

Bond energy, aromatic stabilization energy and strain in IPR fullerenes†

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Various models applied to DFT structures and energies of 2-D and 3-D aromatic molecules shed new light on the effects of strain and aromaticity in these systems. The cyclic π electron delocalisation does not stabilize the fullerene C₆₀ formation; and 5–6 and 6–6 CC bonds have near-identical bond stretch potentials.

The nature and magnitude of the 3-D aromatic stabilization effects of fullerenes has been a topic of considerable interest.^{1–6} Key theoretical developments include the $2(N + 1)^2$ rule (3-D analogue of the Hückel rule), and the insights that have followed from application of indices such as NICS^{7,8} and TRE.³ Despite this body of work, it would be fair to say that to date there is no widely-accepted value for the aromatic stabilization energy (ASE) of even the archetypal fullerene C₆₀. Moreover there is no reliable quantitative treatment of strain energy (SE) in fullerenes. At the root of these problems is the fact that both strain and aromatic effects in these systems are large and operate simultaneously, such that a formal separation of their contributions to the overall stability is very difficult.^{9,10}

In order to make some headway with this problem we optimized structures and energies of the 12 lowest energy isomers of the neutral, closed-shell IPR fullerenes C₆₀–C₉₆ (full details provided in the ESI†) at B3LYP/6-31G* level. Table 1 reports: the average POAV pyramidalization angles according to Haddon,^{11,12} the strain parameter, h , which measures the average height of each atom above the plane defined by the three atoms bonded to it; the mean cavity radius, R ; geometry-based aromaticity index, HOMA,¹³ the HOMO–LUMO gap, $\Delta\epsilon$; and the absolute endohedral chemical shift $\delta(^3\text{He})$ of a helium nucleus placed at the geometrical centre of each cage.

Evidently these various parameters describing changes in

Table 1 B3LYP/6-31G* data for 12 ground state IPR fullerenes

Fullerene C _N	POAV ^{11/12}	R ^a /Å	h ^b /rad ²	HOMA	$\Delta\epsilon$ /au	$\delta^3\text{He}^d$ ppm
C ₆₀ I _h	11.64	3.550	2.632	0.263	0.1015	69.2
C ₇₀ D _{5h}	10.82	3.837	2.720	0.341	0.0988	87.3
C ₇₂ D _{6d}	10.76	3.894	2.811	0.270	0.0916	78.6
C ₇₄ D _{3h}	10.51	3.943	2.774	0.363	0.0260	93.6
C ₇₆ D ₂	10.43	3.999	2.788	0.320	0.0729	79.3
C ₇₈ C _{2v}	10.25	4.051	2.823	0.339	0.0607	78.2
C ₈₀ D ₂	10.20	4.104	2.782	0.304	0.0495	70.6
C ₈₂ C ₂	10.03	4.152	2.835	0.321	0.0599	72.5
C ₈₄ D _{2d}	9.88	4.202	2.899	0.328	0.0754	71.2
C ₈₆ C ₂	9.79	4.251	2.881	0.320	0.0565	72.8
C ₉₀ C ₂	9.57	4.350	2.934	0.346	0.0611	74.0
C ₉₆ D ₂	9.29	4.492	2.941	0.371	0.0590	75.2

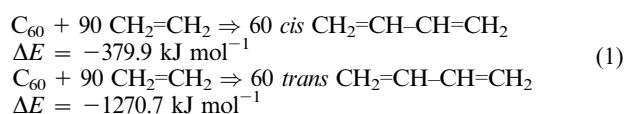
^a Average distance of an atom from the geometric cage centre.

^b Strain parameter calculated as sum of square deviations of angles from 120° ^c B3LYP/6-31G* Homo–lumo gap. ^d GIAO/B3LYP/6-31G* absolute chemical shift, ³He.

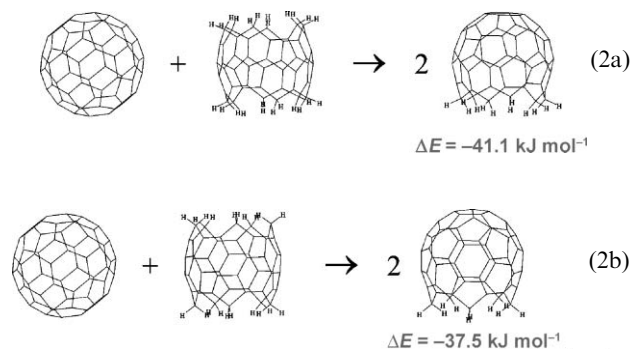
† Electronic supplementary information (ESI) available: Data for attempted fittings. See <http://www.rsc.org/suppdata/cc/b4/b408903k/>

π -electron delocalisation contain diverse information. Increasing the size of the system geometry-based index HOMA indicates an increase of aromaticity from 0.263 for C₆₀ up to 0.371 for C₉₆. The HOMO–LUMO gap decrease with an increase of the size up to 0.059 au, while the variance of the endohedral chemical shift $\delta(^3\text{He})$ shows even more complicated pattern. Factor analysis reveals that three orthogonal factors are necessary to describe the variance of these aromaticity descriptors. Hence, the case of fullerenes well-exemplifies the multidimensional character of aromaticity.¹⁴ Interestingly, contrary to the $2(N + 1)^2$ rule¹ none of the indices predicts the C₇₂ fullerene to be the most aromatic. However, the rule strictly applies to icosahedral fullerenes, whereas in the case of lower symmetries the local substructures can also significantly affect stability.¹

The estimation of the stabilisation energy due to cyclic π -electron delocalisation of fullerene C₆₀ has been proposed⁹ on the basis of the homodesmotic reaction formalism.



The deficiency of this approach is obvious: (i) the extracted values are strongly biased by strain which is impossible to separate out, and (ii) the choice of reference system impacts dramatically on the findings. Since *trans* butadiene is more stable than the *cis* isomer by 14.9 kJ mol⁻¹, the two ASE estimates differ by *ca.* 890 kJ mol⁻¹! We suggest using reference systems of the same topology and therefore similar strain, for deriving the extra stability of the fullerene upon sphere closure:



Both reference compounds are fragments of fullerene C₆₀ with one six- or one five-membered ring omitted, in eqns. (2a) and (2b). The last shell is terminated with six (or five) CH₂ groups imposing electron delocalisation on half of the sphere. On the left side of eqns. (2a) and (2b) the central part of fullerene with top and bottom six- (or five-) membered rings omitted is required to fulfil the standard homodesmotic reaction requirements, and CH₂ groups similarly terminate these systems. Both (2a) and (2b), utilizing subtly different reference compounds with presumably differing

electron delocalisation effects, accomplish sphere formation. They predict far lower destabilization of C_{60} , by *ca.* 0.6 kJ mol⁻¹ per π -electron, as compared with the reference systems. In the case of bigger fullerenes a similar estimation of ASE is much more difficult, because the number of possible topologically different reference systems significantly increases.

We apply a simple method of estimating the equilibrium distribution of bonding energy,^{15,16} namely parameterizing the vibrationless atomization energies $\sum D_e$ using the set of bond lengths. Modelling $\sum D_e$ as a sum of C–C bond energies, $\sum D_e = \sum E_{CC}(r)$, means that the bond energies derived implicitly contain the effects of π -electron delocalisation and strain in some average sense. The fitting is done by a minimization of a normalised statistic $\chi^2 = (\sum_{15} D_e^{calc} - \sum D_e)^2$ where the summation is over all the molecules.

A linear bond energy–bond length relationship gives a poor rms deviation of 58 kJ mol⁻¹ on predicted $\sum D_e$ values. A quadratic term improves things dramatically (rms 13.1 kJ mol⁻¹).

$$E_{CC}(r) = 23105.9 - 28074.4 r + 8556.7 r^2 \text{ kJ mol}^{-1} \quad (3)$$

This function is monotonically decreasing (*i.e.* no minimum present) over the 1.34 Å < r < 1.48 Å range of the data that it is fitted to. The worst predictions of $\sum D_e$ are found for C_{76} and C_{78} (errors of 22–24 kJ mol⁻¹). Further fits with a cubic term in r proved unsuccessful, since the resulting least-squares matrix is ill-conditioned.

IPR fullerenes possess two bond types: ‘5–6’ bonds shared between adjacent five- and six-membered rings, and ‘6–6’ bonds shared between adjacent six-membered rings. Arguably they might have different bond stretch potentials, so we consider different $E_{CC}(r)$ forms for each type of bond. A bi-linear model suggests these *are* distinct:

$$\begin{aligned} E_{CC,5-6}(r) &= 2780.9 - 1616.5r \text{ kJ mol}^{-1} \\ E_{CC,6-6}(r) &= 2277.0 - 1284.0r \text{ kJ mol}^{-1} \end{aligned} \quad (4)$$

However, given that the rms deviation on $\sum D_e$ of 26.9 kJ mol⁻¹ is much worse than the single quadratic function just discussed, this is a poor model. A bi-quadratic fit yields an rms deviation of 12.6 kJ mol⁻¹ a slight improvement over a single quadratic. However, the two fitted bond energy formula

$$\begin{aligned} E_{CC,5-6}(r) &= 25094.5 - 30670.4r + 9398.9 r^2 \text{ kJ mol}^{-1} \\ E_{CC,6-6}(r) &= 28176.6 - 34894.1r + 10847.1 r^2 \text{ kJ mol}^{-1} \end{aligned} \quad (5)$$

shows very little difference between the two functions (see Fig. 1 in the ESI†). Given also that the fit quality only slightly improves compared to a single quadratic function, despite doubling the number of parameters, we conclude that a single quadratic function for both bond types is most suitable.

The same approach is now applied to predict $\sum D_e$ values of B3LYP/6-31G* optimized planar reference compounds, which contain the same adjacent five- and six-membered ring motifs found in IPR fullerenes (details given in the ESI). The best four-parameter model includes a fitted constant C–H bond energy of 427.2 kJ mol⁻¹, and for the CC bonds

$$E_{CC}(r) = 5378.62 - 5048.01r + 1124.78r^2 \text{ kJ mol}^{-1} \quad (6)$$

with an rms of just 8.5 kJ mol⁻¹. Applying this model to CC bonds in fullerenes predicts fullerene $\sum D_e$ values ‘in error’ due to three factors: (i) differences in strain between 2-D and 3-D compounds (ii) 2-D *versus* 3-D delocalisation and (iii) additional 3-D π -electron delocalisation effect due to sphere formation.¹⁷

The predicted difference is in the range $-449 \text{ kJ mol}^{-1} < \Delta < -276 \text{ kJ mol}^{-1}$ (see Table 2), which quantifies the extent to which

Table 2 The $\sum D_e$ values for fullerenes and their planar analogues

Fullerene C_N	$\sum D_e(\text{exact})^a/$ kJ mol ⁻¹	$\sum D_e(\text{calculated})^b/$ kJ mol ⁻¹	Δ^c/kJ mol ⁻¹	$\Delta(\pi\text{-electron})^d/$ kJ mol ⁻¹
C_{60}	40422.9	40814.4	-391.5	-6.53
C_{70}	47429.5	47819.6	-390.1	-5.58
C_{72}	48663.7	49057.1	-393.4	-5.47
C_{74}	50141.7	50590.9	-449.1	-6.07
C_{76}	51554.5	51934.1	-379.6	-5.00
C_{78}	52973.4	53332.2	-358.8	-4.60
C_{80}	54315.6	54663.1	-347.5	-4.35
C_{82}	55768.0	56083.0	-315.0	-3.85
C_{84}	57217.1	57500.3	-283.2	-3.38
C_{86}	58571.1	58866.3	-295.2	-3.44
C_{90}	61396.0	61678.6	-282.6	-3.14
C_{96}	65607.4	65883.8	-276.4	-2.88

^a The atomisation energies of fullerenes defined as: $NE_C - E_{SCF}$, where $E_C(^2P) = -37.84628$ au and E_{SCF} is the energy of the fullerene C_N (both calculated at B3LYP/6-31G* level). ^b The predicted $\sum D_e$ of the model planar analogues of fullerenes (with use of eqn. (6)). ^c The difference defined as $\sum D_e(\text{exact}) - \sum D_e(\text{calculated})$

strain dominates the properties of the fullerenes. Deviation from planarity leads to a lowering of the extent of π -electron delocalisation,¹⁸ whilst sphere formation causes further lowering of the stability. If differences between 2-D and 3-D aromatic effects were very small (almost certainly they are not) then Δ would be a good estimate of the strain energy. We note fairly good correlations of Δ per one carbon atom (alternatively one π -electron) and the Haddon POAV, the h parameter of strain and the mean cavity radius R , with the correlation coefficients 0.942, 0.916 0.947, respectively. This indicates that the changes in $\sum D_e$ are strongly dominated by strain, whereas the 2-D and 3-D aromaticity effect varies across these compounds to a much smaller extent. The Δ may be treated as an *upper limit* for the strain energy in these molecules.

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