

Stone–Wales Pyracylene Transformations of the Isomers of C₈₄

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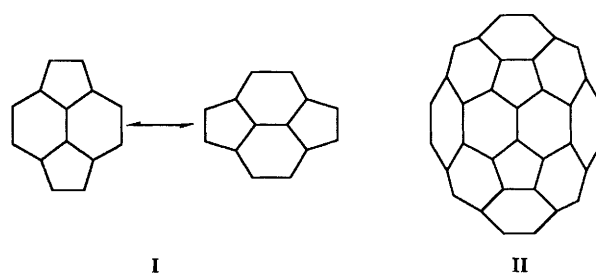
Under the Stone–Wales (pyracylene) transformation, the 24 isolated-pentagon isomers of C₈₄ fall into two disjoint families, each containing one leapfrog closed shell, suggesting that the experimental product will consist of a mixture of two isomers.

Of the many thousands of conceivable isomers of a general large fullerene C_n, few if any are expected to be stable. Stable fullerenes are thought to share three features: (1) isolation of pentagons; (2) high delocalisation energy and a significant HOMO–LUMO gap; (3) low steric strain.^{1,2} Structures obeying the isolated-pentagon criterion can be catalogued by the ring-spiral algorithm.³ A subset of isolated isomers have properly closed electronic shells, and these are specified by the geometric leapfrog and carbon cylinder constructions^{4,5} for certain ‘magic’ numbers. Other pseudo-closed electronic configurations with large HOMO–LUMO gaps can be identified by explicit Hückel calculations on isolated-pentagon isomers.⁶ Apart from the requirement for pentagon isolation, this elementary theory offers little guidance on treatment of the steric factor. Steric and electronic effects in fullerene stability may be in fine balance; it is found for example that C₇₆ adopts the electronically favoured *D*₂ structure,^{6,7} whereas C₇₈ seems to prefer the low steric strain of a C_{2v} isomer⁸ over the electronic stability of the closed-shell leapfrog *D*_{3h} isomer.⁹

Recently, Diederich *et al.*⁸ put forward a novel picture for stability in isomers of C₇₈, which it is suggested will have more general applicability. They suppose that isolated-pentagon isomers undergo facile interconversion by the Stone–Wales (pyracylene) transformation¹⁰ under the conditions of the graphite-arc synthesis, and that the number of isolable products reflects the number of closed families of interconverting isomers. Within each family only the most stable

isomer will then occur in the product. We have used group theory in conjunction with the ring-spiral algorithm to provide complete computer maps of the isomerisation pathways for fullerenes up to C₉₀, and report here our treatment of C₈₄ and its implications for experimental assignment.

The Stone–Wales transformation **I** effects pairwise interchange of pentagons and hexagons. It was first proposed¹⁰ as a mode of isomerisation of C₆₀ and has been used to generate a class of non-icosahedral structures for this cluster by Coulomb and Rassat.¹¹ Whilst isomers of C₆₀ are not found in experiment, the transformation can be carried out on any fullerene isomer with an appropriate four-ring motif. Transformations from one isolated-pentagon isomer to another *via* forms with abutting pentagons are possible, but since they pass through high-energy intermediates will have small rates



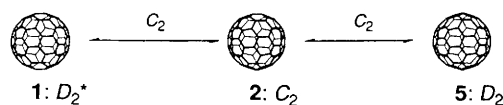


Fig. 1 The smaller family of isolated-pentagon isomers of C_{84} interconverted by the pyracylene transformation. Each isomer is labelled (at the bottom right) by point-group symmetry and by position in the complete listing of ref. 14. Each arrow represents a feasible transformation and is labelled by the site symmetry of the active SW patch. The number of patches of given symmetry in a structure is the ratio of the orders of molecular and site point groups. A star denotes a properly closed electronic shell.

compared with direct routes involving only isolated-pentagon isomers. The model of Diederich *et al.*,⁸ amounts to a contention that only these latter routes are fast enough to affect the outcome of the annealing process by which fullerenes are formed. In this spirit, we confine attention to interconversions between isomers with isolated pentagons. This is mathematically well-defined: we treat only patches where the central bond ('the SW bond') is embedded within the larger 12-ring patch **II**.

Some useful properties of the transformation are summarised below. A fullerene may have up to 30 SW bonds in overlapping copies of the small patch **I** (realised only in icosahedral C_{60}) but a maximum of 12 at the centres of larger patches **II** (realised, for example, in D_{6h} C_{84}). The SW bonds form sets of equivalent edges of the fullerene polyhedron (orbits of the point group¹²), each characterised by a site symmetry C_{2v} or one of its subgroups C_s , C_2 or C_1 . The site symmetry of a particular SW bond is preserved during the transformation centred on it. This places restrictions on the isomers that can be connected by the transformation. The number of orbits of SW bonds present in a given isomer is equal to the number of isomerisation pathways leading from it. A corollary is that isomers of high symmetry tend to be found at the ends of the branches on the isomerisation map whereas low-symmetry isomers tend to be at junction points. In fact, it is easily shown that isomers of the highest possible symmetries, I and I_h , are connected to *no* other isolated-pentagon isomer and so always form families of one member. Direct transformation in a single Stone–Wales step from one leapfrog isomer is impossible, and isomers formed by two or more iterations of the leapfrog construction are unconnected by the transformation to *any* other isomer. On the picture advanced in ref. 8, therefore, all double leapfrog and icosahedral isomers would be in principle experimentally isolable. As n grows very large the number of SW patches on a typical isomer dwindles, and so the number of single-member families grows. On the other hand, no isolated-pentagon isomers below C_{78} can contain a larger patch of type **II**. The transformation picture of fullerene stability has, therefore, a natural limit to its range of application.

A computer program was written to search for, and identify, all Stone–Wales patches on the full set of isolated-pentagon structures generated by the ring-spiral algorithm. Within the program all possible Stone–Wales transformations are carried out at the level of the adjacency matrix and maps of connections between isomers constructed. The maps generated in this way for C_{84} are shown in Figs. 1 and 2.

The maps summarise a great deal of information. Some interesting features are: (1) the 24 isomers fall into two disjoint sets, each containing one leapfrog isomer; (2) the smaller family in fact comprises two separate chiral pathways $D_2 \leftrightarrow C_2 \leftrightarrow D_2$ each linking one enantiomer of each of the three structures; (3) the larger family contains both chiral and achiral isomers so that any chiral structure within the family can be converted to its mirror image by a finite sequence of steps to the nearest achiral junction and back; (4) the T_d and D_{6h} closed-shell leapfrog and cylinder isomers (structures 20 and 24) are very closely related—they interconvert in just

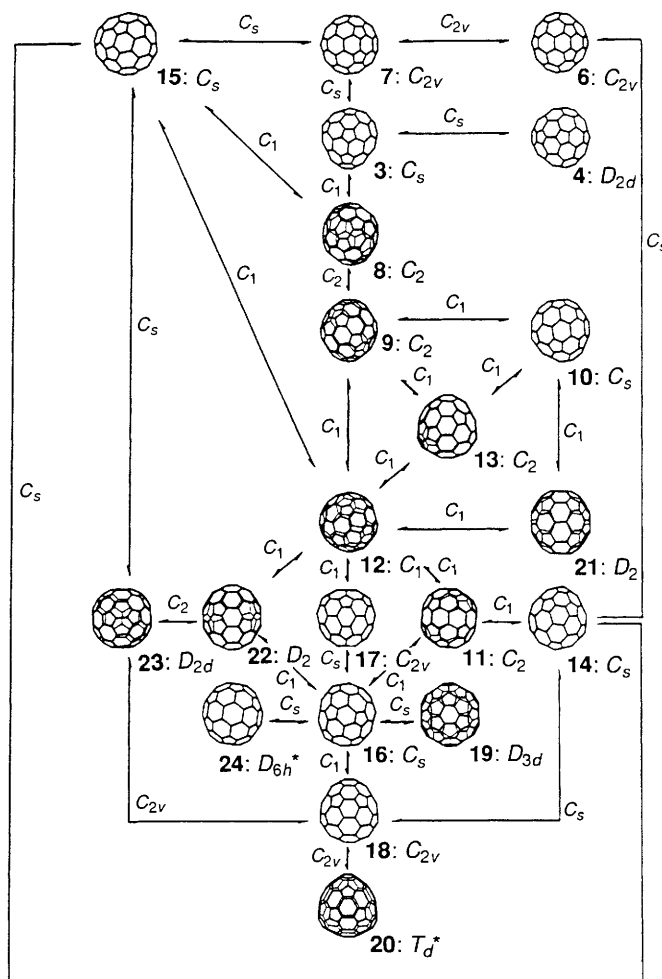


Fig. 2 The larger family of isolated-pentagon isomers of C_{84} interconverted by the pyracylene transformation. Notation and symbols as in Fig. 1.

three SW steps; (5) the fact that the maps are *closed* gives further informal reassurance of the correctness of the ring-spiral conjecture.³

The ^{13}C NMR spectrum of C_{84} has not yet been published but is reported to contain ~ 25 peaks.¹³ It is not possible to account for this number with a single isomer of the 24, and the possible mixtures leading to 25 peaks are quite limited.¹⁴ The most plausible suggestion in view of our calculated map would appear to be a mixture of two isomers, with one D_2 isomer (21 peaks¹⁵) form the small family and one, more symmetrical structure (*e.g.* T_d with 4 peaks)¹⁵ from the larger. This combination would be favoured on electronic grounds if the D_2 isomer were structure **1**, as both candidates would then have properly closed shells and satisfy the criterion of non-interconvertibility. Steric factors may favour the other D_2 isomer in the small family, and just one overlapping pair of resonances would allow the D_{6h} structure 24 from the larger family. In any event a mixture of isomers seems most likely.[†]

Automated computation of Stone–Wales maps will be of considerable utility in the unravelling of the structural puzzle for this and higher fullerenes. A comprehensive account of the maps for a range of cage sizes is in preparation.

[†] Note added in proof: In a presentation at the *First Italian Workshop on Fullerenes* (Bologna, February 1992), Professor Yohji Achiba showed a 31-line NMR spectrum of C_{84} consistent with a mixture of D_{2d} (23) and D_2 (5) isomers, *i.e.* one from each SW family.

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