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Synthetic strategies toward buckybowls and C_{60}: benzannulation is remarkably facile compared to cyclopentannulation

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Abstract—Computations on a model buckybowl, pinakene ($C_{28}H_{14}$) unequivocally predict that in general, benzannulation is a significantly facile process compared to cyclopentannulation in the ring closure synthetic strategy towards buckybowls. © 2001 Published by Elsevier Science Ltd.

Fullerenes have generated tremendous attention from various sectors in the last decade. Synthetic organic chemists around the world, not particularly satisfied with the way in which this beautiful molecule is prepared, have taken up the arduous task of synthesis of C_{60} and their serious attempts to achieve the synthesis have not yet solved the impasse in this direction. Nonetheless, these attempts have led to the syntheses of many novel bowl shaped polycyclic aromatic hydrocarbons, especially those which map onto the surface of fullerenes.[1]

The most successful and extensively used synthetic strategy towards buckybowls is that of ring closure to generate the characteristic curvature usually starting from a suitably substituted polycyclic planar hydrocarbon moiety. Thus, cyclopentannulation and benzannulation, to close five- and six-membered rings, respectively, proved to be vital steps in achieving the synthesis of buckybowls. Also, the strategies such as transition metal template mediated synthesis[2] or starting with a precursor which was bent by tethering the extreme ends[3] of an otherwise planar hydrocarbon moiety have been conceived; the ring closure strategy seems to be the only practical alternative at present. One major impediment to effect ring closure is high strain energy build-up, so an ideal ring closure strategy aims at reducing the high strain energy build-up in any single step.[4,5]

We used theoretical studies to assess the relative ease of cyclopentannulation and benzannulation by taking pinakene as a target compound.[4] Pinakene (**P**), $C_{28}H_{14}$, a curved bowl type molecule possessing an optimal number of five- and six-membered rings was chosen as the model compound to test the feasibility of the twin ring closure protocols, namely cyclopentannulation and benzannulation. Six idealized retrosynthetic routes were conceived and are given in Scheme 1. The sequential stepwise ring closure reactions, which involve dehydrogenations and isomerizations along these routes and the concomitant strain energy build-up were evaluated using the semiempirical self-consistent field calculations at MNDO level.[6] The geometries of all the structures considered in this study were fully optimized without any symmetry constraints and characterized as minima on the potential energy surface. The trends in energetics and the conclusions obtained are essentially independent of the theoretical procedure adopted. The routes 1 and 2 have all the five-membered rings in the precursor, and thus each ring closure will correspond to a benzannulation. However, routes 4–6 start from an all six-membered skeleton and similarly each step involves a cyclopentannulation. The build-up of strain energy in a sequential ring closure process are depicted in Fig. 1 for all the routes considered here. Figures 1a and 1b show a substantial decrease in the strain energy followed by benzannulation, which may be traced to the aromatic stabilization of the product as well as the reduction in the *peri*-hydrogen repulsion in going from the reactant to product upon ring closure. One striking feature is that in routes 1 and 2, most of the steps involve substantial lowering of strain, with the final ring closure showing a marginal increase in the strain energy. In contrast, Figures 1c–f show a consistent build-up of

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Keywords: pinakene; strain energy; buckybowl; theoretical calculations; synthetic strategy.

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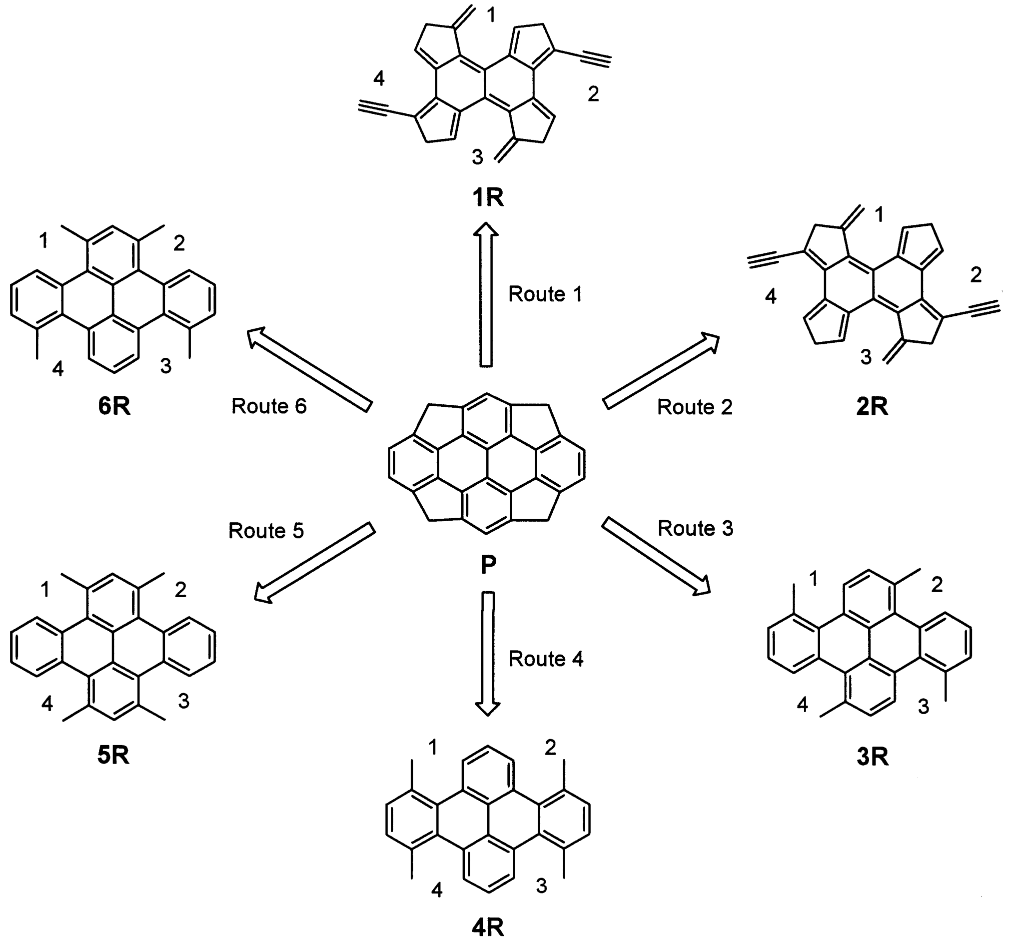

Scheme 1.

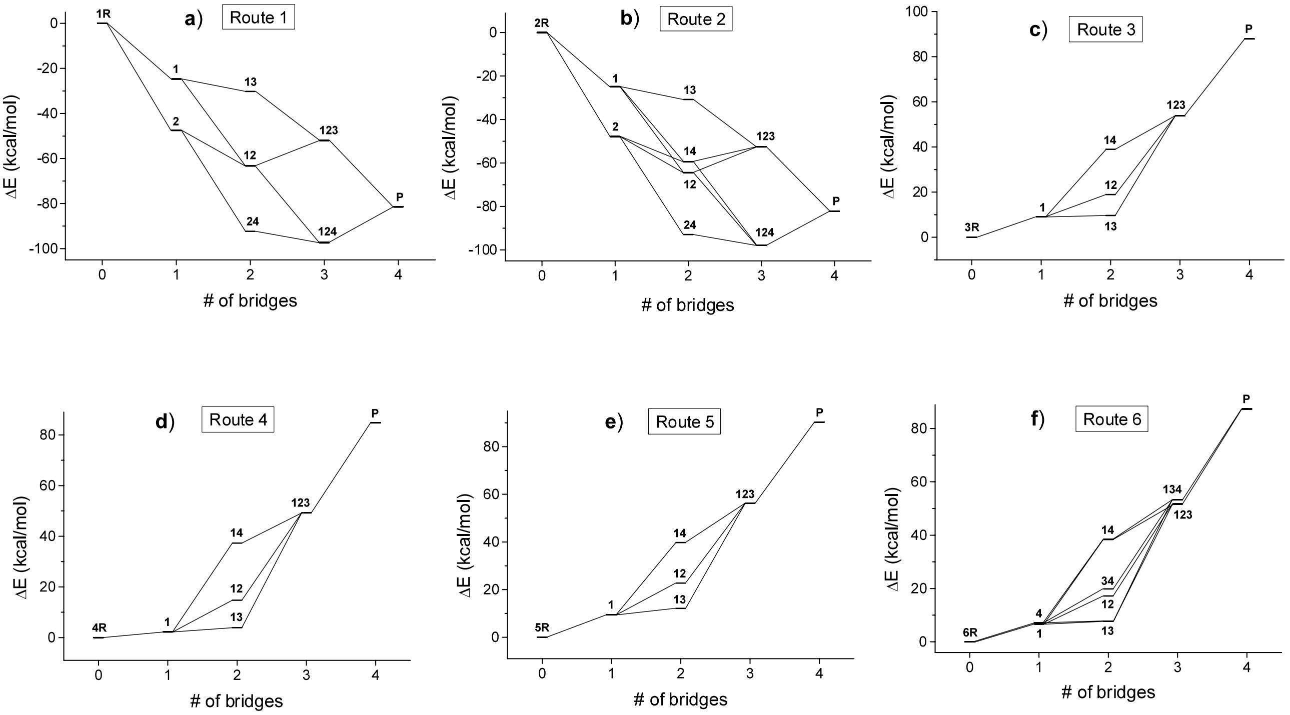

Figure 1. The MNDO plots showing the strain energy build-up in sequential ring closure strategies towards pinakene (**P**) along routes 1–6. Each route involves four ring closures. The number of bridges in the axis correspond to the number of ring closures. The numbering for specific rings is derived from Scheme 1.

strain energy right from the first ring closure, and continual increase in the strain energy with each bridging. Thus, all the routes, which involve cyclopentannulations, encounter severe strain energy in the final step, which means that these routes are not expected to be very successful for the synthesis of buckybowls in general.

These observations account for the futility of synthetic efforts towards pinakene and sumanene in synthetic strategies involving sequential cyclopentannulations starting from a planar all six-membered skeleton.[5,7] Among more than half a dozen successful syntheses of corannulene, apart from one procedure, all the other routes have precursors possessing a five-membered ring.[8]

Perhaps, the synthesis of the precursors for routes 3–6 are easier compared to those for routes 1 and 2. However, once the precursor is successfully synthesized for either route 1 or route 2, the sequential benzannulations and the eventual synthesis of pinakene is very likely to be successful. Thus, this analysis infers that wherever possible the syntheses of buckybowls are easier to achieve when starting from a precursor possessing the maximum number of five-membered rings. In this direction, the recently conceived strategy of Ferrier et al. towards C_{60} through a 'tetramer' of trindane which provides the 12 five-membered rings in the precursor seems to be very promising, and could potentially provide the much required breakthrough in the synthesis of the soccerball.[9]

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