

Organic Thermochemistry at High ab Initio Levels. 2. Meeting the Challenge: Standard Heats of Formation of Gaseous Norbornane, 2-Norbornene, 2,5-Norbornadiene, Cubane, and Adamantane at the G2 Level

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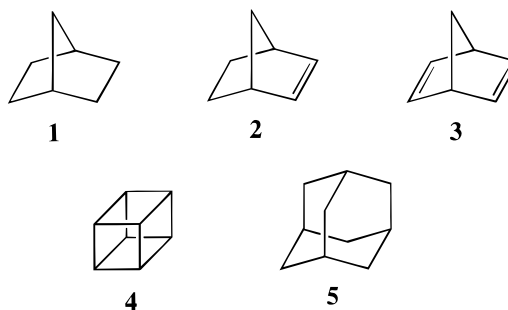
Norbornane (**1**), 2-norbornene (**2**), 2,5-norbornadiene (**3**), cubane (**4**), and adamantane (**5**) are large molecules for high-order computational studies and are subject to widely different degrees of strain. Ab initio studies at the G2(MP2) and G2 levels provide purely computational values of the standard enthalpies of formation in the gas phase for these compounds. These results are compared to the available experimental data in order to further assess the reliability of the thermochemical data obtained at these (reasonably high) computational levels.

Introduction

As indicated in our preceding paper,¹ G2-calculated standard enthalpies of formation in the gas phase of organic compounds are generally extremely close to the experimental values.^{2–5} It was found that the standard heat of formation in the gas phase of a compound M [the standard molar enthalpy of formation in the gas phase, $\Delta_f H_m^\circ(M, g)$] computed at the G2 level, by means of the bond separation isodesmic reaction scheme, agrees within 1.7 kcal mol⁻¹ or better with the experimental calorimetric values. In the case of organic molecules, it is of extreme importance to assess the ability of G2 theory to quantitatively describe the effect of internal strain. This is so, because strained species are often difficult to synthesize and, obviously, reliable computational methods should provide an ideal alternative to destructive calorimetric techniques.

Here we have examined five paradigmatic molecules: bicyclo[2.2.1]heptane (norbornane, C₇H₁₂, **1**), bicyclo[2.2.1]hept-2-ene (2-norbornene, C₇H₁₀, **2**), bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene, C₇H₈, **3**), pentacyclo[4.2.0.0.2.5.0.3.8.0.4.7]octane (cubane, C₈H₈, **4**), and tricyclo[3.3.1.1.3.7]decane (adamantane, C₁₀H₁₆, **5**) (see Chart 1). Internal strain in these molecules can be estimated in a variety of ways.⁶ Here, we use the experimental standard enthalpies of formation in the gas phase reported in Table 1 and the Schleyer⁸ and Ibrahim⁹ (values in parentheses) methods. The estimated stabilization energies (that

Chart 1



include the strain energy and any stabilizing interactions in the molecule) are, respectively, 16.9 (16.4), 23.3 (22.6), 34.0 (33.0), 166.0 (164.7), and 7.4 (6.6) kcal mol⁻¹ for **1**, **2**, **3**, **4**, and **5**. These compounds represent, therefore, a wide range strain effects. In regard to their sizes, we believe they are the largest systems ever treated at this level of theory.

Computational Details

1. G2 Techniques. Standard ab initio molecular orbital calculations¹⁰ were performed with the Gaussian94 series of programs.¹¹ Energies were obtained at the G2¹² and G2(MP2)¹³ levels of theory. The two methods differ in their implementation of additivity approximations, but each corresponds

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Table 1. G2(MP2) and G2 Total Energies at 0 K and Enthalpies at 298 K of Norbornane, 2-Norbornene, 2,5-Norbornadiene, Cubane, and Adamantane^a

compd	G2(MP2)		G2	
	E_0	H_{298}	E_0	H_{298}
norbornane, 1	-273.372 48	-273.365 69	-273.377 87	-273.371 08
2-norbornene, 2	-272.157 73	-272.151 40	-272.162 94	-272.156 60
2,5-norbornadiene, 3	-270.934 75	-270.928 81	-270.939 80	-270.933 86
cubane, 4	-308.847 60	-308.842 01	-308.853 24	-308.847 65
adamantane, 5	-389.889 90	-389.881 58	-389.897 41	-389.889 10

(a) All values in hartrees. 1 hartree = 627.5 kcal mol⁻¹.**Table 2.** G2(MP2)- and G2-Calculated Heats of Formation, at 298 K, of Norbornane, 2-Norbornene, 2,5-Norbornadiene, Cubane, and Adamantane^a

method	norbornane		2-norbornene		2,5-norbornadiene		cubane		adamantane	
	G2(MP2)	G2	G2(MP2)	G2	G2(MP2)	G2	G2(MP2)	G2	G2(MP2)	G2
atomization	-10.7	-14.1	22.5	21.1	61.0	59.6	149.6	148.1	-29.6	-31.7
bond separation	-13.4	-16.8	19.2	18.8	57.1	56.5	145.0 ^b	144.1	-33.8	-34.4
experimental ^c	-13.13 ± 0.25 ^d		19.7 ± 0.5 ^f		58.4 ^g		148.7 ± 1.0 ^p		-32.12 ± 0.56 ^q	
	-13.07 ± 1.12 ^e		20.4 ^g		57.4 ^h				-31.93 ± 0.60 ^r	
			21.4 ^h		59.18 ± 0.74 ^m				-30.79 ± 0.90 ^s	
			21.65 ± 0.81 ^e		58.5 ± 1.4 ⁿ				-32.96 ± 0.19 ^t	
			19.14 ± 0.37 ⁱ		58.64 ± 0.64 ^o					
			21.1 ± 0.65 ^j		50.59 ± 0.26 ^k					
			15.12 ± 0.42 ^k							
			28.9 ^l							

^a All values in kcal mol⁻¹. ^b There is a previous calculated value of 142.8 kcal mol⁻¹, obtained at G2(MP2,SVP) level; see ref 19. ^c Values taken from the compilation in ref 20. ^d Value taken from ref 21. ^e Value taken from ref 22 and reanalyzed in ref 23. ^f Value taken from ref 24. ^g Value taken from ref 25. ^h Value taken from ref 26. ⁱ Value taken from ref 27. ^j Value taken from ref 28. ^k Value taken from ref 29. ^l Value taken from ref 30. ^m Value taken from ref 22. ⁿ Value taken from ref 31. ^o Value taken from ref 28 and reanalyzed in ref 23. ^p Value taken from ref 32. ^q Value taken from ref 33 and reanalyzed in ref 23. ^r Value taken from ref 34 and reanalyzed in ref 23. ^s Value taken from ref 35. ^t Value taken from ref 36

fectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies and a so-called higher-level correction to accommodate remaining deficiencies.

Treatment of electron correlation in G2 theory is by Møller–Plesset (MP) perturbation theory at the MP2 and MP4 levels, and quadratic configuration interaction (QCI). G2(MP2) theory is based on reduced order of Møller–Plesset perturbation theory and has larger deviations, but saves computational time and disk space.

G2(MP2) and G2-calculated energies, at 0 K, for all the studied compounds (see Chart 1) are given in Table 1. All of these structures are minima on the potential energy surface.

To calculate enthalpy values at 298 K, the difference between the enthalpy at temperature T and 0 K can be evaluated according to standard thermodynamics.¹⁴ The thermal correction in G2 theory is made using scaled (0.8929) HF/6-31G(d) frequencies for the vibrations in the harmonic approximation for vibrational energy,¹⁵ the classical approximation for translation ($3/2RT$) and rotation ($3/2RT$ for nonlinear molecules and RT for linear molecules), and an additional RT for converting energy to enthalpy (the PV term).

G2(MP2) and G2 energies at 0 K, and enthalpies at 298 K, are collected in Table 1.

2. Standard Heats of Formation in the Gas Phase. (a) From Atomization Reactions. In standard G2 theory, theoretical enthalpies of formation at 0 K are calculated through atomization reactions. This procedure has been described in detail in our preceding paper.¹

G2(MP2) and G2-calculated heats of formation at 298 K of norbornane, 2-norbornene, 2,5-norbornadiene, cubane, and adamantane are given in Table 2.

(b) From Bond Separation Isodesmic Reactions. There has been some evidence in recent years that there is an

accumulation of errors in the application of G2 theory (or similar approaches) to larger molecules.^{2,4,16,17} Glukhovtsev and Laiter¹⁶ have shown that more accurate heats of formation for benzene and 1,3-butadiene can be derived using isodesmic or homodesmotic reactions rather than atomization energies as in standard G2 theory. The cancellation of errors for such cases involving similar chemical bonds obviously improves the agreement with experiment.

As Raghavachari et al.⁵ have pointed out, one of the deficiencies of the isodesmic reaction approach is that many different isodesmic reactions can be set up for the same molecule yielding different results. These authors have very recently proposed the use of simpler, but better defined reactions to assess the performance of theoretical methods in a more systematic manner. A standard set of isodesmic reactions are "bond separation reactions",¹⁰ where all formal bonds between nonhydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages. They demonstrated⁵ that the combination of such bond separation reactions with G2 theory generally leads to a significant improvement in the accuracy of theoretically evaluated heats of formation.

In the case of norbornane, the bond separation reaction using its effective valence bond structure is



The bond separation reaction energies are then evaluated at G2, or G2(MP2), levels of theory

$$\Delta H_{\text{BS}}^{\circ} = 8\text{G2}(\text{CH}_3\text{CH}_3, 298 \text{ K}) - 9\text{G2}(\text{CH}_4, 298 \text{ K}) - \text{G2}(\text{C}_7\text{H}_{12}, 298 \text{ K}) \quad (2)$$

and using the experimentally known heats of formation for the reference molecules, as given in ref 1:

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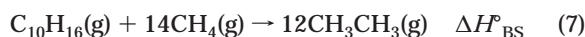
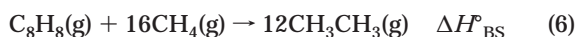
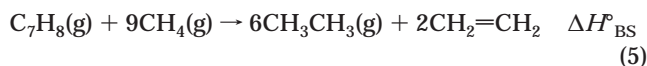
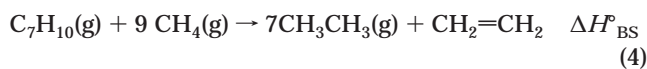
(15) Each normal mode contributes $Nh\nu/(e^{h\nu/kT} - 1)$ to thermal correction, where N is Avogadro's constant, h is Planck's constant, ν is the frequency, k is Boltzmann's constant, and T is the temperature.

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$$\Delta_f H_m^\circ(\text{C}_7\text{H}_{12}, 298 \text{ K}) = \text{G2}(\text{C}_7\text{H}_{12}, 298 \text{ K}) + 9\text{G2}(\text{CH}_4, 298 \text{ K}) - 8\text{G2}(\text{CH}_3\text{CH}_3, 298 \text{ K}) - 9\Delta_f H_{m,\text{exp}}^\circ(\text{CH}_4, 298 \text{ K}) + 8\Delta_f H_{m,\text{exp}}^\circ(\text{CH}_3\text{CH}_3, 298 \text{ K}) \quad (3)$$

In the cases of 2-norbornene, 2,5-norbornadiene, cubane, and adamantane, the process is similar, using the corresponding bond separation reactions, (4), (5), (6) and (7), respectively:



G2(MP2)- and G2-calculated heats of formation using bond separation reactions are collected in Table 2.

Notice that the coefficients of CH₄ and C₂H₆ in eqs 1, 4–7 are large. This necessarily introduces some systematic errors¹⁸ since the $\Delta_f H_m^\circ(\text{g})$ values of these compounds bear some experimental uncertainty (of the order of 0.1 kcal mol⁻¹).

Discussion

At variance with the experimental results reported in the preceding paper, the experimental uncertainties on the $\Delta_f H_m^\circ$ values of the compounds studied herein seem appreciably larger, as shown by the substantial scatter of the data. In the case of cubane, only one experimental datum is available for comparison.

The results obtained using the bond separation scheme are consistently smaller than those given by the atomization method and this applies to both the G2(MP2) and G2 values. This might be partially related to the experimental errors involved in the data for the ancillary compounds CH₄, C₂H₆, C₂H₄, etc. used in the computation of the $\Delta_f H_m^\circ$ values.

G2(MP2) data treated by the bond separation technique provides values of $\Delta_f H_m^\circ$ in very satisfactory agreement with experiment, except in the case of cubane (see below). Interestingly, the G2 method does not seem to perform better than G2(MP2).

Norbornane, 2-Norbornene, and 2,5-Norbornadiene. These compounds allow the examination of the performance of the computational methods in systems featuring internal strain and a variable number of double bonds.

In the case of norbornane, the two available experimental values agree remarkably well. For 2-norbornene, there are eight available experimental $\Delta_f H_m^\circ$ values. Excluding the last two values reported in Table 2, the mean experimental value is 20.6 ± 1.9 kcal mol⁻¹. In the case of 2,5-norbornadiene, there are six available experimental values. Excluding the last one reported in Table 2, the mean experimental value is 58.4 ± 2.2 kcal mol⁻¹.

In these three compounds, the bond separation scheme at the G2(MP2) level leads to values in very good agreement with experiments. However, in the case of G2 calculations the atomization method performs best, but the bond separation scheme leads to values lower than the experimental ones.

It is rewarding to see that the quality of the computational results does not seem to be affected by the presence of strained double bonds.

Cubane. There is only one direct experimental determination of $\Delta_f H_m^\circ$ for this compound. It is clear that in this case the atomization method performs best. Interestingly, the quality of the agreement is quite comparable to that found⁴ in the cases of cyclopropane (a difference between experiment and theory of -0.9 and -1.5 kcal mol⁻¹, at G2 and G2(MP2), respectively) and cyclobutane (-0.2 and -1.1 kcal mol⁻¹, at G2 and G2(MP2), respectively).

$\Delta_f H_m^\circ$ for 1,4-dimethylcubane dicarboxylate has been used³⁷ to estimate a value of 159.0 kcal mol⁻¹ for the $\Delta_f H^\circ$ of cubane. Our results as well as those of Wang and Law¹⁹ do not seem to support this estimate. The discrepancy likely originates in the internal repulsion between the two carbomethoxy groups of the diester³⁸ and, perhaps, as pointed out by a reviewer, in the estimate of the enthalpy of phase change involved in the “transplanting” of the ester moiety from cubane to cyclobutane and bicyclobutane.

Adamantane. The four available experimental data spans a range of 2.2 kcal mol⁻¹. The mean value is -32.0 ± 1.2 kcal mol⁻¹. As in the case of cubane, the atomization method performs best, the calculated value at the G2 level being approximately the mean value of the experimental ones.

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Conclusions

In the case of cage hydrocarbons:

1. The computational results, particularly at the G2 level using the atomization reactions and the G2(MP2) level using the bond separation reactions, seem of "experimental quality".

2. There seems to be no definite relationship between the size of the molecule and the difference between the experimental and calculated values of $\Delta_f H_m^\circ$.

3. Internal strain does not seem to affect the quality of the calculated $\Delta_f H_m^\circ$ values.

4. A useful practical conclusion derived from this and the preceding paper is the fact that "modest" level

G2(MP2) data treated by means of the bond separation scheme leads to $\Delta_f H_m^\circ$ values having the "chemical accuracy" (i.e., within ca. 2 kcal mol⁻¹) level of quality.

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