On the Lack of Reactivity of Buckminsterfullerene. A Theoretical Study

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The lack of reactivity of buckminsterfullerene, a C_{60} cluster, towards addition reactions is attributed to the high values of the bond localization energies of its bonds.

Buckminsterfullerene, the recently discovered[1] soccer ball-shaped molecule with sixty carbon atoms (see Figure 1), appears to be remarkably stable under relatively severe reaction conditions.[1–4] It has also been predicted, by a number of theoretical studies,[5–10] to have a degree of aromaticity close to that of benzene.

Since aromatic stability does not necessarily preclude reactivity, we have investigated the lack of reactivity of buckminsterfullerene towards the addition reactions using the bond localization energy concept.[11] The inertness of C_{60} towards the substitution reactions is clearly due to the unavailability of replaceable hydrogens capable of electrophilic and oxidative reactions normally characteristic of aromatic compounds. Therefore, the molecule can only undergo substitution reactions after the cage network has been ruptured.

Bond Localization Energy.—The concept of bond localization energy may be introduced in the following way. Addition reactions occur at bonds with significant double bond character in aromatic substrates. During addition at a double bond, the π-electronic energy of the substrate is reduced and this is related to an energy loss. This π-electron energy loss is called the bond localization energy and is denoted by L. The localization energy of the bond i, $L(i)$, can be calculated by equation (1), where E_π

$$L(i) = E_\pi(\mathrm{S}) - E_\pi(\mathrm{S} - i) \qquad (1)$$

is the π-electron energy, S the aromatic substrate and (S − i) the aromatic substrate without the bond at which the addition reaction has occurred. $L(i)$ is an index which measures the ease with which the bond i can be localized. Or, in other words, the smaller the value of the bond localization energy $L(i)$, the greater probability of the addition reaction occurring at the bond i. E_π may be computed by a variety of MO methods.[12] In this report we obtained E_π values for S and (S − i) using the standard form of the HMO method.

We also point out here that the HMO calculations on buckminsterfullerene and the corresponding two substructures (each obtained by deleting the appropriate bond in the C_{60} cluster) were performed in the same way as for most other HMO studies[8,10,13] on fullerenes, *i.e.* all non-zero entries (reflecting the connectivity between sites in the C_{60} cluster) in the Hückel determinant were taken to be identical and equal to unity.

Results and Discussion

We have calculated bond localization energies of buckminsterfullerene and a number of polycyclic conjugated systems. Their structures are given in Figure 2. These polycyclic systems are introduced for the purpose of comparison with buckminsterfullerene. In Table 1 are given $L(i)$ indices and the corresponding bond orders for buckminsterfullerene and the polycyclic structures in Figure 2.

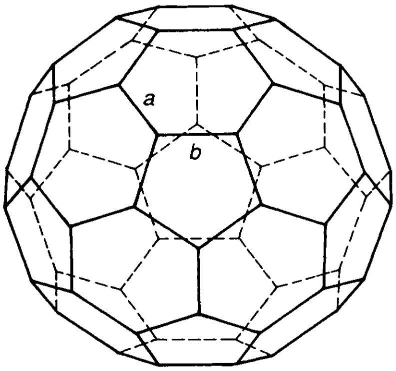

Figure 1. The truncated icosahedron as a model of buckminsterfullerene, a conjugated sixty-carbon cluster C_{60}. Label *a* denotes a bond between two hexagons and *b* between the pentagon and hexagon.

The relationship between bond localization energies and the corresponding bond orders is approximately linear (r = 0.87) as can be seen from Figure 3. This is not surprising because $L(i)$ may be also expressed in terms of bond orders. Since the Hückel energy of S and (S − i) can be represented (in the normalized form $\alpha = 0$ and $\beta = 1$) by equations (2) and (3)[14]

$$E_\pi(\mathrm{S}) = 2\sum_l p_l(\mathrm{S}) \qquad (2)$$

$$E_\pi(\mathrm{S} - i) = 2\sum_l p_l(\mathrm{S} - i) \qquad (3)$$

it follows that the bond localization energy is also calculable from equation (4).

$$L(i) = 2\sum_l [p_l(\mathrm{S}) - p_l(\mathrm{S} - i)] \qquad (4)$$

This confirms the empirical observation that the addition reactions in aromatic systems occur most readily at those bonds which show the most pronounced double-bond character. These bonds are shorter than traditional aromatic bonds[15] and possess smaller values of $L(i)$ and higher bond orders. The region of reactive bonds in Figure 3 belongs to bonds in (rectangular) cyclobutadiene [(**11**): L(a) = 2.00; p_a = 1.00] and the cyclobutadiene parts of benzocyclobutadiene [(**12**): L(a) = 2.38; p_a = 0.90], 2,3-naphthocyclobutadiene [(**13**):

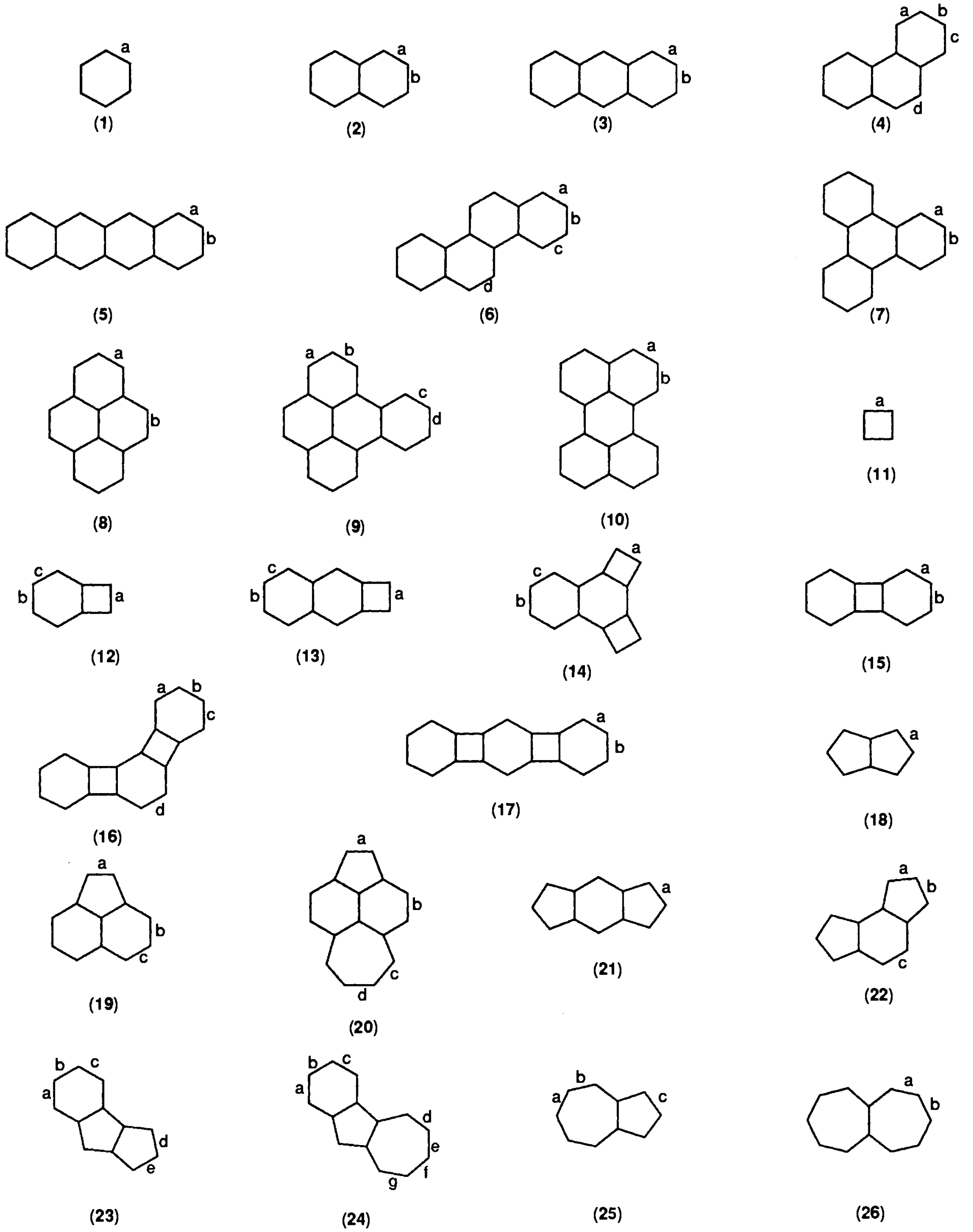

Figure 2. Structures of the polycyclic conjugated molecules studied.

L(a) = 2.52; p_a = 0.84] and 1,2,3,4-naphthodicyclobutadiene [(**14**): L(a) = 2.68; p_a = 0.71]. The reactivity of such bonds towards the addition reactions has been confirmed experimentally.[16,17]

The area between reactive bonds [bonds with low values of $L(i)$] and inert bonds [bonds with high values of $L(i)$] is populated by 'aromatic' bonds[15] and covers the range of L values between 3.00 and 4.00. These bonds are to a great extent resistant to addition reactions. The inert bonds possess L values higher than 4.00. The bonds of buckminsterfullerene fall in the region of inert bonds which possess L values of 4.11 or 4.45. It is interesting to note that the bonds between two hexagons have a bond order corresponding to 'aromatic' bonds, but an L value (4.11) corresponding to inert bonds. Bonds between the pentagons and hexagons have L values and p values characteristic of unreactive bonds. To conclude, therefore, the lack of reactivity of buckminsterfullerene towards addition reactions can be reliably attributed to the presence of bonds with high localization energies.

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Table 1. Bond localization energies $L(i)$ and bond orders p_i for buckminsterfullerene and the polycyclic conjugated systems shown in Figure 2.

Molecule	Bond	$p_i(i = \mathrm{a, b, \ldots})$	$L(i)$ (in β units)
(1)	a	0.67	3.53
(2)	a	0.72	3.26
	b	0.60	3.73
(3)	a	0.74	3.20
	b	0.59	3.78
(4)	a	0.70	3.34
	b	0.62	3.65
	c	0.71	3.32
	d	0.77	3.06
(5)	a	0.74	3.19
	b	0.58	3.80
(6)	a	0.712	3.30
	b	0.62	3.67
	c	0.707	3.32
	d	0.75	3.12
(7)	a	0.69	3.38
	b	0.64	3.60
(8)	a	0.67	3.42
	b	0.78	3.06
(9)	a	0.68	3.375
	b	0.65	3.49
	c	0.69	3.384
	d	0.64	3.59
(10)	a	0.71	3.28
	b	0.63	3.57
(11)	a	1.00	2.00
(12)	a	0.90	2.38
	b	0.73	3.17
	c	0.56	3.78
(13)	a	0.84	2.52
	b	0.64	3.55
	c	0.69	3.37
(14)	a	0.71	2.68
	b	0.57	3.82
	c	0.75	3.15
(15)	a	0.62	3.60
	b	0.69	3.35
(16)	a	0.635	3.54
	b	0.68	3.40
	c	0.636	3.53
	d	0.59	3.67
(17)	a	0.61	3.61
	b	0.70	3.33
(18)	a	0.65	2.99
(19)	a	0.80	2.94
	b	0.63	3.52
	c	0.70	3.28
(20)	a	0.74	3.11
	b	0.713	3.21
	c	0.715	3.17
	d	0.58	3.67
(21)	a	0.66	3.18
(22)	a	0.64	3.32
	b	0.66	3.28
	c	0.77	3.07
(23)	a	0.67	3.32
	b	0.651	3.42
	c	0.650	3.40
	d	0.56	3.26
	e	0.74	2.97
(24)	a	0.714	3.27
	b	0.61	3.65
	c	0.706	3.295
	d	0.62	3.44
	e	0.67	3.330
	f	0.60	3.54
	g	0.698	3.20
(25)	a	0.64	3.42
	b	0.664	3.31
	c	0.656	3.37
(26)	a	0.67	3.04
	b	0.62	3.14
Buckminsterfullerene	a	0.60	4.11
	b	0.48	4.45

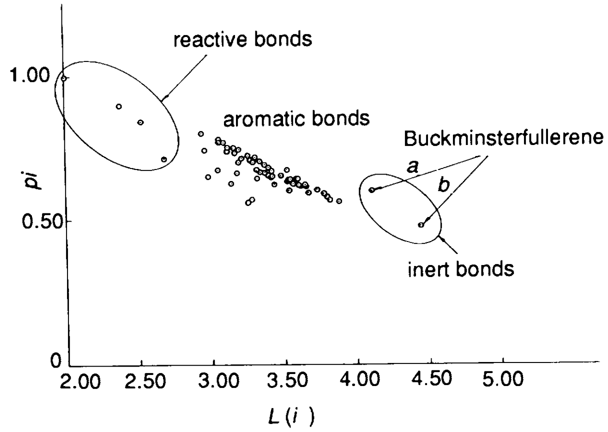

Figure 3. A plot of p_i *vs.* $L(i)$.

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