ARTICLE

Chemistry of the Fullerenes: The Manifestation of Strain in a Class of Continuous Aromatic Molecules

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Within the π-orbital axis vector theory, the total rehybridization required for closure of the fullerenes is approximately conserved. This result allows the development of a structure-based index of strain in the fullerenes, and it is estimated that about 80 percent of the heat of formation of the carbon atoms in C_{60} may be attributed to a combination of σ strain and steric inhibition of resonance. Application of this analysis to the geometries of structurally characterized organometallic derivatives of C_{60} and C_{70} shows that the reactivity exhibited by the fullerenes may be attributed to the relief of a combination of local and global strain energy. C_{60} is of ambiguous aromatic character with anomalous magnetic properties but with the reactivity of a continuous aromatic molecule, moderated only by the tremendous strain inherent in the spheroidal structure.

The chemistry of the fullerenes is beginning to emerge. In the original work, it was suggested that C_{60} was an aromatic molecule (*1*). Of the many connotations of this term, perhaps the most important relates to chemical reactivity. There seems to be no doubt that the molecule is highly electronegative, but recently, the chemistry of C_{60} has been characterized as that of an electron-deficient polyalkene without significant delocalization and in terms of substructures such as [5]radialene and pyracylene (*2, 3*) (Fig. 1). Such characterizations are based on planar analogs and therefore do not capture the chemical and physical nature of the fullerenes. Furthermore, the fullerenes are without boundary conditions; just as in an ideal graphite sheet, there are no peripheral atoms to serve as sites of preferred reactivity. The fact that the fullerenes are composed solely of triconjugate carbon atoms that form a continuous aromatic sheet is reflected in the very low reactivity indices of C_{60} (*4, 5*). Without curvature, the fullerenes would be no more reactive than an ideal graphite sheet. The chemistry of the fullerenes is best described as that of a class of strained and continuous aromatic molecules.

The geometric and electronic structures of the carbon atoms and bonds in the fullerenes primarily differ in two respects from those in graphite. First, the carbon atoms are nonplanar (pyramidalized), and second, 12 five-membered rings (5-MRs) must be accommodated to allow closure of the fullerene. The second of these differences relates to the topological properties of the π system and is conveniently treated with Hückel molecular orbital (HMO) theory. The pyramidization of the carbon atoms is the factor that changes the character of the π orbitals and can be viewed as a source of strain in the fullerene geometry. Although a rigorous separation of these two effects is not possible, it is useful in a heuristic sense. For example, models of the electronic structure that rely on polyalkenes or pyracylene substructures clearly focus on the topology of the fullerene, whereas an analysis of the strain must be primarily concerned with the pyramidalization of the carbon atoms.

POAV Analysis

The π-orbital axis vector (POAV) analysis was developed in an effort to treat nonplanar conjugated organic molecules in the usual σ–π separability approximation (*6*). The POAV analysis extends σ–π separability into three dimensions with the use of the orbital orthogonality relations that are the basis of standard hybridization theory. In POAV2 theory, a π orbital is defined as the hybrid orbital that is locally orthogonal to the σ orbitals, whereas in the POAV1 analysis, the π orbital is the hybrid orbital that makes equal angles with the σ orbitals at a conjugated carbon atom (Fig. 2).

The present approach relies on the structures of known fullerene compounds, which are examined with POAV analysis (*6*). Although the first structurally characterized C_{60} derivative involved the formation of bonds from the oxygen atoms of an osmylate ester to the carbon atoms of C_{60} (*7*), most of the best characterized structures that are available in the literature are organometallic compounds with direct metal-to-carbon bonds (*8, 9*). A one-center POAV analysis (*10*) of organometallic derivatives of the fullerenes is collected in Table 1.

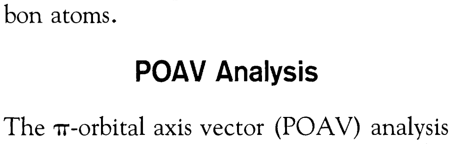

Fig. 1. The Flat-Earth Society: [5]radialene, pyracylene, and the polyalkenes. Models for C_{60} chemistry?

The carbon atoms of the fullerenes are either free (f), tetrahedral (t), or complexed (η) and are first characterized by their pyramidalization angle ($\theta_{\sigma\pi} - 90$), where $\theta_{\sigma\pi}$ is the common angle made by the π-orbital axis vector and the three σ bonds (Fig. 2). Also included in Table 1 are the fractional hybridizations ($m/m + 1$) of the atomic π orbitals ($s^m p$) obtained from the orthogonality relations of the POAV2 analysis. All of the quantities in Table 1 are calculated analytically from the experimental atomic coordinates of the molecules supplied by the authors of the original fullerene structure determination (*7–9*). Structural characterization of fullerenes is a difficult undertaking, and a number of the symmetry-related parameters exhibit large standard deviations. In the cases where the standard deviations do not warrant their separation, nonsymmetry-related parameters are included in the same set of average values.

Theory of Fullerene Strain and the Conservation of Hybridization

An index of strain based on the POAV analysis has been reported; Schmaltz *et al.*

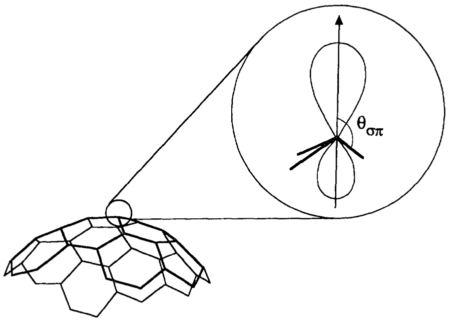

Fig. 2. In the POAV1 approximation, the π-orbital axis vector is defined as the vector that makes equal angles to the three σ bonds at a conjugated carbon atom (*4*). The common angle to the three σ bonds (which are assumed to lie along the internuclear axes) is denoted $\theta_{\sigma\pi}$.

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(*11*) obtained the following approximate relation for fullerenes, C_n (in our notation)

$$\sum^{n}(\theta_{\sigma\pi} - \pi/2)^2 \sim 4\pi/(3\sqrt{3}) = 2.418 \quad (1)$$

where $(\theta_{\sigma\pi} - \pi/2)$ is expressed in radians. This relation works best in situations where the bond angles between the σ bonds are equal and suggests that in spheroidal clusters there will be conservation of curvature. These workers (*11*) went on to suggest that the strain attributable to nonplanarity can be assessed with the parameter $\sum^{n} (\theta_{\sigma\pi} - \pi/2)^2$, and they inferred a nonplanar strain energy for fullerenes of 461 kcal/mol, which is 77% of the heat of formation (ΔH_f) of C_{60} [$\Delta H_f \sim 600$ kcal/mol (*12*)]. The total strain energy for C_{60} was estimated to be ~100% of ΔH_f (*11*).

Bakowies and co-workers (*13*) have shown by computation that Eq. 1 holds reasonably well for the fullerenes that have been isolated and characterized. From an examination of a number of fullerenes (C_n), they established that the relation

$$\frac{1}{n}\Delta H_f = a\frac{1}{n}\sum^{n}(\theta_{\sigma\pi}-\pi/2)^2 + b \quad (2a)$$

or

$$\Delta H_f = a\sum^{n}(\theta_{\sigma\pi}-\pi/2)^2 + nb \quad (2b)$$

provides a reasonably accurate estimate of thermodynamic stability from structural data. For those fullerenes without fused 5-MRs, a regression analysis with Eq. 2a gave a standard error of 0.6 kcal/mol. Equation 2 suggests that ΔH_f of the common fullerenes may be partitioned between a term attributable to the strain of pyramidalization of the conjugated carbon atoms and a term related to the number of π bonds. Equation 2b suggests that 78% of the excess ΔH_f of the carbons in C_{60} above those in graphite originates in the strain of pyramidalization. Remarkably, if the reference point of Eq. 2 is changed from bulk graphite to that of a single two-dimensional sheet of graphite, then the pyramidalization term alone accounts for the excess energy of the carbon atoms in fullerenes (*13*).

I have therefore further examined the quantity defined in Eq. 1. In the POAV1 approximation, the π-orbital hybridization (s^mp) is related to the pyramidalization angle (*10*)

$$m = \frac{2\sin^2(\theta_{\sigma\pi} - \pi/2)}{1 - 3\sin^2(\theta_{\sigma\pi} - \pi/2)} \quad (3)$$

The fractional hybridization is then

$$m/(m + 1) = 2\tan^2(\theta_{\sigma\pi} - \pi/2) \sim 2(\theta_{\sigma\pi} - \pi/2)^2 \quad (4)$$

Hence, from Eq. 1

$$\sum^{n}m/(m + 1) \sim 8\pi/(3\sqrt{3}) = 4.837 \quad (5)$$

Thus, there is not only an approximate curvature conservation in the fullerenes but also an approximate hybridization conservation. The POAV1 and POAV2 approximations give similar results in most situations, but the POAV2 analysis seems to give a slightly better description of the orientation and hybridization of the π orbitals in nonplanar conjugated organic molecules in which the σ bond angles are unequal (as in the fullerenes) (*6*). The POAV2 value for $\sum^{n}m/(m + 1)$ in C_{60} is in excellent agreement with the result in Eq. 5 (Table 1); the POAV1 value for this parameter is 5.093. Examination of Eq. 5 suggests that there will be a constant amount of *s* character mixed into the π molecular orbitals formed from the carbon atomic orbitals of all fullerenes.

Pyramidalization and Rehybridization

The *s* character in the π molecular orbitals exerts an important effect on a number of fullerene properties and contributes to the high electron affinity of these molecules (*4*, *14*). The conservation of hybridization in the fullerenes provides a partial explanation of the finding by Wudl *et al.* (*15*, *16*) that C_{60} and C_{70} show the same electrochemistry. The localization of the spin density in benzyl C_{60} radicals (*17*) may originate from pyramidalization and strain relief of the carbon atoms near the site of addition.

Quite apart from influencing the properties of the fullerenes (*18*), pyramidalization and rehybridization are known to play an important role in the chemistry of many nonplanar conjugated organic molecules (*6*, *19–26*). Pyramidalized alkenes show an enhanced electron affinity (*23*) and lead to the formation of epoxides on exposure to molecular oxygen (*24*). The rehybridization of the benzene carbon atoms in [2.2]paracyclophane shifts the π-electron density to the outside faces of the molecule (*27*), and the molecule readily undergoes cyclopropanation reactions (*27*, *28*). Related reactions are known for the fullerenes (*16*, *29*). In spite of the strain-induced reactivity of the cyclophanes (*25–28*), the degree of pyramidalization is modest (*30*) compared with the fullerenes (Table 1), and even superphane (*25*) (Fig. 3) only shows a pyramidalization angle of $(\theta_{\sigma\pi} - 90) = 7°$ (*31*).

Fig. 3. Superphane, average pyramidalization angle $(\theta_{\sigma\pi} - 90) = 6.7°$ (*31*).

The conservation of hybridization in fullerenes allows a simple approach to the part played by tetrahedral [$sp^3 \equiv s^{1/3}p$; ideal fractional *s* character, $m/(m + 1) = 0.25$ (s^mp)] carbon atoms in the relief of the strain in fullerenes. The saturation of a fullerene carbon atom contributes 0.25 to the total *s* character required for closure, and therefore, the presence of 20 tetrahedral carbon atoms almost satisfies Eq. 5 [$\sum^{20}m/(m + 1) = 5.0$]. It is well known that the carbon-carbon σ bonds in dodecahedrane ($C_{20}H_{20}$) are virtually strain-free (*32*).

Strain in Fullerenes

The strain in the fullerenes can be assessed with either $\sum^{n} (\theta_{\sigma\pi} - \pi/2)^2$ or $\sum^{n}m/(m + 1)$, and from the numbers quoted, the strain in C_{60} accounts for between 78 and 100% of the excess energy of the carbon atoms relative to graphite. An intermediate value was chosen, and purely for convenience, the strain in the fullerenes was set to 200 × 2.418 kcal/mol (Eq. 1) and 100 × 4.837 kcal/mol (Eq. 5), which amount to 81% of the excess energy in C_{60}. Thus, multiplication of the quantity $(\theta_{\sigma\pi} - \pi/2)^2$ by 200 kcal/mol and the quantity $m/(m + 1)$ by 100 kcal/mol allows a direct order-of-magnitude estimate of the strain in the carbon atoms in the derivatives tabulated. This approximation sets the strain energy in the fullerenes to 484 kcal/mol; these compounds are the most strained organic molecules ever isolated (*33*). The strain per carbon atom in C_{60} is 8 kcal/mol.

Although the present development makes use of the geometry of the σ bonds, strain in the fullerenes is not confined to the carbon atoms. Curvature-corrected HMO theory also accounts quite well for the ΔH_f of the fullerenes (*13*). However, the adjustment of the resonance integrals depends on the pyramidalization angles, and it therefore seems best to use the atomic terms directly. In this view, the modifications to the conjugation in the fullerenes are considered as steric inhibition of resonance.

Bakowies and co-workers (*13*) have applied a simplified version of the three-dimensional HMO theory (*34*) to the fullerenes, and this curvature-corrected HMO theory makes use of a cluster-reduced resonance integral based on the graphite resonance integral (β_G). Let β be the resonance integral between a bonded pair of cluster carbon atoms. Then, taking graphite as reference, the reduction in resonance integral may be written

$$\Delta\beta = \beta_G - \beta \quad (6)$$

With the use of the high degree of π-orbital alignment (*35*) in the fullerenes and assuming a common pyramidalization angle and graphite bond length, Eq. 6 may be written (*11, 13*)

$$\Delta\beta \sim \sin^2(\theta_{\sigma\pi} - \pi/2)\beta_G \sim (\theta_{\sigma\pi} - \pi/2)^2\beta_G \qquad (7)$$

Thus, the scaling of the resonance integral attributable to curvature is identical to that obtained for the σ strain (Eqs. 1 and 4), and therefore, the effect of strain on the one-center (atomic, σ bond) and two-center (resonance integral, π bond) terms should be strongly correlated. To a first approximation, therefore, these two seemingly distinct approaches depend on the same basic quantities: pyramidalization and rehybridization. It is therefore to be expected that they will both perform fairly well (either singly or together) describing the fullerenes (*13, 36*).

As noted earlier, this means that a treatment of strain based on pyramidalization and rehybridization includes steric inhibition of resonance by means of the scaling of the resonance integrals in addition to σ strain. Thus, the entire problem is characterized in terms of quantities that are obtained analytically from fullerene structures (Table 1). What is omitted from this analysis is an energy calculation: for example, utilization of the π-electron resonance integrals (β) in an HMO calculation (*4, 13*). In other words, apart from an overall scaling, the resonance contribution to the carbon clusters is taken to be equal to that of graphite. Detailed calculations on fullerene isomers (*13, 37–40*) show that except in the most pathological cases, the differences in total energy rarely amount to 1 kcal/mol per carbon atom, and conjugation effects are therefore at least an order of magnitude less important in a chemical sense than the cluster strain, which in the case of C_{60} is estimated as 8 kcal/mol per carbon atom. However, it should be noted that by neglecting resonance differences entirely, it will be impossible to capture fine distinctions in fullerene reactivity and stability where steric factors are similar. For example, placement of double bonds in 5-MRs is known to be unfavorable (*41, 42*). The isolated pentagon rule also identifies fused 5-MRs as energetically unfavorable (*11, 43*), although the pyramidalization angles suggest that this is partially a result of strain (*18, 39*). Furthermore, for bonds involving carbon atoms with a given degree of pyramidalization, the shorter bonds (of higher bond order) will be more strained.

Local and Global Strain in Fullerenes

It is first necessary to assess the strain associated with formation of (η^2-ethylene)metal complexes. Many of these compounds have been characterized, and their structures have been reviewed by Ittel and Ibers (*44*). Of the structures they tabulated, four compounds with sufficient bond-angle information and with relevance to the molecules of interest were examined. Let θ_{12}, θ_{23}, and θ_{31} (= θ_{23}) be the angles made by the σ bonds to a conjugated carbon atom (*10, 31*). The pyramidalization angle is given by

$$\cos(\theta_{\sigma\pi} - \pi/2) = 2\sin^2(\theta_{23}/2) \times [4\sin^2(\theta_{23}/2) - \sin^2(\theta_{12}/2)]^{-1/2} \qquad (8)$$

The pyramidalization angles of the ethylene carbon atoms were calculated: for $Pt[(NC)_2C{=}C(CN)_2](PPh_3)_2$, ($\theta_{\sigma\pi} - 90$) = 10.9° and 11.4°; for $Pt[Cl_2C{=}CCl_2](PPh_3)_2$, 14.5° and 14.5°; for $Ir[(NC)_2C{=}C(CN)_2](PPh_3)(CO)(Br)$, 12.1° and 13.1°; and for $Ir[(NC)_2C{=}C(CN)_2](PPh_3)(CO)(C_6HN_4)$, 10.9° and 12.7°. As a check, the experimental unit-cell coordinates of $Pt[Cl_2C{=}CCl_2](PPh_3)_2$ (*45*) were transformed, and the results of a direct POAV analysis of the atomic coordinates are given in Table 1. Zeise's salt, $K[(H_2C{=}CH_2)PtCl_3]$, was previously analyzed, yielding ($\theta_{\sigma\pi} - 90$) = 6° (*46*). On the basis of these values, it appears that the potential surface for pyramidalization of the carbon atoms in (η^2-ethylene)metal complexes, particularly with electron-deficient alkenes, is quite flat in the region of values found for fullerene complexes (Table 1) (*47*), and we therefore assume that the complexed carbon atoms are strain-free.

The η^2-complexation reaction of the fullerenes can now be compared with that of planar, unstrained alkenes, such as those discussed above. In planar alkenes, the geometry at the actual site of complexation requires that these carbon atoms initially have fractional *s* character, $m/(m + 1) = 0$. In the case of the fullerenes, the free ligand has already achieved the geometry required for complexation of the η carbon atoms, and the energy that is normally required to force pyramidalization will enhance the reactivity

Table 1. Fullerene geometrical parameters.

Compound	Atoms		($\theta_{\sigma\pi}$ − 90)		$\frac{1}{n}\sum^{n}(\theta_{\sigma\pi} - \pi/2)^2$	$\frac{1}{n}\sum^{n} m/(m+1)$		$\sum^{n} m/(m+1)$
	Position and type*	No. (*n*)	Avg. (deg)	SD (deg)	(rad²)	Avg.	SD	
C_{60}†	f	60	11.64	—	0.0413	0.0807	—	4.839
PtC_{60}‡	1, η	2	15.4	1.3	0.073	0.142	0.032	0.284
	2, f	58	11.5	1.1	0.041	0.078	0.015	4.513
Pt_6C_{60}(a)§	1, η	12	15.1	0.9	0.070	0.135	0.015	1.622
	2, f	24	10.2	0.7	0.032	0.063	0.008	1.490
	3, f	24	11.3	1.1	0.039	0.076	0.016	1.830
	f	48			0.036	0.069		3.321
Pt_6C_{60}(b)‖	1, η	12	14.9	1.4	0.068	0.132	0.021	1.588
	2, f	24	10.3	0.6	0.033	0.064	0.007	1.526
	3, f	24	11.3	1.1	0.039	0.076	0.015	1.828
	f	48			0.036	0.070		3.354
Pd_6C_{60}¶	1, η	12	14.69	0.08	0.066	0.127	0.002	1.523
	2, f	24	10.23	0.19	0.032	0.062	0.002	1.500
	3, f	24	11.51	0.17	0.040	0.079	0.002	1.886
	f	48			0.036	0.071		3.386
C_{70}#	1, f	10	11.96	—	0.0435	0.0854	—	0.854
	2, f	10	11.96	—	0.0436	0.0841	—	0.841
	3, f	20	11.46	—	0.0400	0.0784	—	1.567
	4, f	20	10.06	—	0.0308	0.0594	—	1.187
	5, f	10	8.78	—	0.0235	0.0476	—	0.476
	f	70			0.0360	0.0704		4.925
IrC_{70}**	1, η	1	14.4	—	0.064	0.109	—	0.109
	2, η	1	17.0	—	0.088	0.168	—	0.168
	3, f	68	10.7	2.6	0.037	0.070	0.034	4.770
PtC_2Cl_4††	1, η	2	14.45	0.06	0.127	0.128	0.007	0.257
OsO_2C_{60}‡‡	1, t	2	18.4	0.8	0.104	0.203	0.011	0.407
	2, f	4	9.0	1.4	0.025	0.045	0.013	0.181
	3, f	54	11.6	0.9	0.041	0.080	0.014	4.302
	f	58			0.040	0.077		4.483

*Atoms are numbered away from the point of addition. C_{70} is numbered from the apical to the equatorial carbons. The analysis was effected with Release 3.0 of the POAV3 program. Copies of a PC beta-test version are available from the author. Carbon atom types: η (complexed), t (tetrahedral), and f (free). For pure trigonal hybridization (sp^2 σ bonds), ($\theta_{\sigma\pi} - 90$) = 0.0°, $(\theta_{\sigma\pi} - \pi/2)^2 = 0.0$, and $m/(m + 1) = 0.0$. For pure tetrahedral hybridization (sp^3 σ bonds), ($\theta_{\sigma\pi} - 90$) = 19.47°, $(\theta_{\sigma\pi} - \pi/2)^2 = 0.1155$, and $m/(m + 1) = 0.25$. †Determined by symmetry (*4, 31*). ‡$(Ph_3P)_2PtC_{60}$ (*8*). §$[(Et_3P)_2Pt]_6C_{60}$, molecule A (*8*). ‖$[(Et_3P)_2Pt]_6C_{60}$, molecule B (*8*). ¶$[(Et_3P)_2Pd]_6C_{60}$ (*8*). #(*37*). **2.5 $(C_6H_6)[(Ph_3P)_2(CO)(Cl)IrC_{70}]$ (*9*). ††$(Ph_3P)_2Pt(Cl_2C{=}CCl_2)$ (*45*). ‡‡(*tert*-C_4H_9-4-$C_5H_4N)O_2OsO_2C_{60}$ (*7*).

of the fullerenes in comparison with normal alkenes. For the η^2 complexes in Table 1, $m/(m + 1)$ therefore gives the change in fractional hybridization required for complexation of an initially planar alkene. This amounts to 0.13 to 0.14 and is constant irrespective of whether there is one or six metals attached to the cage. If the paramaterization given is adopted, the energetic advantage of the fullerene complexation reaction for the pyramidalization of the two carbon atoms is $2 \times 100 \times 0.13 = 26$ kcal/mol. Hence, relative to normal alkenes, the strain in the carbon atoms at the site of complexation predisposes the fullerenes to η^2 complexation by 26 to 28 kcal/mol. Furthermore, the present analysis explains the selectivity observed in the η^2 complexation of C_{70} (9); the results for free C_{70} (Table 1) show that the site of reaction involves the carbon atoms with the most strain.

However, as discussed above, the hybridization and strain in the fullerenes are approximately conserved. Hence, the increased pyramidalization at the η^2 carbon atoms should lead to a decrease in pyramidalization and strain throughout the remaining atoms of the cage. The difficulty with this analysis is that relief of strain is now spread over many carbon atoms. Consider the 58 free carbon atoms in PtC_{60} relative to those in C_{60}. On the basis of the $m/(m + 1)$ values, the decrease in strain is given by $58 \times 100 \times (0.081 - 0.078) = 17$ kcal/mol. A similar analysis on the other complexes yields a strain relief value for Pt_6C_{60}(a) of 58 kcal/mol; for Pt_6C_{60}(b), 53 kcal/mol; for Pd_6C_{60}, 48 kcal/mol; and for IrC_{70}, ~0. Thus, in the case of the C_{60} organometallic derivatives, the relief of strain in the cluster contributes between 8 and 17 kcal/mol per metal complexed.

When these two factors, the local relief of strain in the η carbons and the global relief of strain in the remainder of the molecule, are taken together, it is apparent that relative to normal unstrained alkenes, the strain in the fullerenes produces a tremendous driving force for these complexation reactions. Although no attempt has been made to treat the loss of resonance energy caused by complexation, the fact that benzene derivatives undergo such reactions (48) suggests that this is not a major factor in the determination of the feasibility of these reactions.

The osmylation reaction (7) is not quite so clear-cut because the carbon atoms at the site of reaction become tetrahedrally hybridized during the reaction and are therefore removed from conjugation. However, organic functionalization reactions that lead to saturated carbon atoms will be strongly assisted by the local strain of pyramidalization present in the fullerenes. The global strain relief in the remaining 58 carbon atoms of the osmate molecule is pronounced, with a value of 23 kcal/mol in OsO_2C_{60}, and clearly, this favors the osmylation of C_{60} over unstrained alkenes.

Hawkins and co-workers (*49*, *50*) have recently shown that the regiochemistry of the osmylation of C_{70} and C_{76} are dictated by the pyramidalization angle. In particular, they demonstrated that under conditions of kinetic control, only those double bonds involving pairs of carbon atoms with $(\theta_{\sigma\pi} - 90) > 11.5°$ are attacked by OsO_4. In the parameterization of Eq. 1 given above, this amounts to a local strain energy of 16 kcal/mol for the two fullerene carbon atoms. This finding provides support for the approach adopted here because the regiochemistry of C_{70} is driven by degree of pyramidalization rather than bond length or bond order (*49*).

The global relief of strain is primarily responsible for the chemical selectivity exhibited by fullerene reactions. For example, the addition of a single Pt to C_{60} releases 17 kcal/mol of global strain energy, but the addition of six Pt atoms releases less than 10 kcal/mol per Pt. Reactions that exploit this factor will avoid the generation of multiple reaction products; the successful synthesis of $C_{60}H_2$ (*51*) may represent such a case. The strain relief in this compound should follow that discussed above for the osmate ester. However, an analysis based purely on strain seems unlikely to account for the formation of a single isomer of the dihydride or the lowest energy fullerene isomers, where both strain and conjugation are known to be important (*13*, *38*, *42*).

The same principle of strain relief explains why the fullerenes resist other chemical reactions that are normally feasible with planar aromatic molecules. For example, η^5 complexes of the 5-MRs and η^6 complexes of the 6-MRs have yet to be reported. Fagan *et al.* (*8*) have suggested that these compounds are not formed because of the poor overlap between the C_{60} π orbitals and a metal complexed to these rings. Theoretical work on C_{60} supports this argument, and the penta- and hexa-hapto modes of complexation would increase both the local and global strain. We have previously solved for the orientations of the π orbitals in C_{60} with the POAV analysis (*31*). In POAV2 theory, the π-orbital axis vector makes angles of 99.5°, 99.5°, and 105.5° to the bonds that separate 5- and 6-MRs, 5- and 6-MRs, and 6- and 6-MRs, respectively ($3 \times 101.6°$ in the case of the POAV1 analysis). Thus, according to POAV2 theory, the π orbital makes an angle of 106.3° with a vector from the carbon atom through the center of the 5-MR, such that the π orbital is tilted away from the center of the ring. The π orbital is not aligned with an axis of the 6-MR but makes an angle of 9.8° with a ring perpendicular and is also directed away from the center of the ring. The π orbitals are poorly oriented for η^5 and η^6 complexation reactions, and in contrast with the η^2 complexation reactions, improvement of the overlap would increase the strain in the fullerenes. The spacial extent of the actinide 5*f* orbitals might alleviate this problem.

Basis for Aromatic Character of the Fullerenes

Aromaticity and strain are wholely synthetic qualities that are useful because they implicitly provide a conceptual benchmark against which the properties of a new molecule can be measured (*19*, *52–55*). The key to the success of these constructs is the choice of the benchmark or reference molecule. These qualities can scarcely be avoided in connection with the fullerenes, and it is the combination of strain and aromatic character that together make the rationalization of fullerene properties such an intriguing topic.

In the discussion of strain, graphite provided the benchmark. A discussion of fullerene aromatic character is more problematic because of the difficulty in choosing a benchmark. To a limited extent, graphite can also serve as a benchmark for the aromatic character of the fullerenes. The chemistry of graphite is limited by the high stability of this allotrope of carbon, but in terms of what is known, it is not difficult to imagine that fullerene chemistry arises from a strained form of graphite (*56*). On a weight basis, the ring-current diamagnetism of the fullerenes is dwarfed by that of graphite (*57*, *58*). Furthermore, unlike strain, considerations of aromatic character must make contact with the electronic structure of the molecule, and the continuum nature of graphite raises questions regarding the applicability of such a model. However, this point only serves to emphasize that the fullerenes cannot show aromatic chemistry in the conventional molecular sense because there is no periphery and no peripheral hydrogen atoms: The molecules are without boundaries. Thus, they cannot undergo the classical aromatic substitution reaction with "retention of type," and the only derivatives that retain the fundamental fullerene electronic structure are the fulleroids (*16*). In the functionalization chemistry of planar aromatic molecules, derivatization at an internal triconjugate carbon atom is quite rare. For example, Huber and co-workers (*59*) find that of the three common isomers of pyrene, the dianion of only one undergoes internal methylation at triconjugate carbon atoms. The same chemistry leads to hydrogenation and methylation of C_{60} and C_{70} (*60*, *61*).

It is for these reasons that aromaticity of the fullerenes has been controversial, not because of the fullerenes, but because there is no suitable model to serve as a reference compound. I therefore propose a hypothetical reference compound for fullerene aromatic character: a rolled-up molecular ball of graphite. It is only after strain has been allowed for does it make sense to consider aromatic character in fullerenes. Once the 484 kcal/mol of fullerene strain (Eqs. 1 and 5) and the continuity of the electronic structure are factored into the equation, the aromatic nature of C_{60} chemistry becomes apparent. That C_{60} exists at all with 8 kcal/mol of strain energy at every carbon atom is a testament to the aromaticity of the molecule. Furthermore, the molecule does tend to retain its type—C_{60} itself. A number of derivatives revert to C_{60} on heating. It is important to note that the reference compound that is proposed for fullerene aromatic character corresponds to the ideal (infinite) fullerene, rather than the usual nonaromatic model compound. In this formulation, the rolled-up molecular ball of graphite is the three-dimensional (3D) analog of benzene, which is taken as the ideal 2D model aromatic compound. Although the interplay of shape, strain, and aromatic character makes it a difficult undertaking, an assessment of the degree of aromatic character in C_{60} and the higher fullerenes is attempted below.

Degree of Aromatic Character in the Fullerenes

Early theoretical estimates of the resonance energy of C_{60} produced inconsistent results (*4, 62, 63*), although the situation improved once the molecule was isolated. The empirical resonance energy has been largely superseded by the Dewar resonance energy (*64*), which corrects for variations in bond length and hybridization (*65, 66*) by using linear polyenes as nonaromatic reference molecules. As noted above, C_{60} hybridization and strain are highly dependent on functionalization, so it is difficult to draw judgments of the resonance energy on the basis of the heat of hydrogenation. In the case of benzene, the heat of hydrogenation has been measured to be 49.8 kcal/mol (exothermic), whereas that of cyclohexene is 28.6 kcal/mol; this gives an empirical resonance energy for benzene of $3(28.6) - 49.8 = 36$ kcal/mol (*65, 66*) [modern theoretical treatments yield a lower resonance energy (*67*)]. The value for the heat of hydrogenation of cyclohexene is fairly typical of simple olefins, but strained olefins exhibit larger values [olefin strain energy (*19, 21, 68*)]. The heat of hydrogenation of a fullerene has yet to be measured. Although calculations of this quantity are difficult, Matsuzawa and co-workers (*42*) have obtained values of 9 and 22 kcal/mol by semiempirical calculation. Quite apart from the effect of strain relief, the interpretation of the hydrogenation energy of C_{60} is not straightforward because the saturation of two carbon atoms effectively removes five or six bonds from conjugation.

With regard to the suitability of the continuum electronic structure of graphite as a model aromatic reference for the fullerenes, it is important to note that the resonance energy of benzene is 3 to 5 kcal/mol per carbon with use of either finite (polyene) or infinite (polyacetylene) nonaromatic reference compounds (*67*). On the basis of previous arguments, the stable fullerenes seem to lie within 2 kcal/mol per carbon of the hypothetical rolled-up molecular ball of graphite. Thus, if the resonance energy per carbon of graphite is taken to be comparable with that of benzene, then it is apparent that the stable fullerenes possess a resonance energy.

It has only been possible to unify the ring current, resonance energy, and reactivity criteria of aromatic character in the case of the annulenes (*69*). Nonalternants such as the fullerenes occasionally show anomalous magnetic properties, and C_{60} is an extreme case in this respect (*70, 71*), but the demonstration of ring currents in the molecule throws new light on this subject (*72, 73*). In both C_{60} and C_{70}, the 6-MRs are diamagnetic and the 5-MRs are paramagnetic. In C_{60}, the two contributions cancel almost exactly, and there is virtually no ring-current contribution to the magnetic susceptibility. Taken at face value, this might suggest that the 5-MRs should be regarded as antiaromatic, whereas the 6-MRs are aromatic. However, there is currently no discernible relation between the π-electron magnetic susceptibility and other aspects of the electronic structure of the fullerenes (*70, 71*). The bond lengths within the 5-MRs of the fullerenes are similar, and this may enhance the paramagnetic ring currents, particularly in the case of C_{60} [paramagnetic ring currents are strongly quenched by bond alternation (*74*)].

Although the bond lengths in the 5-MRs are all equal in C_{60}, there are two unique bond lengths in the molecule: those between a pair of 6-MRs (1.40 Å) and those between a 5-MR and a 6-MR (1.46 Å) (*75*). These values are reasonably close to the graphite C–C bond length of 1.42 Å (*56*). The degree of bond equalization has formed the basis for a number of approaches to a scale of aromatic character. In the Dewar scheme of resonance energies, linear polyenes form the basis for the nonaromatic model compounds (*64*), and they show a much greater degree of bond alternation (*64–66*) than that found in C_{60}; however, this may not be true of the higher fullerenes (*13, 37, 38, 40, 76*). The variations in bond lengths in C_{60} are reminiscent of those found in aromatic polycyclic hydrocarbons (*40, 64–66, 77, 78*).

The chemistry of the higher fullerenes (*49, 50, 79*) is of considerable interest. If an average fullerene structure is considered, the local strain per carbon atom is reduced with increasing fullerene size (*13, 35*), but at least in the case of the icosahedral fullerenes, the 5-MRs act to concentrate the strain at their vertices (*13, 18, 80*). As the proportion of 6-MRs is increased, the aromatic character is enhanced as the predominant electronic structure tends toward the rolled-up molecular ball of graphite. At the same time, the energy gap contracts toward that of a graphite sheet, and the competition between these effects may be quite subtle insofar as the chemical stability is concerned (*78, 81*).

On the basis of this brief survey of fragmentary data, it seems that real fullerenes fall short of the ideal aromatic fullerene, a rolled-up molecular ball of graphite, but actually do not fare too badly in comparison with graphite once the strain energy of the spheroidal geometry is taken into account.

The reduced forms of the fullerenes provide another challenge to our concept of aromatic character. $C_{60}{}^{6-}$ actually conforms to most of the usual criteria of aromatic character. By calculation, in comparison with the neutral molecule, $C_{60}{}^{6-}$ shows a large π-electron ring-current magnetic susceptibility (*70*), and the bond lengths become more equalized: 1.42 to 1.45 Å (K_6C_{60}) (*82*). The same calculations show a quenching of the ring current in $C_{60}{}^{12-}$ but a further bond-length equalization: 1.445 and 1.435 Å ($Li_{12}C_{60}$) (*83*). The reduced states of C_{60} appear to be even more thermally stable than the neutral molecule itself (*84*).

Conclusion

The chemistry exhibited by the fullerenes is a direct consequence of the drive to reduce strain in this class of continuous aromatic molecules, and the best analogies to fullerene chemistry are to be found in the modified reactivity of other strained aromatic organic molecules (*19*). In comparison with normal planar conjugated organic molecules, the fullerenes greatly favor reactions that decrease strain, whereas those reactions that increase strain are inhibited. Even the reduction of the fullerenes can be viewed as a strain-relief process (*14, 15*) for many carbanions are known to prefer pyramidal geometries.

The vanishingly small ring-current magnetic susceptibility suggested the absence of ring currents in C_{60} (*70, 71*). Recent work has shown the presence of strong diamagnetic (6-MR) and paramagnetic (5-MR) ring currents in the molecule (*73*), which cancel almost exactly in their contribution to the magnetic susceptibilty (*72*). The ring currents found in C_{60} militate against the polyalkene, [5]radialene, and pyracylene descriptions of the molecule. The C_{60} molecule is of ambiguous aromatic character with anomalous magnetic properties but with the reactivity of a continuous aromatic molecule, moderated only by the tremendous strain inherent in the spheroidal structure.

The use of planar conjugated molecules (Fig. 1) as primary reference points demonstrates a failure to capture the significance of the synthesis of the fullerenes (*1, 33*) for organic chemistry. If C_{60} is not to be considered aromatic, benzene will be condemned to a lonely existence (*85*).

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