

## A Prediction of the Structure of $C_{60}H_{36}$

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A proposed structure for  $C_{60}H_{36}$  incorporating four aromatic benzene rings has chiral  $T$  point group symmetry, involves less disruption of the parent fullerene skeleton, gives a better delocalisation energy, and is more closely compatible with experimental evidence than previous candidates; it is also analogous to the recently characterised  $C_{36}H_{36}$  'spheriphane' molecule.

As unsaturated molecules, fullerenes are susceptible to addition of hydrogen, fluorine and other functional groups. Partial hydrogenation of  $C_{60}$  to yield  $C_{60}H_{36}$ ,<sup>1</sup> fluorination giving a series of products  $C_{60}F_n$ ,<sup>2,3</sup> methylation,<sup>4</sup> addition of morpholine,<sup>5</sup> bromination<sup>6,7</sup> and other addition reactions<sup>8</sup> of  $C_{60}$  have been reported. Although characterisation of some of the compounds is incomplete, the experiments have already stimulated several attempts to predict molecular structures of  $C_{60}X_{60}$ <sup>9-12</sup> and  $C_{60}H_{36}$ <sup>12-14</sup> by methods ranging from *ab initio* SCF to density functional and empirical approaches. The present note is concerned with molecules of formula  $C_{60}H_{36}$ . The structures that have been considered for the hydrogenated fullerene  $C_{60}H_{36}$  have not always been the most plausible that could be imagined,\* and it seems that discussion of the factors influencing the probable structure of this molecule could provide a useful starting point for accurate calculation, and serve as a guide to experimental assignment.

Birch reduction of  $C_{60}$  under gentle conditions is reversible and, it is suggested, preserves the structural integrity of the carbon cage.<sup>1</sup> The formula  $C_{60}H_{36}$ , arrived at on the basis of mass-spectroscopic measurements, implies loss of 18 of the 30 double bonds of the  $C_{60}$  cage, and so determination of plausible candidate structures reduces to an investigation of the ways of distributing 12 double bonds over the 90 edges of the initially icosahedrally symmetric framework of sixty carbons. The procedure is mathematically equivalent to counting distributions of 36 H atoms over the 60 vertices with pairing of empty sites, but lends itself more easily to chemical intuition. The number of possible isomers is huge,<sup>17</sup> but many can be rejected on chemical grounds.

The criteria for stability that we propose to use are (i) electronic stability (a high  $\pi$  delocalisation energy) which will favour the more extensively conjugated structures, (ii) positioning of double bonds on the 30 edges *exo* to pentagons rather than on the 60 pentagon edges, which will contribute to electronic stability,<sup>16,18</sup> automatically ensures a degree of conjugation,<sup>†</sup> and also has the advantage of least movement from the  $C_{60}$  structure, (iii) minimum steric strain, which suggests to us that structures with some hydrogens on the inside surface of the cage can be ruled out, and also that relatively high symmetry and a 'geodesic' distribution of strain will be favoured. A less specific indicator of high symmetry is the fact

that a hydrocarbon of definite stoichiometry is produced in the experiment; if the hydrogens were all on one side of the cage then one might expect further reaction until the cage was uniformly covered (as happens in the bromination reaction<sup>7</sup>).

Unrestricted application of the delocalisation criterion would produce a structure of low symmetry, and the isomer of highest symmetry has the poorest delocalisation energy of all, as we will see, and so the criteria (i) and (ii) may lead to conflicting predictions. Given that exhaustive enumeration is not a practical possibility, our strategy is to generate candidates by selecting structures that satisfy each criterion separately.

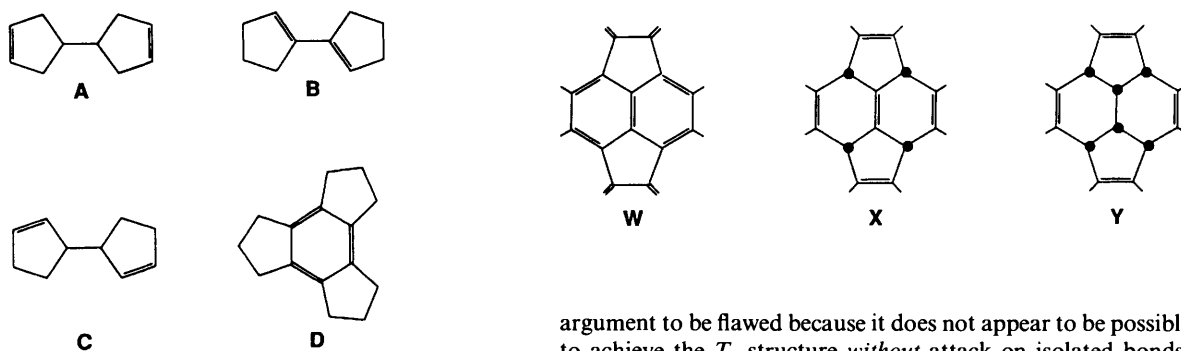
### Symmetry

The central concept we use is that of an orbit of a point group. An orbit is a set of equivalent points or objects transformed amongst themselves by the operations of the group. The number of distinct orbits of a finite group is strictly limited and they have been tabulated for most chemically important point groups. We follow a notation introduced earlier,<sup>19</sup> using  $O_n(G)$  to denote an orbit of size  $n$  in group  $G$ . Members of an orbit share a characteristic site symmetry related to that of the molecule as a whole by (No. of points in orbit)  $\times$  (order of site symmetry group) = (order of full point group). A given orbit with  $C_n$  or  $C_{nv}$  site symmetry may occur at most twice in a pseudospherical cluster, whereas orbits of  $C_s$ ,  $C_i$ ,  $C_1$  symmetry may occur in one, two or more copies. In  $I_h$ , for example, the possible orbits are  $O_{120}$ ,  $O_{60}$ ,  $O_{30}$ ,  $O_{20}$  and  $O_{12}$ , with site symmetries  $C_1$ ,  $C_s$ ,  $C_{2v}$ ,  $C_{3v}$  and  $C_{5v}$ , respectively. Since the site symmetry of a bond (single or double) must be  $C_{2v}$  or a subgroup, there is no arrangement of 12 double bonds in  $C_{60}H_{36}$  that preserves the full icosahedral symmetry. Isomers of  $C_{60}H_{36}$  that retain the basic carbon topology of  $C_{60}$  therefore correspond to decorations of the original icosahedron that belong to subgroups of  $I_h$ . The 60 pentagon-hexagon edges of  $C_{60}$  span  $O_{60}(I_h)$ ; the 30 hexagon-hexagon edges span  $O_{30}(I_h)$ .

Enumeration of structures reduces to following the fate of the sets of edges of the truncated icosahedron as we successively remove symmetry elements of  $I_h$ . A general fullerene may belong to one of 28 point groups<sup>20</sup> and a fullerene derivative to one of the 36 subgroups of these 28. Of the 22 subgroups of  $I_h$ , 15 have orbits compatible with sets of 12 bonds. A hydrogenated fullerene with 12 pairs of adjacent empty sites must therefore belong to one of  $T_h$ ,  $T$ ,  $D_{3d}$ ,  $D_{2h}$ ,  $D_3$ ,  $C_{3v}$ ,  $S_6$ ,  $D_2$ ,  $C_{2h}$ ,  $C_{2v}$ ,  $C_3$ ,  $C_2$ ,  $C_s$ ,  $C_i$  or  $C_1$ . At first, in the higher subgroups, the 12 bonds are equivalent and form a single orbit. As the order of the group falls the 12 split into smaller orbits 6 + 6, 6 + 3 + 3, 3 + 3 + 3 + 3, etc. until eventually in  $C_1$  they span twelve orbits 1 + 1 + 1 + ... Fortunately, the chemically interesting structures occur in the higher reaches of this complicated branching diagram.

\* The structure that we believe to be the most stable isomer of  $C_{60}H_{36}$ ,<sup>4</sup> is proposed in ref. 15 and was apparently first suggested in print by Taylor in ref. 16.

† The set of 30 *exo* bonds has the topology of the edges of a dodecahedron. Selection of 12 edges from the 30, each of which has 4 neighbours, forces at least two adjacencies of selected edges, corresponding to conjugated bonds on the  $C_{60}$  surface.



The highest subgroup of  $I_h$  compatible with equivalence of 12 double bonds is the centrosymmetric tetrahedral group  $T_h$ . In this group the orbits of  $I_h$  split as  $O_{60}(I_h) \rightarrow O_{12}(T_h) + 2O_{24}(T_h)$ ,  $O_{30}(I_h) \rightarrow O_6(T_h) + O_{24}(T_h)$  and  $O_6(T_h)$  can occur at most once. Therefore in this symmetry a structure with 12 double bonds is possible, but they must lie in pentagonal rings. The orbit  $O_{12}(T_h)$  can be realised as 6 copies of motif A in the isomer 1 (Fig. 1). It is the most symmetrical arrangement of one double bond per pentagon, suggested as the Birch reduction product by Smalley *et al.*,<sup>1</sup> and used as a starting point for optimisation in calculations.<sup>12-14</sup> It suffers from the unfavourable feature of double bonds in pentagons and has 12 isolated (non-conjugated)  $\pi$ -bonds and therefore a Hückel  $\pi$  energy of only  $24\alpha + 24\beta$ . Moreover, the structure was based on the premise that Birch reduction does not take place at isolated double bonds, and reduction therefore ceases once an array of isolated double bonds is achieved. We believe this

argument to be flawed because it does not appear to be possible to achieve the  $T_h$  structure *without* attack on isolated bonds.  $C_{60}$  comprises six pycnolene units (W), Birch reduction of which will produce X but not Y and so  $C_{60}H_{24}$  but not  $C_{60}H_{36}$ ; there appears to be no example of such a reduction in planar chemistry.<sup>21</sup> Isolated double bonds can be reduced under more drastic conditions, *e.g.*, using lithium in alkylamines<sup>21</sup> and it is possible that on the curved surface of  $C_{60}$  the normal Birch conditions (sodium in ammonia) will reduce isolated double bonds, but then reaction should not cease at  $C_{60}H_{36}$  unless this yields a particularly stable structure, such as that which we propose in this paper. Evidence that the structure has some special stability comes from fluorination, where even through the mechanism is probably quite different, the structures  $C_{60}F_{36}$ ,  $C_{60}F_{36}O$  (and  $C_{60}F_{18}$  and  $C_{60}F_{18}O$ ) can be dominant in the mass spectrum under some conditions;<sup>22</sup> it is significant in relation to the latter two species that  $C_{60}H_{18}$  was also observed under the Birch conditions.<sup>1</sup>

Equivalence of 12 double bonds is, however, also possible in the pure rotational group  $T$ . The orbits of  $I_h$  split as  $O_{60}(I_h) \rightarrow 5O_{12}(T)$ ,  $O_{30}(I_h) \rightarrow O_6(T) + 2O_{12}(T)$  [and again  $O_6(T)$  may occur at most once] and so 12 equivalent

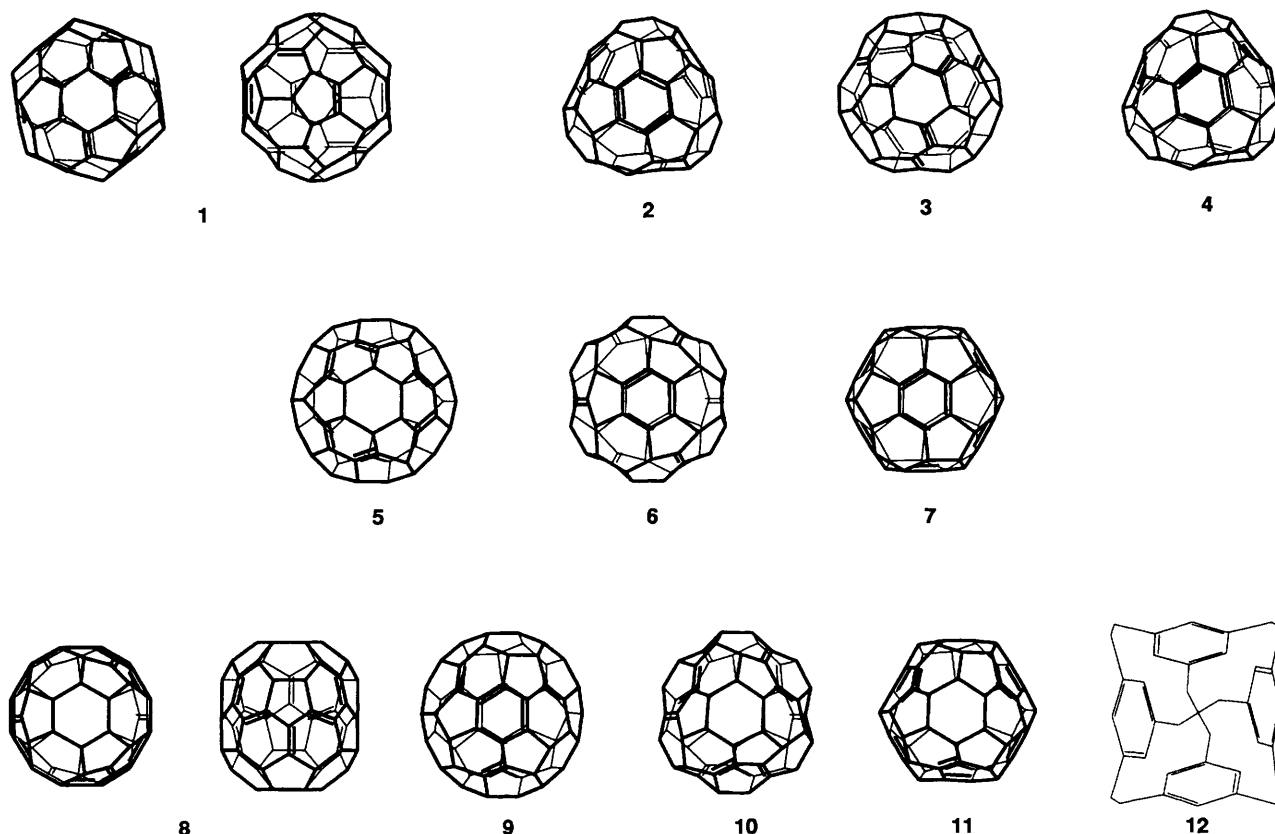


Fig. 1 Cage structures for  $C_{60}H_{36}$  (1-11) and for  $C_{36}H_{36}$  (12). The symmetries and properties of 1-11 are discussed in the text where it is concluded that 4 is the best candidate for  $C_{60}H_{36}$  on a combination of steric and electronic arguments.

bonds are present in structures containing 6 copies of motif **B** (isomer **2**), **C** (isomer **3**) or **D** (isomer **4**). Isomers **2** and **3** again suffer from the presence of double bonds in pentagons. Isomer **4**, on the other hand, has all pentagons constructed with single-bond edges and has 4 benzenoid hexagons, one on each face of the (twisted) master tetrahedron. It implies the least re-adjustment of carbon-carbon bond lengths as all its formal double bonds are short in  $C_{60}$ , and 60 of its 78 formal single bonds are long in  $C_{60}$ . This isomer is dissymmetric (as are **2** and **3**) and at equilibrium would be in one of two enantiomeric forms. The possibility of their resolution would depend on details of the potential hypersurface. Structure **4** is clearly a strong candidate for  $C_{60}H_{36}$  or  $C_{60}F_{36}$ . It has a total  $\pi$  energy of  $24\alpha + 32\beta$  and is therefore stabilised with respect to **1** by a delocalisation energy of  $8\beta$ .

The carbon atoms in **4** fall into 5 sets of 12 and the substituents are in 3 sets of 12, giving characteristic  $^{13}C$  and  $^1H$  (or  $^{19}F$ ) NMR signatures with equal peak heights if relaxation and other effects can be ignored. The vibrational representation for the cluster is  $\Gamma_{vib} = 24A + 24E + 70T$  giving 70 IR-active and 94 Raman-active fundamentals (24 polarised), with 70 coincidences. In contrast, the  $T_h$  isomer (**1**) would have 3 distinct  $^{13}C$  chemical shifts (in the ratio 24:24:12) and 2  $^1H$  shifts (in the ratio 24:12), a vibrational representation  $\Gamma_{vib} = 13A_g + 13E_g + 34T_g + 11A_u + 11E_u + 36T_u$ , giving 36 IR-active and 60 Raman-active fundamentals (13 polarised), obeying a rule of mutual exclusion. These spectroscopic predictions are confronted with experimental data in a later section of the present paper.

The process of descent in symmetry can be continued. Subgroups  $D_{5d}$  and  $D_5$  are incompatible with 12 double bonds. In  $D_{3d}$  the set of 30 hexagon-hexagon edges splits  $30 \rightarrow 12 + 6 + 6 + 6$  and 4 distinct structures are possible (**5**, **6**, **7** and **8**). Reduction to  $D_3$  symmetry splits the bonds into 5 sets of 6 and 3 new chiral structures are found (**9**, **10** and **11**). If the pentagon criterion is relaxed these isomer counts rise to 10 ( $D_{3d}$ ) and 33 ( $D_3$ ). None of the  $D_3$  or  $D_{3d}$  structures has the benzene rings of the best  $T$  isomer, but one (**8**) has all bonds involved in a conjugated girdle that runs around its equator ( $E_\pi = 24\alpha + 29.5875\beta$ ).

### Conjugation

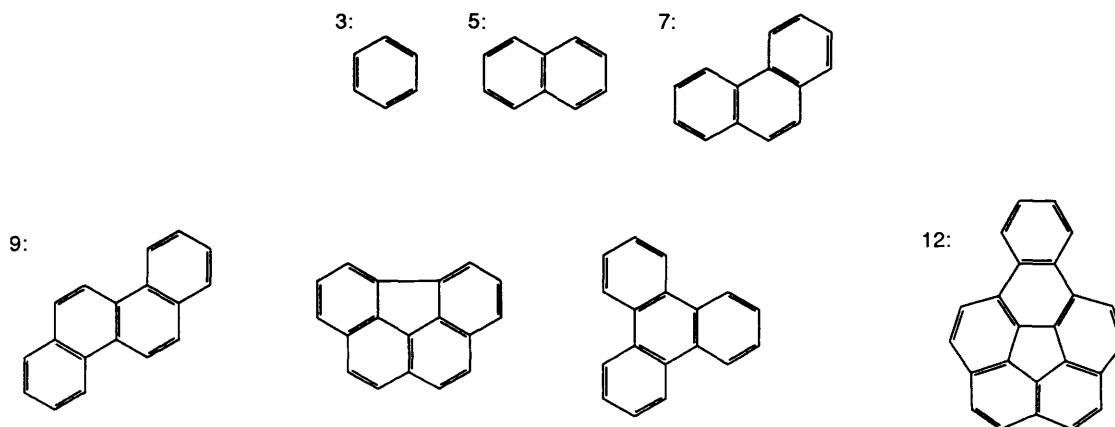
Even within the *exo*-pentagonal criterion (ii), a huge variety of conjugated structures could be postulated for  $C_{60}H_{36}$ , and in general their delocalisation energy will reflect the degree of

clustering of the double bonds on the fullerene surface. If attention is confined to structures in which every double bond is part of at least one benzenoid hexagon, then the possibilities are limited to (see Fig. 2) (a) four benzene rings ( $3 + 3 + 3 + 3 = 12$  double bonds), (b) one naphthalene and one phenanthrene fragment ( $5 + 7 = 12$ ), (c) one benzene and one chrysene fragment ( $3 + 9 = 12$ ), (d) one benzene and one triphenylene fragment ( $3 + 9 = 12$ ), (e) one benzene and one benzo[*g,h,i*]-fluoranthene fragment ( $3 + 9 = 12$ ), and (f) a single benzo[*a*]corannulene fragment (12 double bonds). In cases (a) to (e) the fragment ring systems could either be isolated or joined by biphenyl-type linkages. With isolated rings the Hückel  $\pi$  energies are (a)  $E_\pi = 24\alpha + 32\beta$ , (b)  $E_\pi = 24\alpha + 33.1315\beta$ , (c)  $E_\pi = 24\alpha + 33.1922\beta$ , (d)  $E_\pi = 24\alpha + 33.2745\beta$ , (e)  $E_\pi = 24\alpha + 33.6042\beta$ , and (f)  $E_\pi = 24\alpha + 34.5389\beta$ . By linking the ring systems the  $\pi$  energies can be increased to at most (a)  $E_\pi = 24\alpha + 33.5298\beta$ , (b)  $E_\pi = 24\alpha + 33.9532\beta$ , (c)  $E_\pi = 24\alpha + 34.0117\beta$ , (d)  $E_\pi = 24\alpha + 33.6611\beta$  and (e)  $E_\pi = 24\alpha + 34.4152\beta$ . However, in all cases (b) to (f) the possible structures have very low symmetries ( $C_{2v}$  or lower) and so suffer from the disadvantage of large 'bald' patches which seem ripe for further hydrogenation. In case (a) the most symmetrical possibility is the  $T$  isomer **4**.

Without explicit *ab initio* or semiempirical calculations on all possible isomeric structures it is not possible to give a definitive prediction, but none of the more highly conjugated candidates seems to achieve the required compromise between steric and electronic factors apparent in structure **4**.

### Spectroscopic evidence

Hydrogenation of fullerite (a mixture of  $C_{60}$  and  $C_{70}$ ) in a recent study<sup>23</sup> using radical conditions gave products that included  $C_{60}H_{36}$  (identified by mass spectrometry). Whilst this method of production is potentially cleaner than the Birch reduction, in that there is no possibility of amination of  $C_{60}$ , the use of a mixed starting material makes characterisation problematic. A  $^{13}C$  NMR spectrum of the product mixture was recorded by Attalla *et al.*<sup>23</sup> and is roughly consistent with a formula  $C_{60}H_{36}$  (it integrates to  $C_{60}H_{38}$  if intensity variations are ignored) and shows four signals in the  $sp^3$  region [31, 38 (weak), 44 and 49 ppm] and at least two intense signals in the  $sp^2$  region (134 and 138 ppm, with a broad, weak peak at 128 ppm). If the two weak peaks are attributed to other components of the mixture (*e.g.*, hydrogenated  $C_{70}$ , other  $C_{60}H_x$  isomers) then the main part of



**Fig. 2** Polycyclic benzenoid fragments on the surface of  $C_{60}$ . The systems of 1, 2, 3, 4 and 6 hexagons account for 3, 5, 7, 9 and 12 double bonds, respectively. The patterns of hexagons shown are those with formal double bonds *exo* to pentagonal rings and compatible with the requirement that all 12 double bonds of  $C_{60}H_{36}$  appear in a conjugated hexagon. Thus, a 5-ring system is disallowed as it would leave too few bonds to form a separate benzene ring. Linking of the smaller fragments by formal single bonds to form larger conjugated systems is allowed.

the spectrum is consistent in number and position of peaks with the *T* isomer **4**. The authors of ref. 23 note the presence of three strong CH stretching absorptions in the IR spectrum of the product; this is again consistent with the presence of three equivalent sets of CH bonds in **4**. Other proposals made in ref. 23 would produce many more NMR and IR peaks than are observed. We conclude that the hypothesis of a chiral *T* isomer is compatible with the limited available experimental evidence. It would be interesting to see the results of a repeat experiment in which pure C<sub>60</sub> was the starting material.

### Conclusions

A search of both highly symmetric and highly conjugated systems yields one especially suitable candidate for C<sub>60</sub>H<sub>36</sub>. The chiral *T* structure has a delocalisation energy of  $8\beta$ , compared with a theoretical maximum of  $10.5389\beta$  and a minimum of zero, and is symmetric under 12 operations, the maximum for a conjugated structure. It is also interesting to note that the same disposition of benzene rings occurs in the molecule C<sub>36</sub>H<sub>36</sub> (**12**) recently characterised by workers at the University of Bonn.<sup>24</sup> This 'spheriphane' has 4 benzene rings, each one linked by (-CH<sub>2</sub>CH<sub>2</sub>-) chains at 1, 3, 5 positions to the other three. It can be imagined to be constructed from **4** by removal of 24 of the saturated carbon sites. It has the same Hückel  $\pi$  energy as **4**, though the elimination of most of the saturated rings allows **12** to achieve full *T<sub>d</sub>* symmetry, so that **12** is achiral where **4** is not, and has two <sup>13</sup>C and two <sup>1</sup>H NMR peaks<sup>24</sup> where **4** has five and three, respectively.

Another structural analogy can be drawn between isomer **4** of C<sub>60</sub>H<sub>36</sub> and the hexasubstituted organometallic compounds of C<sub>60</sub> {e.g.<sup>7</sup> [(Et<sub>3</sub>P)<sub>2</sub>Pt]<sub>6</sub>C<sub>60</sub> and [(Et<sub>3</sub>P)<sub>2</sub>Pd]<sub>6</sub>C<sub>60</sub>}. In these molecules addition of six metals in  $\eta^2$  fashion removes an octahedral array of six formal double bonds from C<sub>60</sub> and leaves an aromatic<sup>16,25</sup>  $\pi$  system consisting of 8 benzene rings in a cubic array, each ring connected to three others by single bonds at 1, 3, 5 positions. The same pattern of rings would exist in a *T<sub>h</sub>* isomer of C<sub>60</sub>H<sub>12</sub>. In the latter case, saturation of rings on alternate vertices of the cube would lead to one of the two *T* enantiomers of **4**. This purely formal analysis may give a clue to one mechanism of hydrogenation, as it suggests that the reaction is driven by progressive aromatisation of the initially non-aromatic C<sub>60</sub> cage.<sup>25</sup>

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