Spherical Aromaticity of Buckminsterfullerene

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Synopsis. Aromatic stabilization of buckminsterfullerene is not large enough to guarantee isolation in macroscopic amounts. This does not rule out the possibility that such carbon clusters are formed in sooting flames and/or in dark interstellar space.

Carbon clusters are produced in a pulsed supersonic beam apparatus using laser vaporization of a graphite disk.[1] Kroto et al. presented evidence for the existence of a remarkably stable C_{60} cluster in the vaporization products.[2-4] The stability has been presumed to arise from the ability of a graphitic sheet to close into a spheroidal shell, thereby eliminating its reactive edges.[2-4] The structure proposed was a truncated icosahedron with 12 pentagons and 20 hexagons arranged on the surface of a sphere. The ultraviolet spectrum of C_{60}[5] and the photoelectron spectrum of its anion[6] are apparently consistent with this structure. Kroto et al. named the molecule having this structure (**1**) buckminsterfullerene.[2,7] If the C_{60} cluster is really buckminsterfullerene, it will be of great interest in connection with the problem of spherical aromaticity.

Various molecular orbital (MO) methods have been used to obtain the energy structure of buckminsterfullerene.[8-24] Dewar resonance energy was estimated by use of Herndon–Simpson and conjugated circuit resonance theories[10,12] and by the Hess–Schaad method based on Hückel MO theory.[10,13] The topological resonance energy (TRE) is known to be an excellent measure of aromatic stabilization.[25-29] It can be calculated exactly within the Hückel framework. However, no one has ever calculated the TRE of buckminsterfullerene because it is not easy to evaluate the non-adjacent numbers[30,31] of a very large conjugated system.

The situation has changed recently. Hosoya overcame this difficulty,[32] and succeeded in construct ing the matching polynomial (i.e., the reference polynomial[25]) of buckminsterfullerene, which is shown below:[32]

$$\begin{aligned}R(X)=&X^{60}-90X^{58}+3825X^{56}-102120X^{54}+1922040X^{52}\\&-27130596X^{50}+298317860X^{48}-2619980460X^{46}\\&+18697786680X^{44}-109742831260X^{42}+534162544380X^{40}\\&-2168137517940X^{38}+7362904561730X^{36}\\&-20949286202160X^{34}+49924889888850X^{32}\\&-99463457244844X^{30}+165074851632300X^{28}\\&-227043126274260X^{26}+256967614454320X^{24}\\&-237135867688980X^{22}+176345540119296X^{20}\\&-104113567937140X^{18}+47883826976580X^{16}\\&-16742486291340X^{14}+4310718227685X^{12}\\&-783047312406X^{10}+94541532165X^{8}-6946574300X^{6}\\&+269272620X^{4}-4202760X^{2}+12500 \qquad (1)\end{aligned}$$

According to our standard interpretation,[25-29] this is a characteristic polynomial for an olefinic reference structure of buckminsterfullerene. Here, an olefinic reference structure stands for a hypothetical molecule obtained by replacing all bonds in a given molecule by those found in acyclic polyenes.

Hückel MO calculations of buckminsterfullerene have been published repeatedly.[8-13,16,18,19,33] Total π-electron energy of this molecule is $60\alpha+93.1616\beta$. That of its olefinic reference structure is $60\alpha+91.5189\beta$, which was obtained from the roots of the equation $R(X)=0$. The TRE is then given as the difference between these two energies. It is 1.6427β for buckminsterfullerene. Since this molecule is more stable than its olefinic reference structure, it can be classified as an aromatic molecule or a molecule of spherical aromaticity.

However, an aromatic molecule is not always stable enough to exist in the condensed phase. In order to see relative stabilities of buckminsterfullerene and related molecules, we evaluated the percent resonance energies (%RE's). The %RE of a given molecule is defined as 100 times the TRE, divided by the total π-electron energy of its olefinic reference structure.[28,34-36] Owing to the wide variation in the size of molecules compared, we feel that %RE is a better way of comparing stabilities than using the total TRE's. The %RE's calculated for buckminsterfullerene and related species are listed in Table 1.

The %RE of buckminsterfullerene is 1.79, which is smaller than those of typical benzenoid hydrocarbons

Table 1. Topological Resonance Energies of Buckminsterfullerene and Related Hydrocarbons

Species	TRE/β	%RE
Buckminsterfullerene (**1**)	1.643	1.79
Buckminsterfullerene*	1.010	1.10
Buckminsterfullerene^{2+}	0.530	0.58
Buckminsterfullerene^{2-}	1.489	1.63
Corannulene (**2**)	0.735	2.63
Naphthacene	0.553	2.27
Pentacene	0.630	2.11
Hexacene	0.706	1.99
Heptacene	0.783	1.91
Acenaphthylene (**3**)	0.354	2.18
Cyclopenta[*cd*]pyrene (**4**)	0.565	2.27
Pyracylene (cyclopent[*fg*]-acenaphthylene) (**5**)	0.106	0.55

(2.2—3.3).[35,36] In the benzenoid hydrocarbons, a %RE of this size does not guarantee stability or isolability in macroscopic amounts.[28] In the polyacene series, even hexacene and heptacene have a larger %RE. Note that hexacene (%RE=1.99) must be handled under nitrogen and that heptacene (%RE=1.91) is so unstable that it has never been obtained in a pure state. Hess and Schaad also noted insufficient stability of buckminsterfullerene.[13] Thus, this molecule is predicted not to be isolable although it has as many as 12500 Kekulé structures.[10,12,32]

Each carbon in buckminsterfullerene is equivalent to every other carbon, being the vertex joining one pentagon and two hexagons. As in graphite, each atom is involved in two single bonds and one double bond to its neighbors. Graphite has a total π-electron energy per carbon of $\alpha+1.5746\beta$.[37] If we assume that the olefinic reference structures of buckminsterfullerene and graphite have the same total π-electron energy per carbon, the %RE of graphite is calculated to be 3.23, which is slightly less than twice the %RE of buckminsterfullerene. This again suggests insufficient stability of the icosahedral C_{60} cluster.

To make matters worse, each C–C resonance integral in buckminsterfullerene cannot take the standard value (β) since all C–C bonds are bent on the surface of the sphere. Taking this structural factor into account, Haddon et al. showed that the resonance integrals in buckminsterfullerene must be reduced to 0.877β.[11] This further decreases the TRE of buckminsterfullerene. The TRE of buckminsterfullerene in Table 1 must likewise be multiplied by 0.877.

The structural unit of the truncated icosahedron is a pentagon surrounded by five hexagons. Corannulene (**2**) is a hydrocarbon in such a structure. This molecule is shaped like a bowl,[38] and isolable in accord with its large %RE (2.63). As stated by Hess and Schaad,[13] the isolation of corannulene which has a considerably larger %RE than buckminsterfullerene does not imply the potential isolation of buckminsterfullerene.

Heath et al. obtained evidence for the formation of stable complexes of the formula $C_{60}M$ by laser evaporation of a graphite disk impregnated with M, where M=La, Ba, Sr, Ca, etc.[39] Stability of the dianion in a supersonic beam might be rationalized well by the %RE, which is comparable to that of the neutral species. As can be seen from the structure, buckminsterfullerene has a nonalternant hydrocarbon skeleton but without hydrogens. The dication has a much smaller %RE than the dianion.

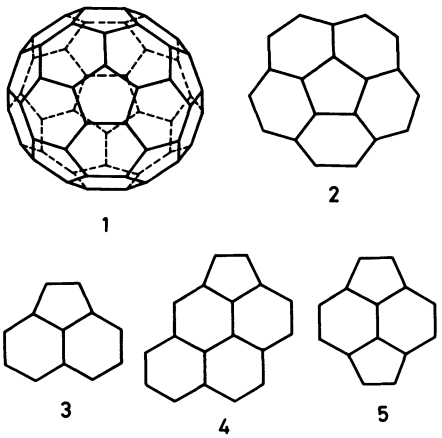
Kroto et al. speculated about the possibility that the C_{60} cluster might be the carrier of the diffuse interstellar ultraviolet band.[2,40] As in a supersonic beam, buckminsterfullerene may be formed somewhere in the hydrogen-deficient interstellar or circumstellar medium. At present, there is no reason to doubt the existence of this molecule in dark interstellar space. In fact, the C_{60} cluster in a supersonic beam is very resistant to chemical attack by such small molecules as NO, H_2, CO, SO_2, O_2, and NH_3.[3]

Léger and Puget[41] and Allamandola et al.[42] proposed recently that there must be abundant polycyclic aromatic hydrocarbons (PAH's) in the interstellar medium. In previous papers,[35,36] Aihara suggested that such interstellar PAH's must have a large %RE both in the ground and excited states since they are placed in the intense radiation field. As shown in Table 1, the %RE of buckminsterfullerene is very small in the first excited state. Therefore, it does not seem stable enough to exist in the intense radiation field. Buckminsterfullerene* in Table 1 indicates the excited-state species.

Soot is formed by incomplete combustion of organic matter. One of the striking features known about soot is that it is almost always found in the form of spheres, arranged in strands of beads or more complicated structures.[2,43] The polycyclic hydrocarbons are detectable in high concentrations in sooting flames. They may adopt pentagonal rings as they grow, so as to generate spheroidal structures which maximize the number of C–C linkages.[2]

Acenaphthylene (**3**) and cyclopenta[*cd*]pyrene (**4**) are formed in sooting flames.[43] Even pyracylene (cyclopent[*fg*]acenaphthylene) (**5**) is suspected to exist in flames.[43] These molecules are not highly aromatic PAH's. Synthetic pyracylene is far from isolable from solution.[44,45] Fluorene and indene are also detectable in flames.[43] Since in flames there are many such hydrocarbons with pentagonal rings, it seems likely that soot or large spheroidal carbon clusters are formed starting from these molecules. However, this does not imply that buckminsterfullerene is isolable even if it is formed in flames.[46] As pointed out above, the %RE of buckminsterfullerene is too small.

Localization energy is a typical reactivity index for aromatic molecules.[47] The cation and anion localization energies of buckminsterfullerene are 2.767 and 2.490, respectively, at all constituent carbons. These values are very large as compared with those at the peripheral carbons of polycyclic benzenoid hydrocarbons (1.90—2.55).[47] It should be noted that most reactions of benzenoid hydrocarbons occur at these peripheral carbons. If in future buckminsterfullerene is found to be isolable, the stability will be ascribed to the absence of peripheral reactive carbons,



thereby being kinetic rather than thermodynamic in nature.

In this connection, Iijima prepared a spherical particle of graphitic carbon by arc discharge between two carbon rods, and found that there seems to be a C_{60} cluster at the core of the particle.[48] The innermost carbon cluster is obviously protected from danger by many outer spheres made of carbon atoms.

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