Simple structural and bonding representations of fullerenes

A Rathna & J Chandrasekhar*
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012
Received 20 February 1992

Bonding in buckminsterfullerene, C\textsubscript{60}, can be described in terms of a unique canonical representation in which all six membered rings have a benzenoid Kekule structure while the pentagons are all made of exclusively single bonds. The corresponding valence bond structure reflects the full symmetry of the molecule and is consistent with the observed bond length variations. Computational support for the bonding description is provided using localized MO's obtained at the MNDO level. The requirement of benzenoid structures for all the hexagons can be used as a criterion of stability of fullerenes which complements the pentagon isolation rule. A convenient two-dimensional representation of the fullerene structures incorporating the above bonding description is suggested, especially for use in mechanistic discussions.

The first report\textsuperscript{1} of the mass spectral characterisation of a sixty carbon cluster along with the remarkable structural proposal derived from the geodesic dome of Buckminster Fuller (1) immediately attracted the attention of numerous theoretical chemists\textsuperscript{2}. The intriguing question concerning the nature of bonding in the truncated icosahedral framework was the focus of many of these studies. Simple valence rules can be satisfied if all the carbon atoms of C\textsubscript{60} are considered to be uniformly \(sp^2\) hybridized, with 60 \(p\) orbitals of pseudo \(\pi\) symmetry participating in a three-dimensional aromatic interaction. Effectively, 60 electrons are delocalized over the surface of the spheroidal molecule. In fact, the free electron model\textsuperscript{3} reproduced the essential features of the electronic structure of the molecule, viz., the symmetry and the associated degeneracy of all the molecular orbitals. Huckel calculations confirmed the pattern\textsuperscript{4}, while more sophisticated methods like the INDO\textsuperscript{5}, PRDDO\textsuperscript{6}, MNDO\textsuperscript{7,8}, AM1\textsuperscript{8}, and ab initio\textsuperscript{9,10} procedures provided additional details. These calculations led to reliable structural and spectral parameters, in particular those associated with vibrational, electronic and photoelectron spectra. Many of these insights were obtained even before the recent explosion of activity involving the fullerenes following the development of simpler procedures for their synthesis and experimental study\textsuperscript{11}.

While the theoretical results mentioned above have been quite useful, a simpler representation of the structure and bonding of fullerenes is probably of greater value, especially for understanding their reactivity patterns. The formation of new bonds and the reorganisation of existing bonds in these compounds following a chemical reaction are rather difficult to visualize at present within the delocalized bonding models. For example, the mechanistic details of a reaction such as the Birch reduction of C\textsubscript{60} appear complicated, while the corresponding information for a typical aromatic molecule is textbook material. In this paper, we consider a simple approach based on localized molecular orbitals for understanding the structure, stability and reactivity of fullerenes. We discuss previous studies employing related concepts and also provide additional details.

Computational details
The standard MOPAC package\textsuperscript{11} was implemented on a CYBER 992 computer and enhanced to handle molecules containing more than 60 non-hydrogen atoms. Using this program, the geometry of C\textsubscript{60} was fully optimized imposing \(I_h\) symmetry at the MNDO level. The wave functions were successively transformed until a set of localized molecular orbitals was obtained\textsuperscript{12}. The default criteria for localization built in the program was used without modification. Convergence occurred in 48 cycles.

A modified version of Jorgensen's program\textsuperscript{13}, installed on the VAX 8810 computer, was employed to plot the contours of the MNDO localized wave functions. The PERGRA program\textsuperscript{14}, developed for a PC, was also used to pictorially represent the relative coefficients of the AO's in the various types of localized molecular orbitals.

Results and Discussion
A convenient starting point for understanding the bonding in C\textsubscript{60} is provided by the experimental and computed structural parameters of this molecule (Table 1). Many of the more quantitative
theoretical methods clearly predict the presence of bond alternancy in \( \text{C}_{60} \). The bond shared by two hexagons (6-6) is relatively short, while the common bond between a hexagon and a pentagon (6-5) is long. NMR studies\(^{15} \) and the more recent neutron\(^{16} \), X-ray\(^{17} \) and electron diffraction\(^{18} \) results also confirm that there are effectively two types of bond lengths in \( \text{C}_{60} \). A range of distances is observed in the solid state, due to intermolecular interactions\(^{16,17} \). However, the general pattern follows the calculated data, which refer to the gas phase.

The bond length variations suggest the presence of alternating single and double bonds in \( \text{C}_{60} \). The computed bond orders reflect the changes in lengths. A linear muffin-tin orbitals (LMTO) calculation gave bond orders of 1.54 and 1.41, respectively for the 6-6 and the 6-5 bonds\(^{19} \). The corresponding values computed by us at the MNDO level (1.51 and 1.10) show a larger difference. This is also reflected in the greater degree of bond alternancy obtained at this theoretical level (Table 1).

In addition to bond orders, another criterion can be used to qualify the differences in the nature of bonds in a molecule. The individual molecular orbitals can be transformed into localized orbitals leaving the total wave function unchanged. Although the nature of the transformed MO's sometimes depend on the localization procedure employed, especially in polycyclic aromatic compounds and three-dimensional polyhedral boron hydrides\(^{20} \), the results are quite instructive. A previous study using the Boys method of maximising the sum of squares of orbital centroids at the PRDDO level showed that the MO's of \( \text{C}_{60} \) can be localized as efficiently as in benzene\(^{5} \). The calculations led to three types of localized bonds in \( \text{C}_{60} \), viz., a well defined 6-5 \( \sigma \) bond and a pair of \( \tau \) bonds. The latter correspond to a bent bond representation of the 6-6 double bond. The pyramidality at carbon makes the two \( \tau \) bonds non-equivalent. The nature of hybridization of the three unique bonds were compared with the corresponding data obtained for benzene at the same theoretical level\(^{6} \).

The localized bonds obtained in the present study using MNDO wave functions correspond to an even simpler bonding description. Again, three unique types of localized MO's were obtained. The orbital contour diagrams (Fig. 1) clearly indicate that one of them is the 6-5 \( \sigma \) bond found in the earlier study. However, the 6-6 double bond appears as a \( \sigma \) bond and a pseudo \( \pi \) bond, rather than as a pair of \( \tau \) bonds. An alternative pictorial representation of these orbitals which reflects the relative atomic orbital coefficients and coordinates.

<table>
<thead>
<tr>
<th>Method</th>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MNDO</td>
<td>1.400</td>
<td>1.474</td>
<td>2,7</td>
</tr>
<tr>
<td>AMI</td>
<td>1.385</td>
<td>1.464</td>
<td>8</td>
</tr>
<tr>
<td>PRDDO</td>
<td>1.360</td>
<td>1.436</td>
<td>6</td>
</tr>
<tr>
<td>LMTO</td>
<td>1.410</td>
<td>1.440</td>
<td>19</td>
</tr>
<tr>
<td>HF/STO-3G</td>
<td>1.376</td>
<td>1.463</td>
<td>8a,9a</td>
</tr>
<tr>
<td>HF/DZ</td>
<td>1.368</td>
<td>1.451</td>
<td>9b</td>
</tr>
<tr>
<td>HF/DZP</td>
<td>1.372</td>
<td>1.453</td>
<td>9c</td>
</tr>
<tr>
<td>HF/TZP</td>
<td>1.370</td>
<td>1.448</td>
<td>9c</td>
</tr>
<tr>
<td>MP2</td>
<td>1.405</td>
<td>1.445</td>
<td>9d</td>
</tr>
<tr>
<td>Solid State NMR</td>
<td>1.40</td>
<td>1.45</td>
<td>15</td>
</tr>
<tr>
<td>Single crystal</td>
<td>1.340-1.391</td>
<td>1.378-1.561</td>
<td>17</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>1.355</td>
<td>1.467</td>
<td>18</td>
</tr>
<tr>
<td>Electron diffraction</td>
<td>1.401</td>
<td>1.458</td>
<td></td>
</tr>
<tr>
<td>Neutron powder</td>
<td>1.366-1.412</td>
<td>1.420-1.487</td>
<td>16</td>
</tr>
<tr>
<td>Diffraction</td>
<td>av.1.391</td>
<td>av.1.455</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1—Contours of the localized orbitals of \( \text{C}_{60} \). Only a small fragment of the molecule is shown for clarity [(a) 6-5 \( \sigma \) bond; (b) 6-6 \( \sigma \) bond; (c) 6-6 \( \pi \) bond]
hybridization (Fig. 2) is also instructive. The extent of localization and the nature of orbital distortions are clearly seen. For example, the $\pi$ bond is not completely localized, as evident from the small lobes on the adjacent atom orbitals. The $\pi$ bond is also splayed outwards on the exterior of the spheroidal molecule, reflecting the pyramidality at the carbon atoms. The orbital contours indicate significant differences in the distortion of the $\sigma$ and $\pi$ MO's. The former has a greater density on the outside, while the reverse is true or the $\pi$ bond. Such orbital effects have been associated with interesting chemical consequences in many organic systems$^{21}$. In the case of C$_{60}$, endohedral interactions are expected to be quite different in magnitude compared to interactions of the $\pi$ cloud with reagents on the exterior.

The above analysis clearly implies that buckminsterfullerene consists of 60 single and 60 double bonds. The pentagons are constructed of exclusively single bonds. On the other hand, the hexagons are made of alternating single and double bonds. In effect, the electronic structure of C$_{60}$ is well represented by a single canonical structure, which remarkably reflects the icosahedral symmetry of the molecule. In contrast, resonance structures such as the Kekule forms for benzene do not have the full symmetry of the molecule. Multiple related structures have to be invoked to restore the molecular symmetry. For buckminsterfullerene, alternative resonance forms probably do not contribute as much as the unique highly symmetric pairing scheme which parallels the localized molecular orbital description.

The localized bonding description has been used to advantage earlier$^{16,17,22}$. For example, pentagon faces are readily recognised as being relatively electron deficient, while the hexagons are electron rich. Intermolecular interactions, in solid fullerene$^{16,17}$ and perhaps also in a donor-acceptor complex$^{23}$, are determined by these electron density variations.

The valence bond description also enables the extension of previous rules of stability of polycyclic conjugated compounds to the fullerene family. For example, the known antiaromatic character of pentalene has been invoked by Taylor$^{22}$ to suggest that structures with shared pentagons are unstable. This factor can be used to rationalize the 'pentagon isolation rule' and the uniqueness of the C$_{60}$ structure. Buckminsterfullerene represents the smallest closed structure with exclusively five and six membered rings in which no two pentagons are adjacent. Extending the argument, it has been proposed that structures with a double bond in a pentagon face are destabilized. This proposal was used to rationalize the relative stabilities of several of the larger fullerenes, C$_n$ ($n > 60$).

We prefer an alternative interpretation of the factors contributing to the relative stabilities of fullerenes. The reference system, graphite, is of course aromatic with its planar sheets of hexagons. The structure can be folded to yield a closed surface by introducing 12 pentagons. In order to have maximum stability for the cluster, it is essential that all the hexagons retain benzenoid character. Alternative canonical structures like the quinonoid forms do not lead to stabilization. That is, the spin pairing scheme as in the Kekule structure 2a is more stable than those in 2b-2e. The smallest closed structure made of pentagons and hexagons in which every double bond is optimally part of a benzenoid structure such as 2a is the fullerene, C$_{60}$. Such an ideal bonding situation is not possible in the larger clusters, say C$_{70}$ or C$_{80}$.
In the $D_{5h}$ form of $C_{70}$, for any given resonance structure, at least five of the hexagons would not retain their Kekule-type benzenoid spin pairing. Hence, the presence of additional hexagons in this cluster relative to $C_{60}$ does not lead to correspondingly greater stability. The same reasoning applies to the larger clusters as well. Ten hexagons of the $C_{80}$ cluster (assuming a five-fold symmetric structure) would lose benzenoid character.

In our revised proposal for rationalizing the relative stabilities of fullerenes, the focus has been shifted from the pentagons to the hexagons. Rather than suggesting that double bonds avoid pentagons, we insist that hexagons should adopt benzenoid structures for stability. The latter is a well known empirical rule for understanding the stabilities of polycyclic aromatic molecules. It is interesting that it can be used for three-dimensional clusters as well. However, as emphasized by earlier workers, conjugation contributes only partly to the stabilization of fullerenes. Strain effects associated with the $\sigma$ skeleton, pyramidality at the carbon, and the varying magnitude of $\pi$ overlap must all be taken into account for a complete understanding of the stability of these compounds. In the gas phase, entropic and other factors have also been suggested to be important.

The localized bonds of $C_{60}$ can be incorporated in an exploded view of the molecule, employed earlier by Saunders. The procedure of drawing such a structure (Fig. 3) is similar to that used occasionally for dodecahedrane, $C_{20}H_{20}$. A pentagon is first drawn, followed by five bonds from each of the vertices. In the case of dodecahedrane, additional 10 atoms are drawn staggered with respect to the first set and all the bonds are suitably connected to complete the structure. On the other hand, for pictorially representing fullerene, a set of 5 bonds (two-carbon units) is drawn parallel to the edges of the base pentagon. Connecting the nearest atoms would lead to corannulene, with a pentagon surrounded by 5 hexagons. Another set of 10 atoms (5 bonds) is drawn, staggered with respect to the previous set of bonds and maintaining five-fold symmetry. The nearest bonds are connected and the process is repeated up to $C_{50}$. The five bonds (10 atoms) of the final set are drawn radially. The nearest atoms are connected and finally the outermost five atoms are linked as a pentagon. The localized bonds, alternating single and double bonds, can then be easily inserted by ensuring that no double bonds are placed in any pentagon. For $C_{70}$ or $C_{80}$, the same procedure can be employed, with additional sets of 10 carbon units inserted beyond $C_{50}$ before drawing the outermost ten atoms. The structure of $C_{70}$ drawn following this procedure with a representative canonical structure is shown in Fig. 4.

The projected views of course do not reflect the spheroidal shape of the fullerenes. In particular, the above representations (Figs 3 and 4) emphasize only the five-fold symmetry of the molecules. However, it is a straightforward exercise to redraw the structures with three-fold or two-fold symmetry being highlighted. These may be appropriate in some discussions, e.g., structures of the trianion and the dianion of buckminsterfullerene or some partially hydrogenated forms.

The exploded representations have several advantages. All the atoms, bonds, pentagons and hexagons are visible in these structures. Thus, the key structural features can be recognized without the use of three-dimensional models. The pedagogical value hardly needs to be emphasized. More importantly, it would be possible to consider and evaluate bond reorganizations which may accompany chemical reactions involving fullerenes using these simplified structures. We recommend the routine use of these representations, including
the alternating single and double bonds, for mechanistic discussions.

Acknowledgement
We thank the Supercomputer Education and Research Centre, IISc, for help and cooperation. Discussions with P Balaram and S Chandrasekaran were valuable.

References
2 For a comprehensive list of theoretical studies and MNDO results on numerous fullerenes, see: Thiel W & Bakowies D, J Am chem Soc, 113 (1991) 3704.
(b) McKee M L & Herndon W C, J Mol Struct (Theochem), 153 (1987) 75.
14 For typical applications of this program, see: Sustmann R & Sicking U, Chem Ber, 120 (1987) 1323, 1471, 1653.
(b) Lipscomb W N, Science, 196 (1977) 1047.