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Resonance Stabilization Study of Some Fullerenes $C_n(20 \leqslant n \leqslant 88)$: Is $n = 32$ a 'Magic' Number?†

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A π-orbital axis vector (POAV) analysis used in Hückel molecular orbital approximation calculations indicates that the cutoff in the fullerene mass spectrum at C_n ($n = 32$) must naturally occur with no need to define a 'magic' number.

Initial studies on carbon clusters and carbon cages were performed by laser vaporization of graphite in a high pressure supersonic jet which was skimmed into a molecular beam and probed by mass spectrometry.[1,2] One of the first mass spectra, reported by Rohlfing *et al.* in 1984, has been explained in many articles.[3–6] This spectrum is composed of two parts: the first part contains carbon cluster peaks C_n^+ ($n \leqslant 30$) and they are separated by one carbon atom mass or 12 mass units. The second part of the spectrum shows peaks separated by two carbon atom mass or 24 mass units and contains C_n^+ clusters for which $n \geqslant 32$. The first region of the spectrum consists of carbon chains, single and multiple planar rings and so there is no obstacle as to how many carbon atoms can exist in the cluster. However, the peak spacing in the second region follows the general formula (C_{20+2h}), which implies the existence of fullerene cages (h indicates the number of six-membered rings).

The cutoff is noticed as an abrupt change in fragment pattern at C_{32}^+ for laser photofragmentation of C_{60}^+ using 266 nm radiation with three different laser powers.[7] Also, the low-mass portion of the daughter ion fragments produced by intense laser excitation of C_{60}^+ by Curl *et al.*[8] clearly show this cutoff.

In none of the stability studies of various carbon chains and carbon cages has the reason for the cutoff in the mass spectrometric results been explained.[9–12]. In this report we have employed Hückel molecular orbital calculations using π-orbital axis vector (POAV) approximations[13–15] to explain the abrupt change in the spectrum. These calculations are performed for various possible cage structures in the range C_{20}–C_{88} (Fig. 1). Stabilities due to resonance of the conjugated π-structure as well as pyramidalization factors for each cage and per bond are calculated and the results are tabulated (Table 1).

Our calculations illustrate the fact that only carbon cages with masses greater than C_{30} can possess more relative resonance stability than localized π-conjugated planar systems. Clusters with $n \leqslant 30$ are less stable relative to the localized π-conjugated planar analogues, which explains the preference of planar multi-ring structures for these latter clusters. These results are consistent with the experimental observations.

Computational Scheme

Several fullerenes in the range C_{20}–C_{88}, each with a known symmetry were chosen. A geometry optimization to find the lowest energy configuration using the MM$^+$ method was performed. For each atom in a molecule, the pyramidalization angle $\theta_{\sigma\pi}$ (Fig. 2) relative to a planar geometry was calculated. Using the POAV1 method of references,[13–15] the m factor which is an indicator of the degree of s orbital participation in the atomic orbital that takes part in the π-system, was computed. The m factor was applied as an average value to the whole cage in each case. Next, using the Hückel approximation method and by obtaining the π-energy states of the system, the resonance stabilization energies in terms of β for each molecule were calculated.

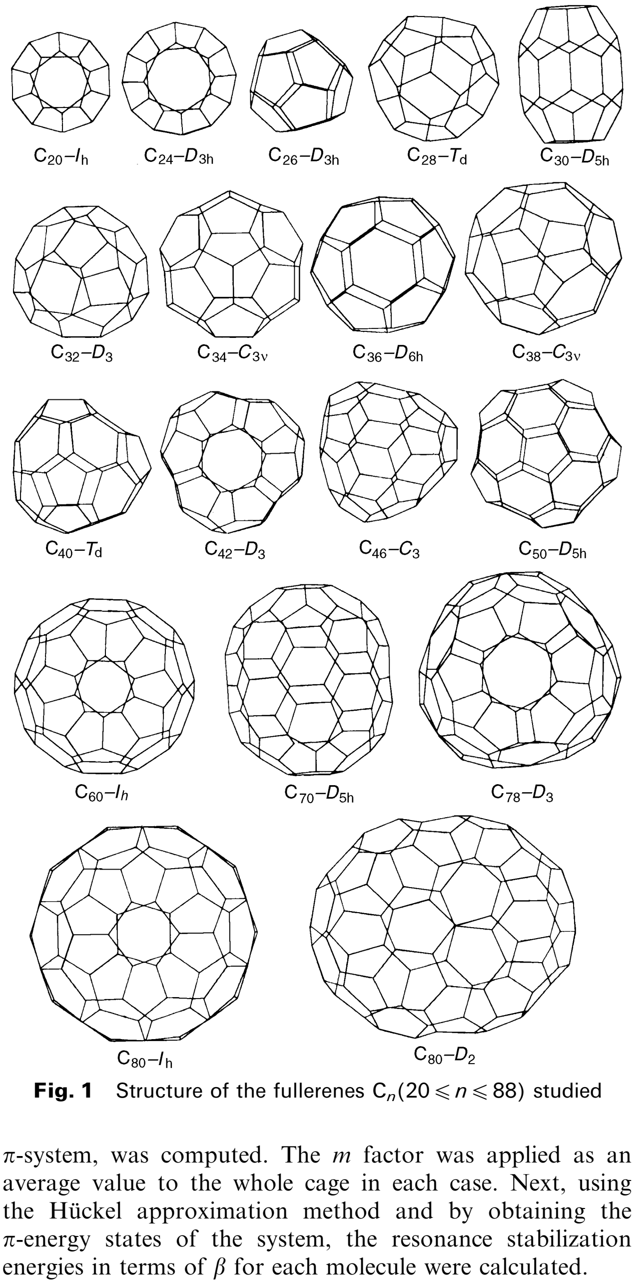

Fig. 1 Structure of the fullerenes $C_n(20 \leqslant n \leqslant 88)$ studied

Results and Discussions

In order to achieve a more stable structure, the following changes are predicted to take place in the annealing process of carbon clusters in a plasma:

(i) Coalition and thereby formation of carbon chains, carbon single and multiple rings, and carbon cages.
(ii) Side chain omission.
(iii) Stone–Wales rearrangement to a proper five-membered ring distribution.

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Table 1 Calculated resonance stabilization energies, pyramidalization angles, and *m* factors for some fullerenes

C_n—Sym.	$\langle\theta_{\sigma\sigma}\rangle$	$\langle\theta_{\sigma\pi}\rangle$	*m*	R.E. (β)[a]	B.R.E. (β)[b]
C_{20}—I_h	108.0000	110.9052	0.4244	−5.5017	−0.1834
C_{24}—D_{6d}	109.7740	109.1667	0.3277	−3.5642	−0.0990
C_{26}—D_{3h}	110.5939	108.3238	0.2882	−2.4696	−0.0633
C_{28}—T_d	111.3628	107.5061	0.2539	−1.1119	−0.0265
C_{30}—D_{5h}	111.2756	107.6003	0.2577	−1.4397	−0.0320
C_{32}—D_3	112.3193	106.4463	0.2148	1.3038	0.0272
C_{34}—C_{3v}	112.4793	106.2638	0.2086	1.6407	0.0322
C_{36}—D_{6h}	113.1431	105.4887	0.1840	3.4049	0.0631
C_{38}—C_{3v}	113.1936	105.4284	0.1822	3.7031	0.0650
C_{40}—T_d	113.5906	104.9481	0.1684	4.8497	0.0808
C_{42}—D_3	114.0668	104.3547	0.1525	6.7225	0.1067
C_{46}—C_3	114.4298	103.8883	0.1409	8.3935	0.1216
C_{50}—D_{5h}	115.0285	103.0892	0.1227	11.5507	0.1540
C_{60}—I_h	116.0000	101.6947	0.0955	17.3978	0.1933
C_{70}—D_{5h}	116.3407	101.1700	0.0866	22.1618	0.2111
C_{78}—D_3	116.6648	100.6498	0.0784	26.5030	0.2265
C_{80}—I_h	116.8655	100.3159	0.0735	27.6463	0.2304
C_{88}—D_2	116.6782	100.6278	0.0781	30.0800	0.2279

[a]Total resonance stabilization energy. [b]Bond resonance stabilization energy.

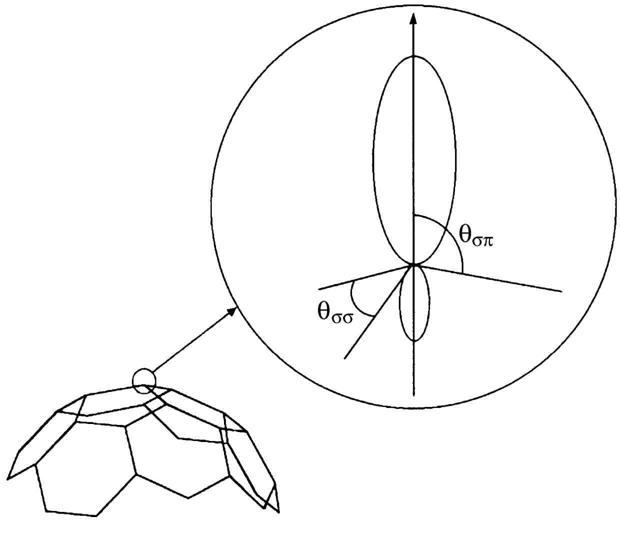

Fig. 2 π-Orbital axis vector diagram, illustration of pyramidalization angles $\theta_{\sigma\pi}$ and $\theta_{\sigma\sigma}$

(iv) C_n fragment omission from a structure in order to achieve a more stable geometry with no adjacent five-membered rings.

It is also found that the above changes as well as three important factors: inert gas atmospheric pressure, plasma temperature and plasma concentration are responsible for formation of a particular annealing product.

None of the preceding conditions can allow the structures, which are negative in terms of resonance stabilization energy β, and also have streak hindrance, coalesce to form cages.

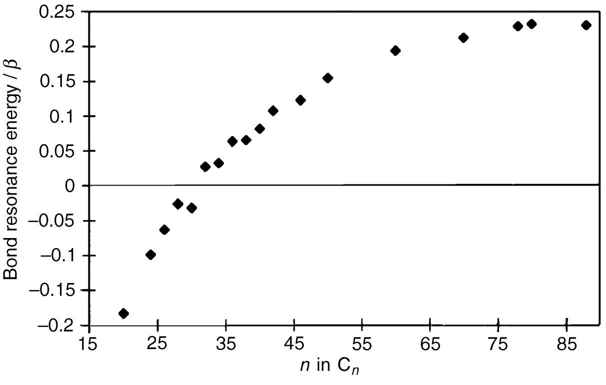

Fig. 3 Bond resonance stabilization energies (β) *vs.* *n* for the fullerenes studied $C_n(20 \leqslant n \leqslant 88)$

As the results of our calculation show (Table 1), the total bond resonance energy β, as well as β per bond, is calculated to be negative for $n \leqslant 30$ and positive for $n \geqslant 32$. Also calculated pyramidalization angles $\theta_{\sigma\pi}$ and m values indicate that as $\theta_{\sigma\pi}$ decreases towards less pyramidalization, the degree of s orbital participation in the π system also decreases, thereby causing the resonance energy to increase as expected. These results are depicted in Fig. 3 which more clearly illustrates the fact that the cut-off in the mass spectrum must occur naturally due to the resonance stabilization energy trend which is the most important factor in the annealing process. As a result, other factors such as conformational hindrance and the isolated pentagon rule (IPR) are less effective factors in determining the structure of annealing products while the major factor in carbon cage formation with $n \geqslant 32$ from the low-mass chains and rings with $n \leqslant 30$ is the resonance stabilization energy of bonds.

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References

1 T. G. Dietz, M. A. Duncan, D. E. Powers and R. E. Smalley, *J. Chem. Phys.*, 1981, **74**, 6511.
2 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
3 E. A. Rohlfing, D. M. Cox and A. Caldor, *J. Chem. Phys.*, 1984, **81**, 3322.
4 W. Weltner Jr. and R. Van Zee, *J. Chem. Rev.*, 1989, **89**, 1713.
5 H. W. Kroto, A. W. Allaf and S. P. Palm, *Chem. Rev.*, 1991, **91**, 1213.
6 R. F. Curl, *The Fullerenes*, ed. H. W. Kroto, J. E. Fisher and D. E. Cox, Pergamon Press, 1993, p. 11.
7 S. C. O'Brien, J. R. Heath, R. F. Curl and R. E. Smalley, *J. Chem. Phys.*, 1988, **88**, 220.
8 R. F. Curl and R. E. Smalley, *Science*, 1988, **242**, 1017.
9 P. Ballone and P. Milam, *Phys. Rev. B*, 1990, **42**, 3201.
10 B. L. Zhang, C. H. Xu, C. Z. Wang, C. T. Chang and K. M. Ho, *Phys. Rev. B*, 1992, **46**, 7333.
11 B. R. Eggen, R. L. Johnston and J. N. Murrell, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3029.
12 K. Balasubramanian, *J. Phys. Chem.*, 1995, **99**, 6509.
13 R. C. Haddon, *J. Am. Chem. Soc.*, 1987, **109**, 1676.
14 R. C. Haddon, *J. Am. Chem. Soc.*, 1990, **112**, 3385.
15 R. C. Haddon, *Acc. Chem. Res.*, 1992, **25**, 127.