(0)
17c(5/6)c X = O	247.06 [1.520]	33.8	*a*		*a*	
17o(6/6)c X = O	224.64 [2.214]	11.4	*a*		256.41 [2.175]	−0.8
17c(6/6)c X = O	213.82 [1.514]	0.6	268.95 [1.535]	0.6	257.36 [1.528]	0.2
17o(5/6)d X = C=O	226.42 [2.282]	(0)	270.42 [2.231]	(0)	258.32 [2.245]	(0)
17c(5/6)d X = C=O	257.43 [1.567]	31.0	*a*		*a*	
17o(6/6)d X = C=O	239.89 [2.328]	13.5	*a*		253.40 [2.265]	−4.9
17c(6/6)d X = C=O	228.77 [1.468]	2.4	268.39 [1.586]	−2.0	256.27 [1.578]	−2.1
17o(5/6)e X = BCN	*b*		*b*		325.71 [2.322]	(0)
17o(6/6)e X = BCN	*b*		*b*		322.98 [2.337]	−2.7
17c(6/6)e X = BCN	*b*		*b*		326.10 [1.592]	0.4
17o(5/6)f X = $CtBu_2$	231.17 [2.166]	(0)	312.91 [2.151]	(0)	*b*	
17c(5/6)f X = $CtBu_2$	254.32 [1.533]	23.2	*a*		*b*	
17o(6/6)f X = $CtBu_2$	242.92 [2.216]	11.8	*a*		*b*	
17c(6/6)f X = $CtBu_2$	224.90 [1.524]	−6.3	291.67 [1.559]	−21.2	*b*	
17o(5/6)g X = CPh_2	294.05 [2.189]	(0)	358.51 [2.186]	(0)	*b*	
17c(5/6)g X = CPh_2	326.73 [1.526]	32.7	*b*		*b*	
17o(6/6)g X = CPh_2	307.49 [2.239]	13.4	*b*		*b*	
17c(6/6)g X = CPh_2	294.00 [1.517]	−0.1	344.85 [1.555]	−13.7	*b*	

[a] Structure not an AM1 minimum. [b] Not calculated.

Table 6. Calculated Substituent Effects on Model Fullerene Monoadducts of Structure **18**

	theoretical method					
	MMPI		RAM1		UAM1	
compd	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}	ΔH_f, kcal [$r_{1,6}$, Å]	E_{rel}
18o(5/6)b X = CMe_2	305.40 [2.259]	(0)	374.10 [2.213]	(0)	348.97 [2.253]	(0)
18c(5/6)b X = CMe_2	349.72 [1.534]	44.3	*b*		*b*	
18o(6/6)b X = CMe_2	315.75 [2.312]	10.4	376.91 [2.144]	2.8	349.59 [2.274]	0.6
18c(6/6)b X = CMe_2	310.61 [1.531]	5.2	374.58 [1.598]	0.5	353.21 [1.579]	4.2
18o(5/6)c X = O	291.87 [2.207]	(0)	363.08 [2.160]	(0)	344.46 [2.181]	(0)
18c(5/6)c X = O	331.48 [1.525]	39.6	*b*		*b*	
18o(6/6)c X = O	301.27 [2.250]	9.4	372.67 [2.130]	9.6	343.07 [2.212]	−1.4
18c(6/6)c X = O	294.15 [1.524]	2.3	372.73 [1.569]	9.7	351.70 [1.550]	7.2
18o(5/6)d X = C=O	302.61 [2.326]	(0)	361.33 [2.256]	(0)	342.31 [2.273]	(0)
18c(5/6)d X = C=O	339.62 [1.576]	37.0	*b*		*b*	
18o(6/6)d X = C=O	317.12 [2.368]	14.5	366.41 [2.218]	5.1	341.51 [2.305]	−0.8
18c(6/6)d X = C=O	311.63 [1.475]	9.0	371.54 [1.641]	10.2	350.06 [1.611]	7.8
18o(5/6)e X = BCN	*b*		431.81 [2.316]	(0)	412.12 [2.336]	(0)
18o(6/6)e X = BCN	*b*		434.28 [2.286]	2.7	405.57 [2.395]	−6.6
18c(6/6)e X = BCN	*b*		441.07 [1.663]	9.3	419.53 [1.630]	7.4
18o(5/6)g X = CPh_2	372.02 [2.233]	(0)	448.83 [2.210]	(0)	*b*	
18c(5/6)g X = CPh_2	414.42 [1.530]	42.4	*b*		*b*	
18o(6/6)g X = CPh_2	385.56 [2.287]	13.5	451.81 [2.136]	3.0	*b*	
18c(6/6)g X = CPh_2	375.96 [1.527]	3.9	448.46 [1.592]	−0.4	*b*	
18o(5/6)h X = NH	330.43[c] [2.211]	(0)	395.68[g] [2.173]	(0)	*b*	
18c(5/6)h X = NH	370.85[d] [1.529]	40.4	*b*		*b*	
18o(6/6)h X = NH	338.61[e] [2.284]	8.2	398.63[h] [2.136]	3.0	*b*	
18c(6/6)h X = NH	334.10[f] [1.528]	3.7	398.26[h] [1.591]	2.6	*b*	
18o(5/6)i X = SiH_2	*b*		378.77 [2.362]	(0)	*b*	
18c(5/6)i X = SiH_2	*b*		*a*		*b*	
18o(6/6)i X = SiH_2	*b*		381.23 [2.274]	2.5	*b*	
18c(6/6)i X = SiH_2	*b*		377.41 [1.595]	−1.4	*b*	
18o(5/6)j X = $SiPh_2$	*b*		415.16 [2.348]	(0)	*b*	
18o(6/6)j X = $SiPh_2$	*b*		416.32 [2.217]	1.2	*b*	
18c(6/6)j X = $SiPh_2$	*b*		409.85 [1.591]	−5.3	*b*	

[a] Structure not an AM1 minimum. [b] Not calculated. [c] *endo*-H = H bent toward 4MR; *exo*-H structure not an MMPI minimum. [d] For *endo*-H; *exo*-H structure less than 0.1 kcal/mol higher, with a 58.2 kcal/mol barrier between them ($r_{1,6}$ = 1.65 Å at the transition state). [e] For *exo*-H = H bent toward 4MR; *endo*-H structure is 0.5 kcal/mol higher, with a 2.9 kcal/mol barrier between them ($r_{1,6}$ = 2.29 Å at the transition state). [f] For *exo*-H; *endo*-H structure lies within 0.02 kcal/mol, with a 46.9 kcal/mol barrier between them ($r_{1,6}$ = 1.63 Å at the transition state). [g] *exo*-H (inv. barrier = 9.0 kcal/mol). [h] *exo*-H.

To assess which method, RAM1 or UAM1, gives the more consistent results, one might compare the *change in relative stability* between the open and closed nonbenzannelated systems (i.e., **1**, **2**, **7**, **8**, and **9**) with that for the tetrabenzannelated ones [i.e., **18(6/6)a–e**]. For RAM1, these values are 5.3, −1.6, 8.6, 9.2, and 8.6 kcal/mol, while for UAM1, they are 2.0, −7.4, 9.4, 13.2, and 7.9 kcal/mol, respectively. If the substituent effects are similar for the two structural types, then RAM1 gives the apparently more consistent values.

What about a strategy for making the 6,6-open structure (fulleroid) more stable than the corresponding fullerene? Our data suggest that the carbonyl-bridged derivative is a good candidate. Additionally, an even more electropositive group (e.g., X = BCN) might exist as a 6,6-fulleroid (favored by 14 kcal/mol by UAM1).

Conclusions

In summary, we have shown that *increasing curvature* causes the 5,6-bridged fulleroid structure to become relatively *more stable* than the 6,6-fused fullerene structure. Additionally, the 6,6-bridged fulleroid structure increases in stability relative to the 6,6-fused structure, although the unsubstituted latter one remains more stable at the fullerene level of curvature. Our calculations suggest that bridging by a carbonyl group, or an even more electropositive group, might afford global stability to 6,6-bridged fullerenes.

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