# $C_{60}Br_{24}$ as a chemical illustration of graph theoretical independence

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**If it is assumed that the final product of bromination of $C_{60}$ will obey two rules, (i) that no two $sp^3$ carbons may be adjacent and (ii) that the molecule must have a closed $\pi$ shell, the experimental $T_h$ structure of $C_{60}Br_{24}$ is uniquely selected from 300, 436, 595, 453, 640 possibilities.**

Predictive understanding of fullerene chemistry is hampered by the huge numbers of addition patterns that are compatible with a typical stoichiometry. The formula $C_{60}Br_{24}$, for example, corresponds to 300, 436, 595, 435, 640 distinct decorations of the normal $C_{60}$ cage,[1,2] whereas experiment yields just one isomer, well characterized by X-ray crystallography, which is of $T_h$ symmetry.[3] Theoretical rationalisation of observed structures by brute-force evaluation of energies of all isomers is clearly unfeasible. A more useful rôle for theory is the development and evaluation of rules of thumb to cut this combinatorial explosion down to a manageable number of candidates for more detailed consideration.[4,5] The present communication shows that in the case of $C_{60}Br_{24}$, rigorous application of two simple rules based on chemical intuition leads to precisely the experimental addition pattern. The graph-theoretical concept of independence used in this calculation is expected to have many more applications in chemistry. The Graffiti program has made a number of conjectures on independence numbers of fullerenes, for example.[6]

For a graph of $n$ vertices, the independence number[7] $m$ can be defined as follows. Colour the vertices of the graph black or white at will, subject only to the proviso that no two black vertices may be adjacent. $m$ is then the maximum size of the set of black vertices over all such colourings. Any set of $m$ vertices satisfying this black–black exclusion rule is called a *maximum independent* set. In general a graph will support many such sets. The relevance of independence numbers to problems of fullerene chemical isomerism is straightforward: if a bulky group $X$ on a given site of $C_n$ blocks further addition at all nearest neighbour sites, then a sequential process of addition must stop at $C_nX_m$ if not before. Given the fully eclipsed geometry of *exo* addition to $C_{60}$, a steric constraint of this nature is plausible for Br, $CH_3$ and other large addends.

Icosahedral $C_{60}$ has independence number 24. The proof is as follows. The 12 pentagons of $C_{60}$ include all 60 vertices exactly once. A given pentagon can support at most two black vertices without infringement of the neighbour rule and so $m \leqslant 24$. The existence of at least one such pattern with 24 vertices forming an independent set (Fig. 1) shows that the equality holds and so $m = 24$.

The *stoichiometry* $C_{60}Br_{24}$ for the endpoint of bromination of [60]fullerene would thus be predicted by a rule such as Rule (i): addition of a bromine atom to a site in $C_{60}$ blocks further addition to the three neighbouring sites.

However, the *pattern* of bromine atoms is not fixed by this rule. Enumeration of all possible maximum independent sets yields 1085 distinct possibilities, classified by point group in Table 1. This count was made by assigning a Br pair to one diagonal of each pentagon and then making a depth-first search of the tree of $5^{12}$ possibilities to exclude Br adjacencies. The 126 715 survivors of this procedure were then reduced to the above count by application of 120 projection operators, one for each operation of $I_h$.

A further restriction on likely addition patterns is imposed by electronic structure. Initially, the 60 $\pi$ electrons of $C_{60}$ occupy 30 molecular orbitals distributed over the 90 edges of the molecular graph. Addition of each Br removes a $\pi$ electron from the count and cuts out one vertex and three edges from the graph. After successive additions, the molecule has several separate $\pi$ systems, corresponding to disjoint subgraphs. If the final product is not to be a multiple radical, the addition pattern should have an overall closed-shell $\pi$ structure with all electrons of each subgraph paired up in orbitals corresponding to positive eigenvalues of the local adjacency matrix. Barring energetically unlikely zwitterionic states, the pattern should therefore obey Rule (ii): each separate $\pi$ system in the addition pattern should have a closed $\pi$ shell.

A weaker condition, implied by Rule (ii), is that each subgraph should have an even number of vertices. Any configur-

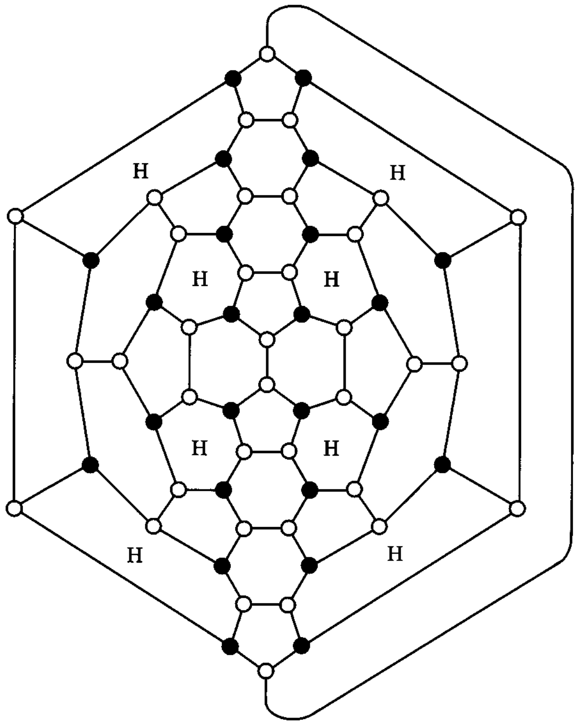

**Fig. 1** A maximum independent set for $C_{60}$. At most 24 vertices of the cage can be coloured black without producing black–black adjacencies. The particular set shown corresponds to the tetrahedrally symmetric experimental structure of $C_{60}Br_{24}$ (filled circles represent brominated and empty circles bare carbon atoms and 'H' labels a tribrominated hexagonal ring).

**Table 1** Possible symmetries of isomers of $C_{60}Br_{24}$ resulting from addition to a topologically unchanged $I_h$ $C_{60}$ cage. Of the 22 subgroups of $I_h$, 15 are accessible when no neighbour restrictions are imposed, eight if the pattern must be a maximum independent set and just one if the pattern must be both a maximum independent set and closed-shell.

| $H^a$ | $\lvert H\rvert$ | $N_t{}^b$ | $N_i$ | $N_{ii}$ |
|---|---|---|---|---|
| $T_h$ | 24 | 2 | 1 | 1 |
| $D_{3d}$ | 12 | 10 | 0 | 0 |
| $T$ | 12 | 4 | 1 | 0 |
| $D_{2h}$ | 8 | 21 | 0 | 0 |
| $S_6$ | 6 | 98 | 3 | 0 |
| $C_{3v}$ | 6 | 212 | 0 | 0 |
| $D_3$ | 6 | 100 | 1 | 0 |
| $C_{2h}$ | 4 | 2 460 | 0 | 0 |
| $C_{2v}$ | 4 | 5 044 | 0 | 0 |
| $D_2$ | 4 | 822 | 0 | 0 |
| $C_3$ | 3 | 31 280 | 17 | 0 |
| $C_i$ | 2 | 1 440 284 | 5 | 0 |
| $C_s$ | 2 | 43 090 979 | 0 | 0 |
| $C_2$ | 2 | 21 618 198 | 20 | 0 |
| $C_1$ | 1 | 300 436 529 264 126 | 1 037 | 0 |
| Total | | 300 436 595 453 640 | 1 085 | 1 |

[a] For each subgroup $H$ of order $\lvert H\rvert$, $N_t$ is the total count without restriction, $N_i$ the count of independent sets and $N_{ii}$ the number of such sets obeying Rule (ii). Only one member of each enantiomeric pair is included in each count. [b] The counts $N_t$ are taken from ref. 1 and the total for this column agrees with the number of distinct positional isomers counted without separation into symmetry groups in ref. 2.

ation of Br atoms that traps a single carbon atom or an allylic triplet of atoms is ruled out, for example. It is possible to envisage even-carbon patches with open shells, but it happens that these do not occur in the present problem. In fact, an even weaker form of Rule (ii)—that no final pattern should include an isolated carbon atom—is sufficient in the present case.

Application of the even-subgraph form of the rule to the 1085 maximum independent sets produces a startlingly simple result. Only *one* pattern, the experimentally observed $T_h$ structure, is compatible with both (i) and (ii). This structure has 18 isolated double bonds, one in each pentagon and six in an octahedral set of hexagon–hexagon edges and self-evidently a closed shell. Thus just two simple restrictions are sufficient to reduce an apparently intractably large set of isomeric possibilities to a unique solution.

The fully localised nature of the π bonding in the favoured $T_h$ structure is in fact an inevitable consequence of Rule (ii). This can be proved as follows. Let $a_i$ be the number of bare carbons adjacent to exactly $i$ brominated sites of a maximum independent set. Counting bare carbons in $C_{60}Br_{24}$ yields eqn. (1), where

$$a_1 + a_2 + a_3 = 36 \qquad (1)$$

$a_0$ must be zero if the set is maximum, otherwise extra bromine atoms could be added without breaking Rule (i). Counting the edges in $C_{60}Br_{24}$ emanating from bare carbon sites yields eqn. (2). Now, from Rule (ii), isolated bare carbons are

$$a_1 + 2a_2 + 3a_3 = 72 \qquad (2)$$

forbidden and $a_3 = 0$. Hence, $a_1 = 0$ and $a_2 = 36$ and bare carbons occur in 18 localised double-bond pairs. [The number 18 occurs naturally here, as the independence number of the 90-vertex edge-dual (line graph) of $C_{60}$ under the assumption that each included edge excludes all its first and second neighbours.] Once one edge of $C_{60}$ is fixed as a double bond, the extension of the solution to the rest of the ball turns out to be unique (up to the five settings of $T_h$ in $I_h$), as the explicit construction given above shows.

Another feature of the favoured structure also relates to

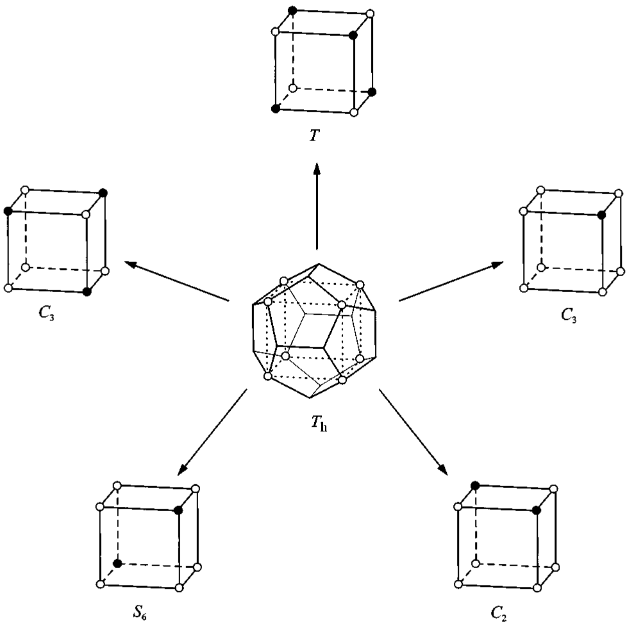

**Fig. 2** A family of isomers of $C_{60}Br_{24}$ related by rotation of hexagons. The central figure shows the dodecahedral configuration of the 20 hexagons of $C_{60}$, with unfilled circles picking out the eight disjoint tribrominated rings of the experimental structure of $C_{60}Br_{24}$ (Fig. 1). Rotated hexagons in the derived isomers are shown as filled circles.

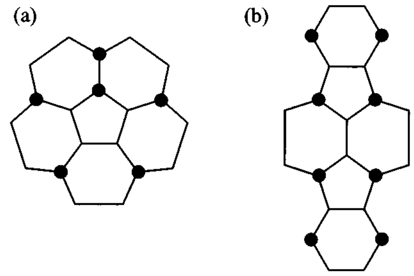

**Fig. 3** Patterns of brominated sites in the experimental[8] structures of $C_{60}Br_6$ and $C_{60}Br_8$

independence arguments. The 20 hexagonal rings of $C_{60}$ are connected to each other in the same way as the vertices of a dodecahedron. Five cubic subsets of 8 disjoint vertices can be found within a dodecahedron (8 is the independence number) and inspection of Fig. 1 shows that the eight hexagons corresponding to one such set share a specific property: they are 1,3,5-brominated and together they account for the 24 bromine addends.

Isomers with this ‘spanning’ property are rare and all can be derived from the $T_h$ pattern by a sequence of 1,3,5→2,4,6 ‘rotations’ of the disjoint hexagons. At most four of the hexagons can be rotated simultaneously, as hexagons on adjacent vertices of the cube may not rotate together (Br adjacencies would be produced) and the cube has independence number 4. Fig. 2 shows the complete family of five ‘rotated’ isomers derived from $T_h$ $C_{60}Br_{24}$. Each rotation isolates three bare carbon sites and so all five of these isomers violate Rule (ii).

Finally, we note that a combination of similar rules may be useful for lower derivatives. Bromination of [60]fullerene in the absence of solvent yields $C_{60}Br_{24}$, but when solutions of the fullerene are mixed with bromine, two less highly functionalised products can be formed. The initial hexabromo derivative disproportionates on being warmed in solution to an octabromo compound. The addition pattern in $C_{60}Br_6$ [Fig. 3(a)] has an $sp^3$–$sp^3$ adjacency which is thought to result from the final stage of a mechanism in which the sixth Br atom quenches a cyclopentadienyl radical that has been isolated by the first five.[8] In $C_{60}Br_6$, it seems, the closed-shell requirement overrides the steric repulsion of adjacent bromines at the final stage of addition.

It is significant however that this compound accepts more bromine and that in $C_{60}Br_8$ the addends have rearranged to a pattern of isolated $sp^3$ atoms, also with a closed $\pi$ shell. The pattern in the octabromo derivative [Fig. 3(b)] is a subset of the unique $T_h$ maximal independent set of $C_{60}Br_{24}$, though the pattern of 24 bromo positions is not a simple superposition of three octabromo sets.

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