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Theory provides a clue to accomplish the synthesis of sumanene, $C_{21}H_{12}$, the prototypical C_{3v}-buckybowl

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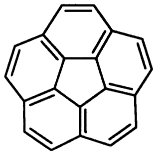
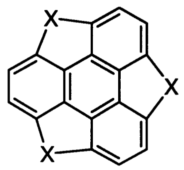
Abstract—Two possible synthetic routes, namely a triphenylene route and a trindene route for the synthesis of sumanene, $C_{21}H_{12}$ (**$2CH_2$**) and trithiasumanene, $C_{18}S_3H_6$ (**2S**) are analyzed in detail. Theoretical calculations unequivocally predict that the synthesis of sumanene may be easily achieved through a trindene route. © 2001 Elsevier Science Ltd. All rights reserved.

Corannulene **1** and sumanene **$2CH_2$** represent the fundamental structural motifs of buckminsterfullerene possessing five- and three-fold symmetry, respectively.[1] Corannulene **1** has been known for more than three decades; the discovery of fullerenes marked the onset of a flurry of activities towards buckybowls, following which more than half-a-dozen alternative routes towards the synthesis of corannulene were reported in the last decade.[2] In sharp contrast, sumanene **$2CH_2$** although long recognized as a key structural motif of C_{60} has not yet been conquered. One attempt towards a synthesis of sumanene was that of Mehta et al., wherein they start from a suitable triphenylene derivative and adopt a sequential ring closure strategy.[3] Only the first two bridges could be assembled in this strategy and closure of the crucial third bridge could not be achieved, which was attributed to the enormous build-up of strain energy.[1] McGlinchey and co-workers' attempt towards sumanene starting from an organometallic precursor also did not provide the breakthrough.[4] In a different context, Klemm et al. made an attempt to get **2S** by S bridging to triphenylene, however this yielded only the mono- and di-bridged isomers, and the crucial C_3 symmetric trithiasumanene **2S** could not be prepared.[5] However, Otsubo et al. have successfully conquered the synthesis of **2S**, the first reported heterobuckybowl, through an entirely different route, namely starting from a benzotrithiophene.[6] It occurred to us that the pristine hydrocarbon counterpart, triscyclopentadienobenzene (or trindene **$4CH_2$**, $C_{15}H_{12}$), may be taken as a precursor for the synthesis of sumanene **$2CH_2$**.

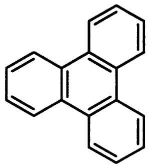
We decided to evaluate the relative ease using computational methods of accomplishing the synthesis of sumanene **$2CH_2$** and trithiasumanene **2S** by triphenylene and trindene routes (Fig. 1). Standard quantum mechanical calculations[†] were done using the



1, C_{5v}



2X, C_{3v}



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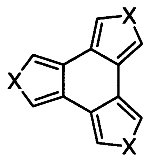

4X

X = CH_2, **S**

Keywords: buckybowls; sumanene; trindene; theoretical calculations; heterobuckybowls.

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[†] The B3LYP/cc-pVDZ optimizations are performed for all the structures considered in Fig. 2. However, for the structures considered in Fig. 1, B3LYP/cc-pVDZ calculations are reported on MNDO optimized structures. Exploratory benchmark calculations at various levels indicate that the results obtained here are independent of the level of theory employed.

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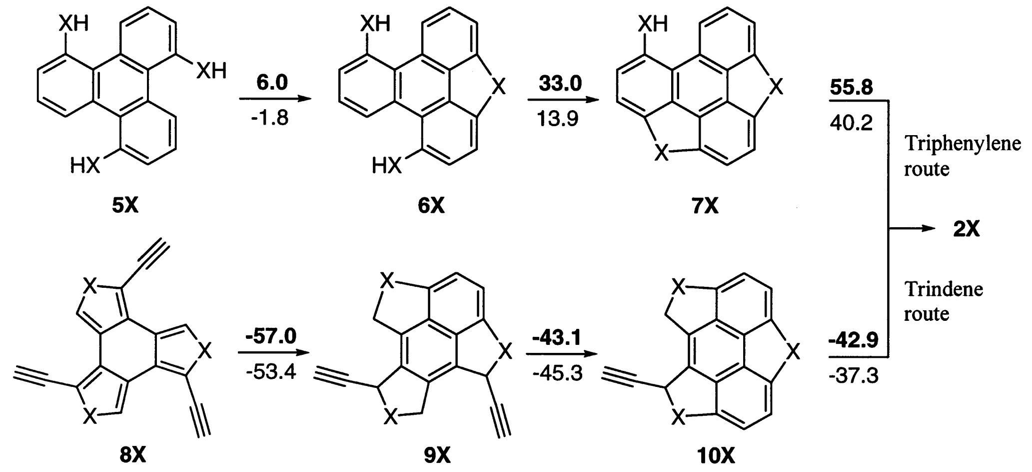

Figure 1. Strain energy (kcal/mol) build-up in a sequential ring closure strategy in triphenylene routes and in trindene routes towards the synthesis of **2X** at the B3LYP/cc-pVDZ//MNDO level. Bold and ordinary are for X=CH_2 and S, respectively.

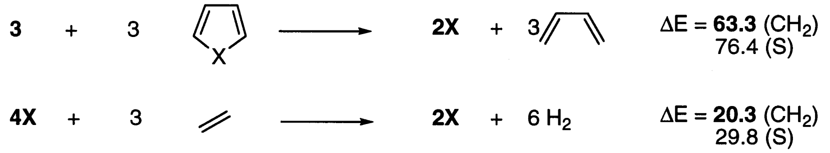

Figure 2. The strain energies (kcal/mol) computed for sumanene **2CH$_2$** and trithiasumanene **2S** via the triphenylene and trindene routes at the B3LYP/cc-pVDZ level. Bold and ordinary are for X=CH_2 and S, respectively.

Gaussian 94 program package.[7] The strain energy build-up in each of the steps in sequential ring closure pathways, obtained from the reaction energies, for both the routes are given in Fig. 1. In the triphenylene route, all steps lead to an increase in strain with the third step endothermic by more than 50 kcal/mol, which makes the task of the synthesis almost impossible. In the thia-analogue, while the first two steps have much less strain energy build-up, the final step requires almost 40 kcal/mol, which accounts for the failure of the attempt by Klemm et al.[5] The lower strain energy for the thia-analogue can be traced to the fact that larger atoms substituted at the rim of the bowl facilitate ring closure.[8]

Astonishingly, the trindene route shows substantial negative reaction energies indicating the ease with which its synthesis can be accomplished. The reported synthesis can easily be understood looking at the huge exothermicities of −53.4, −45.3 and −37.3 kcal/mol for the first, second and third bridge closures en-route to **2S**. What is more important is that the steps in the route towards the hydrocarbon compound are more exothermic when compared to the thia-analogue. Therefore, according to these calculations, once the synthesis of the precursor **8CH$_2$** is achieved, the sequential ring closures will follow immediately to accomplish the elusive sumanene, $C_{21}H_{12}$. Calculations indicate that in the trindene route, the hydrocarbon analogues have lower strain energies compared to the thia-analogues.

To examine the inherent strengths/weaknesses of the two strategies adopted, the isodesmic equations are set up as given in Fig. 2. Beyond any doubt, these calculations indicate that the trindene route is definitely a better choice to achieve the synthesis of sumanene. The lower strain energy for the hydrocarbon analogue may be traced to the presence of aromaticity in the thia-analogue, which is absent in the former. We feel that this computational study gives boost to the synthetic efforts towards sumanene using the trindene route.[4,9]

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