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Thermochemistry of Bridged-Ring Substances. Enthalpies of Formation of Some Diamondoid Hydrocarbons and of Perhydroquinacene. Comparisons with Data from Empirical Force Field Calculations

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Abstract: The enthalpies of combustion and of sublimation of nine bridged-ring hydrocarbons of the diamondoid class and of perhydroquinacene have been determined. The derived solid and gas-phase enthalpies of formation in kcal/mol at 298.15 K follow: adamantane, −46.02 ± 0.07, −31.76 ± 0.32; 1-methyladamantane, −56.72 ± 0.30, −40.57 ± 0.34; 2-methyladamantane, −51.80 ± 0.29, −35.66 ± 0.62 (recommended value −36.89); 1,3,5,7-tetramethyladamantane, −86.54 ± 0.47, −67.15 ± 0.50; protoadamantane, −36.04 ± 0.41, −20.54 ± 0.60; diamantane, −57.80 ± 0.61, −34.87 ± 0.64 (recommended value −34.54); 4-methyldiamantane, −62.51 ± 0.17, −43.53 ± 0.30; 3-methyldiamantane, −62.24 ± 0.48, −37.60 ± 0.58 (recommended value −39.67); 1-methyldiamantane, −59.12 ± 0.78, −39.85 ± 0.85; perhydroquinacene, −37.99 ± 0.76, −24.46 ± 0.86. Trends and methyl group increments within the diamondoid series are discussed. Enthalpy differences within the methyladamantanes and methyldiamantanes are compared with existing data from equilibration studies. The enthalpy of isomerization of protoadamantane into adamantane is discussed in the light of indirect estimates from existing experimental data on derivatives in solution. Comparisons are made between the experimental gas-phase enthalpies of formation and those obtained by molecular mechanics calculations based on the MM1 (1971), EAS (1973), WB (1977), and MM2 (1977) force field models. With the exception of perhydroquinacene, the MM2 force field gives predictions in excellent agreement with the experimental data. The enthalpy of formation of perhydroquinacene is discussed in the light of experimental data for cyclopentane and *cis*-bicyclo[3.3.0]octane and force field predictions for peristylane and the unknown hydrocarbon dodecahedrane.

Thermochemical data for some classes of chemical compounds are plentiful and reliable while for others the data are nonexistent, sparse, or of unacceptable quality. Even within individual classes there are notable gaps. In organic chemistry, for example, normal and branched-chain saturated hydrocarbons are reasonably well covered, whereas for cyclic structures, particularly those with unusual features such as severe angle strain, intramolecular overcrowding, or multiple bridging, the available data are limited and scattered.[2] At a time when experimental data are being collected only slowly it is important that reliable methods for predicting and correlating thermochemical properties be developed.[3] Clearly, if precise reliable structure–energy relationships could be established, further thermochemical measurements would scarcely be necessary, since enthalpies of compounds not studied experimentally could be estimated from their structures. Alkanes and cycloalkanes provide an important testing ground for such structure–energy relationships: these substances form the structural backbone of many organic compounds and reliable predictions of their thermochemical properties thus become a prerequisite to applications to molecules containing functional groups.

One approach to structure–energy relationships which is now being used extensively in organic chemistry is based on molecular mechanics (or empirical force field) calculations. In this method, pioneered by Westheimer[4] and later enlarged and extended by Hendrickson[5] and Wiberg,[6] a molecule is viewed as a collection of particles held together by simple harmonic or elastic forces. Electrons are not considered explicitly. Equations based on classical mechanics are used to define stretching, bending, torsional, nonbonded, and stretch–bend potential functions, the sum of which gives the geometry of a single minimum-energy conformation and the total steric energy of the molecule. Corrections for the chemical binding energy, the vibrational zero-point energy, and the thermal energy of translation, rotation, and vibration are then made to convert steric energies into enthalpies of formation in the gas phase at 25 °C.[7]

For organic chemists the ultimate objective of the molecular mechanics approach is the development of a simple generally applicable force-field model, extensively substantiated by experimental data, of predictive value for the structures, enthalpies, and spectral properties of a wide range of molecules representing a diversity of structural types and all the important functional groups. The greatest emphasis in this endeavor so far has been on saturated hydrocarbons. Of the many force-field models available, those devised by Henrickson,[5] Lifson,[8] Allinger (MM1[9] and MM2[10]), Boyd,[11] Schleyer (EAS[12]), and White (WB[13]) and their respective collaborators have been applied to the enthalpies and structures of alkanes and cycloalkanes. The molecular mechanics approach has several commendable features, not the least of which is the freedom to probe structures and energies of molecules either unknown or not at hand; furthermore, through the use of modern computers quite large polycyclic hydrocarbons are accessible within minutes, contrasting with the experimental approach through synthesis and combustion calorimetry which may require months of effort. The general acceptance of data from calculations and their use in quantitative interpretation of chemical phenomena depend on their reliability. A recent survey[12] of the use of the MM1[9] and EAS[12] force field models lists the enthalpies of formation and strain energies of some 84 cyclic hydrocarbons none of which has been measured experimentally. The molecular mechanics approach is, of course, a method of interpolation and extrapolation from existing experimental data and the general lack of sufficient, reliable experimental values makes accurate parametrization of the force field difficult. For this and other reasons to be discussed in this paper we have selected ten bridged-ring hydrocarbons with which to evaluate experimentally the predictive power of existing force-field models, while at the same time making available more data in the polycyclic series. For comparative

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purposes the list contains adamantane (**1**) and diamantane (**6**), for which experimental gas-phase enthalpies of formation were already available.

Experimental Section

Preparation and Purification of Hydrocarbons. Adamantane[14a] was obtained commercially. 1- and 2-methyladamantane (**2**[14b] and **3**),[14c] 1,3,5,7-tetramethyladamantane (**4**),[14b] protoadamantane (**5**),[14d] diamantane (**6**),[14e] 4-, 3-, and 1-methyldiamantane (**7**,[14b] **8**,[14f] and **9**),[14b] and perhydroquinacene (**10**)[14g] were prepared by published procedures and subjected to rigorous purification by column chromatography over alumina, recrystallization, fractional sublimation, and, with the exception of tetramethyladamantane (**4**), which was distilled twice and sublimed six times, multiple zone refining (30 molten zone passes). Purity was checked by GLC and DSC analysis and judged to be 99.99 mol %.[15] 2-Methyladamantane (**3**) and 3-methyldiamantane (**8**) are waxy solids which were very difficult to purify; waxy solids frequently form solid solutions with closely related compounds and in the case of the two compounds in question it is possible that undetectable amounts of impurities remained (vide infra).

Calorimetry. The calorimeter used was the Belfast Mark I[16] aneroid rotating bomb in the static mode. The calorimeter was extensively modified for the present work. The dc bridge used previously[16] was replaced by an Automatic Systems Ltd. H8 ac bridge coupled to a quartz crystal dual display (to $^1/_{100}$ s) digital clock. The jacket temperature was continuously monitored by a platinum resistance thermometer coupled to an Automatic Systems Ltd. H6 ac bridge. The copper jacket was thermostated manually throughout each combustion experiment. The data from the bomb calorimeter, clock, and jacket thermometer were processed by a Fortran IV program which first corrects the bomb temperature readings for deviations of the jacket from the standard isothermal jacket temperature and then calculates the bomb temperature rise under adiabatic conditions. The program uses previously determined calibration constants to relate the two resistance thermometer scales and the experimental Newton cooling constant for the bomb-jacket system. These constants were checked at regular intervals throughout the work. This arrangement allowed us to thermostat the jacket conveniently by computer rather than try to control its temperature manually within fine limits.

As all the compounds investigated were volatile solids they were burned in vacuum-formed polyethylene "pillboxes" with tightly fitting lids. These had been found to prevent sublimation while removing the need for sealing the boxes. A weight-time experiment on a pillbox containing 0.551 360 g of adamantane showed a weight loss of 0.000 002 g after 1.2 h at 25 °C; an uncovered sample of 0.392 710 g decreased in weight by 0.002 203 g over the same period at the same temperature. The polyethylene used was I.C.I. Ltd. sheet Alkathene. Two sheets were used: one for all compounds except the repeat measurements on diamantane for which the second sheet was used. Combustion analysis showed that the polyethylene was $(C_{1.00}H_{2.00})_n$ and control experiments showed no significant deviation of $\Delta E°_c$ within each sheet. The experimental energies of combustion, $\Delta E°_c$, follow: sheet 1, −11.1132 ± 0.0009 kcal/g; sheet 2, −11.1204 ± 0.0020 kcal/g. For all combustions, Whatman's no. 1 filter paper was used as the fuse with an enthalpy of combustion of 3995 ± 6 cal/g. All combustions were initiated by a platinum wire and a filter paper fuse. The oxygen supply was fitted with a complete purification system to remove both water and combustible impurities. The system contained two catalysts in series, followed by molecular sieves. The catalysts were 5% platinum adsorbed on alumina and finely divided copper oxide on carbon. Both were packed into one stainless steel tube 1 ft long, $^3/_4$ in. internal diameter, maintained at 250 °C. The catalysts were followed by another stainless steel tube, 6 in. long, of the same internal diameter, containing molecular sieves, type 5A, held at −78 °C. Before the bomb was charged with oxygen, the heating element around the catalysts was switched on for at least 45 min, and the molecular sieves were held at −78 °C for the same period. For each compound, with the exception of perhydroquinacene (**10**), the bomb was flushed with oxygen three times before charging to an initial pressure of 40 atm. Test runs showed that this procedure eliminated nitric acid formation. After each combustion the bomb was checked for soot and carbon monoxide. With perhydroquinacene the bomb was not flushed before charging with oxygen and the amount of nitric acid formed was determined by titration. Water (0.6 mL) was placed in the bomb prior to each run.

The energy equivalent of the calorimeter, Σ(calor), was determined by combustion of 0.5-g pellets of BDH thermochemical grade benzoic acid, batch no. 503 341. The value of Σ(calor) for the first calibration was 3968.83 ± 0.14 cal/Ω; that for the second calibration was 3905.92 ± 0.20 cal/Ω. The second calibration was necessary because of an accidental disconnection of the bomb thermometer and subsequent repair. The initial and final temperatures of combustion were 22.0 and 25.7 °C, respectively.

Results and Discussion

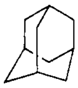
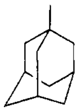
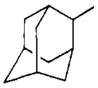
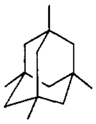
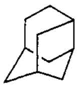
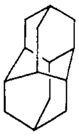
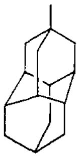
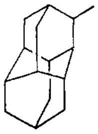
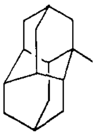
A summary of typical combustion experiments and of combustion results is available as supplementary material in Tables S1 and S2. The $-\Delta E°_c$ values refer to the following reaction:

$$C_aH_b(c) + (a + b/4)O_2(g) \rightarrow aCO_2(g) + b/2H_2O(l)$$

Table III lists the results derived from the experimental data at 298.15 K with uncertainties calculated as recommended by Rossini and Deming.[17] The values of $\Delta E°_c$ and $\Delta H°_c$ are for the idealized reaction above. Since all the substances are solids at 25 °C, the standard enthalpies of formation, $\Delta H°_f(c)$, include the intermolecular binding energies of the condensed state. Intermolecular binding energies can vary considerably even within closely related systems, thus masking true orders of thermochemical stability; and since we wished to compare our data with those from molecular mechanics calculations, which refer to the ideal gas state at 298.15 K, it was necessary to measure the enthalpies of sublimation, ΔH_{sub}. This was done on a Pye 104 gas chromatograph using the temperature scanning technique described previously.[18] The derived gas-phase enthalpies of formation, $\Delta H°_f(g)$, for all ten compounds are collected in Table III. After the completion of this research and the publication of a preliminary report,[19] Steele and Watt[20] reported $\Delta H°_f(g)$ data for six methyl-substituted adamantanes, three of which are pertinent to our studies. As we shall show presently, there are some inconsistencies in the measurement of Steele and Watt (Table VI).

Adamantane (**1**) is unique among bridged-ring saturated hydrocarbons in that its enthalpy of combustion has been the object of four independent investigations; and there have been at least six determinations of its enthalpy of sublimation (Table IV). Agreement within the latter is excellent, but in the former the values range over more than 2 kcal/mol. Within the error limits our value of −1441.01 kcal/mol for the standard enthalpy of combustion is in excellent agreement with two of the three earlier measurements, that due to Mansson et al[21] being most out of line. Our value of −31.76 kcal/mol for the gas-phase heat of formation of adamantane will be used in this discussion. The $\Delta H°_f(g)$ data for 1-methyladamantane (**2**) and 1,3,5,7-tetramethyladamantane (**4**) are entirely consistent with the adamantane value. This is presented in Table V in the form of bridgehead methyl group increments. Adamantane possesses four equivalent bridgehead hydrogen atoms and replacement of one of these by a methyl group produces an experimental enthalpy increment of −8.81 kcal/mol. In thermochemical terms, successive replacement of each of the three remaining tertiary hydrogen atoms by methyl groups should be accompanied by the same enthalpy increment provided that there are no nonbonded interactions between bridgehead substituents. The molecular geometry would appear to preclude any such interactions in adamantane; accordingly, we have assumed that the methyl group increment is constant. That this is a reasonable assumption is supported by the molecular mechanics calculations in Table V, which show that, notwithstanding differences among the various force fields, within each the methyl group increment is predicted to be constant or nearly so. The experimental data for the tetramethyl compound **4** (entry ii, Table V) show that replacement

Table III. Derived Thermochemical Daia at 298.15 K (kcal/mol)

	 1	 2	 3	 4	 5	 6	 7	 8	 9	 10
					Experimental					
$-\Delta E^\circ_c$(c)	1438.64	1590.01	1594.93	2046.40	1448.62	1939.10	2096.46	2096.73	2099.85	1446.67
	± 0.09	± 0.30	± 0.29	± 0.47	± 0.41	± 0.61	± 0.17	± 0.48	± 0.78	± 0.76
$-\Delta H^\circ_c$(c)	1441.01	1592.68	1597.60	2049.95	1450.99	1942.06	2099.72	2099.99	2103.11	1449.04
	± 0.09	± 0.30	± 0.29	± 0.47	± 0.41	± 0.61	± 0.17	± 0.48	± 0.78	± 0.76
$-\Delta H^\circ_f$(c)	46.02	56.72	51.80	86.54	36.04	57.80	62.51	62.24	59.12	37.99
	± 0.07	± 0.30	± 0.29	± 0.47	± 0.41	± 0.61	± 0.17	± 0.48	± 0.78	± 0.76
ΔH_{sub}	14.26	16.15	16.14	19.39	15.50	22.93	18.98	24.64	19.27	13.53
	± 0.20	± 0.12	± 0.50	± 0.22	± 0.42	± 0.19	± 0.30	± 0.24	± 0.10	± 0.31
(at T/K)	(323)	(321)	(320)	(305)	(322)	(319)	(322)	(316)	(322)	(307)
$-\Delta H^\circ_f$(g)	31.76	40.57	35.66	67.15	20.54	34.87	43.53	37.60	39.85	24.46
	± 0.32	± 0.34	± 0.62	± 0.50	± 0.60	± 0.64	± 0.30	± 0.58	± 0.85	± 0.86
recommended value	31.76	40.57	36.89[a]	67.15	20.54	34.54[a]	43.53	39.67[a]	39.85	24.46
					Molecular Mechanics Predictions					
−MM1[b]	33.82	42.89	39.04	70.21	22.63	38.13	47.21	43.35	44.43	19.74
ΔMM1	2.06	2.32	2.15	3.06	2.09	3.59	3.68	3.68	4.58	−4.72
−EAS[c]	32.50	41.82	37.94	70.26	21.13	37.37	46.82	42.91	43.56	23.74
ΔEAS	0.74	1.25	1.05	3.11	0.59	2.83	3.29	3.24	3.71	−0.72
−MM2[d]	31.55	40.25	36.89	66.46	20.73	34.30	43.03			22.08
ΔMM2	−0.21	−0.32	0.00	−0.69	0.19	−0.24	−0.50			−2.38
−WB[e]	29.61	38.90	35.69	67.05	19.45	33.06	42.43	39.31	40.46	23.46
ΔWB	−2.15	−1.67	−1.20	−0.10	−1.09	−1.48	−1.10	−0.36	0.61	−1.00

[a] See text. [b] Data from ref 12 obtained with the force field described in ref 9. [c] Data from the force field described in ref 12. [d] Data from the force field described in ref 10. [e] Data from the force field described in ref 13.

Table IV. Thermochemical Data for Adamantane (kcal/mol)

ΔH°_c(c)	ΔH_{sub}	ΔH°_f(g)
−1439.89 ± 0.17[a]	14.18 ± 0.04[a]	−32.96 ± 0.19[a]
−1441.95 ± 0.68[b]	14.45 ± 0.30[b]	−30.65 ± 0.98[b]
−1442.01 ± 0.48[c]	14.23 ± 0.20[c]	−30.57 ± 0.90[c]
−1441.01 ± 0.09[d]	14.26 ± 0.20[d]	−31.76 ± 0.32[d]
	14.00[e]	
	14.21[f]	

[a] Data from ref 21. [b] Data from ref 22. [c] Data from ref 23. [d] This work. [e] Data from ref 24. [f] Data from ref 25.

of all four tertiary hydrogen atoms by methyl groups produces an enthalpy change of −35.40 kcal/mol, or −8.85 kcal/mol for each methyl group. This result establishes that the data for adamantane, 1-methyladamantane, and 1,3,5,7-tetramethyladamantane are internally consistent. If, however, we apply the same treatment to the data of Steele and Watt (Table VI), using Steele's earlier value of −30.57 kcal/mol[23] for the enthalpy of formation of adamantane, a quite contrasting picture emerges: increments (kcal/mol), adamantane (−11.23) → 1-methyladamantane (−10.5) → 1,3-dimethyladamantane (−8.6) → 1,3,5-trimethyladamantane (−9.6) → 1,3,5,7-tetramethyladamantane. These differences suggest that there are inconsistencies in the data of Steele and Watt. On the basis of our data, we predict 1,3-dimethyladamantane and 1,3,5-trimethyladamantane to have ΔH°_f(g) values of −49.38 and −58.19 kcal/mol, respectively. The bridgehead methyl-group increment in the adamantane series provides a useful link with the diamantane series. Diamantane (**6**) possesses two distinctly different types of bridgehead, C-1 and C-4, and replacement of a hydrogen atom on the latter by a methyl group produces a structural change exactly equivalent in thermochemical terms to the adamantane–1-methyladamantane case. In a preliminary communication[19] we quoted a value of −32.60 ± 0.58 kcal/mol for the gas-phase enthalpy of formation of diamantane. This value is mutually inconsistent with the adamantane methyl-group increment of −8.8 kcal/mol and the measured ΔH°_f(g) value of −43.53 kcal/mol for 4-methyldiamantane (**7**). As it was essential that a reliable ΔH°_f(g) value for diamantane be established, we repeated the combustions and obtained a new ΔH°_c(c) value of −1942.06 ± 0.60 kcal/mol. At the same time, Dr. W. Good of the Bartlesville Energy Center, Oklahoma, kindly offered to conduct an independent series of combustions which produced a ΔH°_c(c) value of −1942.58 ± 0.32 kcal/mol. Weighing these two results on the basis of the uncertainties we obtain a value of −57.46 ± 0.36 kcal/mol for ΔH°_f(c); combining this value with the enthalpy of sublimation gives −34.54 ± 0.41 kcal/mol for the gas-phase enthalpy of formation of diamantane. The bridgehead methyl-group increment for diamantane → 4-methyldiamantane thus becomes −8.99 kcal/mol, in excellent agreement with the adamantane case. These methyl-group increments agree rather well with that of −9.12 kcal/mol for norbornane → 1,4-dimethylnorbornane (**2**) (entry v, Table V), the only other case among bridged-ring compounds to have been measured experimentally; topologically, the bridgehead positions of norbornane resemble the 1 position of adamantane and the 4 position of diamantane *vis-à-vis* methyl substitution. The simplest comparable case in the acyclic series is isobutane → neopentane (entry ix, Table V) for which the methyl group increment is −7.86 kcal/mol, about 1 kcal/mol less exothermic than values (i)–(iii) in the bridged ring series. For 3-methylpentane → 3-ethyl-3-methylpentane (entry x, Table V) the increment is only −6.1 kcal/mol. This pair provides a better model than isobutane–neopentane for the distinction between nonbonded interactions involving the relevant groups in the acylic and cyclic series. The least favorable conformation of 3-ethyl-3-methylpentane is that shown in A, which is formally analogous to the arrangement of the corresponding groups in

Table V. Increments for Adding Methyl Groups to Adamantane, Diamantane, Norbornane, and Isobutane (kcal/mol)

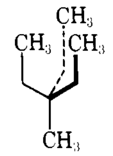
			molecular mechanics calculations			
		exptl	MM1[a]	EAS[a]	MM2[b]	WB[c]
(i)	adamantane → 1-methyladamantane	−8.81[d] −11.23[e]	−9.07	−9.32	−8.70	−9.27
(ii)	adamantane → 1,3,5,7-tetramethyladamantane/4	−8.85[d] −9.98[e]	−9.07	−9.44	−8.73	−9.38
(iii)	diamantane → 4-methyldiamantane	−8.99[d]	−9.08	−9.45	−8.79	−9.37
(iv)	norbornane → 1-methylnorbornane		−9.30	−9.56		
(v)	norbornane → 1,4-dimethylnorbornane/2	−9.12[f]	−9.31	−9.57		
(vi)	diamantane → 1-methyldiamantane	−5.31[d]	−6.30	−6.19		−7.40
(vii)	diamantane → 3-methyldiamantane	−3.06[d] (−5.13)[g]	−5.22	−5.54		−6.25
(viii)	adamantane → 2-methyladamantane	−3.90[d] (−5.13)[g] −6.83[e]	−5.44	−5.22	−5.40	−6.08
(ix)	isobutane → neopentane	−7.86[h]	−8.80	−7.74	−8.30	
(x)	3-ethylpentane → 3-ethyl-3-methypentane	−6.10[h]				

[a] Data from ref 12. [b] Data from ref 10. [c] Data from ref 13. [d] This work. [e] Data from ref 20. [f] Data from ref 26. [g] Corrected value; see text. [h] Data from the compilation of Cox and Pilcher, ref 2a.

Table VI. Thermochemical Data of Steele and Watt[20] (kcal/mol)

	$\Delta H^\circ_f(g)$
1-methyladamantane	−41.8 ± 0.5
2-methyladamantane	−37.4 ± 0.5
2,2-dimethyladamantane	−43.7 ± 0.7
1,3-dimethyladamantane	−52.3 ± 0.7
1,3,5-trimethyladamantane	−60.9 ± 1.0
1,3,5,7-tetramethyladamantane	−70.5 ± 0.9

1-methyladamantane. In A, 1,3-diaxial-type interactions exist between the three terminal methyl groups. These interactions can be relieved by rotation about two of the bonds to the quaternary carbon atom, giving the more favorable conformation B. However, B cannot be free of strain either: in this conformation there are now three gauche butane interactions with the tertiary methyl group. Therefore the methyl group increment in the acyclic pair should be, and is, less exothermic than that in adamantane–1-methyladamantane, the difference of ~2.8 kcal/mol being roughly equal to three gauche butane interactions.



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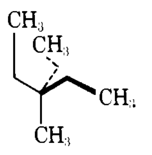
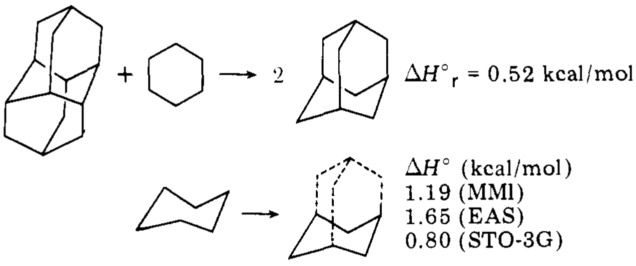


B

The enthalpy increment for placing a methyl group at the 1 position of diamantane is less than that for the 4 position. This is due to stability differences caused by the environments of the methyl group in the two isomers: in the 4 isomer **7** the substituent occupies an equatorial position with respect to three cyclohexane rings of the nucleus whereas in the 1 isomer **9** the substituent is axially located with respect to one cyclohexane ring of the nucleus. Accordingly, isomer **9** should be, and is, less thermochemically stable than isomer **7** and the bridgehead methyl-group increment should be smaller in the latter case (entry vi, Table V). The remaining entries in Table V relate to nonbridgehead methyl-group increments in adamantane and diamantane. Here the exothermicity of replacing a hydrogen atom of any methylene group by a methyl group is smaller than that observed for replacing a tertiary hydrogen atom. Bridgehead methyladamantanes and diamantanes are more stable thermochemically than are their nonbridgehead counterparts (see Table VII). However, the measured increment for diamantane → 3-methyldiamantane (entry vii, Table V) is about 1 kcal/mol less than that obtained for the thermochemically equivalent change in adamantane (entry viii, Table V). This discrepancy casts doubt on the reliability of the experimental $\Delta H^\circ_f(g)$ data for either 3-methyldiamantane or 2-methyladamantane or both (vide infra).

That the gas-phase enthalpies of formation of adamantane and diamantane are mutually consistent can be demonstrated in a quite different way. Consider the hypothetical metathesis reaction whereby 1 mol of gaseous diamantane combines with 1 mol of gaseous cyclohexane producing 2 mol of gaseous adamantane. Using our $\Delta H^\circ_f(g)$ data for adamantane and diamantane and the recommended value of −29.50 kcal/mol for cyclohexane[2a] we find that the reaction as written is endothermic by 0.52 kcal/mol. In other words, incorporating a cyclohexane ring into a diamondoid framework is thermochemically unfavorable. Cyclohexane itself does not exist in a perfect chair conformation with ideal tetrahedral bond angles; rather, the flexible nature of the molecule enables it to relax into a somewhat flattened geometry in which the best balance is struck between angle, nonbonded, and torsional strain.[27] The MM1 and EAS calculations indicate that this relaxation process in cyclohexane is enthalpically favorable by 1.19 and 1.65 kcal/mol, respectively. A recent STO-3G calculation by Pople and co-workers[28] gives a value of 0.80 kcal/mol for the same change. The rigidity of the diamondoid skeleton precludes any comparable relaxation of the cyclohexane rings of adamantane and diamantane and, as Schleyer et al.[29] have pointed out, this factor contributes very considerably to the existence of strain in diamondoid hydrocarbons. Accordingly, we should expect that constraining "normal" cyclohexane into "diamondoid" cyclohexane (dotted lines in the scheme above) will be an endothermic process as is indicated by the enthalpy change for the hypothetical reaction of cyclohexane with diamantane.



We return now to the inconsistencies apparent in the $\Delta H^\circ_f(g)$ data for 2-methyladamantane (**3**) and 3-methyldi-

Table VII. Isomerization Enthalpies from Enthalpy of Formation Differences ($\Delta\Delta H^\circ{}_f(g)$), Direct Equilibration ($\Delta H^\circ{}_i$), and Molecular Mechanics Calculations (kcal/mol)

	exptl		molecular mechanics $\Delta\Delta H^\circ{}_f(g)$			
	$\Delta\Delta H^\circ{}_f(g)$	$\Delta H^\circ{}_i$	MM1	EAS	MM2	WB
3 → **2**	-4.91 ± 0.71[a] -3.68[c] -4.4 ± 0.8[f]	-2.77 ± 0.20[b] (-2.63,[d] -3.37[e])	-3.85	-3.88	-3.36	-3.21
9 → **7**	-3.68 ± 0.90[a]	-2.14 ± 0.20[b] (-2.00[d])	-2.78	-3.26		-1.97
8 → **7**	-5.93 ± 0.65[a] -3.86[c]	-2.70 ± 0.20[b] (-2.63[d])	-3.86	-3.91		-3.12
8 → **9**	-2.25 ± 1.03[a] -0.18[c]	-0.64 ± 0.20[b] (-0.57[d])	-1.08	-0.65		-1.15
5 → **1**	-11.22 ± 0.68[a]	(-11.0,[g] -7.5[h])	-11.19	-11.37	-10.82	-10.16

[a] This work. [b] Data from ref 33. [c] Corrected values using the recommended $\Delta H^\circ{}_f(g)$ data in Table III. [d] Data from ref 34. [e] Data from ref 32. [f] Data from ref 20. [g] Data from ref 36. [h] Data from ref 37. [i] Data in parentheses are solution values.

amantane (**8**), in particular, the methyl-group increments obtained with these systems. Prior to these combustion studies, some thermodynamic data had already been collected from equilibration measurements with all the methyladamantanes and methyldiamantanes. It was known that the substituent in a variety of substituted compounds is prone to peripheral shift under the influence of acidic catalysts.[30] The first example was observed with 1- and 2-methyladamantane which interconvert in the presence of aluminum bromide, producing a preponderance of the bridgehead isomer at equilibrium.[31] A study of the temperature dependence of this equilibrium,[32] and of the corresponding equilibria between the three methyldiamantanes both in the gas phase[33] and in solution,[34] produced the isomerization enthalpies, $\Delta H^\circ{}_i$, summarized in Table VII. Comparison of these data with isomerization enthalpies expressed as the difference between the gas-phase enthalpies of formation of each pair isomers, $\Delta\Delta H^\circ{}_f(g)$, and with the molecular mechanics calculations shows that, although the $\Delta\Delta H^\circ{}_f(g)$ value for **8** → **9** obtained from the recommended $\Delta H^\circ{}_f(g)$ values in Table III is quite small, these three sources are in complete agreement on the order of thermochemical stability in the two series. 1-Methyladamantane (**2**) is more stable than 2-methyladamantane (**3**); and 4-methyldiamantane (**9**) > 1-methyldiamantane (**8**) > 3-methyldiamantane (**7**). These orders of stability reflect the substitution type (secondary or tertiary) and location (axial in **3**, **8**, and **9** and equatorial in **2** and **7**). The final entry in Table VII refers to the very exothermic change of protoadamantane (**5**) into adamantane. The equilibrium constant for this isomerization, which forms the basis of a number of synthetically useful routes to 1,2-disubstituted adamantanes,[35] has not been measured directly, the two $\Delta H^\circ{}_i$ values quoted being indirect estimates from measurements with derivatives in solution. Schleyer's estimate[36] from solvolysis data of −11.0 kcal/mol is in excellent agreement with both the $\Delta\Delta H^\circ{}_f(g)$ value and the molecular mechanics predictions.

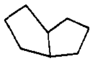
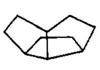
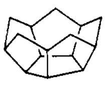
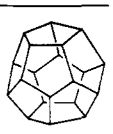
However, there are clearly major discrepancies with the methyladamantanes and methyldiamantanes. Notwithstanding the rather large uncertainties associated with the experimental $\Delta\Delta H^\circ{}_f(g)$ values, it does appear that the enthalpy difference of −4.91 kcal/mol between 2- and 1-methyladamantane is much too large. Our $\Delta H^\circ{}_i$ value from equilibration in the gas phase was −2.77 kcal/mol, more or less identical with the solution value but somewhat less than that of −3.37 kcal/mol obtained in solution by Schleyer and coworkers[32] over a shorter temperature range. These data and the molecular mechanics predictions of −3.21 to 3.88 kcal/mol for **3** → **2** cast doubt on the reliability of the experimental $\Delta\Delta H^\circ{}_f(g)$ value. Similarly, the $\Delta\Delta H^\circ{}_f(g)$ value of −5.93 kcal/mol for the 3-methyldiamantane → 4-methyldiamantane isomerization is clearly in conflict with both the $\Delta H^\circ{}_i$ measurement and the molecular mechanics predictions. On the basis of the bridgehead methyl-group increments already discussed we believe that the enthalpies of formation of 1-methyladamantane and 4-methyldiamantane are securely established; furthermore, the good measure of agreement on isomerization **9** → **7** suggests that the $\Delta H^\circ{}_f(g)$ value for 1-methyldiamantane is also reasonably accurate. The error must lie, therefore, in the heats of combustion of 2-methyladamantane and 3-methyldiamantane. Although both these compounds, which are waxy solids, were subjected to rigorous purification, they were difficult to purify and it is possible that minute amounts of impurities persisted with consequential effects on the $\Delta E^\circ{}_c$ or ΔH_{sub} values or both. These compounds were not reinvestigated when it became clear that developments in the MM2 force field calculations made it possible to recommend the following $\Delta H^\circ{}_f(g)$ values: 2-methyladamantane, −36.89 kcal/mol; 3-methyldiamantane, −39.67 kcal/mol (vide infra).

Let us now consider the comparative data in Table III, excluding for the moment perhydroquinacene (**10**), the only nondiamondoid member of the group. The comparisons are expressed as differences between the experimental enthalpies of formation and those predicted by the four force fields: ΔMM1, ΔEAS, ΔMM2, and ΔWB. It is immediately clear that there is a systematic trend in the MM1 and EAS predictions inasmuch as both force fields predict greater thermochemical stability for all nine compounds than is indicated by the combustion measurements. ΔMM1 is 2.1–3.1 kcal/mol for the five adamantyl systems and 3.6–4.6 kcal/mol for the four diamantyl systems. The EAS force field does notably better with adamantane and protoadamantane but does not reproduce well the enthalpies of tetramethyladamantane and the four diamantyl systems. Allinger[10] has referred to MM1 and EAS as "first generation force fields", pointing out that, although the general usefulness and versatility of the molecular mechanics method are beyond doubt, these first-generation force fields contain various flaws which are revealed in different ways. Each force field is composed of a different balance of the various nonbonded interactions (H···H, H···C, and C···C): the MM1 force field uses a hydrogen atom which is both large and hard and a carbon atom which is small whereas the EAS force field employs a more repulsive C···C nonbonded potential function. The WB force field gives substantially better predictions overall with adamantane being most out of line with our experimental value (ΔWB = 2.15 kcal/mol); for tetramethyladamantane there is complete agreement. In the latest force field, Allinger's MM2, the problem of simultaneously obtaining a sufficiently large gauche butane interaction energy while keeping the hydrogen atoms small enough for good structural predictions has been solved by utilizing the V_1 and V_2 terms in the torsional potentials. Allinger's claim[10] that these new torsional terms can correct most of the defects in MM1, producing structural predictions competitive with the best of extant force fields and enthalpy predictions superior to any previously reported for hydrocarbons, is substantiated: for a list of 42 selected hydrocarbons of diverse structure the standard deviation between calculated and experimental enthalpies of formation is 0.42 kcal/mol, compared with an average experimental error for the same group of compounds of 0.40 kcal/mol.[10] Certainly, the agreement between MM2 predictions and our experimental data (ΔMM2 in kcal/mol) for adamantane (0.21), 1-methyladamantane (0.32), 1,3,5,7-tetramethyladamantane (0.69), protoadamantane (0.19), diamantane (0.24), and 4-methyldiamantane (0.50) represents a very significant improvement over the MM1 and EAS predictions. This is particularly encouraging since in MM2 adamantane-type structures were given practically no weight in deducing the heat of formation parameters.

This accord highlights the discrepancy in 2-methyladamantane (ΔMM2 = 1.3 kcal/mol), confirming that the problem lies with the experimental enthalpy of formation. We recommend therefore that Allinger's value of 36.89 kcal/mol be taken as an accurate, reliable prediction for 2-methyladamantane. Within the error limits this value is the experimental value of Steele and Watt. Our measured enthalpy of combustion is in error by 0.063%. The adamantane → 2-methyladamantane methyl group increment becomes 5.13 kcal/mol (entry viii, Table V) in excellent agreement with the force field predictions. The rather good agreement within the force fields on all the methyl group increments in Table V follows from the fact that, although calculated absolute enthalpies may differ from one another and from experimental values, agreement among calculated relative energies of closely related systems is much better; cancellation of some of the defects in the force fields causes this effect.[12] Not only does Allinger's value for 2-methyladamantane bring the methyl group increment into line but the 1-methyladamantane ⇄ 2-methyladamantane isomerization enthalpy now becomes 3.68 rather than 4.91 kcal/mol, resulting in good agreement, within the error limits, between $\Delta\Delta H°_f(g)$, $\Delta H°_{isom}$, and the molecular mechanics predictions (Table VII). What has just been said about 2-methyladamantane applies equally well to its counterpart 3-methyldiamantane. Although we do not yet have an MM2 prediction for the larger system, it is already clear from the methyl group increment (entry vii, Table V) and the isomerization enthalpies (Table VII) that the experimental enthalpy of formation of 3-methyldiamantane is in error. Since the nonbridgehead methyl group increment for diamantane should be completely equivalent to that in adamantane (cf. the MM1, EAS, and MM2 predictions in Table V) we recommend a value of 39.67 kcal/mol for the enthalpy of formation of 3-methyldiamantane; the WB prediction is 39.31 kcal/mol. The experimental enthalpy of combustion appears to be in error by 0.095%.

We wish finally to comment on the enthalpy of formation of perhydroquinacene (**10**)[38] and discuss the thermochemical relationship with the unknown, but sought-after, hydrocarbon dodecahedrane (**13**). Perhydroquinacene is a bridged-ring system consisting of three cyclopentane rings mutually cis fused in the shape of a shallow bowl. Perhydroquinacene is thus related to *cis*-bicyclo[3.3.0]octane and also to dodecahedrane, the latter consisting of a symmetrical array of identical cyclopentane rings cis fused so as to form a $(CH)_{20}$ sphere. The relationship between the perhydroquinacene structure and dodecahedrane was first recognized by Woodward et al.,[39] who envisaged the symmetrical triply unsaturated form of the former (triquinacene) as a possible synthetic precursor of the latter. The peristylane system (**12**),[40] consisting of six cis-fused cyclopentane rings, represents an intermediate stage of accumulation of cyclopentane units between perhydroquinacene and dodecahedrane. All the available thermochemical data pertaining to these systems are collected in Table VIII. The experimental enthalpy of formation of cyclopentane itself is accurately reproduced by the MM1, EAS, and MM2 force fields. For *cis*-bicyclo[3.3.0]octane (**11**) the experimental and EAS $\Delta H°_f(g)$ values agree rather well; MM1 appears out of line, but this is corrected in MM2. Interestingly, this same pattern is apparent with perhydroquinacene: experiment and EAS agree satisfactorily while MM1 indicates that the three-ring system is in fact more strained by 4.7 kcal/mol; again MM2 closes the gap but not entirely, leaving a 2.38 kcal/mol difference between the measured value. While we fully accept the possibility that the problem here may be an error in measurement, we also believe that the trends in the data in Table VIII may indicate that the MM1 weakness in dealing with cis-fused cyclopentane rings has not been completely eliminated from MM2. Allinger[10] states that perhydroquinacene is a highly puckered system, i.e., the overall structure is C_3, not C_{3v}, with the implication that it has considerable strain energy, more than, say, norbornane.[41] We are not aware of any evidence for the system being highly puckered. The WB force field prediction for perhydroquinacene is very close to the EAS value.

Table VIII. Gas-Phase Heats of Formation (kcal/mol)

		 11	 10	 12	 13
exptl	−18.44[a]	−22.30[a]	−24.46[b]		
MM1	−18.09	−20.68	−19.74	+14.61	+45.28
EAS	−18.37	−22.61	−23.74	−8.64	−0.22
MM2	−18.27	−22.77	−22.08		+22.15
WB			−23.46		

[a] Data from ref 2a. [b] This work.

There are no experimental thermochemical data for peristylane or dodecahedrane and here the force field predictions are in sharp disagreement. For peristylane, the discrepancy between MM1 and EAS is 23 kcal/mol and, as with perhydroquinacene, MM1 finds the molecule less thermochemically stable than does EAS; an MM2 prediction for peristylane is not yet available. With dodecahedrane, the discrepancy between MM1 and EAS has grown to 45 kcal/mol. Interestingly, the MM2 calculation reduces the difference by 22 kcal/mol. Considering the quite good agreement realized with the EAS and MM2 force fields for many other hydrocarbons it would have been difficult to anticipate such a large discrepancy for dodecahedrane. No satisfactory interpretation of this discrepancy has been put forward. Nevertheless, the MM2 force field does represent a considerable refinement over the first-generation force fields. From the recent literature the reader might be inclined to believe that molecular mechanics calculations now render unnecessary experimental calorimetry of saturated hydrocarbons. On the contrary, new experimental data are clearly needed with which to parametrize the force fields more accurately and provide a basis for understanding the deficiencies revealed by molecules such as peristylane and dodecahedrane.

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Allinger for making available to us the MM2 force field calculations in advance of publication.

Supplementary Material Available: A summary of typical combustion experiments and of combustion results (Tables S1 and S2) (2 pages). Ordering information is given on any current masthead page.

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