The Hückel molecular orbital theory for non-planar conjugated organic molecules has been applied to study the electronic structure and properties of the proposed icosahedral geometry of C₆₀. The results support the suggestion that C₆₀ may be the first example of a spherical aromatic molecule. The molecule is calculated to have a stable closed shell singlet ground electronic state.

1. Introduction

Carbon clusters have been the focus of many experimental studies using a variety of techniques [1–4]. Recently, Kroto, Heath, O'Brien, Curl and Smalley [5] have obtained a remarkably stable cluster containing 60 carbon atoms and have proposed a highly symmetric truncated icosahedral structure (“football or soccerball” like) for this molecule [5,6]. These authors have proposed the name “Buckminsterfullerene” for this unusual structure of C₆₀.

The proposed icosahedral structure of C₆₀ raises a number of particularly interesting questions regarding the electronic structure of the molecule. Perhaps most intriguing is the spherical shape of the non-planar conjugated system which is (formally) solely composed of sp² hybridized carbon atoms. The molecule is comprised of 20 six-membered rings (6-MR) and 12 five-membered rings (5-MR), such that all the atoms are identical. Each atom is at the vertex of one 5-MR and two 6-MRs. There are two independent bond types: 30 bonds which lie solely in 6-MRs, while 60 bonds form the edges of both a 5- and a 6-MR. Particularly noteworthy is the observation that the molecule is non-alternant [7], but that as a result of the symmetry of the molecule the charge densities are all equal. Thus the proposed structure for C₆₀ appears to be unique among non-alternant hydrocarbons in this respect.

Some computed properties of C₆₀ are compared with those of related molecules in table 1. The choice of benzene, the [∞]annulene [11,12] and graphite [13] as reference molecules is clear. The hydrocarbon C₅₆H₂₂ or quateranthrene, is the graphite-like fragment closest in molecular size to C₆₀. Two sets of results are reported for C₆₀. The first set (first column of numbers in the table under C₆₀) refers to calculations with standard Hückel molecular orbital (HMO) theory*, without correction for non-planarity. The second set (final column of numbers in the table) was calculated with the three-dimensional HMO (3D HMO) method [15] in which the HMO resonance integrals (β) are adjusted for the effects of non-planarity by use of the π-orbital axis vector (POAV) analysis [16, 17] (discussed below). Although unsophisticated, the HMO theory [7,18–21] provides a useful starting point for molecular comparisons and the correlation of properties.

2. Planar HMO treatment

The π-bond energy per carbon (or electron) in C₆₀ is slightly less than that of graphite, but greater than that of the graphite fragment (C₅₆H₂₂). The two-dimensional structures (graphite, C₅₆H₂₂ and C₆₀) on the right of table 1 are favored in this comparison.

* A referee has drawn our attention to previous calculations of the eigenvalue spectrum of icosahedral C₆₀ [14].
Table 1
HMO results a)

<table>
<thead>
<tr>
<th>Property</th>
<th>C₆H₆</th>
<th>[∞] Å b)</th>
<th>C₅₆H₂₂ c)</th>
<th>Graphite d)</th>
<th>C₆₀ e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁(π)</td>
<td>8.000</td>
<td>81.820</td>
<td></td>
<td></td>
<td>93.162</td>
</tr>
<tr>
<td>E₁(π)/(C h)</td>
<td>1.333</td>
<td>1.273</td>
<td>1.461</td>
<td>1.576</td>
<td>1.553</td>
</tr>
<tr>
<td>E₁(π)/(B)</td>
<td>1.333</td>
<td>1.273</td>
<td>1.121</td>
<td>1.051</td>
<td>1.035</td>
</tr>
<tr>
<td>λ(k)</td>
<td>0.667</td>
<td>0.637</td>
<td>0.560</td>
<td>0.525</td>
<td>0.518</td>
</tr>
<tr>
<td>E₃(π)</td>
<td>1.0</td>
<td>∞</td>
<td>1.016</td>
<td>u)</td>
<td>0.893</td>
</tr>
<tr>
<td>Fₚ</td>
<td>0.399</td>
<td>0.459</td>
<td>0.566</td>
<td>0.156</td>
<td>0.179</td>
</tr>
<tr>
<td>Lₚ(π) m</td>
<td>2.536</td>
<td>-</td>
<td>1.620</td>
<td>-</td>
<td>2.767</td>
</tr>
<tr>
<td>Lₚ(π) n</td>
<td>2.536</td>
<td>-</td>
<td>1.620</td>
<td>-</td>
<td>2.629</td>
</tr>
<tr>
<td>Δ₀</td>
<td>2.536</td>
<td>-</td>
<td>1.620</td>
<td>-</td>
<td>2.490</td>
</tr>
<tr>
<td>Δ₀(HOMO) p</td>
<td>1.0</td>
<td>0.0</td>
<td>0.051</td>
<td>0.0</td>
<td>0.618</td>
</tr>
<tr>
<td>Δ₀(LUMO) q</td>
<td>-1.0</td>
<td>0.0</td>
<td>-0.051</td>
<td>0.0</td>
<td>-0.139</td>
</tr>
<tr>
<td>IP (eV) s</td>
<td>8.81</td>
<td>-</td>
<td>6.07</td>
<td>-</td>
<td>7.70</td>
</tr>
<tr>
<td>IP (eV) t</td>
<td>9.55</td>
<td>-</td>
<td>7.20</td>
<td>-</td>
<td>8.60</td>
</tr>
</tbody>
</table>


over the linearly conjugated systems (benzene and annulene). This is principally due to the fact that the former structures have more bonds (1.5 bonds per carbon) than the latter forms (1 bond per carbon). As noted above, C₆₀ has two classes of bonds, and the calculated bond orders are found to be: 0.476 (5/6-MR) and 0.601 (6/6-MR). Applying the conventional relationship [7,18–21] between bond orders and bond lengths we calculate C₆₀ to possess 30 bonds of length 1.405 Å (6/6-MR) and 60 bonds of length 1.426 Å (5/6-MR), and the most appropriate Kekulé representation is shown in fig. 1. Particularly important is the prediction that C₆₀ will not undergo a distortion to a point group of lower symmetry as a result of the second-order Jahn–Teller effect [19]. It has been shown [22] that by diagonalizing the bond–bond polarizability matrix, it is possible to ascertain the likely symmetry of distortion (eigenvectors) and the energy gain (eigenvalues, λ) due to second-order Jahn–Teller distortion. In fact, the largest eigenvalue of the bond–bond polarizability matrix (table 1), indicates that C₆₀ has less tendency to break symmetry than benzene. This contrasts with the large aromatic annulenes [11,23,24] where bond alternation is thought to occur in the vicinity of [18]annulene (λcritical ≈ 1.8).

The free valence (Fₚ) provides an index of the unsatisfied valence or residual bonding power at a particular atom (r) in a molecule [7,18–21]. The localization indices provide a measure of the energetic destabilization of the π system when an atom (r) is removed from conjugation by sp³ bond formation with an incoming electrophilic (Lₚ⁺), radical (Lᵣ), or nucleophilic (Lᵣ⁻) reagent [7,18–21]. It is apparent that all of these indices indicate a high chemical stability for C₆₀. This primarily results from the absence of perimeter atoms (two nearest neighbors); as all of the atoms in C₆₀ are “interior”, chemical reaction should be inhibited. The geometry (discussed below), however, does predispose C₆₀ toward chemical attack when
comparison is made with planar conjugated systems as the necessary rehybridization for a tetrahedral transition state is already well advanced in the ground state of C₆₀ (see below).

The non-alternant character of C₆₀ (and the presence of 5-MRs) is reflected in the asymmetric distribution of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) about the zero of energy (fig. 2). The MO energy levels indicate an ionization and oxidation potential comparable to naphthalene (E_{HOMO} = 0.618) and very different from that of graphite. The calculations suggest an exceptionally high electron affinity (facile reduction). For comparison, decacyclene reversibility undergoes addition of six electrons [25] in solution (the lowest three vacant molecular orbitals lie at -0.333, -0.333 and -0.425 β). In C₆₀ there are three MOs at -0.139 β and three at -0.382 β, and thus it is likely that the molecule will add up to twelve

---

Fig. 2. HMO energy level diagram for C₆₀ (unscaled β, see text).
electrons under suitable conditions. The calculated HOMO—LUMO energy gap ($\Delta E$) lies between the values found for anthracene ($\Delta E = 0.828 \beta$) and tetra-
cene ($\Delta E = 0.590 \beta$), although the non-alternant azulene [26,27] ($\Delta E = 0.877 \beta$) may be a more ap-
propriate reference point for C$_{60}$.

3. Three-dimensional HMO treatment

It is now appropriate to consider the way in which the idealized results discussed above are modified when full account is taken of the spherical nature of the $\pi$-electron system. The molecule lends itself to the recently developed POAV/3D HMO analysis [15–
17]. In the POAV approach [16,17] the $\sigma$ bonds are assumed to lie along the internuclear axes, and the orbital orthogonality relationships are used to solve for the $\pi$-orbital hybridization and direction. It has been shown that this analysis provides the logical and natural bridge between the $\sigma-\pi$ separability assumed in planar conjugated systems and the realities of $\pi$ bonding in non-planar situations. The 3D HMO method extends this analysis by utilizing the local POAV hybrids to calculate Slater overlap integrals between nearest neighbors in the $\pi$-electron network. By comparison with the overlap integral for the same bond with “perfect” $\pi$-orbital overlap a reduced resonance integral ($\rho \beta$) may be evaluated which is subsequently used in the (3D) HMO calculation on the molecule. The POAV analysis is non-parametric, and merely requires the molecular coordinates. In the present case we assumed a common carbon—carbon bond length of 1.4 Å. In fact, the molecule has two degrees of freedom, and although the 5-MRs and 6-MRs separately maintain equal bond angles (108° and 120°, respectively), the molecule is expected to exhibit two different bond lengths, so that the 6-MRs become somewhat bond-alternate and the 5-MRs remain bond-
equalized. For the present qualitative discussion, the preceding approximation is expected to be adequate.

The POAV1 analysis [16] of the bond-equalized structure leads to $s^{0.093}p$ hybridization for the $\pi$ orbital and $sp^{2.278}$ hybridization for the three $\sigma$ orbitals. The angle between the $\sigma$ and $\pi$ orbitals ($\theta_{\sigma\pi}$) is found to be 101.6°, and hence the $\sigma$ bonds may be considered to be inclined at an angle of 11.6° below a tangential plane to the surface (this angle is 0° in
graphite and 19.5° in diamond). Thus the rehybrid-
ization in C$_{60}$ is extremely high — much larger than the values found in the most strained bridged annu-
lenes [16,17]. Nevertheless, C$_{60}$ is found to have per-
fected $\pi$-orbital alignment (unlike most non-planar con-
gjugated organic systems), and the reduction in the overlap integrals in C$_{60}$ results from the inclination of the orbitals with respect to the bond axis rather than torsional misalignment. Calculating the Slater overlap integral between the local $\pi$ hybrids gives $\rho = 0.877$ for the $\pi$ bonds in C$_{60}$ (reduced resonance integral = $0.877 \beta$).

As we are treating all bonds on the same basis, it is merely necessary to scale the appropriate quantities for the hypothetical planar structure by $\rho$ to obtain the 3D HMO results (last column of table 1). It is clear from table 1 that the $\pi$ system is de-
stabilized by this perturbation. Nevertheless, the reactivity indices ($F_r$, $L_r$) suggest that the molecule should retain sufficient resistance to chemical at-
tack to be isolable. The only caveat to this predic-
ton concerns the rehybridization, which makes the ground state atoms of C$_{60}$ approach the transition state for reaction (formation of a fourth $\sigma$ bond) much more closely than in normal planar conjugated organic molecules. The molecules is still expected to be stable to a reduction in symmetry, but the bond lengths are now predicted to be 1.418 (6/6-MR) and 1.436 Å (5/6-MR).

It is apparent that our calculations support the proposal by Kroto et al. [5] that C$_{60}$ may qualify as the first example of a spherical aromatic molecule. The $\pi$-electron energy per carbon (or per electron) is 86% of that of graphite and 93% of that of a size-
consistent graphite fragment. Of pivotal importance in this regard is the fact that all of the $\sigma$ bonds are fully satisfied with little strain (ring bond angles of 108° and 120°), after rehybridization. In comparison, the (dehydrogenated) graphite fragment (derived from C$_{56}$H$_{22}$) would have 22 unsatisfied valences. Clearly C$_{60}$ by its topology is a superbly adapted cluster geometry for the bonding characteristics of carbon.

4. Electronic and vibrational spectroscopy

The HMO scheme predicts the HOMO to be com-
pletely filled (fig. 2) and therefore the ground state of C\textsubscript{60} should be diamagnetic $^1A_e$. The icosahedral group is close to spherical symmetry and one can clearly recognize the parentage of the low-lying MOs in spherical harmonics ($Y_{LM}$ where $L$ is the orbital angular momentum quantum number). In particular the $S$, $P$, and $D$ ($L = 0, 1$ and 2) spherical harmonics become $a_g$, $t_{1u}$, and $h_g$ representations in $I_h$. The atomic orbital coefficients in the three lowest MOs are simply the corresponding spherical harmonics evaluated at the angular positions of the carbon nuclei. The $L = 3$ functions split into $t_{2g}$ and $g_u$ as shown. Interestingly, the two components of the $L = 4$ level remain accidentally degenerate at the elementary level of HMO theory. Above $L = 4$, the various components mix strongly. Low-$L$ states have the lowest energies since they have the fewest number of nodes in the wavefunction. The molecular orbitals in C\textsubscript{60} provide a three-dimensional analogy to those found in the annulenes in two dimensions with respect to nodal structure.

The two lowest excited configurations are each fifteen-fold degenerate, $(h_u)^9(t_{1u})^1$ and $(h_u)^9(t_{1g})^1$. These configurations yield eight excited states, each of which is at least three-fold degenerate as shown in fig. 2. The symmetry is so high that among these only $T_{1u}$ is allowed in one-photon absorption from the ground state and only $H_g$ is allowed in two-photon absorption. $T_{1u}$ lies in the second configuration and it is likely that optically forbidden states resulting from the first configuration will lie below it even when more accurate calculations are performed.

The low-lying electronically forbidden degenerate states could undergo Jahn–Teller distortion and acquire some oscillator strength. In general, we expect that vibronic intensity borrowing interactions will be weak, because the electronic states are delocalized over many atoms, and the carbon framework is relatively rigid. There are only two $a_g$ vibrational normal modes in C\textsubscript{60}, and we would expect only modest Franck–Condon progressions in these modes in absorption and fluorescence for allowed transitions. Fluorescence will be depolarized, and photoselection effects absent, from states of either electronic or vibronic $T_{1u}$ symmetry. We conjecture that excited-state radiationless transitions should be relatively slow because excited-state geometries will be very similar to the ground-state geometry, and there are no high-frequency C–H accepting modes.

Planar aromatic hydrocarbons with high symmetry and many rings often have intensely allowed $\pi-\pi^*$ transitions with oscillator strengths of $\gtrsim 1$, and absorption coefficients $\varepsilon \approx 10^5 \text{ g/mol cm}$ [28]. Elementary Hückel theories indicate that maximum oscillator strengths scale with the size of the $\pi$-electron system. Fully allowed $A_g \rightarrow T_{1u}$ transitions in C\textsubscript{60} could be exceedingly strong. The $A_g \rightarrow T_{1u}$ transition in the second configuration lies at an excitation energy of $\approx -1.0\beta$. This is about the same Hückel excitation energy as predicted for anthracene, whose $S_1$ state lies in the near ultraviolet. This crude estimate ignores substantial shifts effected from interelectronic repulsion and configuration interaction. The high symmetry ensures that the electronic spectrum will be “molecule-like” with discrete, well separated transitions.

The high symmetry of C\textsubscript{60} also causes the expected infrared and Raman spectroscopy to be unusually simple. While there are 174 normal modes ($3N - 6$), the infrared spectrum should show only four fundamentals corresponding to the four three-fold degenerate $t_{1u}$ vibrations. The non-resonant spontaneous Raman spectrum should also have an interesting structure. The molecule has only two degrees of freedom that conserve $I_h$ symmetry. These motions are sphere breathing (symmetric bond stretching), and antisymmetric stretching of bonds between 6-MRs out of phase with bonds between 5- and 6-MRs. These $a_g$ motions, especially the antisymmetric mode, should be prominent in the spontaneous Raman spectrum, based upon experience with planar aromatic hydrocarbons. There are also $h_g$ modes that are allowed in the Raman spectrum. The relative displacements of carbon atoms in $a_g$, $t_{1u}$, and $h_g$ normal modes is simply given by the spherical harmonics $Y_{LM}$ for $L = 0$, 1, and 2.

5. Conclusion

Icosahedral C\textsubscript{60} appears to be the first example of a spherical aromatic molecule. The molecule is predicted to be stable, isolable, and capable of accepting up to twelve electrons in solution. The carbon hybridization is calculated to be about $\text{sp}^{0.05}\text{p}$ for the $\pi$ orbitals and $\text{sp}^{2.28}$ for the $\sigma$ system with approximately 90% of the resonance stabilization of an equivalent
planar graphite system. The electronic and vibrational spectra should be comparatively simple due to the high symmetry of the molecule.

References