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Ring closure synthetic strategies toward buckybowls: benzannulation *versus* cyclopentannulation†

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Computations were performed on idealized retrosynthetic routes towards two model buckybowl compunds, sumanene (**I**) and pinakene (**II**). Two possible paths for sumanene (**I**) and six for pinakene (**II**) were analyzed. The computational results unequivocally predict that benzannulation is a significantly easier process compared to cyclopentannulation in the ring closure strategies in both cases. The suitability of the theoretical models for obtaining reliable trends is assessed and generalizations for the synthetic strategies directed towards buckybowls and C_{60} were made.

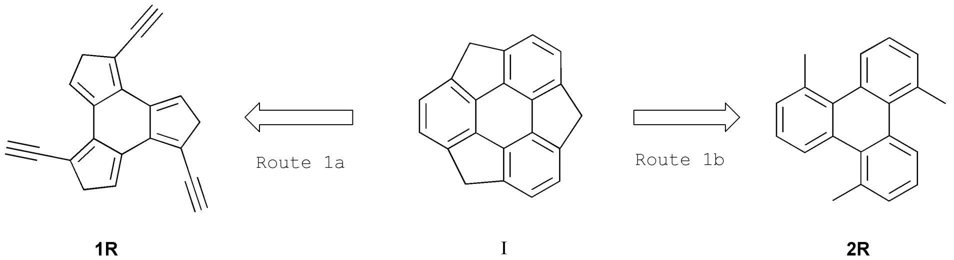
Introduction

The synthesis of C_{60} has been an exigent task for the experimental organic chemists for a considerable time. Although there were isolated attempts towards its synthesis even in the early eighties, attraction and attention burgeoned in the post-fullerene era and several research groups focused their attention on this challenging task.[1–3] While the attempts towards the synthesis of the soccerball were not successful, they opened up a new branch of chemistry in the form of buckybowls.[4–7] The chemistry of buckybowls links that of the closed geodesic dome-fullerenes and the planar polycyclic aromatic hydrocarbons (PAHs). The chemistry of buckybowls is interesting in its own right and these curved polycyclic aromatics are emerging as a promising class of compounds. The incorporation of five-membered rings provides the desired curvature characteristic for the buckybowls. One aspect that distinguishes fullerene and buckybowl chemistries is the general way in which these molecules are prepared. Arcing graphite and soot extraction are ways of accessing fullerenes (methods that may not be regarded as carefully designed synthesis), but traditional synthetic organic chemistry techniques are imperative in realizing the synthesis of buckybowls. The interplay between theory and experiment is essential for the design of workable strategies and also to understand the underlying reasons for the failure of some attempted strategies.[8–13] Although buckybowls were not detected even as fleeting intermediates during the formation of fullerenes, there is no doubt that these entities form important stepping-stones in the synthetic designs toward fullerenes.

Strain energy build-up appears to be the bottleneck in the synthesis of buckybowls, and it is desirable to identify and adopt synthetic strategies that do not encounter strain energy build-up that is too high in any single step.[8–10] Ring-closure protocols are obviously involved in any synthetic strategy towards buckybowls, strating from a suitably substituted polycyclic planar hydrocarbon moiety. Knowledge of the relative ease of cyclopentannulation and benzannulation, *i.e.* closing five- and six-membered rings respectively, will assist in designing optimal retrosynthetic strategies towards the buckybowls. We have used theoretical studies to assess the relative ease of cyclopentannulation and benzannulation by examining two model compounds, sumanene (**I**) and pinakene (**II**). Schemes 1 and 2 depict some of the promising precursors for the syntheses of sumanene (**I**) and pinakene (**II**), respectively. The idealized retrosynthetic routes considered in Schemes 1 and 2 involve suitably substituted symmetric polycyclic frameworks, and each step involves either a cyclopentannulation or a benzannulation. Both the model compounds have a good mix of five- and six-membered rings and are thus ideal substrates for exploring the relative ease of cyclopentannulation *versus* benzannulation. All the sequential ring closure reactions, which involve either dehydrogenations or isomerizations, depicted in Chart 1 and Schemes 3–8, and the reaction energies in both cases effectively indicate the strain energy build-up along these routes.

Computational details

All semi-empirical calculations were performed using the MOPAC 2000 program package.[14] The single point B3LYP calculations were performed using the Jaguar 4.1 program package.[15] For model system 1, the calculations were performed at MNDO,[16] AM1,[17] and PM3[18] levels. The geometries of all



Scheme 1

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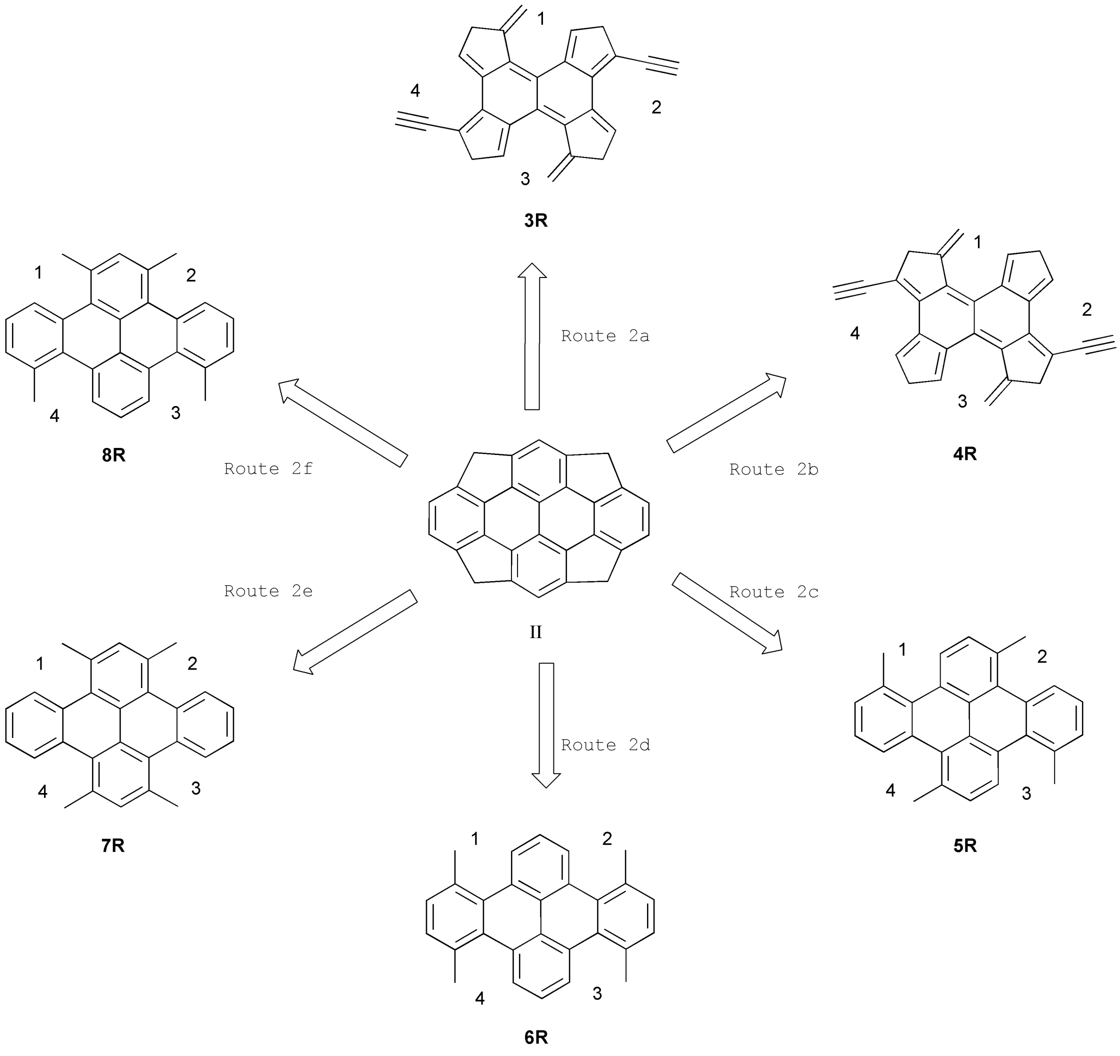
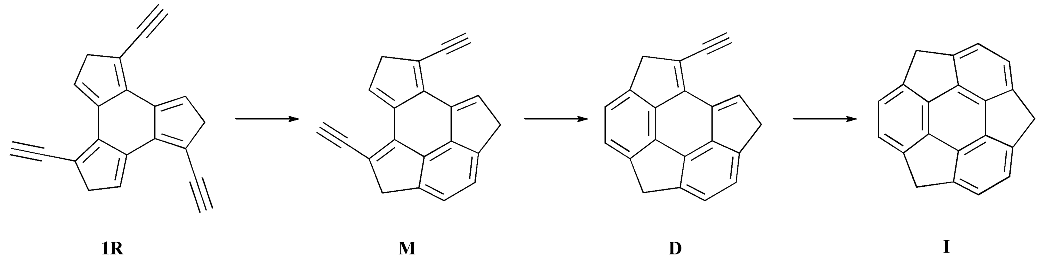
† Electronic supplementary information (ESI) available: the cartesian coordinates of all the MNDO optimized structures considered in the study. See http://www.rsc.org/suppdata/p2/b1/b108030j/



Scheme 2

Route 1a:



Route 1b:

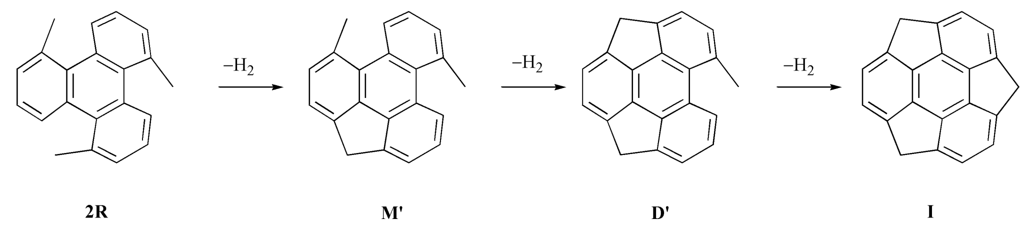
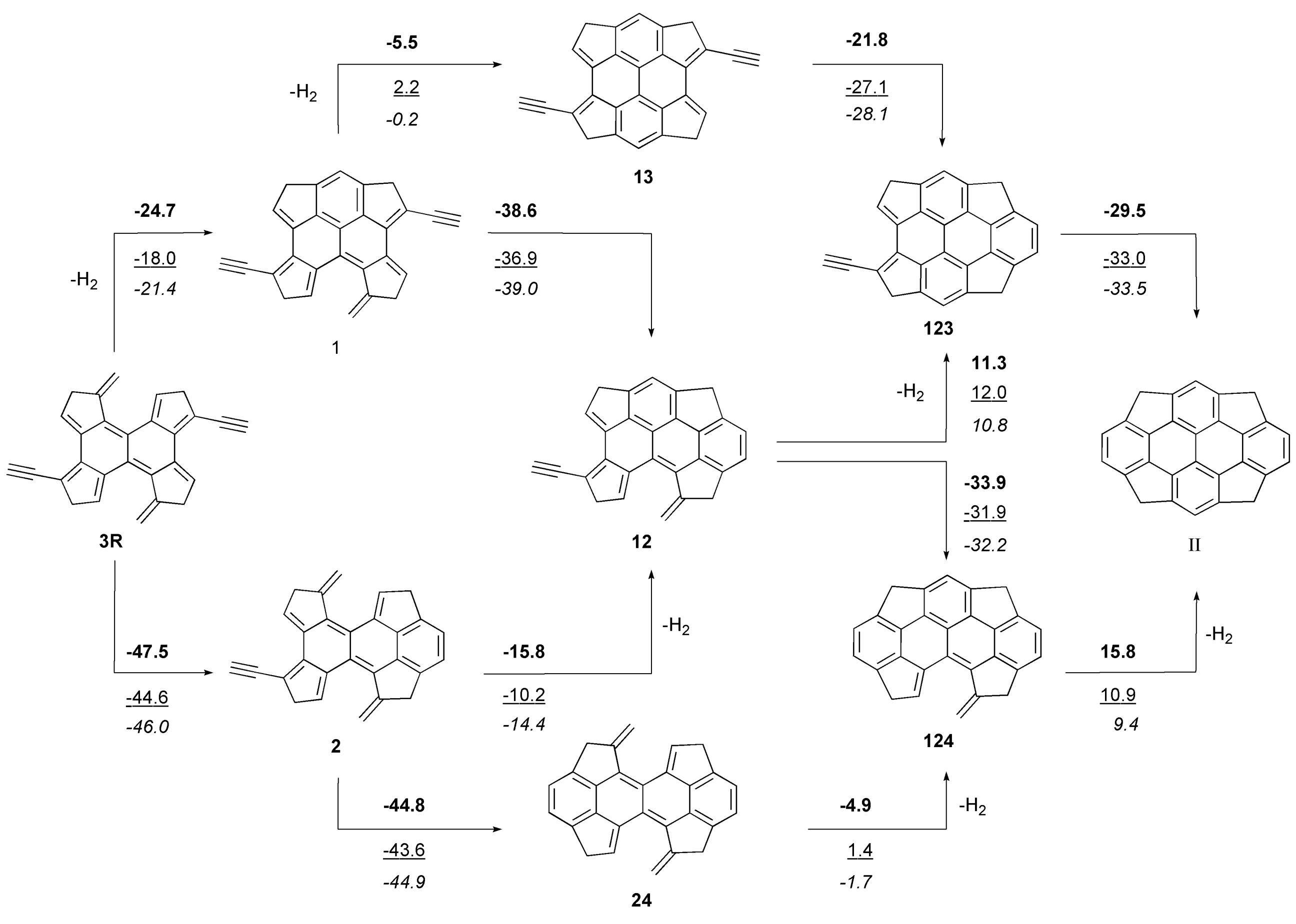
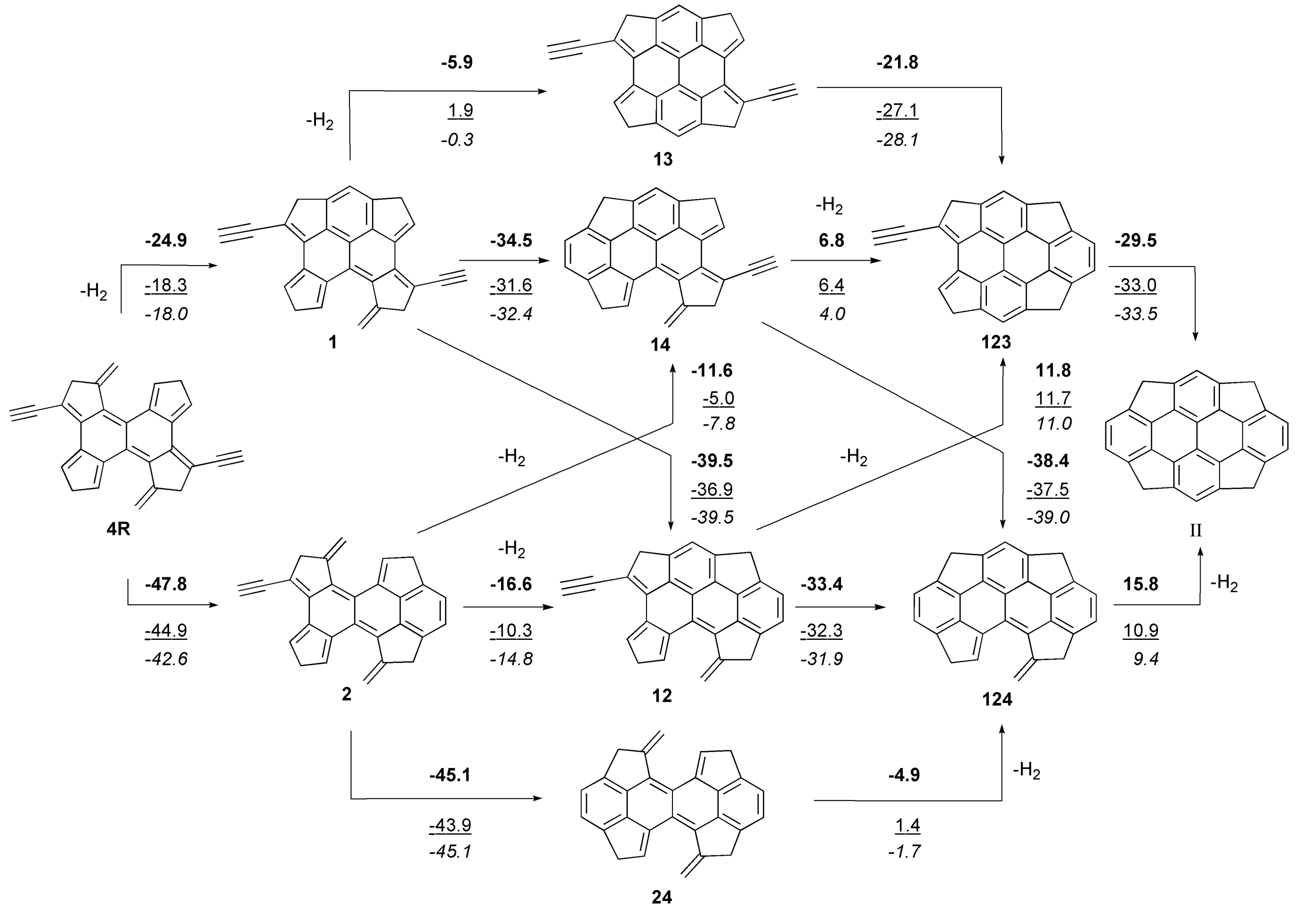


Chart 1

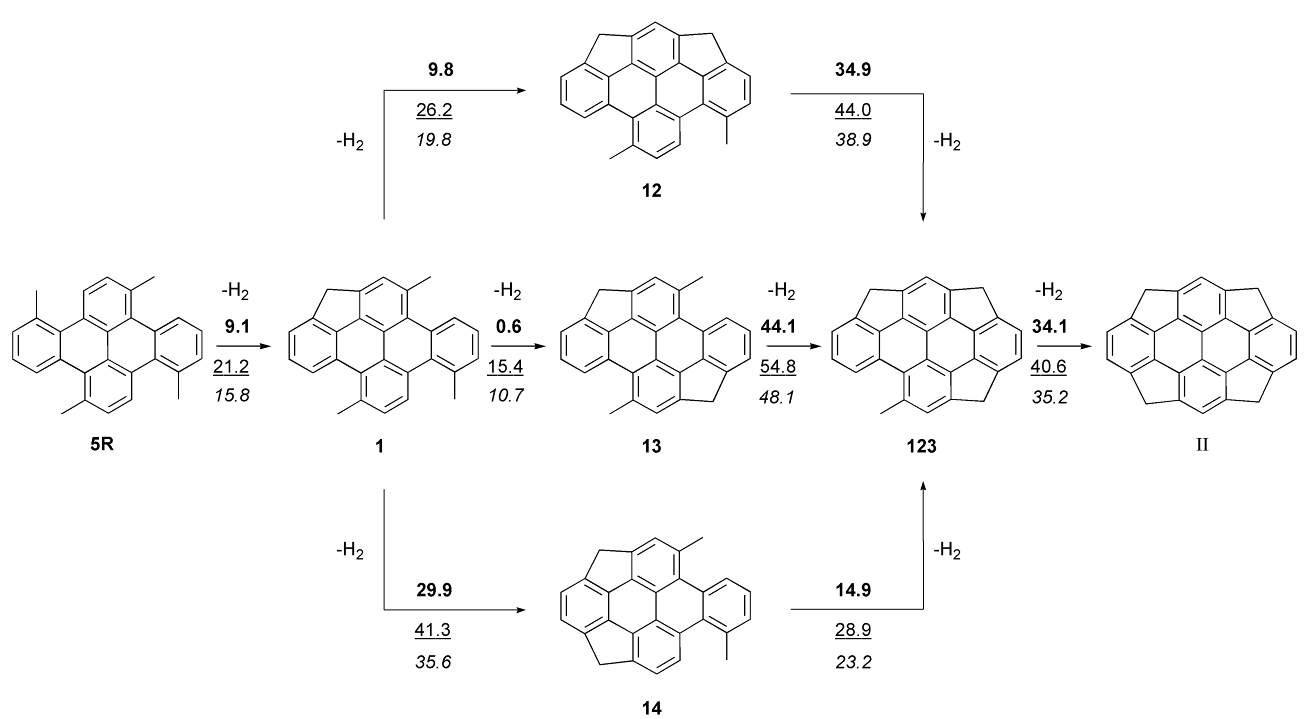
the structures considered in the study were fully optimized without any symmetry constraints and characterized as minima on the respective potential energy surfaces at all the three semi-empirical levels of theory. Single point calculations were performed at the B3LYP/cc-pVDZ level on MNDO and AM1 geometries, for all the points in model system 1, to assess the suitability of semi-empirical methodologies in obtaining reliable trends in energetics of this class of compounds. The results indicate that the broad qualitative features are essentially independent of the theoretical model employed. However, for model system 2, only semi-empirical optimizations were performed and the expensive DFT calculations were avoided.



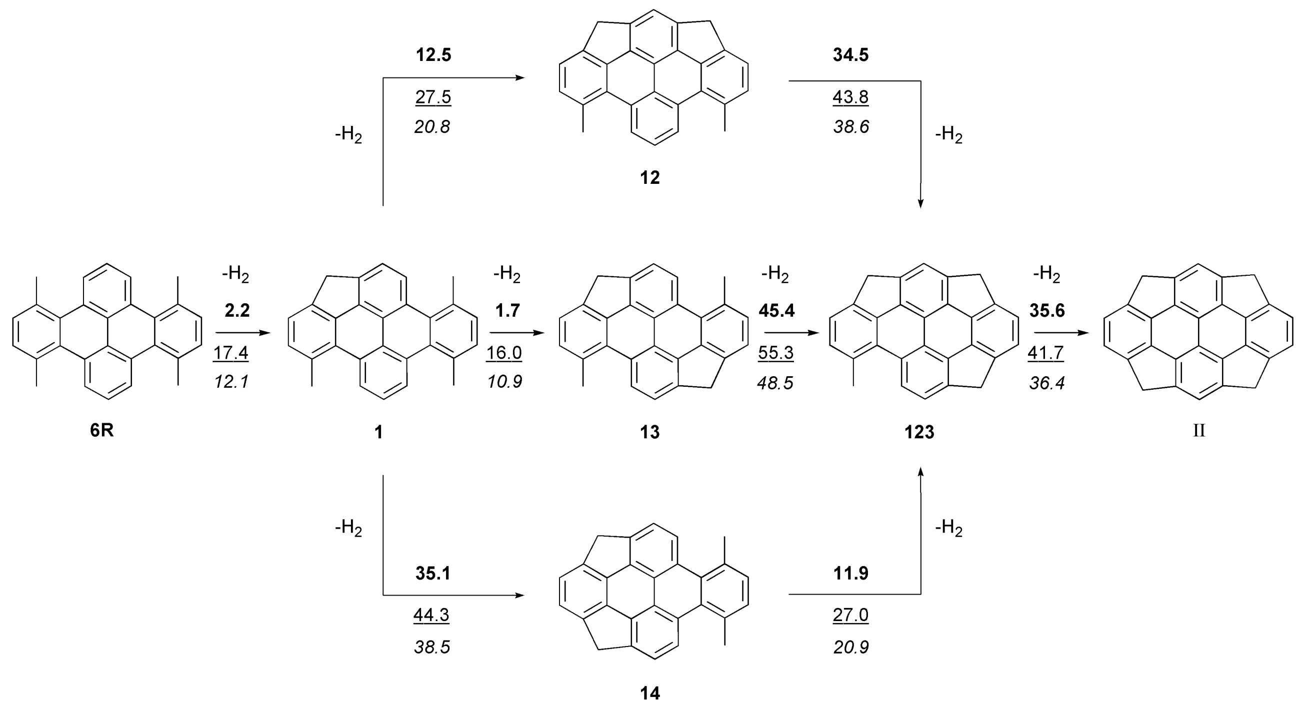
Scheme 3



Scheme 4



Scheme 5

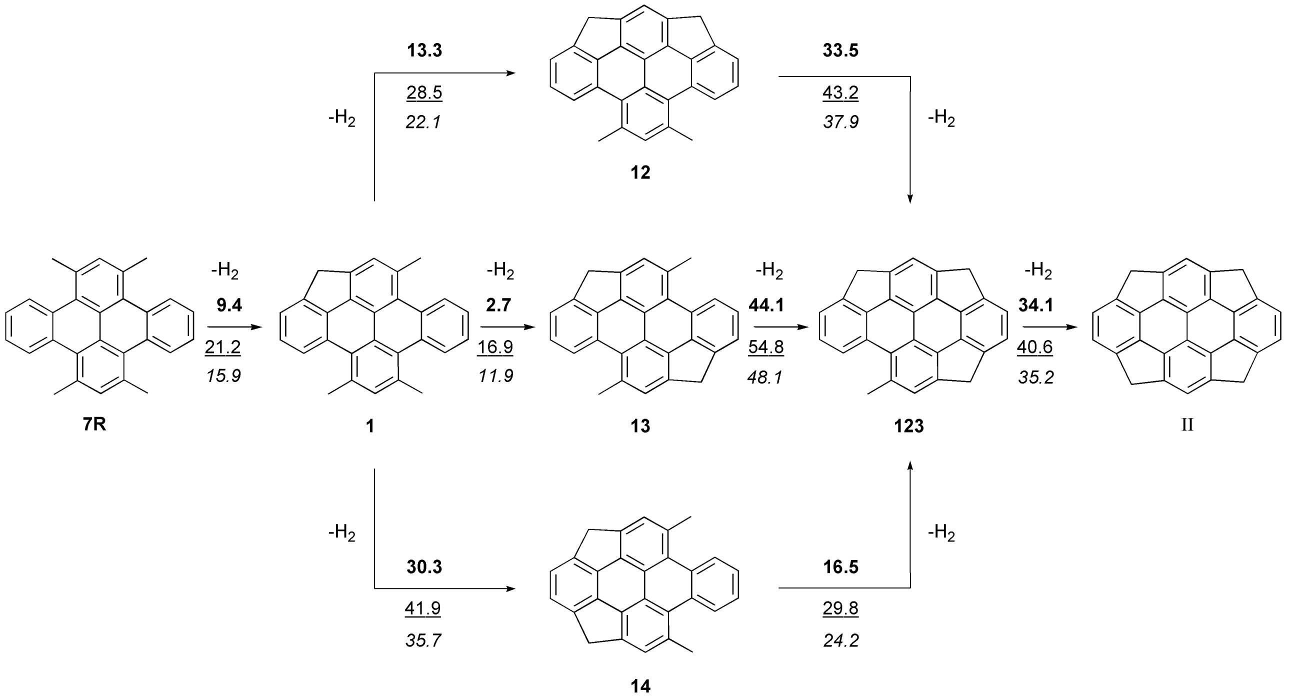


Scheme 6

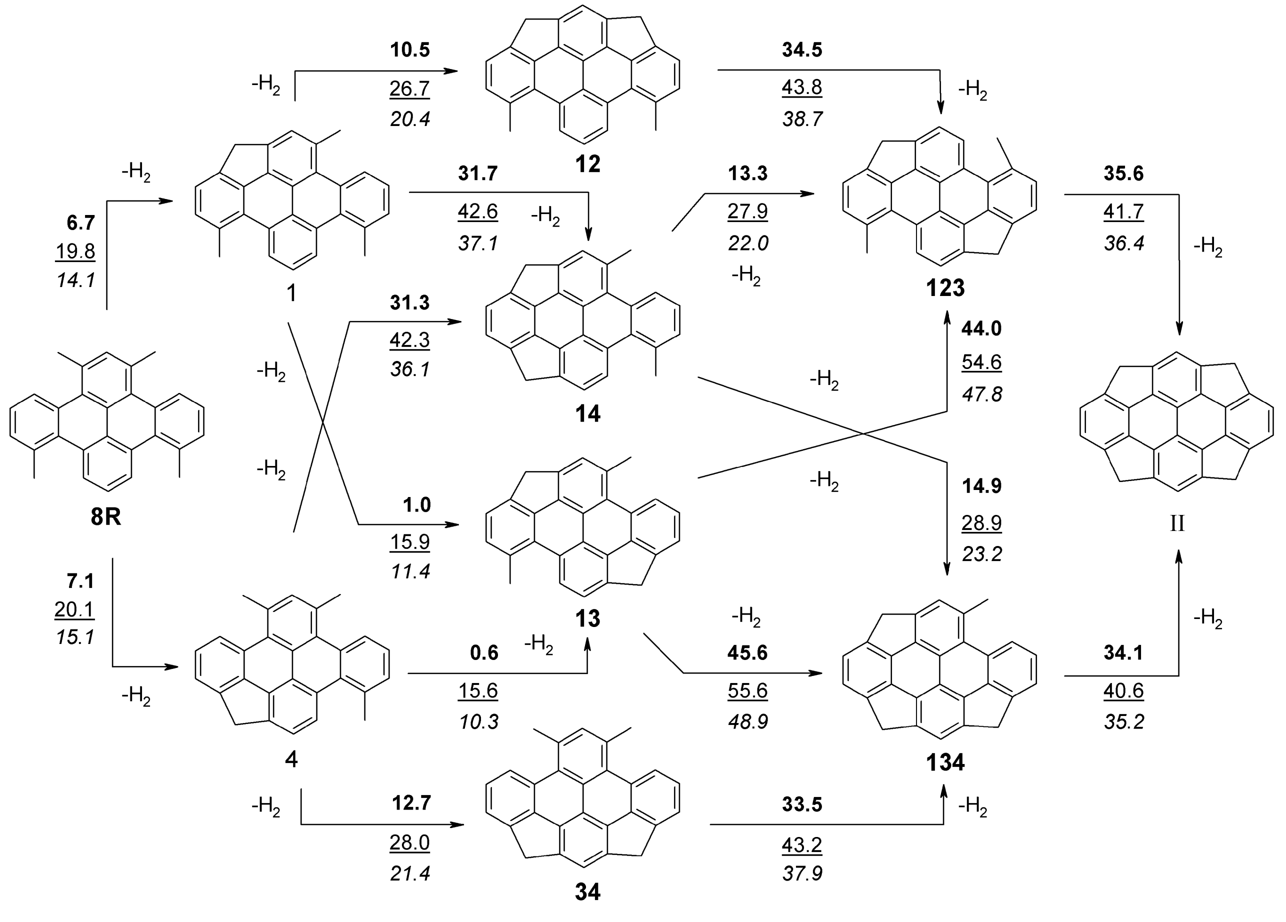
Results and discussion

We analyzed and compared the strain energy build-ups along the two routes in model system 1, sumanene (**I**). The dependence of the results on the computational procedures used was evaluated and this analysis predicts essentially the same qualitative trend at all levels of theory. Therefore, only semi-empirical calculations were performed on model system 2. The results are discussed based on MNDO calculations for uniformity and for its known better performance over AM1 and PM3 in this class of compounds.[19] However, considering any other level of theory employed essentially leads to the same qualitative conclusions.

All the intermediates *en route* to **I** from the precursors **1R** and **2R** along the routes 1a and 1b respectively are given in Chart 1. The strain energy build-ups in each step along the two conceived mechanisms are estimated at various levels and are given in Table 1. Fig. 1 plots the strain energy build-up in the twin pathways at all the levels considered in the study. Examination of Fig. 1 and Table 1 shows that the trends in energetics and conclusions obtained are essentially independent of the theoretical procedure adopted. Thus at all the levels, route 1a, which starts from a suitably substituted trindene and involves isomerizations, shows a substantial decrease in energy with each ring closure. This result accounts for the ease of the synthesis of trithiasumanene, the first heterobuckybowl, through a trindene route (Route 1a).[20] In sharp contrast, route 1b, starting from trisubstituted triphenylene, encounters high strain energy build-ups especially in the penultimate and final steps. This suggests that the ring closures leading to cyclo-



Scheme 7



Scheme 8

pentannulations encounter higher endothermicities and thereby higher activation energies compared to the benzannulations. Thus, the synthetic strategy towards sumanene (**I**) by Mehta *et al.*, which involves sequential cyclopentannulation encounters insurmountable strain build-up in the final step.[11] Recently, we proposed that incorporation of heteroatoms of appropriate size and in an appropriate position is the simplest strategy not only to modulate curvature, bowl rigidity and stability, but also to control the ease of their synthesis.[21,10] Thus, a larger atom substituted at the rim of the bowl facilitates the ring closure to some extent. However, this atom size effect seems to be much smaller compared to the differences between the cyclopentannulation and benzannulation.

The second model compound, pinakene (**II**), which maps on the surface of C_{70} has an ideal mix of five- and six-membered rings and thus becomes a good choice to test the relative ease of

Table 1 The heats of reactions obtained at various levels from **1R** and **2R** to obtain sumanene (**I**) *via* the ring closure strategy (Chart 1)[a]

	Route 1a			Route 1b		
Method	1R ⟶ M	M ⟶ D	D ⟶ I	2R ⟶ M′	M′ ⟶ D′	D′ ⟶ I
AM1	−42.6	−28.1	−30.2	11.8	36.2	50.4
MNDO	−46.2	−29.7	−24.1	−2.3	19.6	46.4
PM3	−41.4	−28.6	−30.6	6.4	30.2	45.0
B3LYP/cc-pVDZ[b]	−56.7	−43.4	−44.8	8.1	33.5	52.7
B3LYP/cc-pVDZ[c]	−56.9	−43.4	−44.8	8.6	32.4	54.5

[a] All values are given in kcal mol^{-1}. [b] Single point calculation on AM1 optimized geometry. [c] Single point calculation on MNDO optimized geometry.

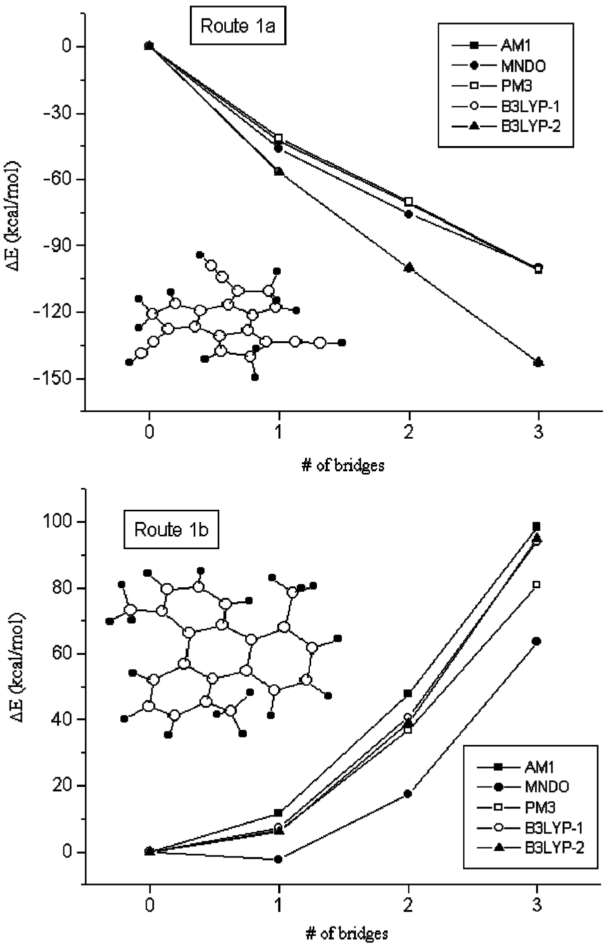


Fig. 1 Plot of strain energy build-ups *via* routes 1a and 1b (Chart 1) towards sumanene (**I**) obtained at various levels of theory (B3LYP-1: B3LYP/cc-pVDZ//AM1 and B3LYP-2: B3LYP/cc-pVDZ//MNDO). The MNDO optimized structures of the precursors (**1R** and **2R**) are given as insets.

cyclopentannulation and benzannulation. Among many possible retrosynthetic pathways, six of the key idealized routes were considered. The routes 2a and 2b contain only five-membered ring precursors and thus all further ring closures involve exclusively benzannulations. In contrast, routes 2c–2f start from skeletons containing only six-membered rings and each step involves a cyclopentannulation. Schemes 3–8 give all the conceived reaction paths and the strain energy build-ups starting from the precursors **3R**–**8R**. Here only semi-empirical optimizations were performed and the build-ups of strain energy in the sequential ring closure processes are depicted in Fig. 2, by taking MNDO values, for all the routes considered. The MNDO, AM1 and PM3 results are given in bold, underlined and italic fonts respectively, in Schemes 3–8. The Schemes indicate that essentially the same qualitative trends are obtained with either AM1 or PM3 studies, albeit with minor quantitative differences. Fig. 2a and 2b show a substantial decrease in the strain energy following benzannulations, which may be traced to the aromatic stabilization of the product as well as the reduction in the *peri*-hydrogen repulsions in going from the reactant to product upon ring closure. Prominently, a substantial lowering of strain is witnessed along routes 2a and 2b in many steps with a marginal increase in the final step. In sharp contrast, but parallelling the case of sumanene, Fig. 2c–2f show a consistent build-up of strain energy from the first ring closure which further increases with each bridging. One directed attempt towards pinakene (**II**) starting from precursor **6R**, did not yield the necessary ring closures to give the desired product.[12]

The optimized structures of the reactants are given as insets in Fig. 1 and 2. A critical examination suggests that the reactants, which are precursors for the benzannulations, were showing a lower degree of out-of-plane distortive tendency compared to the precursors for the cyclopentannulation reactions. *peri*-Hydrogen repulsions in the planar geometry are responsible for the puckering of the reactants considered in the study. If we consider the out-of-plane distortive tendency as a measure of instability, the precursors with all six-membered rings (**2R**, **5R**–**8R**) are less stable than the precursors with all the requisite five-membered rings (**1R**, **3R** and **4R**). In all cases, the major steric problems may be attributed to the CH_3 or CH_2 groups exocyclic to the six- or five-membered rings. Thus, the reactant instability cannot be the reason for the ease with which the benzannulations were taking place and electronic factors should be responsible for such big differences between the two routes. Therefore, the substantial decrease in the strain energy following benzannulations may be attributed to the aromatic stabilization of the product as well as the reduction in the *peri*-hydrogen repulsions upon the ring closure.

Therefore, all routes which involve cyclopentannulations encounter severe strain energy in the final step, which means that in general these routes are not expected to be very successful for the synthesis of buckybowls. These observations account for the futility of synthetic efforts towards pinakene (**II**) and sumanene (**I**) in synthetic strategies involving sequential cyclopentannulations starting from a planar all six-membered ring skeleton.[11,12] More importantly, the present study suggests that the precursors in both cases are very likely to result in the formation of these elusive buckybowls. It may also be noted that among more than half a dozen successful syntheses of corannulene, all but one of the precursors include the requisite five-membered ring, which might point to the fact that the generation of a five-membered ring is a relatively difficult task.[22] It is possible that the syntheses of the precursors for routes 1b and 2c–2f are easier than those for routes 1a, 2a and 2b. Clearly, the only way to solve the bottleneck is to identify the appropriate precursor which can potentially yield the product.

Conclusions

Model studies on two buckybowls, sumanene (**I**) and pinakene (**II**), predict that benzannulation is a significantly easier process than cyclopentannulation. In both cases, aromatic stabilization leads to significant lowering of strain energies on benzannul-

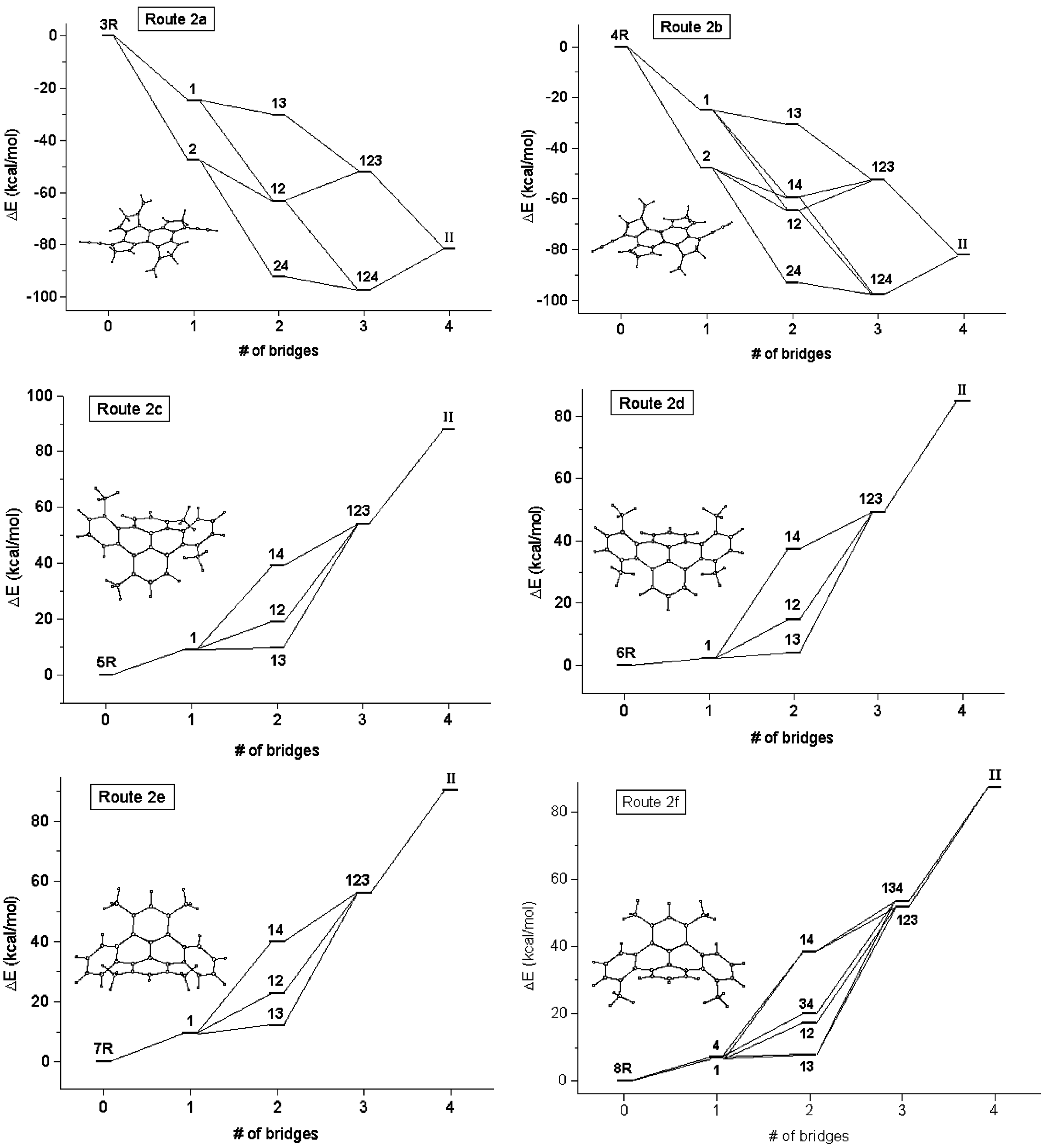


Fig. 2 Plot showing the strain energy buildup obtained at MNDO level in a sequential ring closure strategy towards pinakene (**II**) along routes 2a–2f. The numbering is derived from Scheme 2 (also check in Schemes 3–8). The MNDO optimized structures of precursors (**3R**–**8R**) are given as insets.

ation. In contrast, cyclopentannulation steps involve a high strain energy build-up. Thus, this analysis infers that, wherever possible, the synthesis of buckybowls is easier to achieve when starting from precursors possessing the maximum number of five-membered rings. This is supported by the recently published strategy of Ferrier *et al.* towards C_{60} through a 'tetramer' of trindane, which provides all 12 five-membered rings in the precursor, which appears to be very promising, and could potentially provide the breakthrough in the synthesis of C_{60}.[3]

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References

1 (*a*) A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, New York, 1994; (*b*) R. F. Curl, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1566; (*c*) H. Kroto, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1579; (*d*) R. E. Smalley, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1595.

2 D. Shen, PhD Dissertation, Approaches to Soccerene (I*h*–C_{60}) and Other Carbon Spheres, UCLA, 1990.

3 R. J. Ferrier, S. G. Holden and O. Gladkikh, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3505.

4 R. Faust, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1429.

5 (*a*) G. Mehta and H. S. P. Rao, *Tetrahedron*, 1998, **54**, 13325; (*b*) G. Mehta and H. S. P. Rao, In *Advances in Strain in Organic Chemistry*, ed. B. Halton, JAI Press, London, 1997, vol. 6, pp. 139–187; (*c*) G. Mehta and G. Panda, *Proc. Indian Natl. Sci. Acad., Part A*, 1998, **64**, 587.

6 L. T. Scott, H. E. Bronstein, D. V. Preda, R. B. M. Ansems, M. S. Bratcher and S. Hagen, *Pure Appl. Chem.*, 1999, **71**, 209.

7 P. W. Rabideau and A. Sygula, *Acc. Chem. Res.*, 1996, **29**, 235.

8 (*a*) G. N. Sastry, E. D. Jemmis, G. Mehta and S. R. Shah, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1867; (*b*) E. D. Jemmis, G. N. Sastry and G. Mehta, *J. Chem. Soc., Perkin Trans. 2*, 1994, 437.

9 (*a*) U. D. Priyakumar and G. N. Sastry, *Tetrahedron Lett.*, 2001, **42**, 1379; (*b*) T. C. Dinadayalane and G. N. Sastry, *Tetrahedron Lett.*, 2001, **42**, 6241.

10 (*a*) U. D. Priyakumar and G. N. Sastry, *J. Org. Chem.*, 2001, **66**, 6523; (*b*) U. D. Priyakumar and G. N. Sastry, *J. Mol. Graphics*

Modell., 2001, **19**, 266; (*c*) T. C. Dinadayalane, U. D. Priyakumar and G. N. Sastry, *J. Mol. Struct., (THEOCHEM)*, 2001, **543**, 1.

11 G. Mehta, S. R. Shah and K. Ravikumar, *J. Chem. Soc., Chem. Commun.*, 1993, 1006.

12 G. Mehta, G. Panda, R. D. Yadav and K. Ravikumar, *Indian J. Chem.*, 1997, **36B**, 301.

13 G. J. Bodwell, J. J. Fleming, M. R. Mannion and D. O. Miller., *J. Org. Chem.*, 2000, **65**, 5360.

14 MOPAC 2000 ver. 1.06, J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan, 1999.

15 Jaguar 4.1, Schrodinger, Inc., Portland, Oregon, 2000.

16 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.

17 M. J. S. Dewar, Z. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

18 (*a*) J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209; (*b*) J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.

19 (*a*) T. C. Dinadayalane and G. N. Sastry, *J. Mol. Struct., (THEOCHEM)*, 2002, in the press; (*b*) I. Yavari, E. Taj-Khorshid, D. Nori-Shargh and S. Balalaie, *J. Mol. Struct. (THEOCHEM)*, 1997, **393**, 163.

20 K. Imamura, K. Takimiya, Y. Aso and T. Otsubo, *Chem. Commun.*, 1999, 1859.

21 (*a*) G. N. Sastry, H. S. P. Rao, P. Bednarek and U. D. Priyakumar, *Chem. Commun.*, 2000, 843; (*b*) G. N. Sastry and U. D. Priyakumar, *J. Chem. Soc., Perkin Trans. 2*, 2001, 30.

22 (*a*) L. T. Scott, M. M. Hashemi and M. S. Bratcher, *J. Am. Chem. Soc.*, 1992, **114**, 1920; (*b*) A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldridge and J. S. Siegel, *J. Am. Chem. Soc.*, 1992, **114**, 1921; (*c*) C. Z. Liu and P. W. Rabideau, *Tetrahedron Lett.*, 1996, **37**, 3437; (*d*) G. Mehta and G. Panda, *Tetrahedron Lett.*, 1997, **38**, 2145.