STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 1-2, 2000

HEATS OF FORMATION OF MEDIUM-RING STRAINED CYCLO- AND POLYCYCLOALKANES: COMPARISON OF AB INITIO GROUP EQUIVALENT SCHEMES WITH THE PM3 AND MMX METHODS

LILIANA CRĂCIUN[a,b] and JAMES E. JACKSON[a]

[a] Michigan State University, Department of Chemistry, East Lansing MI 48824-1322, USA
[b] Babes-Bolyai University, Department of Organic Chemistry, 11 Arany Janos Str., 3400 Cluj-Napoca, Romania

ABSTRACT. Optimized structures and energies were calculated for 57 small- and medium-ring strained polycyclic aliphatic hydrocarbons using ab initio HF/3-21G, HF/6-31G* and HF/6-31G** as well as P (semiempirical) and MMX (force field) methods. Best fit CH_2, CH and C group increments relating ab initio total energies to heats of formation were derived from the experimentally known ΔH_f. The ab initio increments deviate little from those previously reported by Wiberg and by Ibrahim and Schleyer, yielding the expected conclusion that the intrinsically isodesmic group increment approach extends efficiently to small- and medium-ring strained systems. For the present data set, the standard deviation between experimental and calculated heats of formation, from ab initio total energies and group increments, is 1.81 kcal/mol for the RHF/6-31G*//RHF/6-31G* calculation, and 1.74 kcal/mol for RHF/6-31G**//RHF/6-31G**, respectively. Less successful results are obtained from the HF/3-21G, PM3 and MMX data. As expected, systems with fused small rings are especially problematic for the latter methods.

INTRODUCTION

In the course of a study of hybridization and ^{13}C-^{1}H NMR coupling constants,[1] we recently obtained RHF/6-31G*//RHF/6-31G* wavefunctions and ab initio total energies for a large number of small- and medium-ring strained polycyclic hydrocarbons. Roughly half of this number have had experimental heats of formation reported. It was of interest to examine the performance of the Wiberg[2] and Ibrahim/Schleyer[3] (IS) hydrocarbon group increments in calculating heats of formation from ab initio energies for these compounds, as most previous work has focused on unstrained or small-ring systems. This

paper provides such an analysis for 57 hydrocarbons, of which several were beyond the range of practical computational tools when the above papers appeared. The new best fits for the CH_2, CH and C fragments deviate little from those previously reported, yielding the expected conclusion that the intrinsically isodesmic group increment approach extends effectively to medium-ring strained systems.

RESULTS AND DISCUSSION

The heat of formation of a compound is a useful characteristic, traditionally determined from combustion measurements. However, the accumulation of computational data at a consistent level for a wide variety of molecules and their correlation with experimental results allow an evaluation of their heats of formation from ab initio energies, as well. The ability to produce reliable estimates depends upon the computational method that is chosen. Molecular mechanics (MM) or semiempirical methods are not as generally useful, since the former method needs good experimental data, not always available, for parametrization,[4] while the latter approximates minimal basis-set calculations which frequently handle strained small-ring compounds unevenly.[5]

Conversion of ab initio calculated energies to heats of formation is commonly done by the use of isodesmic comparisons with closely related compounds of known thermochemistry, such that errors due to inadequacies of basis set or electron correlation treatment largely cancel out.[6] An isodesmic reaction is defined as a hypothetical thermoneutral process in which the number of formal bonds of each type is identical on both sides of the reaction. By appropriately choosing the components of the isodesmic reaction, the unknown heat of formation can be calculated from the corresponding energy differences. The absolute errors are likely to be comparable and can be assumed to cancel in calculation of the energy differences between related molecules. Isodesmic comparisons can provide a test of the reliability of the computational method by comparing the computed results with known experimental values.

The heat of formation of a compound may be estimated from tabulated data pertaining to individual structural fragments. Procedures have been developed for estimating thermodynamic characteristics by summing the contributions of the constituent groups. As was pointed out by Wiberg[2], such group equivalent schemes can be viewed as a subset of isodesmic reactions in which the substitution levels of all C sites are maintained constant. Thus, Wiberg[2] and subsequently, Ibrahim and Schleyer[3], empirically determined sets of group and atom equivalents, which, when subtracted from a compound's ab initio energy, yield its heat of formation, ΔH_f(calcd). Accordingly, ΔH_f(calcd) is expressed as the difference between the molecule's total energy and the summed increments of the component groups, as shown by the following relation:

$$\Delta H_f\,(\text{calcd}) = 627.5\left(E_T - \sum_i n_i E_i \right) \qquad (1)$$

where E_T is the ab initio total energy, *n* represents the number of atoms or groups of each sort, and E is the corresponding atom or group equivalent. Following these reports, simplified schemes with reduced number of parameters have been proposed,[7] and individualized atom or group parameters were developed for particular classes of compounds.[8] Bond/group equivalents have also been derived for alkanes from density functional calculations.[9] In a series of recent articles, Allinger *et al*.[10] outlined an alternative method which combines bond energy with group increments, while it includes terms to explicitly account for statistical mechanical effects of populating a molecule's higher energy conformations and low-lying vibrational states, as well as its translational and rotational motions.

The present study confirms that group equivalent-based heats of formation can be calculated with an accuracy close to that from experiments (see Table 1 and Figure 1). The wide variety of small- and medium-ring strained hydrocarbons used in this work provide a stringent test of the method. Heats of formation may also be estimated for species where experimental values are not available or difficult to obtain. In addition, strain energies have been calculated for all the compounds recorded in Table 1.[11] The experimental heats of formation, ΔH_f(exp), and calculated RHF/3-21G[12], RHF/6-31G*[13] and RHF/6-31G**[13] ab initio total energies for the compounds considered in this study are listed in Table 1. All quantum-chemical calculations (ab initio and semiempirical) were carried out using the SPARTAN program (version 5.0, Wavefunction Inc., Irvine, CA) running on a SGI Indigo2 workstation and include full geometry optimization. Three gaussian basis sets were used in the ab initio calculations; the resulting enthalpies of formation become more accurate with the use of systematically improved basis sets and point to the necessity of inclusion of *d*-type functions (basis sets 6-31G* and 6-31G**) in the basis set for more accurate predictions. The calculated values refer only to the lowest energy conformation, although in several cases the compounds exist as a Boltzmann distribution of different conformational isomers with somewhat different energies.

A least squares fit[14] of experimental vs. calculated heats of formation using equation 1 with the increments for CH_2, CH and C groups as adjustable parameters, yielded ΔH_f(calcd) values at the 3-21G, 6-31G* and 6-31G** basis set levels as listed in Table 1, along with the group increments in Table 2. For a range of ΔH_f(exp) from -60 to +150 kcal/mol, the standard deviation of experimental vs. calculated heats of formation is 1.81 kcal/mol for the RHF/6-31G*//RHF/6-31G* calculation and 1.74 kcal/mol for RHF/6-31G**//RHF/6-31G**, respectively, (see Table 2).

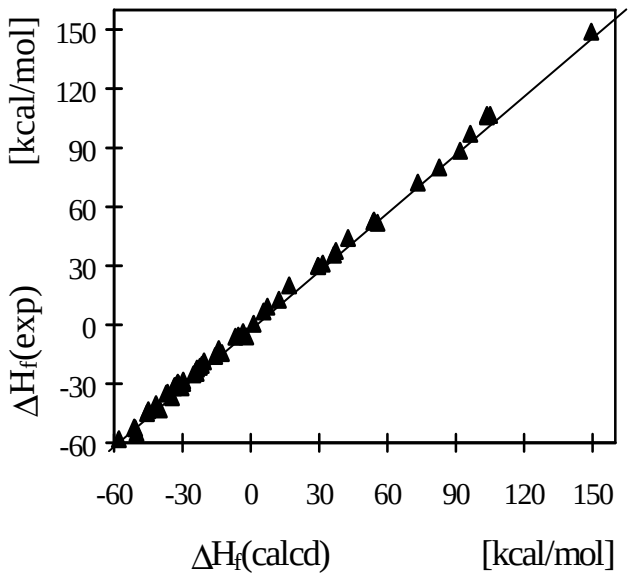

Figure 1. Plot of experimental heats of formation, ΔH_f (exp), vs. calculated values, ΔH_f(calcd), from the HF/6-31G* group equivalents evaluated in this work, for the compounds in Table 1. Slope 1.00 was taken for the correlation line.

The thermochemical measurements recently reported for a variety of spirocyclopropanated cyclopropane and cyclobutane derivatives[15] allowed to establish unambiguously an equivalent for the quaternary carbon atom, which was not available from the work of Ibrahim and Schleyer[3], while Wiberg's[2a] value for this parameter is based only on neopentane and spiropentane. The equivalents derived in this work for the CH_2, CH and C fragments (see Table 2) are essentially unchanged from those previously reported, supporting the consensus that errors due to incompleteness in basis set correlation treatment, and vibrational contributions scale linearly with the numbers of each group. They are absorbed in the group parameters, to yield calculated heats of formation of accuracy comparable to experimental measurements. The

improved 6-31G** basis set gives ΔH_f(calcd) basically unchanged from the 6-31G* values, which appears to be the minimal basis set necessary to appropriately describe systems incorporating small strained rings. The ΔH_f(calcd) values derived for the 3-21G basis set show large errors especially in the case of cyclopropane derivatives, where the flexibility afforded by inclusion of polarization functions into the basis set is essential for a proper description of these compounds.

Analogous values for the semiempirical PM3 method[16] are included in Table 1 for comparison. In general, it can be stated that the ab initio calculations are more reliable whereas semiempirical calculations are faster in terms of computer time. The semiempirical PM3 method is claimed to reliably estimate energies, however, in this work the resulting semiempirical heats of formation show unacceptably large errors; the standard deviation for the best linear fit between PM3 calculated and experimental heats of formation for the compounds listed in Table 1 is 8.0 kcal/mol. Unlike ab initio methods where self-consistency is achieved by iterative procedures and complex calculations with fewer assumptions, the accuracy of empirical methods is limited to the accuracy of the data used in parameterization, whereby parameters are included in the protocol to
adjust the results to match experimental data. Semiempirical methods should be applied with care when employed in prediction of properties or compounds not used in the parameterization, where frequent comparison of calculated and experimental results is imperative.

The MMX method, derived from Allinger's[17] MM2 force field, was also employed to compute heats of formation for the compounds included in Table 1.[18] Usually, MM reproduces well the thermodynamic properties of hydrocarbons; e.g., the new MM4 force field applied to 56 alkanes and cycloalkanes, excluding small rings, calculates ΔH_f with a standard deviation of 0.4 kcal/mol vs. experimental values.[19] However, the MMX results in Table 1 show that although most compounds have MMX ΔH_f(calcd) within experimental accuracy, in some cases there are large discrepancies between experiment and calculation (5 compounds in Table 1 have MMX ΔH_f(calcd) in error vs. ΔH_f(exp) with more than 10 kcal/mol). Thus, the performance of the MMX method (the best linear fit

of ΔH_f(exp) vs. ΔH_f(calcd) gives a s.d. of 4.2 kcal/mol for the compounds listed in Table 1), although much better than that of PM3 or HF/3-21G models, is not entirely consistent, leaving the ab initio HF/6-31G* or HF/6-31G** group equivalent schemes as the most reliable when compared to experiment.

CONCLUSIONS

The estimates of the enthalpies of formation using the 6-31G* or 6-31G** basis sets are in fair agreement with experimental measurements. As expected, the equivalents at the unpolarized 3-21G basis set cannot be used safely for strained compounds since polarization functions are known to be needed to properly describe small ring carbocyclics. These calculations can be used when experimental results for heats of formation are unavailable, or as an independent check when an experimental result of a particular heat of formation is in question.

REFERENCES

1. L. Craciun and J. E. Jackson, *J. Phys. Chem*. *A*, 1998, *102*, 3738.
2. (a) K. B. Wiberg, *J. Comput. Chem*., 1984, *5*, 197. (b) K. B. Wiberg, *J. Org. Chem*., 1985, *50*, 5285.
3. M. R. Ibrahim and P. v. R. Schleyer, *J. Comput. Chem*., 1985, *6*, 157.
4. U. Burkert and N. L. Allinger, *Molecular Mechanics*, ACS Monograph 177, 1982.
5. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc*., 1977, *99*, 4907.
6. (a) W. J. Hehre, R. Ditchfield, L. Radom and J. A. Pople, *J. Am. Chem. Soc*., 1970, *92*, 4796, and subsequent papers. (b) For an example of the use of homodesmic reactions to calculate the heats of formation of 15 representative strained and unstrained medium-sized hydrocarbons, see: R. L. Disch, J. M. Schulman, M. L. Sabio, *J. Am. Chem. Soc*., 1985, *107*, 1904.
7. (a) Z. Yala, *J. Mol. Struct*.: *THEOCHEM*., 1990, *207*, 217. (b) E. A. Castro, *J. Mol. Struct*.: *THEOCHEM*., 1994, *304*, 93. (c) W. C. Herndon, *Chem. Phys. Lett*., 1995, *234*, 82. (d) D. W. Smith, *J. Chem. Soc.*, *Faraday Trans*., 1996, *92*, 1141.
8. (a) J. M. Schulman, R. C. Peck and R. L. Disch, *J. Am. Chem. Soc*., 1989, *111*, 5675. (b) D. A. Armitage and C. W. Bird, *Tetrahedron Lett*., 1993, *34*, 5811.
9. N. L. Allinger, K. Sakakibara and J. Labanowski, *J. Phys. Chem*., 1995, *99*, 9603.

10. (a) N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Phys. Org. Chem*., 1990, *3*, 732. (b) N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Am. Chem. Soc*., 1992, *114*, 2880. (c) N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Comput. Chem*., 1992, *13*, 838. (d) L. R. Schmitz, I. Motoc, C. Bender, J. K. Labanowski and N. L. Allinger, *J. Phys. Org. Chem*., 1992, *5*, 225. (e) R. Liu and N. L. Allinger, *J. Phys. Org. Chem*., 1993, *6*, 551.

11. Strain energy is the difference between the experimental (calculated) heat of formation of a compound and that of a hypothetically “strainless” model, calculated here from Benson’s group equivalents (see S. W. Benson, *Thermochemical Kinetics*; John Wiley: New York, 1976).

12. J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc*., 1980, *102*, 939.

13. P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett*., 1972, *66*, 217.

14. 14.The analysis was done with Microsoft Excel version 5.0 employing the function LINEST, which uses the “least-squares” method to calculate simple or multiple linear regressions that best fit the input data.

15. H.-D. Beckhaus, C. Ruchardt, S. I. Kozhushkov, V. N. Belov, S. P. Verevkin and A. de Meijere, *J. Am. Chem. Soc*., 1995, *117*, 11854.

16. J. J. P. Stewart, *J. Comput. Chem*., 1989, *10*, 209.

17. N. L. Allinger, *J. Am. Chem. Soc*., 1977, *99*, 8127.

18. The MMX calculations were done using the interactive molecular modeling program PCMODEL, version 4.0 (Serena Software, Bloomington, IN).

19. N. L. Allinger, K. Chen and J.-H. Lii, *J. Comput. Chem*., 1996, *17*, 642.

Table 1

Experimental and Calculated Heats of Formation[a]

Alkane (*Symmetry*)[b]	ΔH_f(exp)[c] (SE)[d]	MMX ΔH_f[e]	PM3 ΔH_f[e]	HF/3-21G Total Energy	HF/3-21G ΔH_f[e]	HF/6-31G* Total Energy (SE)[d]	HF/6-31G* ΔH_f[e]	HF/6-31G** Total Energy (SE)[d]	HF/6-31G** ΔH_f[e]
1	2	3	4	5		6		7	
Cyclopropane* (D_{3h})	12.7±0.2 (27.6)	13.4	16.3	-116.40121	20.1	-117.05887	12.3 (27.2)	-117.06906	11.5 (26.4)
Cyclobutane* (D_{2d})	6.8±0.2 (26.6)	6.0	-3.8	-155.23102	8.3	-156.09720	4.6 (24.4)	-156.10818	4.3 (24.1)
Cyclopentane* (C_s)	-18.7±0.2 (6.1)	-18.3	-23.9	-194.08847	-20.8	-195.16358	-20.6 (4.2)	-195.17887	-20.8 (4.0)
Cyclohexane* (D_{3d})	-29.5±0.1 (0.2)	-29.5	-31.0	-232.91691	-31.7	-234.20801	-32.1 (-2.4)	-234.22625	-32.3 (-2.6)
Cycloheptane (C_2)	-28.3±0.1 (6.4)	-28.2	-30.9	-271.72211	-28.0	-273.23036	-29.7 (5.0)	-273.25163	-29.9 (4.8)
Cyclooctane (C_s)	-29.7±0.2 (9.9)	-29.5	-34.3	-310.53228	-27.4	-312.25650	-29.7 (9.9)	-312.28080	-30.0 (9.6)
Cyclononane (D_3)	31.9±0.4[f] (12.7)	-31.9	-39.9	-349.34586	-29.0	-351.28388	-30.5 (14.1)	-351.31122	-30.8 (13.8)
Cyclodecane (C_{2h})	36.9±0.4[f] (12.6)	-37.2	-47.4	-388.16237	-32.4	-390.31683	-34.8 (14.7)	-390.34727	-35.1 (14.4)
Cycloundecane (C_2)	43.1±0.4[f] (11.4)	-43.9	-54.7	-426.98278	-38.2	-429.35147	-40.1 (14.4)	-429.38337	-39.5 (15.0)
Cyclododecane (D_4)	55.0±0.5[f] (4.4)	-52.9	-63.2	-465.81188	-49.6	-468.39383	-50.3 (9.1)	-468.43026	-50.6 (8.8)
Spiropentane* (D_{2d})	44.2±0.2 (63.5)	44.0	43.1	-192.82114	49.3	-193.91776	43.1 (62.4)	-193.93143	42.6 (61.9)
Bicyclo[2.1.0]pentane* (C_s)	37.4±0.3[g] (56.1)	35.9	37.8	-192.83986	46.7	-193.92697	37.3 (56.0)	-193.94020	36.8 (55.5)
Bicyclopropyl (C_{2h})	31±1 (54.6)	36.7	36.1	-231.65313	45.3	-232.96227	31.6 (92.7)	-232.97926	30.6 (92.2)
Spiro[2.3]hexane (C_{2v})	29.9±0.4[i] (54.2)	29.5	21.0	-231.66019	31.8	-232.96504	29.8 (54.1)	-232.98124	29.6 (53.9)
Bicyclo[2.2.0]hexane* (C_{2v})	29.8±0.4[h] (53.4)	26.8	12.1	-231.67441	32.0	-232.96555	29.5 (53.1)	-232.98119	29.3 (52.9)

Table 1 (continued)

1	2	3	4	5		6		7	
Bicyclo[3.1.0]hexane (C_s)	9.2±0.1 (32.8)	8.6	8.1	-231.70454	13.1	-233.00107	7.2 (30.8)	-233.01709	6.8 (30.4)
Tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane (C_s)	88.4±0.4[j] (104.8)	106.0	107.6	-268.07893	110.1	-269.60362	92.0 (108.4)	-269.61814	91.2 (107.6)
Quadricyclane (C_{2v})	80±1 (96.4)	93.4	86.3	-268.10560	93.3	-269.61822	82.9 (99.3)	-269.63239	82.2 (98.6)
trans-Tricyclo[4.1.0.0^{2,4}]heptane (C_2)	35.7±0.4[k] (58.2)	53.4	41.2	-269.31988	47.4	-270.83630	36.5 (59.0)	-270.85294	36.0 (58.5)
Nortricyclane (C_{3v})	20±1 (42.5)	19.5	26.0	-269.36544	18.8	-270.86771	16.8 (39.3)	-270.88387	16.5 (39.0)
Dispiro[2.1.2.0]hep-tane (C_{2v})	72.3±0.8[m] (96.1)	76.0	70.9	-269.24060	78.9	-270.77646	74.1 (97.9)	-270.79359	73.8 (97.6)
cis-Bicyclo[4.1.0]hep-tane (C_1)	0.5±0.5 (29.1)	1.2	1.2	-270.52345	8.2	-272.03677	1.2 (29.8)	-272.05566	0.9 (29.5)
Bicyclo[2.2.1]heptane* (norbornane) (C_{2v})	12.4±0.7[l] (16.2)	-12.8	-13.7	-270.56656	-18.9	-272.06120	-14.1 (42.7)	-272.07947	-14.0 (42.6)
Cubane* (O_h)	149±1 (164.2)	148.9	113.8	-305.69590	143.3	-307.39391	149.5 (164.7)	-307.40775	149.3 (164.5)
Dispiro[2.0.2.2]octane (C_{2v})	53.0±0.2[i] (81.7)	56.6	46.9	-308.08974	55.0	-309.83304	54.9 (83.6)	-309.85298	54.8 (83.5)
Dispiro[2.1.2.1]octane (D_{2h})	52.4±0.3[i] (81.1)	69.4	46.2	-308.08928	55.3	-309.83354	54.6 (83.3)	-309.85351	54.5 (83.2)
cis-Bicyclo[5.1.0]oc-tane (C_s)	-3.8±0.7[n] (29.7)	-4.1	-3.0	-309.34119	4.0	-311.070361	-3.4 (30.1)	-311.09228	-3.8 (29.7)
cis-Bicyclo[4.2.0]oc-tane (C_1)	-6.1±1.0[n] (27.4)	-5.7	-15.8	-309.35566	-5.1	-311.07577	-6.8 (26.7)	-311.09724	-6.9 (26.6)
trans-Bicyclo[3.3.0]oc-tane (C_{2h})	15.9±0.6[n] (17.6)	-15.7	-18.8	-309.37442	-16.9	-311.08985	-15.7 (17.8)	-311.11112	-15.6 (17.9)
cis-Bicyclo[3.3.0]oc-tane (C_{2v})	22.3±0.5[n] (11.2)	-22.5	-31.6	-309.38836	-25.6	-311.10261	-23.7 (9.8)	-311.12391	-23.7 (9.8)
Bicyclo[2.2.2]octane* (D_{3h})	23.7±0.3[j] (9.8)	-22.7	-27.8	-309.39262	-28.3	-311.10360	-24.3 (9.2)	-311.12465	-24.1 (9.4)
Homocubane (C_{2v})	97±2 (117.2)	95.1	75.4	-344.59538	87.9	-346.50449	96.5 (116.7)	-346.52095	96.6 (116.8)
Trispiro[2.0.0.2.1.1]-nonane (C_2)	106.6±0.2[i] (134.8)	108.0	98.7	-345.66021	108.3	-347.63524	104.8 (133.0)	-347.65581	104.9 (133.1)

Table 1 (continued)

1	2	3	4	5		6		7	
Trispiro[2.0.2.0.2.0]-nonane (C_{3h})	105.9±0.3[j] (134.1)	109.2	99.5	-345.65931	108.9	-347.63510	104.9 (133.1)	-347.65566	105.0 (133.2)
cis-Bicyclo[6.1.0]no-nane (C_1)	-5.5±0.2 (33.0)	-7.7	-6.5	-348.15494	2.3	-350.09996	-5.6 (32.9)	-350.12494	-6.0 (32.5)
trans-Bicyclo[6.1.0]no-nane (C_2)	-6.0±0.3 (32.5)	-5.7	-3.0	-348.14956	5.7	-350.09437	-2.1 (36.4)	-350.11931	-2.5 (36.0)
cis-Bicyclo[4.3.0]no-nane (C_1)	-30.0±0.5 (8.5)	-28.8	-36.0	-348.21288	-34.1	-350.14175	-31.8 (6.7)	-350.16598	-31.8 (6.7)
Bicyclo[3.3.1]nonane (C_{2v})	-30.5±0.6[o] (8.0)	-30.5	-35.0	-348.21210	-33.6	-350.14164	-31.8 (6.7)	-350.16575	-31.6 (6.9)
trans-Bicyclo[4.3.0]no-nane (C_2)	-31.0±0.5 (7.5)	-26.5	-34.8	-348.21330	-34.3	-350.14361	-33.0 (5.5)	-350.16784	-32.9 (5.6)
endo-Tricyclo[5.2.1. $0^{2,6}$]decane (C_s)	-14.4±0.9[l] (22.9)	-12.5	-20.1	-385.85945	-19.4	-387.99314	-12.7 (24.6)	-388.01745	-12.4 (24.9)
Protoadamantane (C_1)	-20.5±0.6 (16.8)	-20.7	-25.1	-385.87380	-28.4	-388.00723	-21.5 (15.8)	-388.03132	-21.1 (16.2)
all-cis-Tricyclo[5.2.1. $0^{4,10}$]decane (C_3)	-24.5±0.9[p] (12.8)	-22.1	-35.0	-385.87574	-29.6	-388.01069	-23.7 (13.6)	-388.03504	-23.5 (13.8)
Adamantane (T_d)	-31.8±0.3 (5.5)	-31.5	-34.6	-385.89338	-40.6	-388.02648	-33.6 (3.7)	-389.05042	-33.1 (4.2)
Bicyclo[3.3.2]decane (C_s)	-25.3±1.7[o] (18.1)	-25.2	-28.3	-387.00849	-24.4	-389.15735	-25.2 (18.2)	-389.18452	-25.1 (18.3)
cis-Bicyclo[5.3.0]de-cane (C_s)	-31.1±1.2[n] (12.3)	-31.2	-38.3	-387.02301	-33.5	-389.17060	-33.5 (9.9)	-389.19787	-33.5 (9.9)
trans-Bicyclo[5.3.0]de-cane (C_1)	-31.4±1.4[q] (12.0)	-32.5	-37.7	-387.02141	-32.5	-389.16843	-32.2 (11.2)	-389.19568	-32.1 (11.3)
Spiro[4.5]decane (C_1)	-34.7±0.5[r] (9.4)	-36.8	-42.3	-387.03267	-48.7	-389.17506	-36.4 (7.7)	-389.20235	-36.0 (8.1)
cis-Decalin (C_2)	-40.4±0.5 (3.0)	-41.0	-42.7	-387.03893	-43.5	-389.18357	-41.7 (1.7)	-389.21074	-41.6 (1.8)
trans-Decalin (C_{2h})	-43.5±0.5 (-0.1)	-43.8	-44.5	-387.04355	-46.4	-389.18907	-45.1 (-1.7)	-389.21624	-45.0 (-1.6)
Bicyclo[3.3.3]undecane (manxane) (D_{3h})	-21.3±0.5[s] (27.1)	-24.3	-30.3	-425.81199	-19.6	-428.17907	-22.4 (26.0)	-428.20935	-22.4 (26.0)
Spiro[5.5]undecane (C_2)	-45.0±0.6[r] (4.0)	-46.3	-47.3	-425.85744	-57.3	-428.21535	-45.3 (3.7)	-428.24558	-44.9 (4.1)

Table 1 (continued)

1	2	3	4	5		6		7	
Tetraspiro[2.0.2.0.2.0.2.0]dodecane (D_{4h})	106.6±0.5[i] (144.2)	116.2	100.2	-460.94764	102.1	-463.56650	106.6 (144.2)	-463.59392	106.8 (144.4)
Bicyclohexyl (C_{2h})	-52.2±0.7 (1.1)	-52.0	-54.0	-464.67579	-52.7	-467.25114	-51.3 (2.0)	-467.28436	-51.2 (2.1)
Congressane (diamantane) (D_{3d})	-34.9±0.6[t] (10.0)	-34.3	-38.5	-538.87130	-50.5	-541.84810	-37.1 (7.8)	-541.87788	-36.0 (8.9)
trans-anti-trans-Perhydroanthracene (C_2)	-52.7±1.5[u] (4.4)	-52.0	-53.1	-541.15806	-53.4	-544.15840	-50.8 (6.3)	-544.19452	-50.4 (6.7)
trans-cisoid-trans-Perhydroanthracene (C_2)	-58.1±0.9 (-1.0)	-58.1	-57.9	-541.16868	-60.1	-544.17001	-58.1 (-1.0)	-544.20612	-57.7 (-0.6)

[a] Heats of formation at 298 K in kcal/mol; total energies in hartrees, 1 H = 627.5 kcal/mol. All structures were fully optimized using Spartan 4.0 (Wavefunction Inc., Irvine, CA). The compounds included in the original Wiberg's regression analysis for deriving group equivalents (ref. 2) are marked with asterisk (*).

[b] Symmetry of lowest energy conformation. [c] From NIST Standard Reference Database 25, Structures and Properties, version 2.02, January 1994, by Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. S. A., unless otherwise noted. [d] Strain energy; from experimental ΔH_f and Benson's group equivalents (Benson, S. W., *Thermochemical Kinetics*, John Wiley: New York, 1976). [e] This work; calculated from group equivalents analysis (see Table 2). [f] Heat of formation based on estimated heat of vaporization or sublimation from vapor pressure measurements. Cox, J. D.; Pilcher, G., *Thermochemistry of Organic and Organometallic Compounds*, Academic Press: New York, 1970. [g] Estimated from its heat of hydrogenation to cyclopentane. Roth, W. R.; Klarner, F.-G.; Lennartz, H.-W., *J. Am. Chem. Soc.*, 1982, *104*, 5679. [h] Estimated from its heat of hydrogenation to cyclohexane. See ref. h. [i] Beckhaus, H.-D.; Ruchardt, C.; Kozhushkov, S. I.; Belov, V. N.; Verevkin, S. P.; de Meijere, A., *J. Am. Chem. Soc.*, 1995, *117*, 11854. [j] Estimated from its heat of isomerization to 1,3,5-cycloheptatriene. Christl, M.; Brunn, E.; Roth, W. R.; Lennartz, H.-W., *Tetrahedron*, 1989, *45*, 2905. [k] Pimenova, S. M.; Fogel, L.; Kozina Gal'chenko, G. L., *Russ. J. Gen. Chem.*, 1974, *44*, 1383. [l] Boyd, R. H.; Sanwal, S. N.; Shary-Tehrany, S.; McNally, D., *J. Phys. Chem.*, 1971, *75*, 1264. [m] Luk'yanova, V. A.; Pimenova, S. M.; Kolesov, V. P.; Kuznetsova, T. S.; Kokoreva, O. V.; Kozhushkov, S. I.; Zefirov, N. S., *Russ. J. Phys. Chem.*, 1993, *67*, 1023. [n] Chang, S.-J.; McNally, D.; Shary-Tehrany, S.; Hickey, S. M. J.; Boyd, R. H., *J. Am. Chem. Soc.*, 1970, *92*, 3109. [o] Parker, W.; Steele, W. V.; Watt, I., *J. Chem. Thermodyn.*, 1977, *9*, 307. [p] Clark, T.; Knox, T.; Mackle, H.; McKervey, M. A., *J. Chem. Soc., Chem. Commun.*, 1975, 666. [q] Estimated from its heat of isomerization to *cis*-bicyclo[5.3.0]decane reported in Allinger, N. L.; Zalkow, V., *J. Am. Chem. Soc.*, 1961, *83*, 1144. [r] Pedley, J. B.; Naylor, R. D.; Kirby, S. P., *Thermochemical Data of Organic Compounds*, 2nd Ed., Chapman and Hall: London, 1986. [s] Parker, W.; Steele, W. V.; Stirling, W.; Watt, I., *J. Chem. Thermodyn.*, 1975, *7*, 795. [t] From its heat of combustion reported in Westrum, E. F.; McKervey, M. A.; Andrews, J. T. S.; Fort, R. C.; Clark, T., *J. Chem. Thermodyn.*, 1978, *10*, 959, (considered the most reliable), and its heat of sublimation reported in Clark, T.; Knox, T.; Mackle, H.; McKelvey, M. A.; Rooney, J. J., *J. Am. Chem. Soc.*, 1975, *97*, 3835. In a private communication (1978), McKervey reports a redetermination of the gas-phase heat of formation of diamantane of -34.6±0.6 kcal/mol. [u] Margrave, J. L.; Frisch, M. A.; Bautista, R. G.; Clarke, R. L.; Johnson, W. S., *J. Am. Chem. Soc.*, 1963, *85*, 546.