Dual Graphs and Retrosynthetic Analysis of Regular Polyhedranes

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The dual graphs of Schlegel projections of regular carbon polyhedranes (tetrahedrane, cubane, dodecahedrane), when subjected to the sequential pruning of adjacent vertices of maximum degree, are shown to produce reasonable synthetic pathways to these complex polycyclic structures.

INTRODUCTION

One of the most exciting research fields of chemistry in the second half of the twentieth century has been – and will unquestionably be in the following years – the study of polyhedranes, *i.e.* the closed carbon cages corresponding to the regular or semi-regular polyhedra with vertices of a degree equal to three. Restraining ourselves to regular polyhedra (Platonic solids), the corresponding fully saturated polyhedranes have received the trivial names of tetrahedrane (C_4H_4, **1**), cubane (C_8H_8, **2**) and dodeca-hedrane ($C_{20}H_{20}$, **3**) (See Figure 1).

A convenient way of visualizing these thee-dimensional structures in the plane are the so-called Schlegel diagrams,[1] which are easily constructed for any polyhedrane by suppos-ing that it is resting on one of its faces and that it is viewed from below this particular face, in such a way that all the other faces lie within the one nearest to the observer. The Schlegel diagrams corresponding to the regular polyhedranes **4–6** are shown in Figure 2.
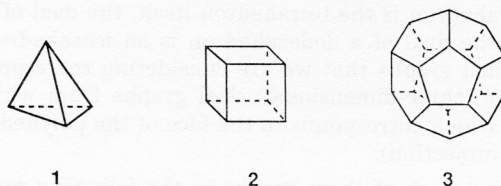

$$1 \qquad 2 \qquad 3$$

Figure 1. The fully saturated regular polyhedranes: tetrahedrane **1**, cubane **2** and dodecahedrane **3**.
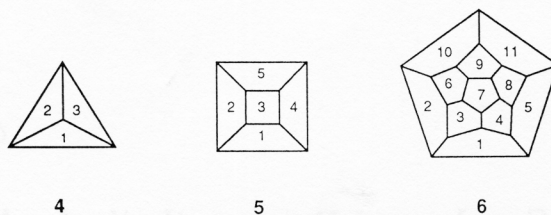
4   **5**   **6**

Figure 2. Schlegel diagrams of regular polyhedranes: tetrahedrane **4**, cubane **5** and dodecahedrane **6**.

These Schlegel diagrams, which allow the representation of polyhedranes in the form of fused polycyclic structures, have been shown to provide a simple way to the naming of polyhedranes according to IUPAC rules.[2,3] In the present paper, we wish to demonstrate that the graph-theoretical analysis of Schlegel diagrams offers a simple way to derive retrosynthetic trees for the parent structures which lead to precursors of minimum topological complexity.

RESULTS AND DISCUSSION

Dual Graphs and Pruning Algorithm.

According to Harary,[4] the dual graph G* of a given planar graph G is constructed by placing a vertex in each ring of G, and joining two vertices of G* by an edge when the corresponding rings of G have an edge in common (*i.e.*, when they are fused). Corey[5,6] has proposed that dual graphs of polycyclic fused ring systems can be used as a basis for their conversion into linear or almost linear precursors, by selecting for retrosynthetic disconnection the peripheral vertex of the dual of maximum connectivity (which corresponds to the peripheral ring with maximum number of fusion bonds), and repeating the process until the resulting dual is linear (*i.e.* it has no rings). We will presently see that a pruning algorithm of the dual graphs corresponding to the Schlegel projection of regular polyhedranes, based on a similar line of reasoning, leads to automatic generation of greatly simplified subgraphs, which are meaningful starting points for their retrosynthetic analysis.

We begin by constructing the dual graphs **7–9** of the Schlegel diagrams **4–6** of regular polyhedranes **1–3**, and by numbering their vertices in an arbitrary way (Figure 3). Note that the graphs generated in this way are not the dual graphs of the three-dimensional polyhedra, which are also Platonic solids: In effect, it is very easy to see that the dual of a tetrahedron is the tetrahedron itself, the dual of a cube is a regular octahedron, and that the dual of a dodecahedron is an icosahedron,, and *vice versa*. In fact, the *reduced* dual graphs that we are considering correspond to the Schlegel projections of *complete* (three-dimensional) dual graphs from which one vertex has been removed (vertex which corresponds to the face of the polyhedron which we have used for the Schlegel projection).

Next, we will submit each of these graphs to the following pruning algorithm: i) Eliminate a peripheral vertex of maximum degree (note that in the case of regular polyhedranes all of the initial peripheral vertices are equivalent and of the same degree). ii) Among the vertices connected to the one eliminated in the preceding step,

eliminate one of maximum connectivity. iii) Repeat step ii), until the resulting graph is a) (*i.e.* it has no rings) or b) disjoint (*i.e.*, it has two or more unconnected subgraphs). iv) If there is a choice in step ii), apply the procedure to each of the suitable vertices, except if they are equivalent by symmetry. This will produce for each graph a pruning tree, whose final points are again converted to the polycyclic form by performing the inverse dual transformation with the appropriate rings (*i.e.*, three-membered in the case of **7**, four-membered in the case of **8** and five-membered in the case of **9**). The resulting structures are then analyzed from the synthetic point of view, and compared to known or proposed routes to regular polyhedranes. In the following sections, we discuss the application of this analysis to each of the regular polyhedranes.

Tetrahedrane

Since the dual graph **7** corresponding to tetrahedrane **1** is simply a triangle, the elimination of a vertex converts it into the trivial linear graph **10** (See Figure 4). The inverse dual transformation of **10** suggests a synthetic pathway to tetrahedrane, which implies the formation of a bond between the positions 2 and 4 of a bicyclo[1.1.0]butane.

Whereas unsubstituted tetrahedrane is still unknown, a completely characterized (NMR, mass spectroscopy, X-ray) derivative, tetra-*tert*-butyltetrahedrane **11**, was synthesized by Maier and co-workers in 1978.[7] The synthetic path **11**, summarized in
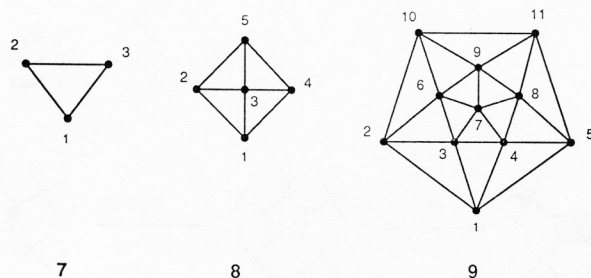

Figure 3. Dual graphs of Schlegel diagrams of regular polyhedranes: tetrahedrane **7**, cubane **8** and dodecahedrane **9**. The numbering of the vertices corresponds to the numbering of the faces shown in Figure 2.
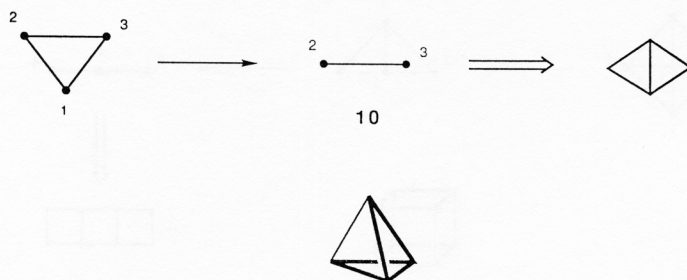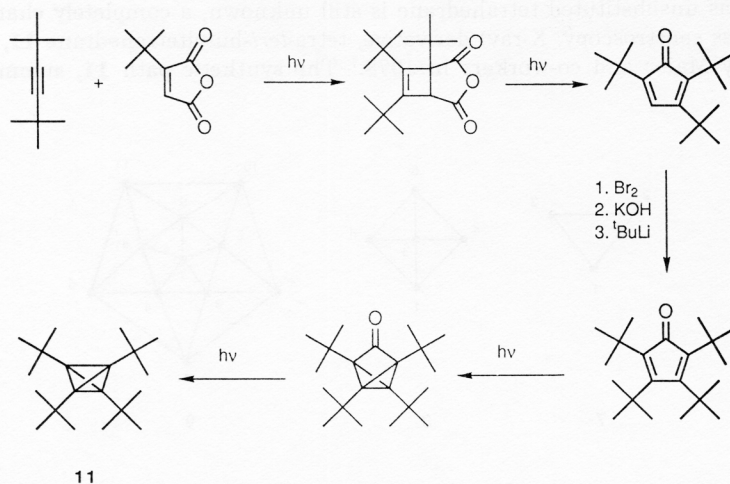

Figure 4. Sequential pruning and inverse dual transformation for tetrahedrane.

Scheme 1, exhibits as the key step the photochemical isomerization and decarbonylation of tetra-*tert*-butylcyclopentadienone, which leads to the key intermediate, a bicyclo-[1.1.0]buta-2,4-diyl biradical. It is, thus, clear that this successful route closely follows the path generated by the pruning algorithm. It is also interesting to note that several frustrated approaches to **1** are based on a similar strategy.[8]

Cubane

The application of the pruning algorithm to the dual graph **8** corresponding to cubane also results in a linear graph, **12**. The inverse dual transformation of **12** suggests a synthetic pathway relying on the formation of two bonds (3–8 and 4–7) within an *all-cis*-tricyclo[4.2.0.0^{2,5}]octane (See Figure 5).

Indeed, the first synthesis of cubane, achieved in the laboratory of P. E. Eaton in 1964,[9] closely follows the topological sequence that we have just described, since the tetracyclic framework is constructed in the key step through an intramolecular [2+2]

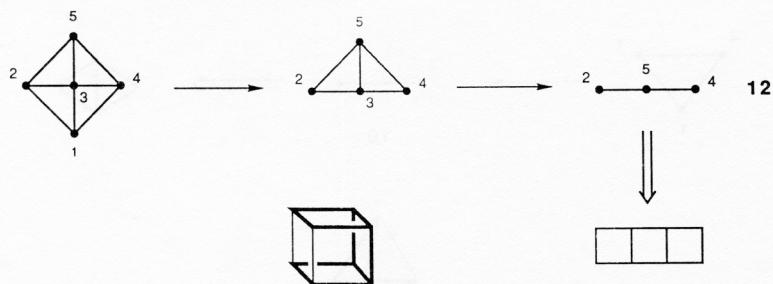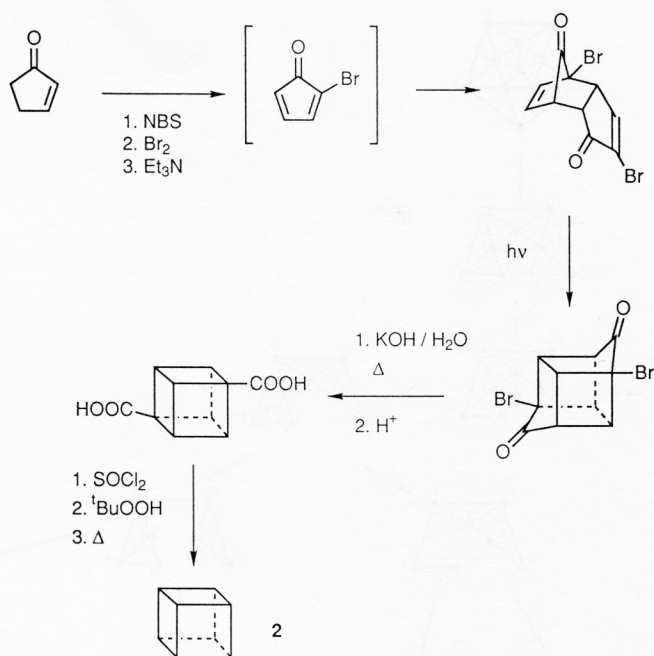Scheme 1: Synthesis of tetra-*tert*-butyltetrahedrane according to Maier (Ref. 7).

Figure 5. Sequentuial pruning and inverse dual transformation for cubane.

Scheme 2: Synthesis of cubane according to Eaton (Ref. 9).

photoaddition of an intermediate topologically equivalent (the ring size is adjusted in the following step by means of a double Favorskii rearrangement) to an *all-cis*-tricyclo-[4.2.0.0^{2,5}]octane (See Scheme 2). As in the case of tetrahedrane, other approaches to **2**[10] and its derivatives[11] are patterned along the same topological strategy.

Dodecahedrane

In the case of the dual graph **10** corresponding to dodecahedrane, the application of the pruning algorithm leads to generation of a relatively complex pruning tree with six different end points, corresponding to a linear graph **13** and to five **14–18** disjoint graphs (See Figure 6). The six corresponding intermediates resulting from inverse dual transformation **19–24** are shown in Figure 7.

When analyzing the synthetic routes to dodecahedrane suggested by the structures shown in Figure 7, one finds that three of them correspond to strategies which have been explored by several research groups.[12]

In effect, the pathway which has the linear hexaquinane **19** as key intermediate has been proposed and attempted (unsuccessfully) by McKervey.[13] On the other hand, the tetracyclic component of the dimerization suggested by **20** has the topology of the »Domino Diels-Alder adduct«, which is the starting material for the first total synthesis of dodecahedrane, achieved in the laboratory of L. A. Paquette.[14] The interesting disconnection suggested by structure **24**, which implies the making of six bonds between two identical, fused triquinane moieties, represents in fact the first suggested
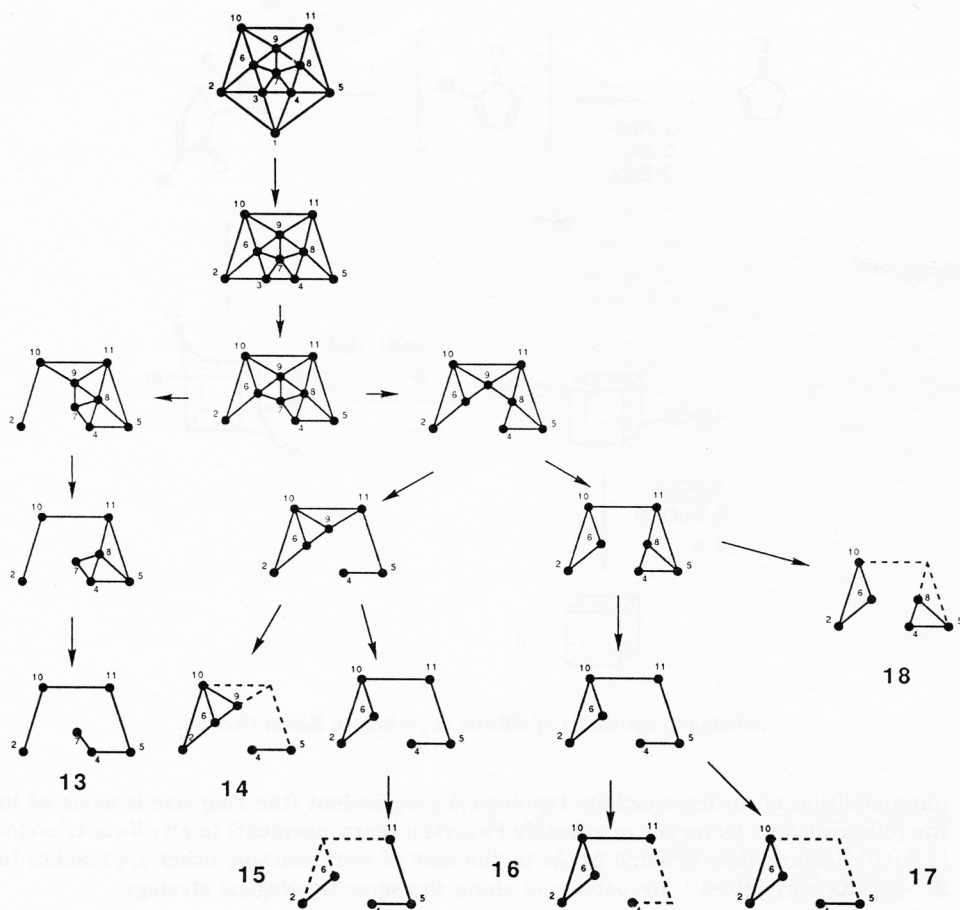
Figure 6. Pruning tree of dodecahedrane.

approach to **3**, and was proposed independently, in the early sixties, by Müller, Jacobson and Woodward.[15] This attractive (but so far unsuccessful) idea has been actively pursued by other research groups.[16] Finally, the strategies suggested by **21 22** and **23**, which imply the trimerization or tetramerization of two fused polycyclic subunits with isolated atoms or bonds, appear to be more difficult to implement, and no proposed routes to dodecahedrane conform to their topological strategy.

CONCLUSIONS

We have seen that the sequential pruning of the dual graphs of Schlegel projections of regular polyheranes generates a set of topologically simple structures, from which one can retrace the vast majority of synthetic approaches proposed for these complex cage structures. In the context of the present interest in large carbon cage
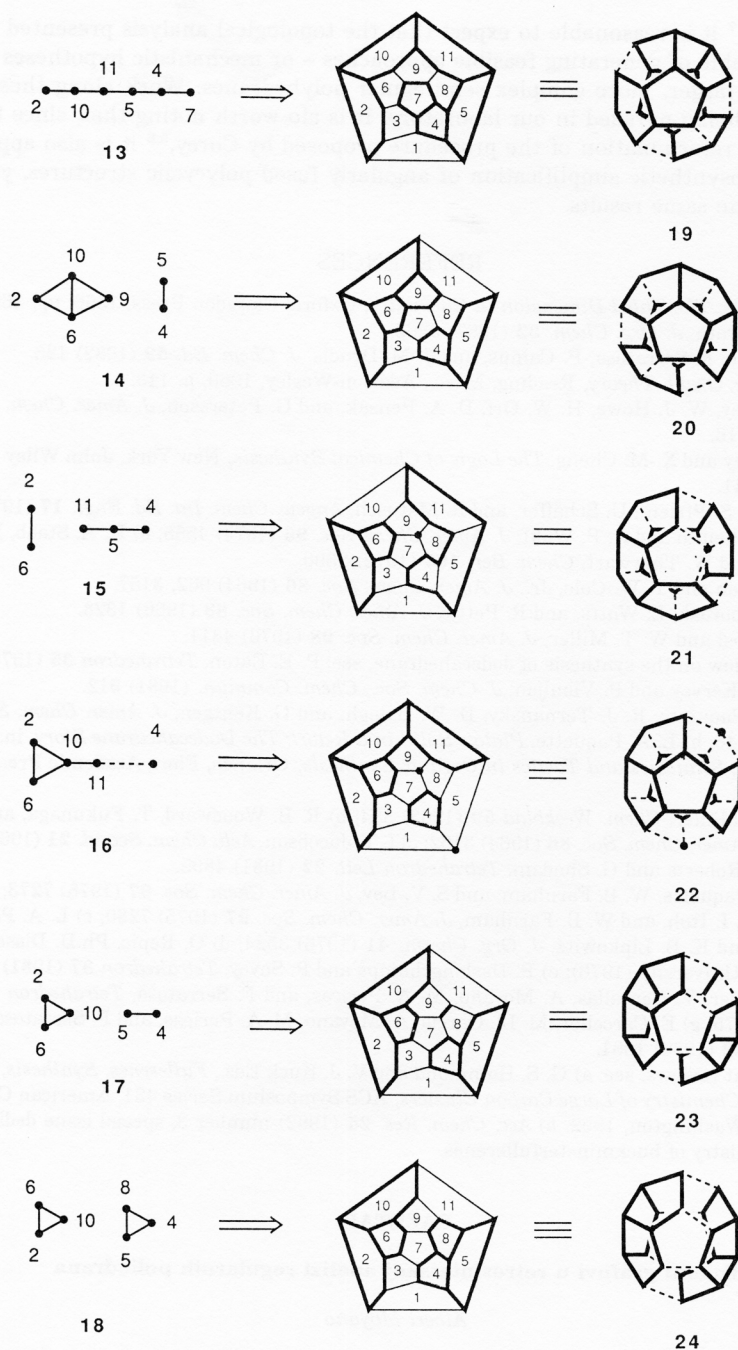
Figure 7. Inverse dual transformation of the six graphs **13–18** generated by the sequential pruning of dodecahedrane.

compounds,[17] it is reasonable to expect that the topological analysis presented in this paper is capable of generating feasible approaches – or mechanistic hypotheses of formation – to larger, more complex semiregular polyhedranes. Work along these lines is currently being pursued in our laboratory. It is alo worth noting that, since this algorithm is a reformulation of the procedure proposed by Corey,[5,6] it is also applicable to the rethrosynthetic simplification of angularly fused polycyclic structures, yielding essentially the same results.

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SAŽETAK

Dualni grafovi u retrosintetskoj analizi regularnih poliedrana

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Pokazano je da se postupnim uklanjanjem susjednih čvorova maksimalnog stupnja u dualnom grafu Schlegelove projekcije regularnog ugljikova poliedrana (tetraedrana, kubana, dodekaedrana), dobiva smislen sintetski postupak za pripravu tih složenih policikličkih struktura.