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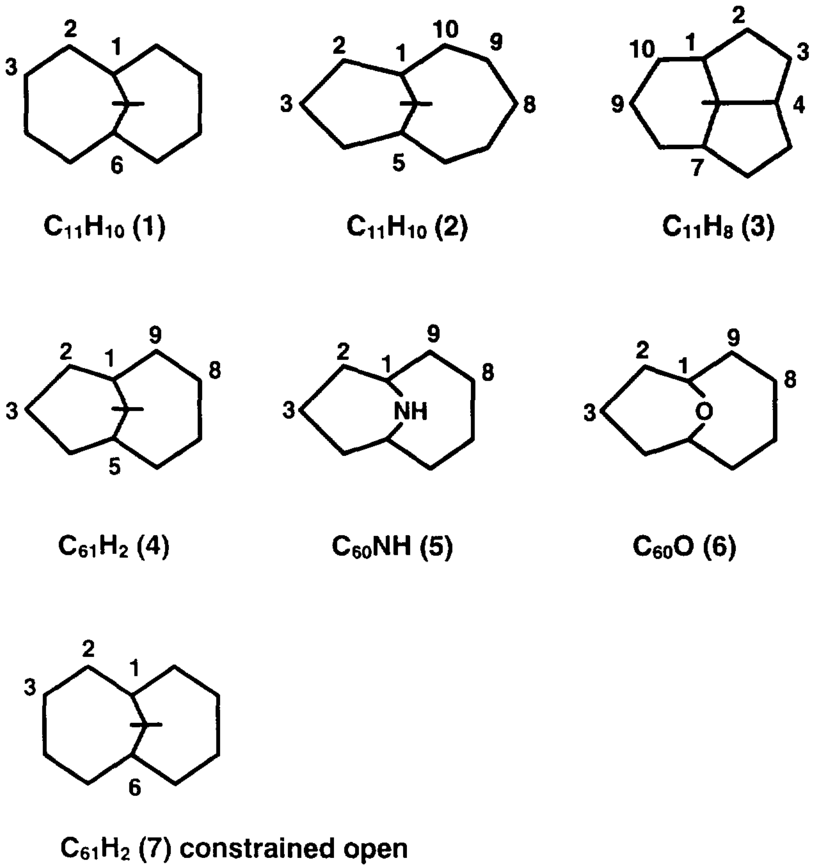
Electronic Structure of the Fulleroids: Homoconjugation in Bridged C_{60} Derivatives

R. C. Haddon and K. Raghavachari

AT&T Bell Laboratories
Murray Hill, N.J. 07974-0636, U. S. A.

Abstract. The electronic structure of the fulleroids is examined with the π-orbital axis vector (POAV) analysis and 3D-HMO theory. Using ab initio HF geometries, we compare the electronic structure of fulleroids with bridge groups attached to [5,6]- and [6,6]-bonds in C_{60}, with the well known bridged annulenes: 1,6-methano[10]annulene, 1,5-methano[10]annulene, and 1,4,7-methino[10]annulene. Although the perimeters of these systems are structurally related, the greater pyramidalization implicit in the fulleroid structure substantially modifies their electronic structure. Copyright © 1996 Elsevier Science Ltd

The fullerenes form a unique class of continuous aromatic molecules.[1] If not for the tremendous strain implicit in their spheroidal structure, they might be expected to be as inert as graphite toward chemical reagents.[1] While the presence of 12 five-membered rings (5-MRs), serves to enhance their ability to accept electrons,[2,3] the extra energy required to transform 60 graphite carbon atoms into a C_{60} molecule is mainly taken up in the strain energy required for carbon atom pyramidalization.[1,4,5] The continuity of the fullerene electronic structure poses a special challenge for chemists who might seek to functionalise these molecules while retaining the basic fullerene bonding pattern. Nevertheless, Wudl[6] has argued that the fulleroids constitute such a class of functionalised fullerenes. Wudl[6] defines the fulleroids as those bridged derivatives of a fullerene that lead to open structures, as opposed to the intact cyclopropane geometry now known to prevail when bridging occurs across a bond common to a pair of hexagons (denoted [6,6]-bridging): "Fulleroid is a term introduced to describe an expanded fullerene where the electronic properties and number of π-electrons remains unchanged with respect to the unexpanded fullerene."



Scheme 1. Numbering scheme for bridged annulenes. Compounds **1** - **3** are isolated annulenes, while structures **4** -**7** show a fragment of the fulleroid molecule. The structure **7** is not an energy minimum, and is included for comparison purposes (see text).

It is of particular importance that the scheme of fulleroid bonding proposed by Wudl depends on the presence of a homoconjugate or homaoaromatic interaction to replace the bond that has been functionalised by fulleroid formation, thereby retaining the fullerene bonding pattern (60 π-electrons and 90 conjugated bonds, one of which is now homoconjugated in C_{60} fulleroids). In fact, in the initial report on fullerene inflation, Wudl considered, and rejected the term "homofullerene", for the fulleroids.[6] Thus the fulleroid field owes much of its inspiration to the class of molecules known as bridged annulenes,[7] where in certain instances the case for homoaromatic interactions has won universal acceptance. In this article we shall build on this body of knowledge by first reviewing the electronic structure of some of the more important members of the bridged annulene class of molecules, and then comparing these rather well-studied compounds with the fulleroids. As representative bridged annulenes we choose 1,6-methano[10]annulene (**1**) (Vogel[8]), 1,5-methano[10]annulene (**2**) (Masamune[9] and Scott[10]), and 1,4,7-methino[10]annulene (**3**) (Rees[11]). These compounds are appropriate for the present work as it is now known that the first two have appreciable homoaromatic interactions while the latter compound shows negligible transannular overlap.[10, 12-15] Thus **1** and **2** are now referred to as homonaphthalene[12, 13] and homoazulene,[10, 14] respectively; whereas **3** qualifies as a genuine bridged annulene with unperturbed peripheral conjugation.[15]

At present, all of the [5,6]-bridged fullerenes are members of the fulleroid family with annulene perimeters as in **4**-**6**, whereas all [6,6]-bridged fullerenes lead to structures with intact cyclopropanes, and are usually referred to as methanofullerenes. The large number of fullerene derivatives of this general type that have been reported in the literature makes the fulleroid-methanofullerene family the most important route to functionalised fullerenes.[16-28] Thus there has been considerable interest in understanding the factors that control the electronic structure of these compounds and their equilibrium geometries. Warner[27] has analyzed the geometries of a variety of fullerene fragments in order to assess the role of curvature (pyramidalization), in determining the preference for methanofullerene or fulleroid structures, and he concludes that curvature actually favors the open, fulleroid structure. Diederich and coworkers[28] have examined the relative energies of the isomers from two standpoints: the electronic preference for the [5]radialene structure with all double bonds exocyclic to the five-membered rings (5-MRs), and the occurrence of Bredt's Rule violations. This latter effect arises when the double bonds involve carbon atoms at the bridgehead of small ring systems, and is energetically unfavorable because the geometric constraints of the system force a misalignment of the π-orbitals that comprise the double bond.

The fulleroids and methanofullerenes add a new feature to considerations of strain in the fullerenes. We have stressed that the π-orbital alignment remains very high in the fullerene family and is perfect in icosahedral C_{60}.[29] This is because the distortions necessary for closure of a fullerene involve carbon atom pyramidalization, rather than a twisting of the carbon-carbon π-bonds. Thus it is possible to approximately model the fullerene strain energy by a consideration of the pyramidalization energy of the carbon atoms (Figure 1), with neglect of torsional energies.[1,4,5,30,31] However, this situation is unlikely to prevail in the fulleroids as the bridge groups may be expected to impose torsional distortions that bring about the type of π-orbital misalignments that are known to occur in the bridged annulenes.[32, 33] The π-orbital axis vector (POAV) analysis[33] provides a measure of the orientation of the π-orbitals in nonplanar conjugated systems and thus it will be possible to directly gauge the degree of π-orbital misalignment in the methanofullerenes and fulleroids, and compare the misalignment angles (ϕ) with those previously reported for the bridged annulenes. The

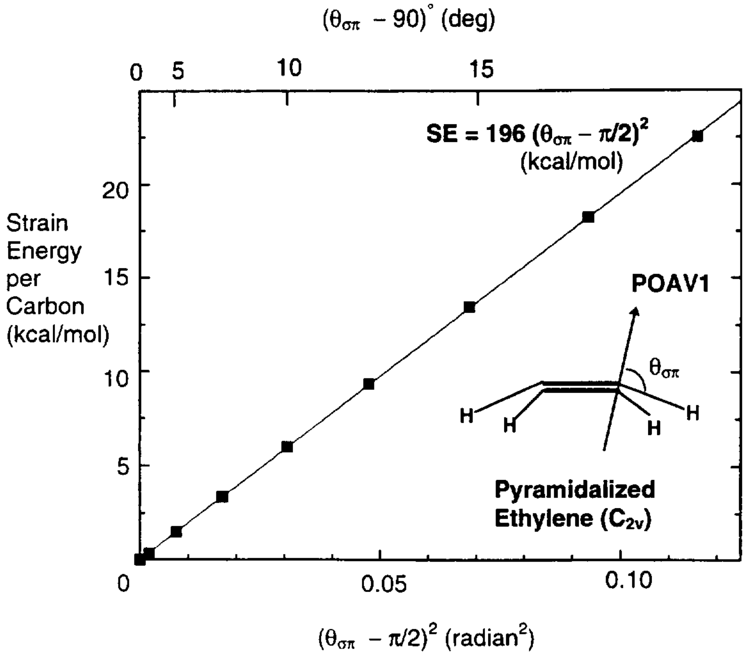
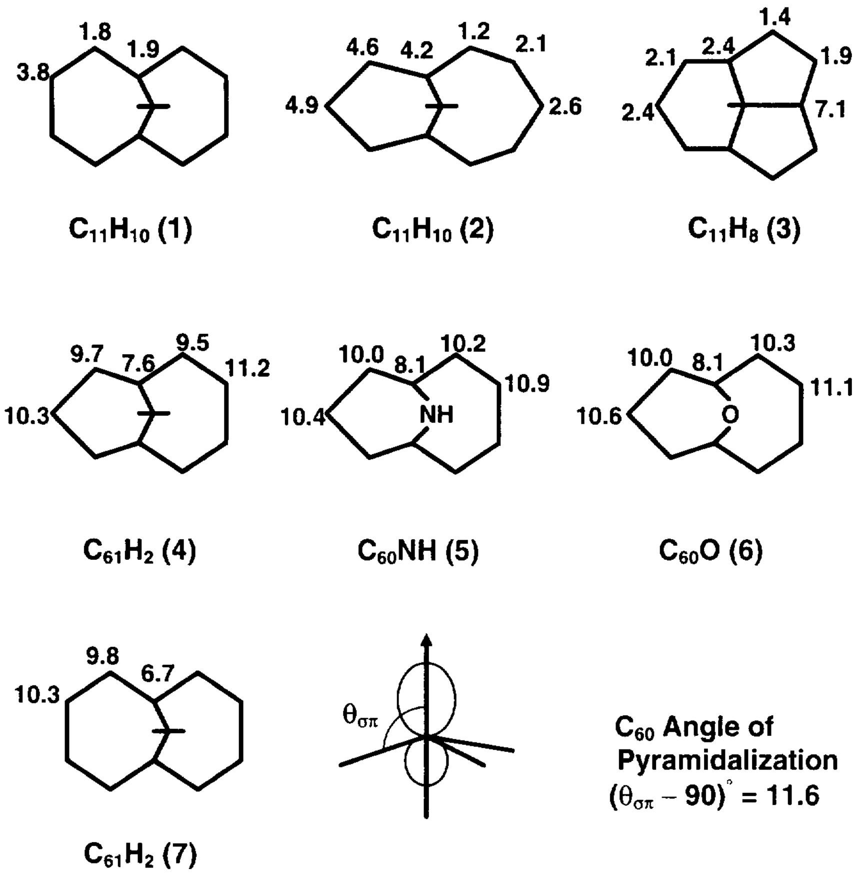


Figure 1. Model POAV1 pyramidalization energies calculated for ethylene.[30,31]

energetic impact of double bonds in the 5-MRs is more difficult to assess. Taylor[34] has noted that within a valence bond approach, C_{60} is the only fullerene in which it is possible to locate all of the double bonds in 6-MRs and none in the 5-MRs, and on this basis C_{60} would be expected to be the most stable fullerene (neglecting the strain energy, which is estimated to vary by no more than 25 kcal/mol among typical fullerenes[1]). The C_{70} valence bond structure requires 5 double bonds in 5-MRs and thus would be expected to be less stable than C_{60}.[34] However, a recent determination of the heat of formation of these two fullerenes showed C_{70} to be more stable than C_{60} by 0.5 kcal/mol on a per carbon basis;[35] calculations give a value of 0.7 kcal/mol C for the same quantity.[36] On the other hand, a theoretical study by Matsuzawa, *et al*. found an 8.5 kcal/mol increase in the heat of formation of the isomers of $C_{60}H_2$, for each double bond placed in a 5-MR on hydrogenation.[37]

CALCULATIONS

The geometries utilized for the bridged annulenes and fulleroids were obtained by use of HF ab initio calculations with extended basis sets. In the case of bridged annulenes **1** (C_{2v}), **2** (C_s), and **3** (C_s) we used the



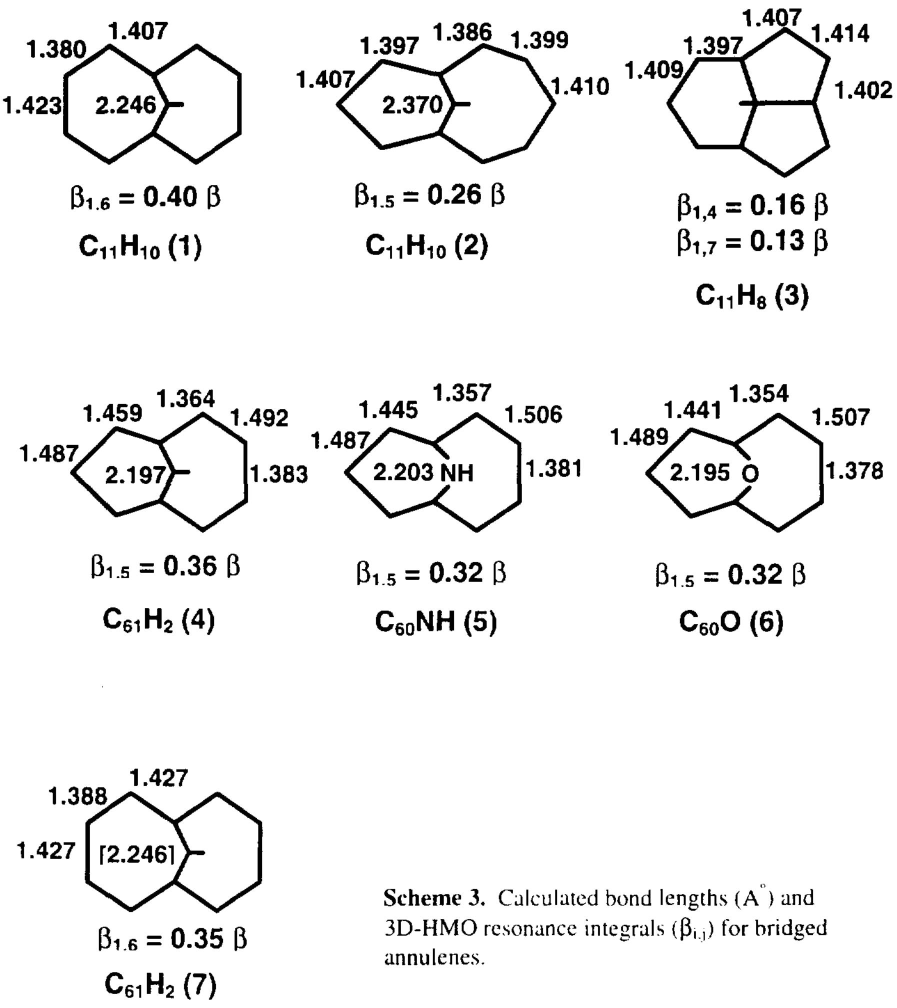
Scheme 2. POAV1 pyramidalization angles [$(\theta_{\sigma\pi} - 90)$, deg] for bridged annulenes.

geometries previously reported at the HF/6-31G level of theory.[38] Whereas for the fulleroids **4** - **6** (C_s), and **7** (C_{2v}), the structures were optimized at the HF/3-21G theoretical level.[16] For [6,6]-fulleroid **7**, the transannular 1,6-distance was constrained to the value of 2.246 Å, which corresponds to the 1,6-distance calculated for **1**.[38] The ground state structure of **7** is known to be closed with an intact cyclopropane; the open structure is used in the present work to provide comparisons with the other fulleroids and bridged annulenes.[16] The POAV1 analysis of the geometrical structures was carried out with Release 3.0 of the POAV3 program, which is now available from QCPE.[39]

RESULTS

Pyramidalization. The POAV1 pyramidalization angles $(\theta_{\sigma\pi} - 90)^{\circ}$, are shown in Scheme 2.[32, 33, 40] The orientation of the π-orbital axis vector in the POAV1 scheme is defined so that it makes equal angles ($\theta_{\sigma\pi}$), to the three σ-bonds at the conjugated carbon atom. In planar conjugated systems, $\theta_{\sigma\pi} \equiv 90°$, and the pyramidalization angle is zero. Even in the isolated bridged annulenes (**1** - **3**), there is appreciable pyramidalization in the conjugated perimeters and this is not restricted to the bridge positions where the carbon atoms are constrained to be nonplanar. Analysis of the π-orbital misalignment angles shows that the nonzero values of the pyramidalization angles at the unconstrained carbons atoms occurs so that the π-orbital overlap around the ring is maintained in spite of the molecular distortions dictated by the bridge group. Nevertheless the pyramidalization angles found in the perimeters of **1** - **3**, are considerably increased when these structural fragments become a part of the C_{61} fulleroid (**4** - **7**). Thus while the topologies of these two sets of compounds are similar, it is clear the degree of strain in the perimeters is quite different. Apart from C-8, the pyramidalization at the conjugated carbon atoms in **5** and **6** is greater than in **4**, but in all cases reduced from the values that are implicit in the parent C_{60} molecule.[2, 29] Thus addition of a bridge group to give a fulleroid serves to decrease the pyramidalization of the atoms in the immediate vicinity of the site of addition to the fullerene. Nevertheless, examination of the atoms more distant from the bridge group than those displayed in Scheme 2 shows that some of the fulleroid carbon atoms have become more pyramidalized than in the parent C_{60} molecule.

Homoconjugation. Scheme 3 shows the calculated bond lengths in the molecules, together with POAV1/3D-HMO transannular resonance integrals.[41] The transannular resonance integrals are calculated from the POAV1 carbon atom hybridizations using Slater orbitals to obtain the overlap integrals. Scaling these overlap integrals with the benzene π-orbital overlap integral gives the reduced resonance integrals as coefficients of the usual benzene resonance integral (β). Analysis of second nearest neighbor (1,3) interactions in the cyclopentadienyl ring shows that $\beta_{1,3} = 0.2\ \beta$, and this value was adopted as the threshold below which transannular interactions are considered negligible; on this basis previous 3D-HMO analyses of **1** - **3** allowed a clear separation of homoaromatic from nonhomoaromatic interactions.[41] Thus **1** and **2**, but not **3**, are classified as homoaromatic by this scheme and these compounds are referred to as homonaphthalene[12,13] and homoazulene,[10,14] respectively. Dewey, *et al*,[12] concluded that for **1**: "The most likely value of the transannular resonance integral was estimated at about 40% of that between $2p_z$ orbitals on neighbors in benzene," in excellent agreement with the value given by 3D-HMO theory (Scheme 3).[15] It should be noted that it is not just the distance between transannular carbon atoms that governs the strength of the homoaromatic interactions in **1** - **3**. At the bridges, the transannular distances in **3** are: $r_{1,4} = 2.371$ Å and $r_{1,7} = 2.550$ Å; the former of these is little different from the value in **2** which has a significant homoconjugate interaction. Inspection of the structures shows that the difference arises from the ring conformations, pyramidalization and POAV orientation in the two compounds.



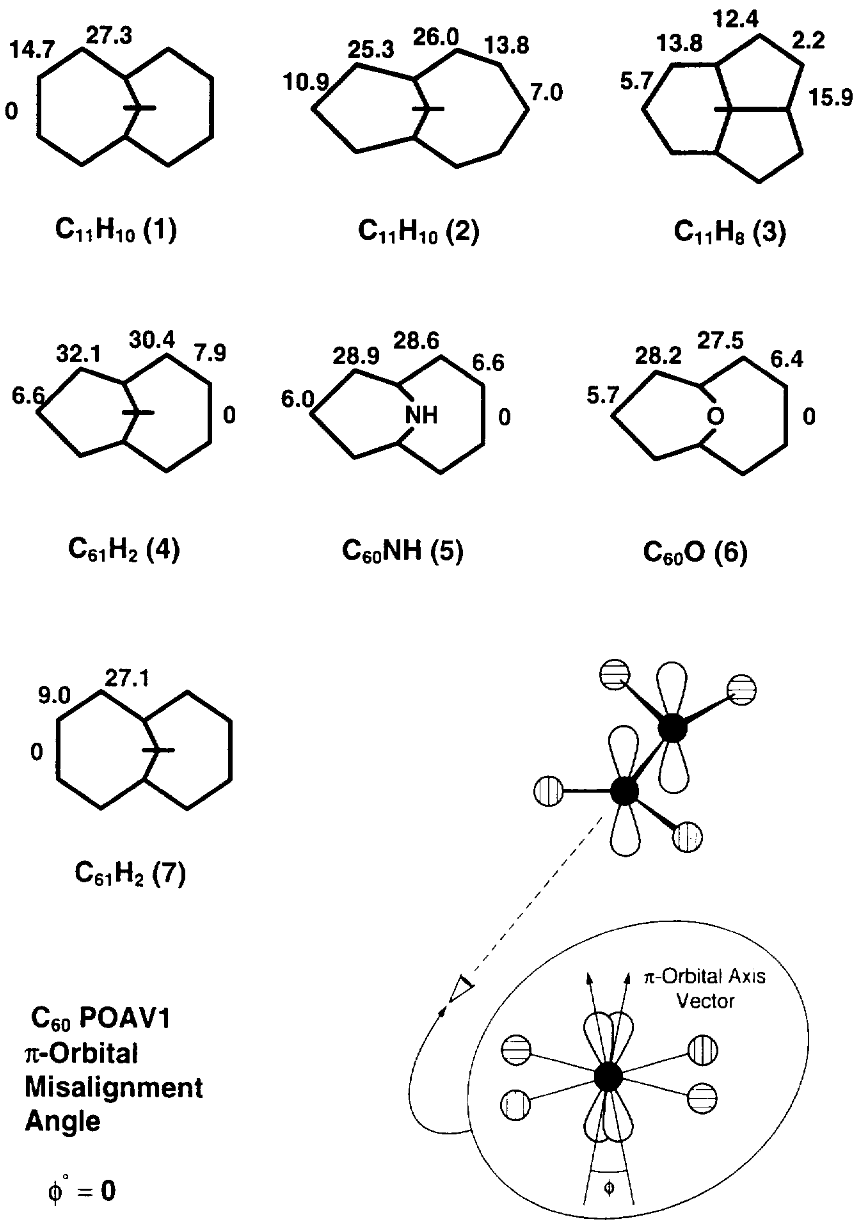
Scheme 3. Calculated bond lengths (Å) and 3D-HMO resonance integrals ($\beta_{i,j}$) for bridged annulenes.

The results in Scheme 3 show that the pattern of (calculated) bond length alternation in **7** is rather similar to that in **1**, whereas there are appreciable differences found in **4** - **6**, perhaps because of the odd-membered periphery found in these fulleroids. The transannular resonance integrals are found to be significant in all of the fulleroids and on the basis of the criteria discussed above for the bridged annulenes, they clearly qualify as homoconjugate and perhaps homoaromatic species. It is interesting to note that even though the transannular distances calculated for **4** - **6** are less than those in **1**, the homoconjugate interactions are found to be weaker and the same remarks apply to **7**. Most of this decrease is due to the greater pyramidalization implicit in the fulleroid structure, although a part is due to the slight misalignment of the homoconjugated orbitals in **4** - **6**. Because the sense of the POAV in all atoms of these compounds[41,42] is in the same direction as the bridge, the strong rehybridization in the bridge orbitals weakens the overlap of the transannular bond in the fulleroids relative to the isolated annulene. The variations in the homoconjugate bond strengths among **4** - **6** have their origin in the calculated bridge bond lengths: 1.491 Å (**4**), 1.421 (**5**), 1.399 (**6**), which in turn affect the angles subtended at the bridge atom: 94.9° (**4**), 101.7 (**5**), 103.3 (**6**). The small bridge angle in **4** enhances the transannular overlap by orienting the p-orbitals so that they make a smaller angle with the internuclear axis between C-1 and C-5. Thus our findings support the early suggestions of homoconjugation in the fulleroids,[6,7] and place the strength of these interactions in the order: **1** > **4** > **5** ~ **6** > **2**.

π-Orbital Misalignment Angles (ϕ). The POAV1 misalignment angles are shown in Scheme 4. These quantities are defined as the two-center dihedral angles between the π-orbital axis vectors on bonded pairs of carbon atoms, and provide a far more reliable index of π-orbital misalignment than the conventional analysis of dihedral angles.[32, 33] In particular, this analysis convincingly demonstrates that the pyramidalization that occurs in **1** - **3** leads to a strong enhancement of the π-orbital overlap in the periphery, and provides a framework for understanding the aromatic character of these highly distorted compounds.[16] In **1** - **3** the pyramidalization angles are modest, and for the non-bridgehead atoms, driven by considerations of π-orbital overlap in the periphery. The pyramidalization in the fulleroids, however, is dictated by the geometry of the remaining structure, and is much larger than that found in **1** - **3**. Thus the geometry of **4** - **7** is not dictated by π-orbital overlap in the periphery, and this is reflected in the π-orbital misalignment angles in **4** - **6**, but not **7** (Scheme 4). The π-orbital misalignment angles in **7** are less than those in the isolated molecule **1**, even though the pyramidalization in **7** is much greater. On the other hand the fragments **4** - **6** are both more pyramidalized and contain greater π-orbital misalignment than their isolated counterparts.

DISCUSSION

Benzene is often cited as the archetypal aromatic molecule, but in reality benzene sets the standard because it may be the one case where aromatic character and strain may be analytically separated, as benzene is taken to be a strain free structure. Thus any discussion of aromatic character must usually take into account the question of strain. The fullerenes represent the most dramatic example of this principle, among the many classes of aromatic compounds studied to date.[1] The strain energy in the fullerenes has been estimated to be ~ 480 kcal/mol, which represents ~ 80% of the excess energy of the carbon atoms in C_{60} over those in graphite and makes the fullerenes the most strained organic molecules ever isolated.[1] The relief of strain drives the chemistry of the fullerenes; the view that fullerene reactivity arises from the localized electronic structure is not tenable. The ring currents that are made apparent in the various NMR and magnetic susceptibility studies provide compelling evidence in favor of a delocalized electronic structure.[1, 19c, 19d, 20, 21c, 21d, 43-45] While the



Scheme 4. POAV1 π-orbital misalignment angles (φ, deg) for bridged annulenes

fullerenes show predominantly paramagnetic and diamagnetic ring currents in the 5- and 6-MRs, respectively, this is quite distinct from the situation in a localized, nonaromatic structure where an absence of ring currents is to be expected. Furthermore, the C_{60} bond lengths of 1.407 and 1.458 Å (Δr = 0.057 Å , electron diffraction[46]), exhibit about the same degree of bond length variation as is found in normal aromatic benzenoid hydrocarbons. For example, naphthalene[47] shows bond lengths, r = 1.371, 1.412, 1.420, 1.422 Å, for a total spread in bond lengths, Δr = 0.051 Å; coronene[47] has r = 1.391, 1.402, 1.413, 1.440, and Δr = 0.049 Å, and hexabenzocoronene[48] has r = 1.376, 1.399, 1.417, 1.418, 1.447, 1.458, and Δr = 0.082 Å. The reactivity of the fullerenes is analogous to that of other strained aromatics,[1] the only difference being the continuity of the fullerene electronic structure.

Apart from partitioning fullerene characteristics between electronic and strain effects, the separation of σ- and π-bonding contributions poses a particular challenge. The POAV analysis provides a rigorous analytical scheme for the isolation of the π-system from the remainder of the molecular electronic structure by defining the π-orbitals to be (locally) orthogonal to the σ-orbitals.[16] In this way it may be shown that the π-orbital misalignment in the parent fullerenes is very small and thus it is to be expected that most of the destabilization of the fullerene structure relative to graphite arises primarily from the pyramidalization energy[1, 2, 29] (Figure 1). As noted above, the pyramidalization angles in the fulleroids are similar to those in the fullerenes but not to those in the isolated bridged annulenes. Furthermore the fulleroids show significant π-orbital misalignment angles, some of which are larger than those found in the isolated bridged annulenes. These two factors introduce new features into considerations of the electronic structure and chemistry to be expected of the fulleroids relative to the behavior of the fullerenes and isolated bridged annulenes.

Relative Energies of the Fulleroids and Methanofullerenes. The nature of the electronic structure of the products of addition of methylene to the fullerenes has received extensive discussion in the literature. The situation now seems to be resolved in favor of the fulleroid structure for [5,6]-bridging and the methanofullerene structure (intact cyclopropane) for [6,6]-bridging. Raghavachari and Sosa[16] noted that the bond strengths of the parent fullerene could account for the open and closed structures of the methylene-bridged products. Diederich and coworkers[28] have drawn attention to two features of the electronic structure of these compounds that may be of importance. First, the observed products avoid placing double bonds in the 5-MRs, whereas the [6,5]-closed structure and the [6,6]-open structure require two and three double bonds in 5-MRs, respectively. Secondly, both of the open, fulleroid structures lead to Bredt's rule violations; that is, placement of a double bond at the bridgehead of a small ring system. This latter effect is destabilizing because of the π-orbital misalignment engendered by this type of structure. However, it is fairly clear that the Bredt's rule violation is not the determining feature in the preferred energy minimum of the [6,6]-bridged structure. Reference to Scheme 4, shows that the π-orbital misalignments in the constrained fulleroid structure **7**, are less than those in the isolated homoannulene **1**. The pyramidalization in **7** is greater than in **1**, but Warner has concluded that pyramidalization favors the open, fulleroid structure. This seems to leave as the only explanation for the occurrence of the closed isomer in the [6,6]-bridged methanofullerenes (apart from the bond strength argument[16]), that this geometry avoids valence bond structures that place double bonds in the 5-MRs. The [5,6]-bridged structures **4** - **6**, experience significantly more π-orbital misalignment (the orbital overlap is approximately proportional to cos ϕ[1,4,5]), than their isolated annulene counterparts **1** - **3**, and the fact that these are the preferred isomers suggests again that it is the placement of double bonds in the 5-MRs, and not the Bredt's rule violations, that determines the final geometry in the $C_{61}H_2$ compounds. Because the bond strength argument[16] preserves the main features of the electronic structure of the original fullerene it leads to much the same conclusions as the rationalisation based on double bonds in the 5-MRs.[28]

Reactivity of the Fulleroids. Recent work by Hummelen, *et al*,[49] has shown that a [5,6]azafulleroid undergoes a regioselective photoxygenation reaction to provide the first example of the controlled opening of the fullerene cage. As shown in Schemes 2-4, the model azafulleroid **5**, shows evidence of substantial strain at the 1-9 bond. First this bond is quite strong and this serves to magnify strain effects such as pyramidalization and π-orbital misalignment as a result of the Bredt's rule violation. The 1-9 bond length of 1.357 Å in **5**, is about 0.01 Å shorter than that calculated for **4** and significantly shorter than the C_{60} bonds (HF/3-21G bond lengths of 1.365 and 1.453 Å[36]). The pyramidalization and π-orbital misalignment angles are far larger than those occurring in the isolated annulenes **1** - **3**. Thus the Bredt's rule violation in **5** is substantial at the 1-9 bond and this is the source of the enhanced reactivity of the molecule. By way of comparison we note that HF/6-31G geometries of *trans*-cyclooctene and 1-norbornene gave POAV1 pyramidalization angles, $(\theta_{\sigma\pi} - 90)^\circ$ = 6.1, 6.1 and 10.9, 20.0, and π-orbital misalignment angles, ϕ° = 20.0 and 37.3 at the double bonds, respectively.[33] Although *trans*-cyclooctene is a well-characterized molecule, 1-norbornene has only been identified as a transient intermediate. While the parent fulleroid, **4**, has a longer 1-9 bond and less pyramidalization than **5**, the severe π-orbital misalignment may also make this a site of preferred reactivity in this compound under certain circumstances.

Prospects. The chemistry and physical properties of the fulleroids and methanofullerenes will continue to be one of the most intensively investigated areas of fullerene science. Recent experiments show that the bridge groups play a part in the electrochemistry of these species,[23, 24] and the reduced forms of these compounds provide evidence for unusual modes of conjugation between bridge substituents and the fullerene electronic structure.[50] While we have focused on the fulleroids derived from C_{60}, Smith and coworkers[21b-d] have already reported regioselective addition of diazomethane to C_{70} to prepare two $C_{71}H_2$ fulleroids and clearly the electronic structure of these compounds will be of relevance to the issues raised in this paper. The chemistry of the buckybowls[51] will also be of great interest: can these compounds be induced to undergo fullerene-type reactivity (internal functionalization at the site of greatest pyramidalization), as opposed to the reactions at the periphery that are typical of noncontinuous (or bounded) aromatics? If so, they could lead to new classes of bridged annulenes that are also fulleroid fragments. The controlled opening of the fullerene cage via an azafulleroid provides a further opportunity for the realization of new classes of functionalised fragments.[49]

Nomenclature. Reference to the literature shows that a clear consensus has yet to be reached on the nomenclature of the fulleroids and methanofullerenes. Based on our studies we believe that the open structures are homofullerenes. If for historical reasons the term fulleroid is retained it should be on this basis. Indeed this was the original rationale for the interest in fulleroids;[6] by including the transannular homoconjugate bond in the electronic structure of $C_{61}H_2$ the bonding pattern of C_{60} is retained in its entirety: 60 π-electrons and 90 π-bonds. Finally one can also question the term methanofullerene, for the resemblance it bears to the term previously adopted for the bridged-annulenes (**1** - **3**). Perhaps cyclopropane could be incorporated in the title of these compounds as this term makes clearest the true geometry of the closed structures.

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