The thermodynamic stabilities of tricyclic tetraene $C_{12}H_{12}$ hydrocarbons

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The thermodynamic stabilities and heats of formation of tricyclic $C_{12}H_{12}$ tetraenes **1**–**6** as well as of a truncated tetrahedron hydrocarbon isomer **7** were computed by various density functional methods in conjunction with a polarized double-ζ basis set. As the DFT stabilities of **1**–**7** differ significantly from the MM2, MM3, MM4 and AM1 results, we conclude that these empirical and semiempirical methods are inappropriate to study such polycyclic hydrocarbons. Compound **6** with only endocyclic double bonds, a potential synthetic precursor of **7**, is found to be less favorable energetically than the other isomers. Although the C_{sp3}–C_{sp3} single bonds in **1**–**6** are rather long (1.601 to 1.620 Å) due to a combination of ring strain and hyperconjugation, the small nucleus-independent chemical shift (NICS) values of **1** and **6** confirm the expectation that cyclic electron delocalization is lacking. In contrast, NICS is unusually large in the cage center (−14.6) of **7**, but this is due to the cumulative diatropic influence of the four cyclopropane rings.

Introduction

The family of tricyclic $C_{12}H_{12}$ tetraenes (**1**–**6**, Chart 1), recently studied by Herb and Gleiter,[1] attracts attention not only for aesthetic reasons. Tetraene **6** has been the target of several unsuccessful synthetic attempts[2,3] since Woodward and Hoffmann[4] suggested in 1969 that the yet unknown dodecane **7** (a truncated tetrahedron) might be accessible from **6** by an allowed $[_{\pi}2_a + {}_{\pi}2_a + {}_{\pi}2_a + {}_{\pi}2_a]$ photocyclization. This reaction was computed later by Schriver and Gerson[5] as well as by Schulman *et al.*[6,7] to be exothermic by 18 (HF/6-31G*//HF-3-21G)[5] or by 24 kcal mol^{-1} (HF/6-31G*//HF/STO-3G).[6,7]

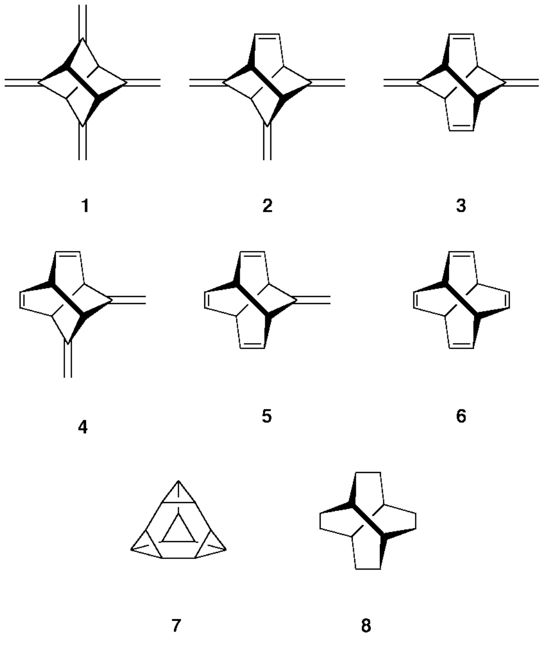

Chart 1 Tricyclic $C_{12}H_{12}$ tetraenes **1**–**6**, the truncated tetrahedron **7**, and saturated hydrocarbon **8**

Herb and Gleiter[1] recently succeeded in preparing **2** and demonstrated that this tricyclic tetraene is a thermodynamically stable species. However, **2** undergoes Cope rearrangements involving the hexa-1,5-diene moieties at room temperature.[1] In an effort to assess the thermodynamic stabilities of **1**–**6**, Herb and Gleiter[1] computed the strain energies of these compounds using an empirical molecular mechanics approach (MMX). They found that the novel compound **2** is the second most highly strained member of this $C_{12}H_{12}$ family; only stellatetraene **1** is more highly strained.[1] Thus, as Herb and Gleiter argued,[1] the less strained isomers **3** to **6** should be stable as well and accessible to synthesis.

Clearly, the limited theoretical data available on the $C_{12}H_{12}$ isomers demands a higher level treatment to give more reliable thermodynamic stabilities of these systems. In this paper we determine the heats of formation and strain energies of isomers **1**–**6** using density functional methods. In contrast to Herb and Gleiter,[1] we find that isomer **6** has the highest strain energy. The successful synthesis of **2** therefore does not necessarily indicate that **6** might be stable as well.

Computational methods

The geometries were completely optimized utilizing various density functional theory (DFT) approaches as implemented in Gaussian 94.[8] Residual Cartesian forces were smaller than 10^{-5} au. Analytic second derivatives were computed for all optimized structures to determine the nature of the stationary points and to obtain thermochemical data for $T = 298$ K using the unscaled harmonic vibrational frequencies. We used Becke's half and half,[9] Becke's three-parameter,[10] and Becke's[11] 1988 exchange functional together with the correlation functional of Lee, Yang and Parr,[12] abbreviated as BHLYP, B3LYP and BLYP, respectively. In addition, the latter two exchange functionals were combined with Perdew's[13] correlation functional (P86) giving rise to the B3P86 and BP86 methods. All computations employed the Huzinaga–Dunning[14,15] double-ζ basis set augmented with one set of polarization functions (DZP) with orbital exponents $a_d(C) = 0.75$ and $a_p(H) = 0.75$. In this paper we only report the B3LYP/DZP+ZPVE results as this density functional method is commonly considered to be the most reliable. Similar energies were obtained with the other functionals and are given in Table 1. In addition, we computed the heats of formation using the MM2,[16] MM3[17] and MM4[18]

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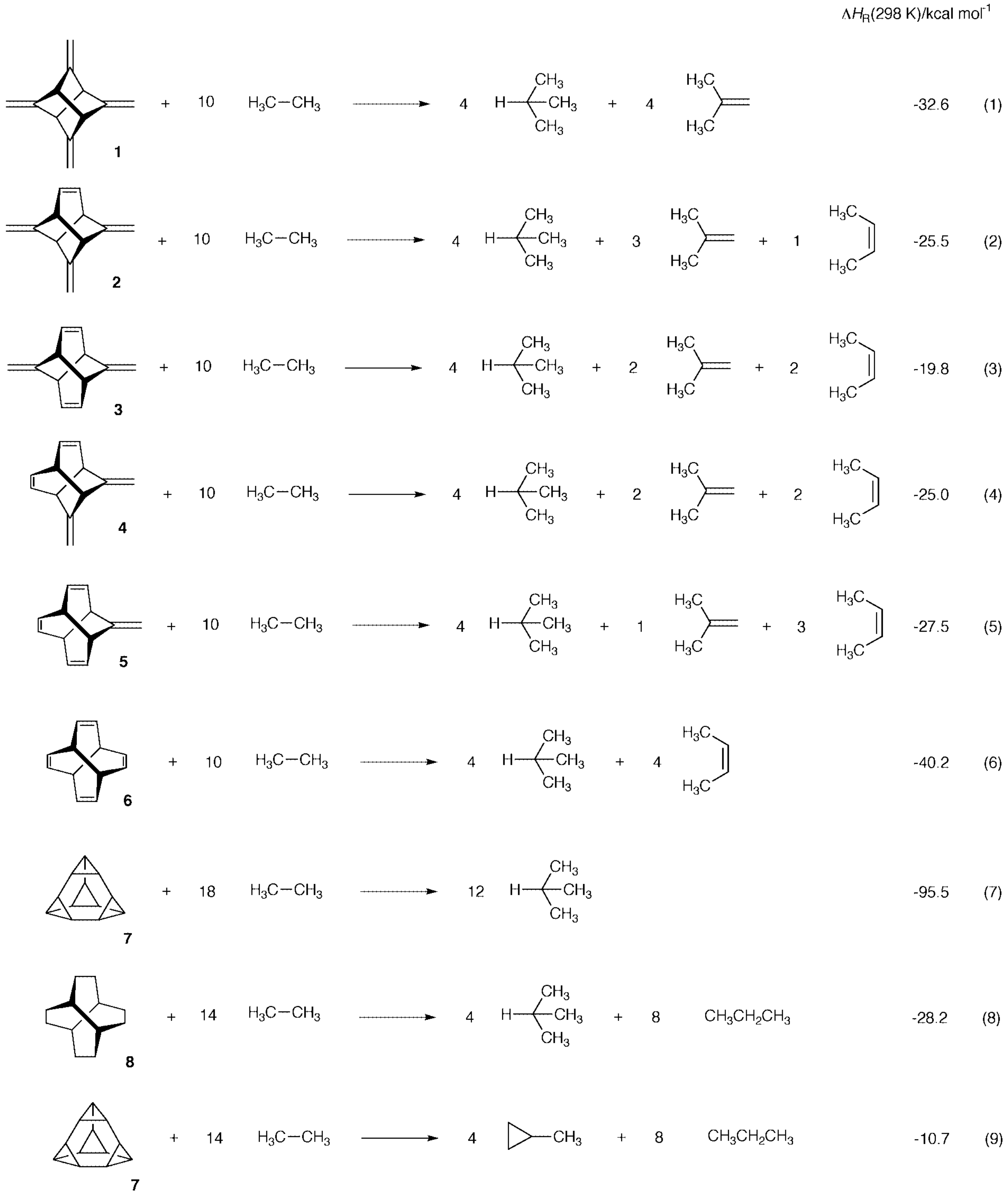


Scheme 1 Reactions (1) to (9) for the evaluation of strain in compounds **1** to **8**.

empirical force fields as well as the AM1[19] semiempirical Hamiltonian as implemented in the Spartan 5.0.3[20] program. The nucleus-independent chemical shifts (NICS)[21] were evaluated at the center of mass for **1**, **6**, **7** and **8** using the GIAO[22] approach at the HF/6-31+G*//B3LYP/DZP level. In addition, the SOS-DFPT-IGLO level using the Perdew–Wang-91 exchange-correlation functional and the IGLO-III TZ2P basis set as implemented in the deMon NMR program was used for NICS computations of **7**.[23–26]

Results and discussion

Energetic properties of $C_{12}H_{12}$ hydrocarbons

All DFT methods employed in this study agree that twistatetraene **3** is the most stable isomer among the six tricyclic $C_{12}H_{12}$ tetraenes (Tables 1 and 2). Although **4** also has two endocyclic and two exocyclic double bonds, it is consistently 5–6 kcal mol^{-1} higher in energy. Compounds **2** and **5** are thermodynamically less stable than **3**, by 6–7 kcal mol^{-1}, respectively. Stellatetraene (**1**) and **6** are even less favorable energetically (13–19 kcal mol^{-1} relative to **3**). Hence, the energetic order of isomers obtained at B3LYP/DZP + ZPVE is: **3** < **4** < **2** < **5** < **1** < **6**.

The heats of formation ΔH_f° (Table 2) of **1**–**6** at $T = 298$ K were evaluated using the reaction enthalpies $\Delta H_R(298\ \text{K})$ (Table 2) of homodesmotic reactions (1) to (6) and the experimental ΔH_f° of ethane, isobutane, 1,1-dimethylethene and (*Z*)-butene.[27] The $\Delta H_R(298\ \text{K})$ values (Table 2) and the strain of the tricyclic tetraenes, increase to the same extent in the order **3** < **4** < **2** < **5** < **1** < **6**. The heats of formation of **1**–**6** follow the same pattern as the total energies: compound **3** is the most stable, **6** is by far the thermodynamically least stable isomer as its $\Delta H_\mathrm{f}^\circ = 105$ kcal mol^{-1} and is well above the 80–90 kcal mol^{-1} range obtained for **1** to **5** (Table 2).

An alternative way to evaluate the strain in **1**–**6** is to compare the computed heats of formation $\Delta H_\mathrm{f}^\circ$ with the heats of formation, $\Delta H_\mathrm{f}^\circ$(increment), estimated with the "strain free" increments[28] of Cohen and Benson[29] (eqn. (10)). We find

$$E_\mathrm{strain} = \Delta H_\mathrm{f}^\circ - \Delta H_\mathrm{f}^\circ(\mathrm{increment}) \qquad (10)$$

twistatetraene **3** to be the least strained compound (Table 2, $E_\mathrm{strain} = 23.1$ kcal mol^{-1}) and **6** to be the most highly strained system among the six tricyclic tetraenes studied ($E_\mathrm{strain} = 46.4$ kcal mol^{-1}). The strain computed for **2** ($E_\mathrm{strain} = 27.3$ kcal mol^{-1}), which has been synthesized by Herb and Gleiter,[1] is significantly smaller than that of **6**.

The relative stabilities of isomers **1**–**6** can be understood qualitatively based on their structures (Fig. 1). Following Wiberg,[30] the total strain can be estimated by considering the number and the nature of the least favorable component rings. For example, the tricyclooctane system in **1** is composed of three five membered rings, and its strain is larger than **2** where only two five membered rings are counted. The C_{sp3}–C_{sp3} bonds are significantly longer (1.626 Å) in the more highly strained stellatetraene **1** than in **2** (1.617 Å). Therefore, the transformation of an exocyclic (**1**) into an endocyclic double bond (**2**) results in a strain-reducing ring enlargement. A second transformation of this kind gives isomers **3** and **4**, which, however, differ in energy by 5 kcal mol^{-1}. But whereas the tricyclic framework of **4** can be considered to consist of one seven, one six and one five membered ring, only six membered rings comprise the most stable isomer **3**. The number of seven membered rings increases from **4** to **5** (two seven membered rings) and reaches its maximum of three for isomer **6**, which is the least stable and most highly strained $C_{12}H_{12}$ compound studied.

The strain of the saturated hydrocarbon cage bishomotwistane **8** evaluated with reaction (8) is 30.8 kcal mol^{-1}. This shows that much of the strain of **6** is due to its carbon skeleton. Note that the related twistane (the basic skeleton of **3**) is strained similarly (18–26 kcal mol^{-1}) according to empirical force field computations.[31,32] The homodesmotic reaction (7) indicates that the truncated tetrahedron **7** is severely strained [ΔH_R(298 K) = −95.5 kcal mol^{-1}, $E_\mathrm{strain} = 100.9$ kcal mol^{-1}]. This is mainly due to the presence of the four strained cyclopropane rings, as reaction (9) is only exothermic by 10.7 kcal mol^{-1}. However, **7** is 12.2 kcal mol^{-1} more stable than **6** at B3LYP/DZP + ZPVE; this reaction energy for **6**→**7** is somewhat smaller than obtained earlier (18–24 kcal mol^{-1}) from HF/6-31G*//HF/3-21G and HF/6-31G*//HF/STO-3G computations.[6,7] A heat of formation $\Delta H_\mathrm{f}^\circ$ of 72.1 kcal mol^{-1} is obtained for **7** from reaction (7); hence, $\Delta H_\mathrm{f}^\circ$ of **7** is 33.1 kcal mol^{-1} less than **6**.

Magnetic properties of $C_{12}H_{12}$ hydrocarbons

The nucleus-independent chemical shift (NICS) is a convenient probe for ring currents arising from cyclic electron delocalization (*e.g.*, aromaticity and homoaromaticity).[21] As the saturated analog (**8**, $E_\mathrm{strain} = 30.8$ kcal mol^{-1}) is only 15.6 kcal mol^{-1} less strained than **6**, the rather long C–C bonds in **1**–**6** (*e.g.*, 1.621 Å in **6**) evidently are not just due to strain (note the shorter 1.590 Å C–C lengths in **8**), but are also due to hyperconjugation.[33,34] This electron delocalization is not expected to be cyclic, as verified by the near zero NICS values found in **1** and **6** as well as in **8** (−3.8, +3.4 and −3.0 ppm, respectively).

The special magnetic properties of cyclopropane rings have been recognized for some time.[19] In particular, hydrogens located above the faces of cyclopropane moieties are shielded, and their NMR chemical shifts are shifted upfield. This behavior is excellent evidence for the σ aromaticity of cyclopropane rings.[35,36] Sauers has used NICS to explore a number of three-membered ring systems recently.[37] Due to its four ideally oriented cyclopropane rings, **7** exhibits an unusually large NICS value, −14.6 ppm, in the center of the cage. We ascribe this to the cumulative diatropic effects of the four three-membered rings (*i.e.* −3.5 ppm each). Indeed, NICS = −3.0 at a point located at the outside of the cage but at the same distance from the center of a three-ring face.

This was also verified by using IGLO to evaluate the contributions of each of the localized orbitals (*i.e.*, CC and CH

Table 1 Relative energies (E_rel/kcal mol^{-1}, corrected for the zero point vibrational energy) of **1**–**6** determined by various density functional methods and the DZP basis set

	E_rel/kcal mol^{-1}				
Compound	BHLYP	B3P86	BP86	BLYP	LSDA
1	16.3	16.3	14.6	12.9	19.9
2	7.5	7.5	6.5	5.6	9.3
3	0	0	0	0	0
4	5.8	5.7	5.1	4.6	6.5
5	6.8	6.8	6.8	6.7	6.8
6	18.6	18.7	18.5	18.1	16.5

Table 3 Heats of formation ($\Delta H_\mathrm{f}^\circ$/kcal mol^{-1}) of **1**–**7** determined by molecular mechanics and semiempirical levels of theory

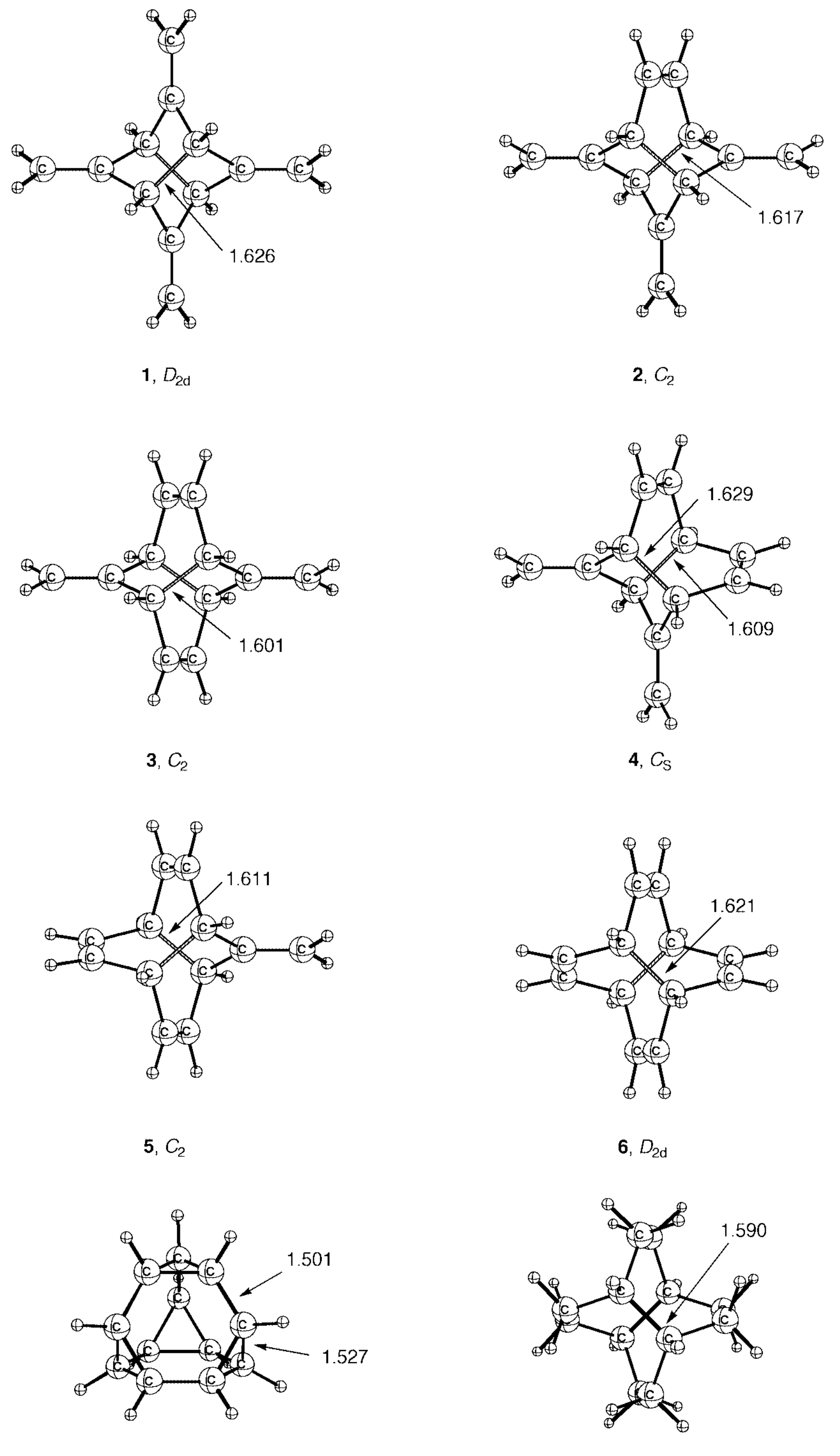
	$\Delta H_\mathrm{f}^\circ$/kcal mol^{-1}			
Compound	MM2	MM3	MM4	AM1
1	122.2	99.6	126.1	141.7
2	111.4	103.0	115.1	118.3
3	101.5	107.0	103.4	96.7
4	105.1	105.9	111.8	102.7
5	100.1	109.2	106.0	90.5
6	102.7	115.0	112.1	89.2
7	77.6	69.6	107.1[a]	104.5

[a] MM4 is not parameterized for three-membered rings.

Table 2 Relative energies (E_rel/kcal mol^{-1}), heats of reaction at 298 K (ΔH_R/kcal mol^{-1}, using reaction (*n*) for compound *n*), heats of formation ($\Delta H_\mathrm{f}^\circ$/kcal mol^{-1}) and strain energies (E_strain/kcal mol^{-1}) of **1**–**8** at the B3LYP/DZP level of theory

Compound	E_rel[a]	ΔH_R(298 K)	$\Delta H_\mathrm{f}^\circ$	E_strain[b]	E_strain (MMX)[c]
1	14.6	−32.6	89.2	33.0	77.6
2	6.6	−25.5	84.2	27.3	65.2
3	0	−19.8	80.6	23.1	53.6
4	5.2	−25.0	85.8	28.3	57.7
5	6.7	−27.5	90.4	32.2	51.2
6	18.3	−40.2	105.2	46.4	52.6
7	6.1	−95.5	72.1	100.9	n.a.
8	—	−28.2	−18.8	30.8	n.a.

[a] All data are corrected for the zero-point vibrational energies. [b] Obtained according to: $E_\mathrm{strain} = \Delta H_\mathrm{f}^\circ - \Delta H_\mathrm{f}^\circ$(increment). [c] From ref. 1.



1, D_{2d} **2**, C_2 **3**, C_2 **4**, C_S **5**, C_2 **6**, D_{2d} **7**, T_d **8**, D_{2d}

Fig. 1 Important geometric parameters (in Å) of tricyclic $C_{12}H_{12}$ tetraene hydrocarbons **1**–**8** obtained at the B3LYP/DZP level of theory.

bonds) in **7** to the total shielding at the center. The total contributions of the twelve cyclopropane-ring CC bonds is −10.2 ppm. The remaining shielding is due to the CH bonds (the other CC bonds have a small paratropic influence).

Conclusions

All empirical and semiempirical approaches employed in this study give energetic orderings of isomers **1**–**6** (Table 3 and Fig. 2) which differ dramatically from those obtained with DFT methods (Tables 1 and 2, Fig. 2). Stellatetraene (**1**) and **2** are the least stable isomers as determined by MM2, MM4 and AM1 methods in agreement with Herb and Gleiter's[1] MMX findings. We find **1** and **6** to be the least, and **3** to be the most stable isomers. Clearly, empirical and semiempirical methods are not suited to investigate the stability of the tricyclic $C_{12}H_{12}$ tetraene hydrocarbons investigated here. The DFT results undermine the energetic basis for the optimistic conclusion expressed by Herb and Gleiter[1] regarding the possible synthesis of isomers **3** to **6**. Of course, many molecules are persistent despite their strain, and the strains in **1** to **6** are only moderately large. The observational stability of such molecules will depend more on the rearrangement barriers to possible alternative structures. The C_{sp3}–C_{sp3} bonds in **1**–**6** are elongated (to 1.60–1.62 Å), in

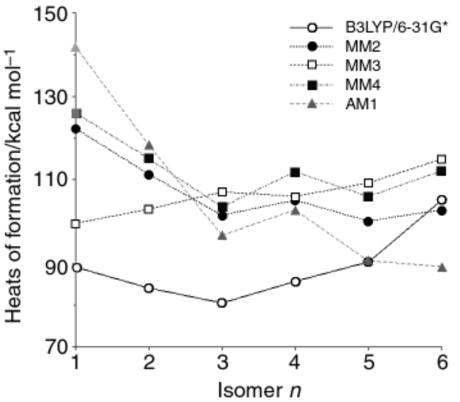


Fig. 2 The heats of formation (ΔH_f°/kcal mol^{-1}) of tricyclic $C_{12}H_{12}$ tetraene hydrocarbons **1**–**6**.

part due to hyperconjugation. Nucleus-independent chemical shifts (NICS) computed in the cage center, are quite small in **1**–**6** indicating there is no cyclic electron delocalization. The same is true for **7**, despite the NICS value of −14.6. This is due to the cumulative effect of the four cyclopropane rings.

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