CAGE GEOMETRY CONTROLLED HYPERSTABILITY IN BRIDGEHEAD OLEFINS[+]

## S. Lalitha,[a] Jayaraman Chandrasekhar*[a], and Goverdhan Mehta*[b]

[a]Department of Organic Chemistry,
Indian Institute of Science, Bangalore 560 012, India
[b]School of Chemistry,
University of Hyderabad, Hyderabad 500 134, India.

Summary : MM2 calculations indicate that roofed polyquinane ring systems containing trans double bonds are hyperstable. The stability results from repulsions at the rim of the cylindrical cage in the hydrogenated forms.

Using molecular mechanics calculations, Maier and Schleyer[1] made the remarkable proposal that certain ring systems enclosing a trans double bond[2] may have less strain than their saturated analogues (i.e. olefin strain, OS, is negative).[3] As an important chemical consequence, such hyperstable olefins were predicted to resist hydrogenation.[4] Numerous examples of bridgehead olefins with the above characteristics have since been experimentally observed.[2,5] Further computational work has led to the generalization that anti-Bredt olefins with the trans double bond in a medium ring (with 10 or more atoms) may all be hyperstable.[6,7]

The above results have considerable significance for the tetraquinane + diquinane approach (**1**)[8] envisaged for the synthesis of dodecahedrane, which involves roofed polyquinanes, **2** and **3**. These systems possess trans double bonds formally enclosed in 10 and 11 membered rings. Any hyperstability associated with these olefins would inhibit the hydrogenation step essential for the eventual construction of the dodecahedrane framework. We have therefore used MM2 calculations[9] for critically evaluating the strain energies in these systems. The relative rigidity of the cage compounds is expected to lead to precise estimates compared to many of the bridgehead olefins studied earlier.[1,6,7,10]

$$\underline{a}: X = CH_2$$
$$\underline{b}: X = CO$$

1   **2**   **3**
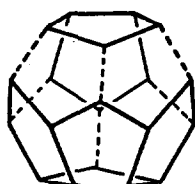
[+]Dedicated to Professor P. v. R. Schleyer on the occasion of his 60th Birthday

The strain energies computed for the trienes, **2a** and **3a**, are substantially lower than those of their saturated analogues, **12a** and **13a**, respectively.[11] Although the reduction per double bond is not as large as in some of the bridgehead systems examined earlier,[6,7] both **2a** and **3a** are clearly hyperstable. Even the partially reduced bridgehead olefins, **4a**, **6a**, **8a**, **5a**, **7a**, and **9a**, have negative OS values ranging from -5.4 to -9.3 kcal/mol (Scheme 1). Thus, the heats of hydrogenation of the trans double bonds in these systems are as low as 17-21 kcal/mol (compared to 26.1 kcal/mol for unstrained trisubstituted olefins[1]).

Scheme 1: Calculated OS values (heats of hydrogenation in parentheses)
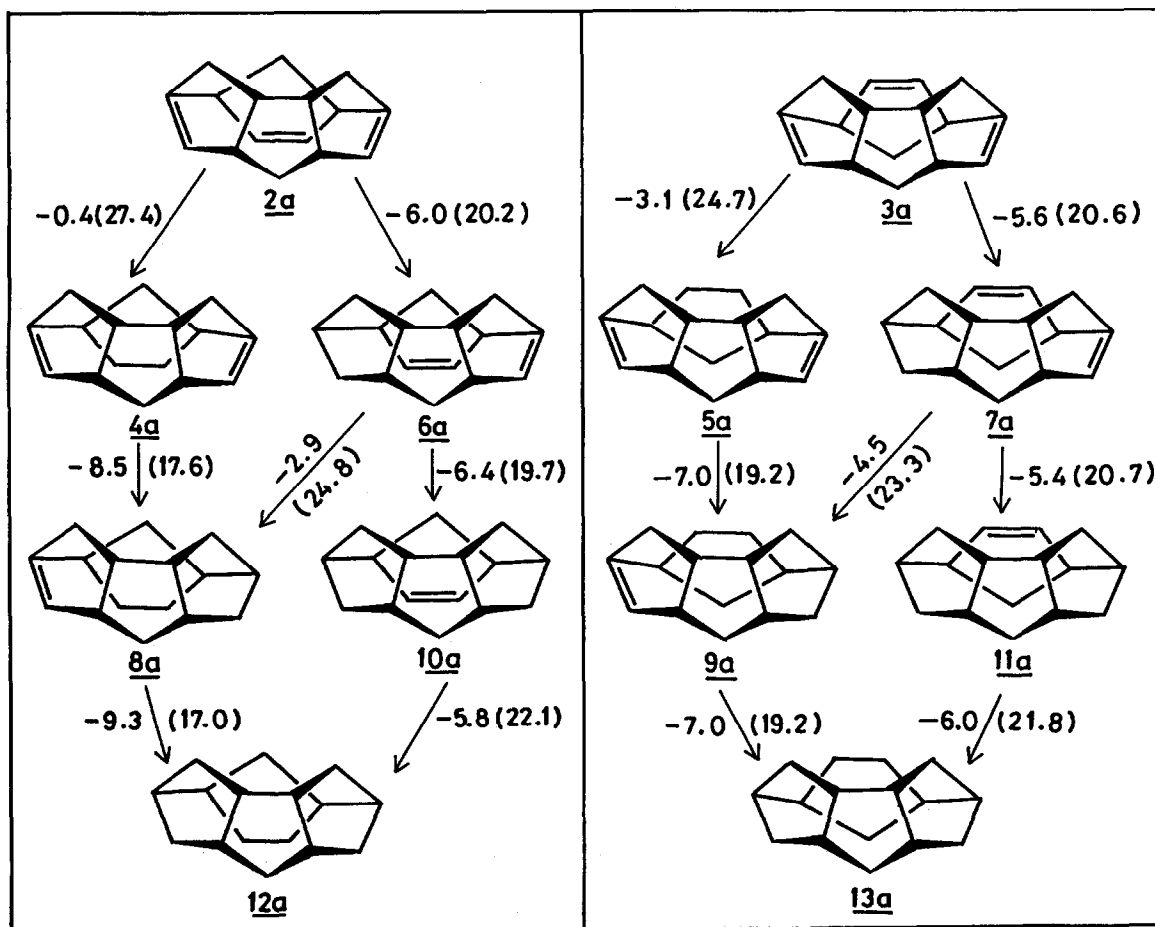
Interestingly, the corresponding dicarbonyl compounds have far less hyperstability. The total OS value for **2b** is only -5.9 kcal/mol, while it is virtually zero for **3b** (Scheme 2). However, some of the hydrogenation steps along the overall reduction pathway may prove to be bottlenecks even in these systems. For example, **10b** can be reached with relative ease from **2b** by the reduction of

the two trans double bonds (ΔH_{hyd} of 29 kcal/mol per step), but the final hydrogenation leads to an increase in strain of 5.5 kcal/mol (ΔH_{hyd} = 22 kcal/mol). A similar trend is found for the hydrogenation steps involving **3b**.

Scheme 2: Calculated OS values (heats of hydrogenation in parentheses)
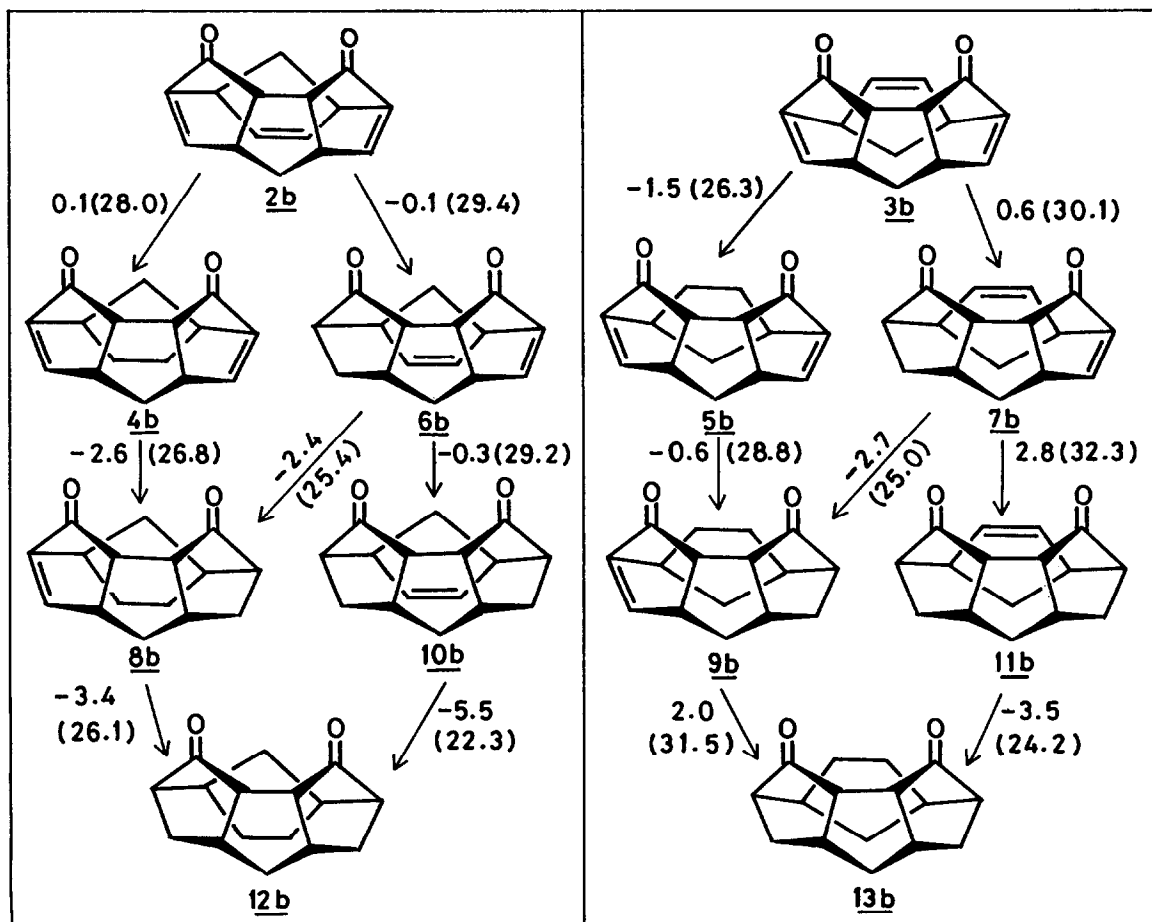
The reduction in hyperstability due to carbonyl groups outside the rings containing the trans double bonds is significant in two respects. For the synthetic strategy **1**, the additional carbonyl groups are indicated to be crucial for the smooth hydrogenation of the double bonds, apart from being needed for the insertion of an additional carbon to complete the tetraquinane subunit.[8,12] Further, the result points to the possible origin of hyperstability in these systems. In these cylindrical molecules, hydrogenation of a double bond leads to enhanced nonbonded repulsions, especially at the rim of the cage. The effect is quite pronounced in **2b** and **3b** due to H..H interactions,[13] but is reduced when two methylene fragments are replaced by carbonyl units.[14] Thus, the hyperstability in these systems is essentially determined by the cage geometry and is significantly modulated by remote substituents at the rim of the cage.

References and Notes

1. W. F. Maier and P. v.R. Schleyer, J. Am. Chem. Soc., **1981**, 103, 1891.

2. Reviews: P. M. Warner, Chem. Rev. **1989**, 89, 1067; W. T. Borden, ibid., **1989**, 89, 1095.

3. OS = Strain energy of olefin - strain energy of the hydrogenated analog.

4. Bond isomerisation during hydrogenation has been suggested to be another indicator of hyperstability: D. K. Johnson and B. P. Mundy, Tetrahedron Lett., **1989**, 30, 6633.

5. H. Kukuk, E. Proksch, and A. de Meijere, Angew. Chem. Int. Ed. Engl., **1982**, 21, 306; Y. Tobe, Y. Ueda, M. Matsumoto, Y. Sakai, and Y. Odaira, Tetrahedron Lett., **1982**, 23, 537; Y. Tobe, T. Kishimura, K. Kakiuchi, and Y. Odaira, J. Org. Chem., **1983**, 48, 551; W. R. Roth, Nachr. Chem. Tech. Lab., **1983**, 31, 964; J. E. McMurry and C. N. Hodge, J. Am. Chem. Soc., **1984**, 106, 609; Z. H. Li and M. Jones, Tetrahedron Lett., **1987**, 28, 753.

6. A. B. McEwen and P. v.R. Schleyer, J. Am. Chem. Soc., **1986**, 108, 3951.

7. P. M. Warner and S. Peacock, J. Comput. Chem., **1982**, 3, 417; P. M. Warner and S. Peacock, Tetrahedron Lett., **1983**, 24, 4169.

8. G. Mehta and K. Raja Reddy, Tetrahedron Letters, **1988**, 29, 5309; K. Raja Reddy, Ph. D. Thesis, University of Hyderabad, 1989.

9. N. L. Allinger, J. Am. Chem. Soc., **1977**, 99, 8127. Inclusion of π calculations for the enones using the MMP1 parameterisation (N. L. Allinger and J. T. Sprague, ibid., **1973**, 95, 3893) does not affect the conclusions, the OS values being altered by less than 2 kcal/mol.

10. The calculated heats of formation and strain energies (in kcal/mol) are : 2a : 65.2, 47.1; 2b : 16.0, 52.4; 3a : 65.4, 47.3; 3b : 17.5, 54.0. The corresponding values for the other systems can be obtained from the Schemes.

11. The perhydro molecules 12 and 13 as well as 10a and 10b do have some conformational flexibility. The values shown in the Schemes correspond to the most stable conformers (two of the cyclopentyl rings are puckered 'in'; the corresponding 'out'conformers are 1-5 kcal/mol higher in energy).

12. Experimental results[8] indicate that 2b and 3b can be hydrogenated to the corresponding perhydro compounds 12b and 13b, respectively, quite uneventfully, although isomerisation also occurs with 3b.

13. For an ultrashort H..H contact in a half cage molecule, see: O. Ermer, S. A. Mason, F. A. L. Anet, and S. V. Miura, J. Am. Chem. Soc., **1985**, 107, 2330.

14. For a study of transannular carbonyl interactions in a cage molecule, see: T. J. Chow and T.-K. Wu, Tetrahedron Lett., **1989**, 1279.