# THEORETICAL STUDIES OF ICOSAHEDRAL $C_{60}$ AND SOME RELATED SPECIES

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There are many stable $C_{60}$ structures other than the icosahedral one proposed by Kroto, Heath, O'Brien, Curl and Smalley. They are related to each other by transformations involving the movement of two atoms. These transformations are thermally forbidden in the Woodward–Hoffmann sense (though photochemically allowed) and the observed $C_{60}$ mass peak is likely to arise from a mixture of isomers.

## 1. Introduction

The truncated-icosahedral $C_{60}$ molecule has recently been proposed as a likely candidate fragment for a $C_{60}$ peak in mass spectroscopic observations of vaporised graphite [1]. A remarkably stable cluster was found on laser irradiation of a graphite target and partial equilibration in a stream of helium, and Haymet [2] argued on the basis of a simple Hückel calculation [3] that the icosahedral $C_{60}$ molecule would indeed be likely to show such stability. This conclusion is supported by various SCF calculations [4]. Although many alternative structures may be proposed, only those with fully $sp^2$ hybridised carbon atoms would be able to benefit from a completely delocalised $\pi$ molecular orbital framework. The proposed icosahedral $C_{60}$ molecule consists of 12 pentagons and 20 hexagons, with the pentagons arranged at the icosahedral vertices. Haymet argues that this structure is the least strained arrangement possible of the hexagons and pentagons, and also reports a Hückel calculation which shows that it would have a large delocalisation energy.

We have found delocalisation energies of very similar magnitude for different arrangements of 12 pentagons and 20 hexagons forming closed, spheroidal molecules. Although all of these isomers have at least one pair of pentagons sharing an edge, some do not appear to be particularly strained. These results suggest that the $C_{60}$ mass peak is likely to be due to a mixture of isomers.

## 2. Alternative $C_{60}$ structures

We consider only spheroidal molecules of $sp^2$ hybridised carbon atoms with different arrangements of the hexagonal and pentagonal rings. A notional process for interchanging the positions of hexagons and pentagons is illustrated in fig. 1. Considered as a pericyclic *chemical* process the concerted shift of sigma bonds gives rise to a four-electron Hückel transition state [5]. Hence it is thermally forbidden, and since unactivated sigma bonds are broken it does not seem to be a likely fluxional mechanism. Nevertheless, we may formally apply this structural transformation to any of the bonds between two pentagons and continue in this way to generate many different species. To identify the resulting molecules unambiguously we

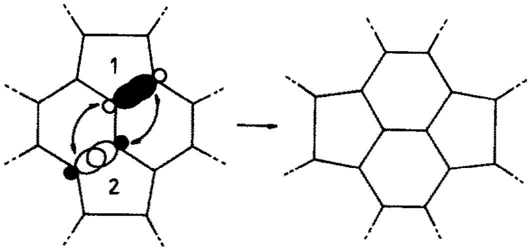

Fig. 1. Structural rearrangement relating isomers of $C_{60}$. The fragment shown includes pentagons 1 and 2 of the twelve pentagons present in the molecule (see fig. 2). The rearrangement formally requires the two sigma bonds shown to be broken, and new bonds to be formed as indicated by the arrows.

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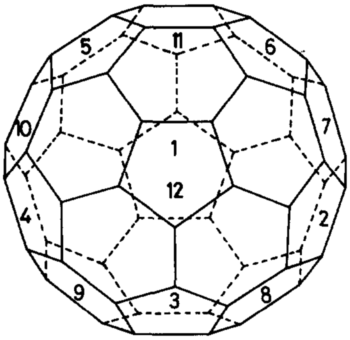

Fig. 2. Icosahedral $C_{60}$. The numbers label the pentagonal faces; faces 1–6 are at the front (solid edges) and faces 7–12 are at the back (dashed edges).

number the pentagonal rings as illustrated in fig. 2 and specify the bonds transformed by the pentagons they originally connect. For example, the molecule produced in fig. 1 is denoted (1,2). If we apply successive transformations to the (1,2), (10,12), (3,9), (6,11), (4,5) and (7,9) bonds we regain icosahedral symmetry, but the two types of bond have been partially interchanged. Unique structures are obtained only from the first three of these transformations, and correspond to the three calculations in table 1 immediately following the icosahedral $C_{60}$ result. If we apply successive transformations in a less symmetrical manner then various other structures are obtained which are probably more strained. For example, the "graphitene" structure suggested by Haymet may be reached from icosahedral $C_{60}$ by a series of six (1,2)-type shifts.

We have carried out Hückel calculations on some of these molecules with the assumption that the parameters $\alpha$ and $\beta$ are the same for all atoms or bonds. In spite of the deficiencies of this theory, this should provide an indication of the response of the frontier orbitals to the differences in geometry between the different species. The results of these calculations for a selection of $C_{60}$ molecules are given in table 1. All the delocalisation energies per atom ($D$) are substantially higher than that of benzene ($0.3333\beta$) and slightly lower than that of graphite ($0.5761\beta$) [6]. Hence it would appear that on the basis of the delocalisation energy criterion $C_{60}$ is likely to be a mixture of different isomers, although the extent to which these isomers are strained is very difficult to estimate. We find that the energies are significantly affected in the frontier-orbital region, and in particular that the HOMO–LUMO gap is much reduced in the less sym-

Table 1
Some alternative $C_{60}$ structures

| Bonds transformed | Point group | $\pi$-electron energy ($\beta$) | $D$ ($\beta$) |
|---|---|---|---|
| none | $I_h$ | 93.162 | 0.5527 |
| (1,2) | $C_{2v}$ | 92.937 | 0.5490 |
| (1,2)(10,12) | $D_{2h}$ | 92.710 | 0.5452 |
| (1,2)(10,12)(3,9) | $D_{2d}$ | 92.721 | 0.5454 |
| (1,2)(7,12) | $C_2$ | 92.715 | 0.5453 |
| (1,2)(11,12) | $C_2$ | 92.711 | 0.5452 |
| (1,2)(3,9) | $C_s$ | 92.866 | 0.5478 |
| (1,2)(3,8) | $C_2$ | 92.607 | 0.5435 |
| (1,2)(3,9)(7,8) | $C_3$ | 92.856 | 0.5476 |

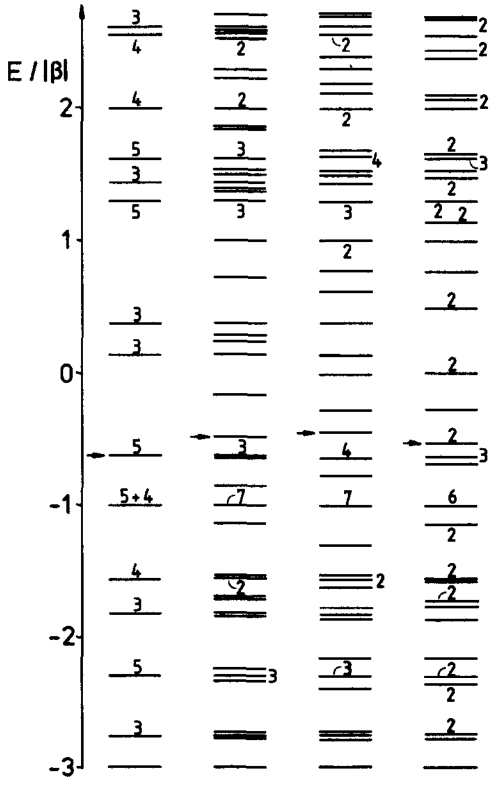

Fig. 3. Orbital energies for (left to right) icosahedral $C_{60}$ and the (1,2), (1,2)(10,12) and (1,2)(10,12)(3,9) isomers. The HOMO is marked with an arrow in each case. The numbers give the degeneracies of the levels.

Table 2
Net atom charges

| Bonds transformed | Range of atom charges |
|---|---|
| none | 0 (no variation) |
| (1,2) | −0.0196 to 0.0492 |
| (1,2)(10,12) | −0.0248 to 0.0476 |
| (1,2)(10,12)(3,9) | −0.0300 to 0.0531 |
| (1,2)(7,12) | −0.0266 to 0.0553 |
| (1,2)(11,12) | −0.0252 to 0.0579 |
| (1,2)(3,9) | −0.0368 to 0.0581 |
| (1,2)(3,8) | −0.0889 to 0.0490 |
| (1,2)(3,9)(7,8) | −0.0275 to 0.0353 |

metrical isomers. Fig. 3 shows the energy level diagrams for the $\pi$ orbitals of icosahedral $C_{60}$ and the next three structures of table 1.

We have also calculated the $\pi$-electron populations, $q_\mu$, and bond orders for these molecules. Simple Hückel theory overestimates the deviation of the $q_\mu$ from unity [7], but despite this deficiency we may take the $\pi$-electron populations as a qualitative measure of the $\pi$-electron polarization. The ranges observed for the net atom charges are given in table 2, and we note that they are generally small. This suggests that these species may be *chemically* stable with respect to attack by polar species. Hence we have both *thermodynamic* and *kinetic* criteria that these molecules may be formed under the conditions prevailing in the experiment.

## 3. Results of SCF calculations

Approximate SCF calculations were performed for the icosahedral structure using the method of Fenske et al. [8]. In this approach a Mulliken population analysis [9] is performed in each iteration and the resulting charge distribution is used to calculate the necessary matrix elements using a ligand-field type of approximation.

For the icosahedral $C_{60}$ molecule we find that the $\pi$ and $\sigma$ orbitals mix very little, and that the lowest energy virtual orbitals are the $\pi^*$ set. The bonding $\pi$ orbitals are generally the highest in energy of the occupied set, and all the $\pi$ orbitals lie in the order predicted by Hückel theory. The energy gap between the $h_u^\pi$ HOMO and the $t_{1u}^\pi$ LUMO is 5.04 eV, whilst the lowest-energy allowed electronic transition to a $t_{1g}^\pi$ orbital is found to have an energy of 7.31 eV. These results give us some confidence in the Hückel results for the other structures, where unfortunately we cannot easily perform better calculations because a geometry optimisation with a large number of independent parameters would be required.

We conclude that $C_{60}$ has a large number of isomeric structures in addition to the icosahedral structure proposed by Kroto et al. [1]. Many of these structures are likely to be nearly as stable as the icosahedral one; it is possible that one or more of them may be more stable. Because the transformation between the structures is a thermally forbidden process, they are unlikely to interconvert under the conditions of the experiment [1], so that the $C_{60}$ peak is likely to arise from a mixture of isomers.

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