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Calorimetric Evaluation of Enthalpies of Formation of Some Bridged-Ring Hydrocarbons. Comparison with Data from Empirical Force Field Calculations

Sir:

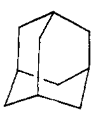
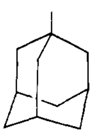
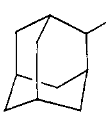
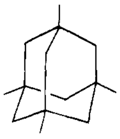
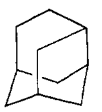
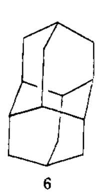
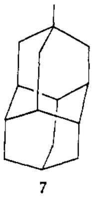
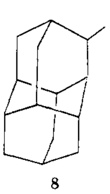
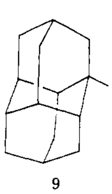
Enthalpies of formation of polycyclic hydrocarbons of diverse structure and moderate size (up to ca. 20 carbon atoms) are now accessible via empirical force field calculations[1-3] in a few minutes using modern computers. In contrast, experimental determination of the enthalpies of formation of such compounds via synthesis, purification, and combustion calorimetry usually takes many months of effort. Furthermore, the force field approach can be used to probe the enthalpies and structures of unknown molecules. The general acceptance of data from this source and their use in the quantitative interpretation of chemical phenomena depend on their reliability. A recent critical evaluation[1] of the use of two general force fields, those of Schleyer[1] and Allinger,[2] lists the enthalpies of formation and strain energies of some 84 hydrocarbons, mainly of the bridged-ring type, none of which has been measured experimentally. Accordingly, we have selected nine compounds for an experimental evaluation of the reliability of the force field data. For comparative purposes, the list includes two compounds, adamantane (**1**) and diamantane (**6**), for which experimental $\Delta H_f°$ values were already available.

Adamantane (**1**),[4a] 1- and 2-methyladamantane (**2**)[4b] and (**3**),[4c] 1,3,5,7-tetramethyladamantane (**4**),[4b] protoadamantane (**5**),[4d] diamantane (**6**),[4e] and 4-, 3-, and 1-methyldiamantane (**7**),[4b] (**8**),[4f] and (**9**)[4b] were subjected to rigorous purification, to 99.99 mol%, by recrystallization, vacuum sublimation, and, with the exception of tetramethyladamantane (**4**) which was redistilled and resublimed several times, multiple zone-refining. Combustions were carried out in the "Belfast" Mark I aneroid bomb,[5] yielding the solid phase enthalpies of formation, $\Delta H_f°$ (c), listed in Table I.

Since the molecular mechanics data relate to the gas phase at 25°, it was essential to have available a quick, reliable method of measuring enthalpies of sublimation. Such a method involving the use of a commercial gas chromatograph and a gas flow technique has now been developed[6] and the $\Delta H°_{sub}$ data obtained in this way are listed in Table I. The value for adamantane is in excellent agreement with literature values: 14.26 vs. 14.45,[3] 14.18,[7] and 14.00 kcal mol^{-1}.[8]

Within the error limits our gas phase enthalpy of formation, $\Delta H_f°$ (g), of adamantane is in complete agreement with two of three earlier determinations: 31.76 ± 0.32 vs. 30.65 ± 0.98,[3] 30.57 ± 0.90,[9] and 32.96 ± 0.19 kcal mol^{-1} [7] whereas that of diamantane, 32.60 ± 0.58 kcal mol^{-1}, differs appreciably from an earlier value of 36.65 ± 2.00 kcal mol^{-1} [10] in which $\Delta H°_{sub}$ was estimated from the enthalpies of fusion and vaporization, corrected to 25° using assumed molar heat capacities, and now shown to be incorrect. Comparison of the experimental $\Delta H_f°$ (g) data for compounds (**1-9**) with the Schleyer (S), $\Delta H_f°$, and Allinger (A), $\Delta H_f°$, results reveals the following features. (i) Both force fields overestimate the thermochemical stability of all nine compounds, Allinger's more so than Schleyer's. Nevertheless, if the errors in the calculated data are taken to be ±1-2 kcal mol^{-1}, there is a notable measure of agreement between $\Delta H_f°$ (g) exptl. and (S) $\Delta H_f°$ for compounds (**1-5**). (ii) Although both force fields predict that the strain energy of tetramethyladamantane (2 kcal mol^{-1}) is less than that of adamantane (6-7 kcal mol^{-1}), they overemphasize the stabilizing influence of the four methyl groups. Using our $\Delta H_f°$ (g) value the strain energy of tetramethyladamantane becomes 5 kcal mol^{-1}. (iii) The enthalpies of the four diamantyl systems are calculated less reliably than

Table I[c]

	 1	 2	 3	 4	 5	 6	 7	 8	 9
					Experimental				
$-\Delta H_f°$ (C)	46.02 ± 0.09	56.72 ± 0.30	51.80 ± 0.29	86.54 ± 0.46	36.04 ± 0.41	55.53 ± 0.55	62.51 ± 0.17	62.24 ± 0.48	59.12 ± 0.78
$\Delta H°_{sub}$	14.26	16.15	16.14	19.39	15.50	22.93	18.98	24.64	19.27
$-\Delta H_f°$ (g)	31.76 ± 0.32	40.57 ± 0.34	35.66 ± 0.62	67.15 ± 0.50	20.54 ± 0.60	32.60 ± 0.58	43.53 ± 0.30	37.60 ± 0.58	39.85 ± 0.85
					Molecular Mechanics				
(S) $-\Delta H_f°$[a]	32.50	41.82	37.94	70.26	21.13	37.37	46.82	42.91	43.56
(A) $-\Delta H_f°$[b]	33.82	42.89	39.04	70.21	22.63	38.13	47.21	43.35	44.43
(S) $\Delta\Delta H_f°$	0.74	1.25	2.28	3.11	0.59	4.77	3.29	5.31	3.71
(A) $\Delta\Delta H_f°$	2.06	2.32	3.38	3.06	2.09	5.53	3.68	5.75	4.58

[a] Calculated $\Delta H_f°$ data from the Schleyer force field in ref 1. [b] Calculated $\Delta H_f°$ data from ref 1 obtained with the Allinger force field in ref 2. [c] Data are in kilocalories per mole.

are the five adamantyl systems, though isomers **7**, **8**, and **9** do emerge in the correct order of stability. (iv) The strain energy of diamantane is larger than expected. Using our $\Delta H_f°$ (g) values and the Schleyer and Allinger strain-free increments, we obtain strain energies of 15.5 and 7.7 kcal mol^{-1} for diamantane and adamantane, respectively. Thus the former is almost exactly twice as strained as the latter. It appears, therefore, that both force fields require some reparameterization.

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On the Isomerization of Pentacoordinated Molecules

Sir:

The isomerizations of a pentacoordinated molecule, MABCDE, with five different ligands have been extensively discussed. Unless all six atoms are coplanar, such a molecule can have no symmetry element other than the identity. Several authors[1] have pointed out that interconversions among the 20 possible isomers can be classified formally in terms of five different types or "modes" of rearrangement: two axial ligands exchange (aa), an axial and an equatorial ligand exchange (ae), an axial and two equatorial ligands exchange cyclically (aee), two independent axial-equatorial exchanges take place simultaneously (aesae), or two axial and two equatorial ligands exchange cyclically (aeae). Both the Berry mechanism[2] and the turnstile mechanism[3] lead to the mode aeae, but the view appears to be held[1] that the other modes must be seriously considered.

At the risk of laboring the obvious we wish to point out here that the first four modes are only to be considered as formal possibilities and may safely be excluded in any discussion of the detailed mechanisms. This is clear from a consideration of the topological properties of the coordination polyhedra;[4] that is, we ignore metrical aspects. We may choose the vertices of the coordination polyhedra either at the atoms bonded to M or at the ends of the five unit vectors that originate at M and lie along the bond directions. Either way, only three topologically distinct kinds of polyhedra are possible: (a) trigonal bipyramid or hexahedron (six triangular faces); (b) tetragonal pyramid or pentahedron (four triangular faces and one quadrilateral face); (c) the degenerate polyhedron with all five vertices in a plane.[4] Since there is no symmetry we shall refer to these as the hexahedral, pentahedral, and planar forms to avoid the symmetry connotations associated with the more familiar names. If the five vectors from M to the vertices A-E remain distinct, that is, no two bond directions ever coincide in the course of the rearrangement, then clearly any interconversion of one hexahedral isomer into another has to pass either through an intermediate pentahedral form or through an intermediate planar form. This follows because the edges that are not common to the polyhedra of the initial and final states must disappear, that is, become diagonals of planar faces, in the intermediate. Single-step mechanisms involving an intermediate pentahedral form are associated exclusively with the aeae mode (Figure 1); hence any single-step mechanism associated with the first four modes must involve an intermediate planar form. The first four modes can, of course, correspond to multistep processes involving pentahedral intermediates, but this is equivalent to replacing them by a sequence of aeae steps. An example is shown in Figure 1.

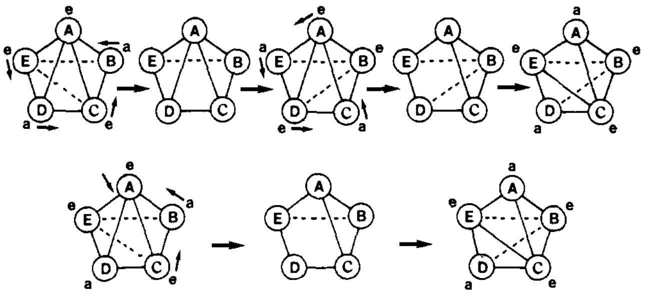

Figure 1. (1-3): an aeae rearrangement proceeding in a single step through a pentahedral intermediate. (6-8), an aee rearrangement proceeding through a single intermediate. Since the intermediate has two quadrilateral faces sharing two edges it must be planar. (1-5), the same aee rearrangement proceeding through two aeae steps.

The conclusion we draw from this is that while five rearrangement modes are formally possible, the chemical improbability of planar intermediates eliminates four of these as serious possibilities, leaving only details of possible aeae mechanisms (Berry and turnstile, for example) to be explained further.

Since a pentahedral form must occur somewhere along the reaction path for all chemically feasible rearrangements, it would appear that the most economical procedure for mapping the reaction pathway by quantum mechanical calculations might be to find the most stable pentahedral form and to proceed from there.

Exactly analogous arguments apply to interconversions between the 30 possible pentahedral isomers, which must proceed either through hexahedral intermediates or through planar ones.

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