Synthetic Strategies Towards C_{60}. Molecular Mechanics and MNDO Study on Sumanene and Related Structures

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Strain energies of the hydrocarbons derived from the fragments of C_{60} along the C_5, C_3 and C_2 symmetry pathways indicate that the strain energy per carbon (E_S) increases gradually along the C_3 and C_2 paths, but has a maximum at $C_{40}H_{10}$ along the C_5 path. C_{21}-Sumanene, **10**, has been recognised as a leading fragment along C_3 route with an inversion barrier of 24.2 kcal mol^{-1} and a bowl depth of 1.15 Å at MNDO level. This contrasts with C_{20}-corannulene, **6**, which is a more shallow bowl with a lower inversion barrier. The bond alternation in the central six membered ring of sumanene resembles that of C_{60}. The higher fragments *en route* to C_{60} are deep bowls with higher barriers for inversion. An approach to sumanene *via* a triphenylene derivative, **26**, has been probed and an increase in strain through sequential placement of methylene bridges has been estimated, using MNDO and MM2 calculations. Synthetic routes to a doubly bridged triphenylene, **28**, and schemes for further elaboration of **26a** and sumanene derivative, **29**, towards C_{60} are considered.

The discovery of buckminsterfullerene,[1] C_{60}, **1**, a new allotropic form of carbon and ready access to it in macroscopic amounts through rapidly improving preparative procedures[2] has generated a great deal of interest and activity at the interfaces of chemistry, physics and material science. While state-of-the-art techniques and modern reagents are being employed to unravel the rich and complex chemistry of C_{60},[3] its preparation based on 'arcing graphite' and 'soot-extraction', by contrast, borders on 'black box' operations. Rational design or classical synthetic approach to this complex and fascinating molecule is a major challenge and synthetic chemists around the world are beginning to bestow attention on this problem.[4-8] In this report we consider some possible synthetic avenues to C_{60}, along different symmetry pathways and evaluate the energies and structures of several key fragments *en route*.

The C_{60}, **1**, can be dismantled in a retro-synthetic sense through three conceptually different routes which retain C_2, C_3 and C_5 symmetry, by successively removing fragments from one side.† The structural fragments are treated as hydrocarbons obtained by adding hydrogens to saturate the σ-valency on the C_n template. Each one of them (Scheme 1, **2–15**) is a fascinating target for synthetic pursuits. The important substructures at the end of the C_5, C_3 and C_2 symmetry routes are corannulene, **6**, sumanene, **10**, and pyracylene, **15**, respectively.[4,6-8] Of these, **6** and **15** are known, have been synthesised and taken note of as C_{60} precursors.[3,4,6,8] On the other hand, sumanene, **10**, has been recognized as the key fragment only recently[7] and its synthesis remains to be accomplished. Herein, attention has been, therefore focused particularly on the structure of sumanene, **10**, and its suitability for further evolution towards C_{60}.

Another dissection that retains C_5, C_3 and C_2 axis removes fragments in pairs from opposite sides of C_{60}, **1**. The interesting 'ribbons' generated are given in Scheme 2. $C_{50}H_{20}$, **17**, has been suggested as a possible synthetic target.[5]

A strain energy analysis of the structures *en route* to C_{60} (Schemes 1 and 2) based on molecular mechanics calculations[9] was carried out and a detailed MNDO[10] study on the structure of sumanene, **10**, and related compounds is presented. The schemes for the synthesis of sumanene and its elaboration towards C_{60} are also given.

Table 1 Strain energies of C_{60} fragments (kcal mol^{-1})

No.	Formula	E_S	E_S (C_n in C_{60})	ΔE_S
1	C_{60}	19.202		
2	$C_{55}H_{10}$	15.53	17.36	1.83
3	$C_{50}H_{10}$	13.38	15.98	2.60
4	$C_{40}H_{10}$	14.43	14.60	0.17
5	$C_{30}H_{10}$	8.83	13.37	4.54
6	$C_{20}H_{10}$	4.30	10.15	5.85
7	$C_{54}H_6$	17.22	17.13	−0.09
8	$C_{45}H_{12}$	12.31	15.56	3.25
9	$C_{36}H_{12}$	8.69	13.50	4.81
10	$C_{21}H_{12}$	5.81	10.67	4.86
11	$C_{54}H_6$	15.89	17.12	1.23
12	$C_{42}H_{12}$	10.26	14.38	4.12
13	$C_{32}H_{12}$	9.78	13.13	3.35
14	$C_{28}H_{12}$	8.64	12.25	3.61
15	$C_{14}H_8$	4.50	8.43	3.93
16	$C_{40}H_{20}$	6.65	11.10	4.45
17	$C_{50}H_{20}$	10.98	15.18	4.20
18	$C_{30}H_{18}$	7.83	8.97	1.14
19	$C_{48}H_{12}$	14.46	14.52	0.06
20	$C_{32}H_{18}$	3.69	9.22	5.53
21	$C_{48}H_{16}$	12.65	14.52	1.87

Results and Discussion

Molecular Mechanics Study of C_{60} *Fragments.*—Table 1 gives the strain energies per carbon (E_S) calculated for the hydrocarbons derived from various C_{60} fragments (**2–21**, Schemes 1 and 2). The optimized carbon skeleta are now different from those of the idealized C_{60} fragments. ΔE_S Values between the optimized hydrocarbon structure and the corresponding carbon skeleton (C_n) kept at the geometry of C_{60} gives an estimate of the deviation of the structure from the standard C_{60}. A large ΔE_S in the smaller hydrocarbons indicates corresponding large reorganizations taking place in the smaller skeletons to reduce strain. Thus, $C_{20}H_{10}$, corannulene, relaxes considerably to a shallow bowl in comparison to the corre-

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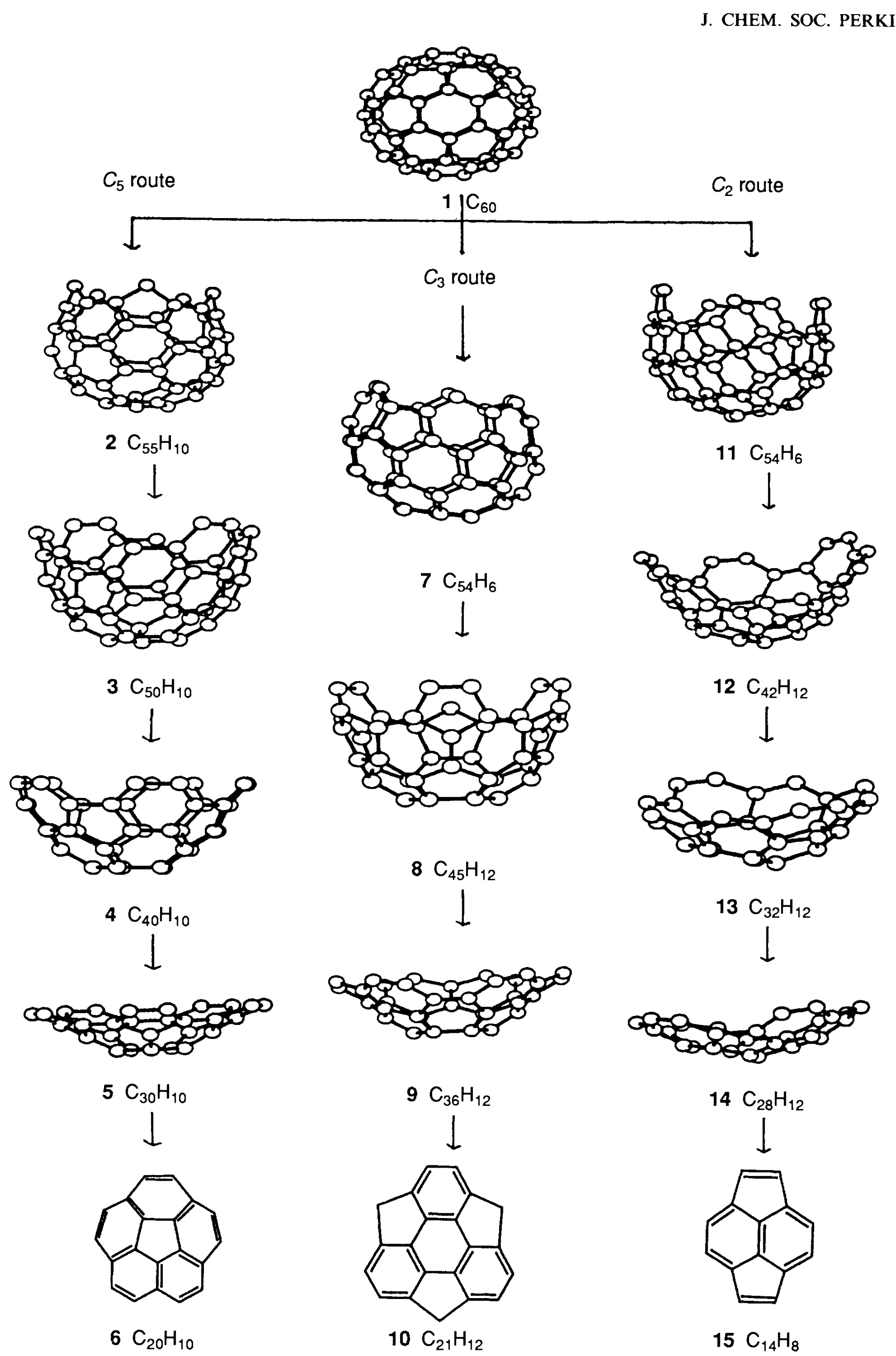
† The trivial fragments, such as cyclopentadiene and [5]-radialene in C_5 route, benzene in C_3 route and ethylene and naphthalene in C_2 route, are not considered here.



Scheme 1

sponding C_{20} fragment of C_{60}.* The corresponding reduction in E_S is 5.85 kcal mol^{-1}.† The lower ΔE_S values between $C_{40}H_{10}$ and C_{40} of 0.17 kcal mol^{-1} correctly points to the similarity between $C_{40}H_{10}$ and C_{60} (**4** and **1**). The structure of $C_{50}H_{10}$, **3**, is especially interesting because it is also a fragment of C_{70}.[3] Addition of [5]-radialene to **3** leads to C_{60} and addition of corannulene, **6**, to **3** leads to C_{70}. The larger fragments have an additional source of strain. The C–H bonds added for completing the valency fall within van der Waals contact, increasing the strain. This is especially significant in **2**, **7** and **11**. In fact the H • • • H non-bonded repulsion makes $C_{54}H_6$, **7**, more strained than the corresponding C_{54} unit in C_{60}.

Fig. 1 gives a plot of the E_S as a function of the fragment. The increase in E_S is gradual along the C_3 and C_2 routes (Fig. 1). The C_5 path involving corannulene has a maximum E_S at $C_{40}H_{10}$, **4**. The E_S decreases in the next higher fragment. In a sequential synthetic route this is not desirable. The E_S values of the fragments, **2**–**21**, as well as C_{60} are to be compared to the E_S values calculated for standard molecules: dodecahedrane, 3.3, [5]-prismane, 14.5, and cubane, 20.7 kcal mol^{-1}.[9,11] The syntheses of all of these molecules have been successful. Likewise, it should be possible to synthesize C_{60} in a stepwise process.

Though C_2 route in Scheme 1 has fragments that follow this

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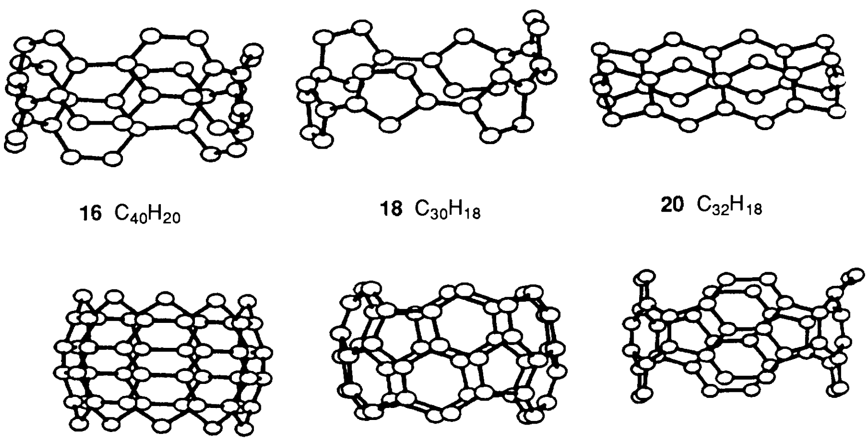
* MM2 calculations incorrectly give a planar structure for corannulene. However the strain energy difference from molecular mechanics between this and the bowl-shaped geometry obtained by the MNDO is very small.

† 1 kcal mol^{-1} = 4.18 kJ mol^{-1}.



16 $C_{40}H_{20}$ **18** $C_{30}H_{18}$ **20** $C_{32}H_{18}$

17 $C_{50}H_{20}$ **19** $C_{48}H_{12}$ **21** $C_{48}H_{16}$

Scheme 2

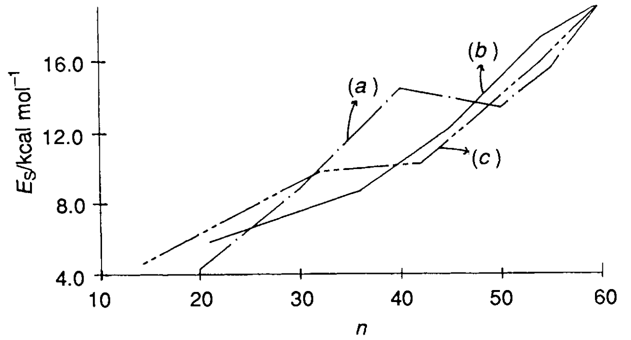


Fig. 1 The plot of the E_S as a function of fragments: (*a*) C_5 route; (*b*) C_3 route; (*c*) C_2 route

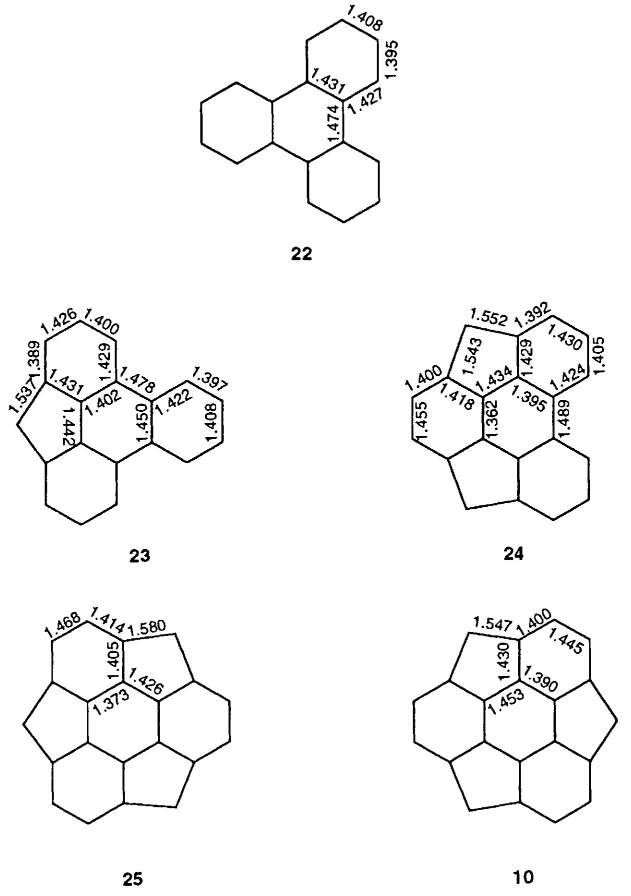


Fig. 2 MNDO bond lengths for **22**–**25** and **10**

symmetry strictly, the individual members may be easily identified with the fragments of the C_3 and C_5 routes. Thus, $C_{28}H_{12}$, **14**, may be considered as a simple extension to sumanene. Similarly $C_{32}H_{12}$, **13**, is an extension of corannulene. Other fragments along the C_2 path can be similarly related to the fragments along the C_3 and C_5 routes. Thus, only two independent pathways, C_3 and C_5, need to be considered seriously.

ΔE_S Values for the ribbon-like fragments indicate that large reorganizations are possible in $C_{40}H_{20}$, **16**, and $C_{50}H_{20}$, **17** which retain the C_5 axis. It may be noted that $C_{40}H_{20}$, **16**, is also a substructure of C_{70}.[12] The minimal ΔE_S values for ribbons that retain the C_3 axis ($C_{48}H_{12}$, **19**, and $C_{30}H_{18}$, **18**) indicate their close resemblance to C_{60}.

Low strain energies in the lower members is an attractive aspect in the initial stages of the synthesis but it becomes less desirable in the final stages where large increases in strain will have to be affected in limited steps. Sumanene, **10**, is a relatively strained molecule compared to corannulene so that the further increase in strain needed to approach the strained C_{60} is relatively small (Table 1). Therefore, it would seem better to build the synthetic strategy, towards C_{60}, around sumanene, **10**. A detailed understanding of the structure of sumanene, **10**, would help in devising a practical route to its synthesis.

Comparison of Sumanene, Corannulene and Related Structures.—Sumanene, $C_{21}H_{12}$, **10**, is calculated to be a bowl-shaped molecule by the MNDO method. The C–C bond lengths of the central C_6 ring are 1.390 and 1.453 Å. These are to be compared to 1.400 and 1.474 Å found in C_{60} itself at the MNDO level.[13] The increase of bond localization in the central C_6 ring by increasing strain is evident from the comparison of bond lengths of sumanene, **10**, to triphenylene, **22**, obtained by removing the methylene bridges. The bond lengths in triphenylene, **22**, are consistent with the description that the 18 π-electrons are localized as three sextets in the three outer rings.[14] We see a gradual increase in the bond length alternation in the central six membered ring going from triphenylene, **22**, to sumanene, **10**, by adding methylene bridges (Fig. 2).* The central ring in triphenylene has C–C bond lengths of 1.431 and 1.474 Å. Addition of one methylene bridge decreases this to 1.402 and 1.442 Å (only the shorter pair is considered here) (**23**).

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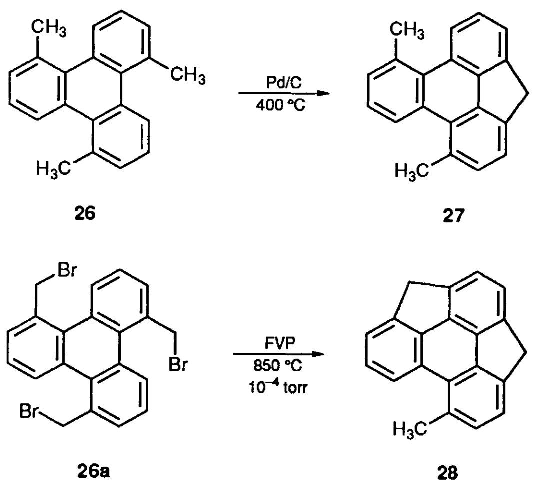
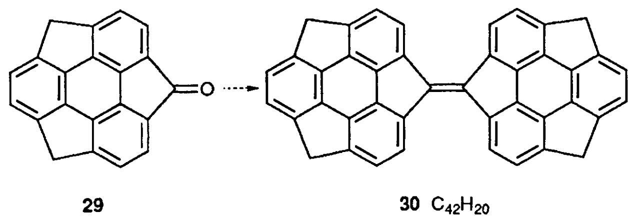
* The variation of bond lengths starting from C_3 1,5,9 trimethyltriphenylene, **26**, through **27** and **28** to sumanene, **10**, follow similar trends.

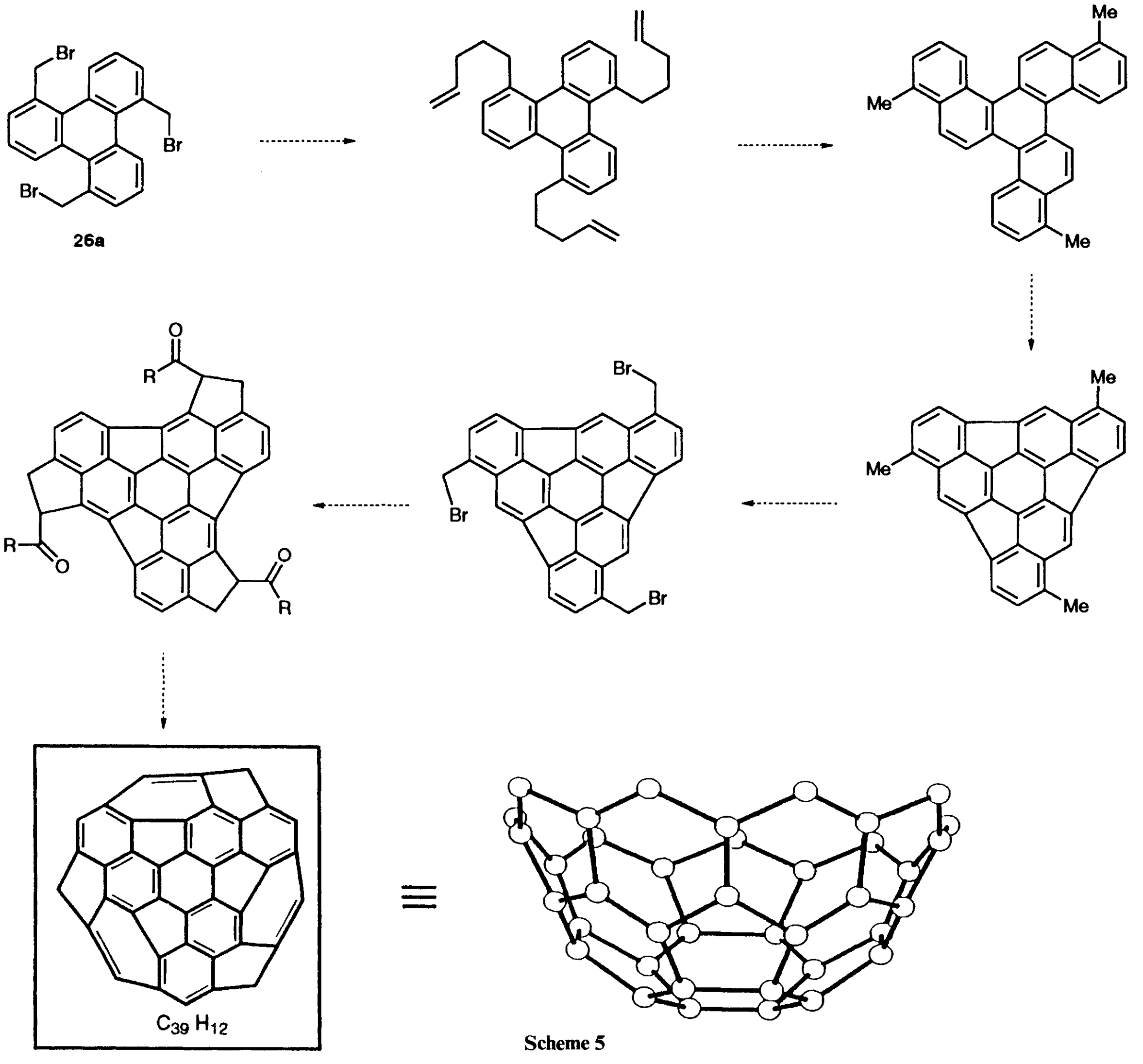


Scheme 3



Scheme 4

A second bridge decreases this further to 1.362 and 1.434 Å (**24**). These are the results of accommodating the newly formed five membered rings. This leads to an abnormally long C–C bond length of 1.489 Å to the 'free' C–C bond of the central ring in **24**. However these structures, **22**–**24**, remain roughly planar. A third methylene bridge forces the molecule to be non-planar. In addition to the constraints in bond lengths, the strain energy of the planar form is also from the inherent tendency of an angularly constrained trigonal carbon to adopt a nonplanar arrangement.[15] The $CH_3^{\bullet}$ radical, for example, prefers a highly pyramidal structure if one of the H–C–H angles is constrained to be much less than 120°. If a planar structure, **25**, is demanded the C–C bond lengths of the central C_6 ring decreases to 1.373 and 1.426 Å. The C–C bonds of the periphery of the molecule are stretched to abnormal lengths. The peripheral CH_2–C single bond lengths increase from 1.537 in **23** to 1.580 Å in **25**. In sumanene, **10**, the central six membered ring now has C–C bond lengths of 1.390 and 1.453 Å. The planar structure, **25**, is 24.2 kcal mol^{-1} higher in energy, and is calculated to be the transition state for the bowl-to-bowl inversion of the sumanene, **10**. Thus, sumanene is not expected to undergo ready inversion. This is to be contrasted to the bowl-to-bowl inversion of corannulene, **6**, that takes place rapidly at room temperature.[6] The inversion barrier of 8.3 kcal mol^{-1} calculated for corannulene at the MNDO level is close to the experimental estimate of 10.2 kcal mol^{-1} and the previous theoretical



Scheme 5

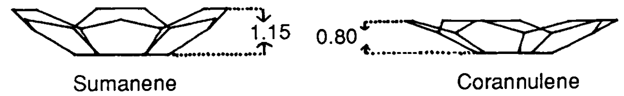


Fig. 3 Bowl depths of sumanene and corannulene (MNDO) (Å)

Table 2

Reaction	$\Delta\Delta H_f$/kcal mol^{-1}	ΔE_S(MM2)/kcal mol^{-1}
27 + $H_2 \longrightarrow$ **26**	−3.8	−4.4
28 + $H_2 \longrightarrow$ **27**	−16.1	−19.9
10 + $H_2 \longrightarrow$ **28**	−46.2	−49.4

studies.[6b] The large difference in the inversion barrier between corannulene, **6**, and sumanene, **10**, can be attributed to the difference in the bowl depths. [The distance between the planes formed by the central ring and the outermost C–C bonds of outer six membered rings (Fig. 3).] The calculated bowl depth of corannulene (0.80 Å) is close to the experimental value of 0.89 Å.[6] Sumanene has a bowl depth of 1.15 Å at the MNDO level (Fig. 3). The bowl depths of corresponding C_{20} and C_{21} of C_{60} fragments are 1.51 and 1.69 Å respectively.[13] This indicates that sumanene, **10**, is a more closed network and its curvature is closer to that of C_{60} than corannulene, **6**.

Our results indicate that sumanene, **10**, is a fairly rigid bowl in contrast to corannulene, **6**. The larger bowls (**2**–**5**, **7**–**9** and **11**–**14**) are extremely rigid, and attempts to evaluate the inversion barriers lead always to bond breaking.

Synthetic Strategies Towards C_{60}.—One of the synthetic strategies, starting from a C_3 1,5,9-trimethyltriphenylene, **26**, and its derivative **26a**, towards sumanene is shown in Scheme 3. The thermally induced cyclo-dehydrogenation has so far led to only singly, **27**, and doubly bridged, **28**, products. MNDO calculations are performed on the structures **26**–**28**. The isodesmic equations (Table 2) indicate the strain energies for the placement of methylene bridges. Molecular mechanics indicate similar trends.[7] Formation of the third bridge does involve greater increase in strain.

Alternative pathways for the synthesis of sumanene are being tried experimentally. Further efforts to access advanced precursors of C_{60} through the coupling of suitably functionalized sumanene, **29**, to furnish $C_{42}H_{20}$, **30**, is shown in Scheme 4. This advanced precursor should be amenable to further tactical elaborations towards C_{60}. Entry into higher fragments *en route* to C_{60} is also planned through several related routes, one of which is indicated in Scheme 5.†

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