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G2 and G3 Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of Bi-, Tri-, and Tetracyclic C_7 Hydrocarbons: The Norbornadiene Cycle

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We have calculated the standard enthalpies of isomerization, hydrogenation, and formation ($\Delta_{\mathrm{hyd}}H^{298}$, $\Delta_{\mathrm{isom}}H^{298}$, and $\Delta_{\mathrm{f}}H^{298}$) of norbornadiene, quadricyclane, norbornene, nortricyclane, and norbornane by the G2, G2(MP2), G2(MP2,SVP), G3(MP2), and B3LYP/6-311+(3df,2p) procedures. Comparison with combustion and hydrogenation thermochemical results shows that agreement between G-*n* theory and experiment remains within the target interval of 1 to 2 kcal mol^{-1} for these C_7 hydrocarbons, but that B3LYP/6-311+(3df,2p) results do not fall within this range.

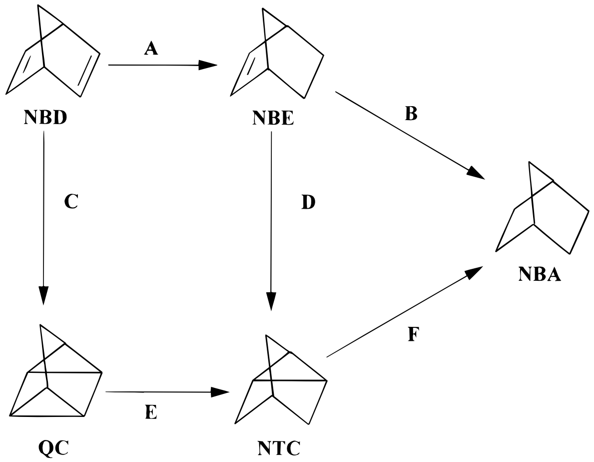
One of the most attractive features of contemporary molecular orbital calculations is the ease with which one can compute fundamental thermodynamic properties that are difficult or impossible to obtain by classical experimental means.[1] Comparison between experimental results and those calculated by the Gaussian-*n* family of procedures (G1, G2, G3, and modifications) has been very encouraging for small molecules, especially for hydrocarbons.[2,3,4] A legitimate question arises, however, as to the validity of the additivity assumptions made in Gaussian-*n* calculations on larger molecules. In particular, the empirical “higher level correction” (HLC) in the G2 method has been questioned.[5]

We have carried out a systematic investigation of the feasibility and accuracy of the G2 family of computational methods (G2, G2(MP2) and G2(MP2,SVP)) in calculating the enthalpies of hydrogenation, isomerization, and formation at 298 K ($\Delta_{\mathrm{hyd}}H^{298}$, $\Delta_{\mathrm{isom}}H^{298}$, and $\Delta_{\mathrm{f}}H^{298}$) of cyclic and acyclic hydrocarbons containing from two to six carbon atoms.[6] Hydrogenation and isomerization reactions have the advantage that they are *isogyric*, that is, they have the same number of α and β spins on the left and the right, causing the HLC to cancel in calculating ΔH.[6c] Raghavachari et al. have shown that use of “bond separation” reactions produces good agreement with experiment[7] in part because of the same HLC cancellation.

So far,[6] we have found that agreement between G2-type calculations and experiment does not deteriorate with a modest increase in molecular size. Those few difficulties that have arisen in hydrocarbon calculations have usually involved cyclic compounds. Here we report G2- and G3-type calculations on a group of C_7 bi-, tri-, and tetracyclic hydrocarbons: norbornadiene (NBD), norbornene (NBE), norbornane (NBA), nortricyclane (NTC), and quadricyclane (QC). See Scheme 1 and Table 3 for structures and systematic nomenclature. Because these compounds are the nodes in a classic thermochemical cycle (Scheme 1), we shall refer to them collectively as the *norbornadiene cycle*.

Practical interest in norbornadiene thermochemistry lies in potential use of the NBD−QC isomerization as an energy storage system. NBD can be converted, even in cold climes, to its high-energy isomer QC by the ultraviolet component of sunlight. It can be stored, then allowed to flow over a catalyst bed in a closed system to be changed back into NBD with evolution of heat. The cycle from NBD to QC and back to NBD can be repeated indefinitely. For a review, see ref 8. More recently, the NBD−QC system has been proposed as a dopant in solid films, with potential applications in photochromic data storage.[9]

SCHEME 1. Norbornadiene Cycle[a]



[a] Taking values from Table 1, A + B − C − E − F add up to zero.

Both CPU time and disk space limit the size of molecules that can be studied by ab initio methods. Because they are single calculations, density functional theoretical (DFT) methods are usually faster than Gaussian-*n* procedures, which are suites of calculations using different basis sets in combination with post Hartree−Fock extensions. Because of the numerous hydrocarbon isomers at higher molecular weights, even a small economy in computer resources produces a rich reward in thermochemical information. The B3LYP method[10] appears to be the most accurate of contemporary DFT methods for thermochemistry.[11] At present, however, there is some conflicting evidence[12] as to how accurate the method will turn out to be in the area of thermochemistry of larger molecules. Therefore, we have included B3LYP density functional calculations with the Gaussian-*n* family of methods presented here.

Thermochemical data must be accurate to be useful, so we have included a critical comparison of the agreement of G2, G2(MP2), G2(MP2,SVP), G3(MP2), and B3LYP results with

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TABLE 1: H^{298} for the Norbornadiene Cycle Shown in Scheme 1[a]

	NBD	NBE	NBA	NTC	QC
G2	−270.93385	−272.15661	−273.37110	−272.16015	−270.89711
G2(MP2)	−270.92881	−272.15140	−273.36570	−272.15502	−270.89217
G2(MP2,SVP)	−270.92940	−272.15011	−273.36236	−272.15332	−270.89216
G3(MP2)	−270.98953	−272.21442	−273.43081	−272.21697	−270.95069
B3LYP	−271.43725	−272.66286	−273.87970	−272.66525	−271.40170

Units are hartrees.

TABLE 2: G2, G2(MP2), G2(MP2,SVP), and B3LYP Values of H^{298} and $\Delta_f H^{298}$(exp) of Methane, Ethene, and Ethane, for Use in Bond Separation Calculations

		ZPE (scaled)	E_0	H^{298}	$\Delta_f H^{298}$ (exp)
methane	G2	0.04270[a]	−40.41086[a]	−40.40704[a]	−17.90 ± 0.1[b]
	G2(MP2)	0.04270	−40.40963	−40.40581	
	G2(MP2,SVP)	0.04270	−40.40764	−40.40383	
	B3LYP	0.04270	−40.49412	−40.49031	
ethene	G2	0.04890	−78.41593	−78.41193	12.54 ± 0.1
	G2(MP2)	0.04890	−78.41430	−78.41029	
	G2(MP2,SVP)	0.04890	−78.41343	−78.40943	
	B3LYP	0.04890	−78.57215	−78.56814	
ethane	G2	0.07122	−79.63089	−79.62640	−20.08 ± 0.1
	G2(MP2)	0.07122	−79.62893	−79.62445	
	G2(MP2,SVP)	0.07122	−79.62608	−79.62159	
	B3LYP	0.07122	−79.79032	−79.78583	

[a] Units: hartrees. [b] Units: kcal mol^{-1}.

TABLE 3: Enthalpies of Formation of the Norbornadiene Cycle[a]

	$\Delta_f H^{298}$		exp − calcd	
	calcd[a,b]	exp[c]	(comb.)	(hyd)
norbornadiene	56.3[d]	59.2 ± 0.7	2.9	0.4
bicyclo[2.2.1]hepta-2,5-diene	57.0	*56.7 ± 1.2*	2.2	−0.3
	56.0		3.2	0.7
	56.0[e]		3.2	0.7
	66.5		−7.3	−9.8
norbornene	18.5[d]	21.8 ± 0.8	3.3	2.2
bicyclo[2.2.1]hept-2-ene	19.1	*20.7 ± 1.2*	2.7	1.6
	18.0		3.8	2.7
	18.5[e]		3.3	2.2
	28.9		−7.1	−8.2
norbornane	−14.1[d]	−13.1 ± 1.1[f]	1.0	
bicyclo[2.2.1]heptane	−13.6		0.5	
	−14.7		1.6	
	−13.8[e]		0.7	
	−3.2		−9.9	
nortricyclane	16.2[d]	19.6 ± 0.5	3.4	1.8[g]
tricyclo[2.2.1.0^{2,6}]heptane	16.9	*18.0 ± 1.2*[g]	3.0	1.1
	15.5		4.1	2.5
	16.9[e]		2.7	1.1
	24.8		−5.2	−6.8
quadricyclane	79.2[d]	81.0 ± 0.5	1.8	−0.4
tetracyclo[3.2.0.0^{2,7}0^{4,6}]heptane	80.1	*78.8±1.2*	0.9	−1.3
	80.1		0.9	−1.3
	80.4[e]		0.6	−1.6
	83.7		−2.7	−4.9

[a] Units are kcal mol^{-1}. [b] Calculated values are given in the descending order G2, G2(MP2), G2(MP2,SVP), G3(MP2), B3LYP. [c] Experimental results were determined by combustion calorimetry[14] and hydrogenation calorimetry (italicized).[13,15c] [d] G2-family and B3LYP were calculated by the bond separation method. [e] G3(MP2) values were obtained by the atomization method. [f] From ref 14, reanalyzed by Pedley et al.,[28] supported by more recent work;[29] see **webbook.nist.gov**. [g] Reference 15c.

experiment. Comparison of calculated results with experimental data requires, at best, a data set that is accurate and reliable, or, at least, a data set that is known to be self-consistent. Quite some time ago, we carried out direct calorimetric determination of $\Delta_{hyd}H^{298}$ of members of the norbornadiene cycle.[13] Here we compare computed values with combustion calorimetric results found by Steele,[14] and with hydrogenation calorimetric results of our group,[13] and those of Turner[15a] and of Roth.[15c]

Theory

The Atomization Method. The most important thermodynamic output of the Gaussian-*n* family of calculations is E_0, the total energy at 0 K, which can be converted to H^{298}, the total enthalpy at 298 K, by a combination of classical statistical thermodynamic terms plus a vibrational energy computed via the harmonic oscillator approximation. These results are converted to energies of atomization at 0 K or enthalpies of atomization at 298 K by comparing E_0 or H^{298} with the total energies of the constituent atoms. These latter values, in turn, are compared to the empirical energy or enthalpy of atomization of the elements from their standard states to the gaseous state at the appropriate temperature[16a] to obtain the thermodynamic quantities $\Delta_f E^0$ and $\Delta_f H^{298}$. Included in this mix of purely ab initio results and empirical energies (enthalpies) is a "high level correction" HLC chosen to make the computed enthalpies best fit the experimental $\Delta_f H^{298}$ values of a selected set of values, presumed to be accurate, called the G2-1 test set, later expanded to the G2-2 test set (vide infra[16]). In developing G3-type procedures, a larger G2/97 test set was used to establish the HLC.[4]

The Bond Separation Method. Very shortly after publication of the G2 test set results, Raghavachari et al. showed that the mean absolute deviation between computation and experiment can be reduced by a factor of about 3 by use of the "bond separation" method[7] for treating the total enthalpy of a molecule, H^{298}, obtained by G2 and G2(MP2) calculations to obtain $\Delta_f H^{298}$. Indeed, bond separation reactions can be used to achieve reasonably good energies for the entire category of molecular orbital calculations, even down to those using the STO-3G basis set, as shown by Hehre et al. in 1970.[17] Accurate calculation of the bond separation enthalpy implies that the $\Delta_f H^{298}$ calculated from it will also be accurate. Examples of atomization and bond separation calculations have been given in a previous paper.[6d]

Raghavachari et al. point out that bond separation reactions bring about cancellation of the HLC so that this empirical factor does not appear in the final result. This is true of all *isogyric* reactions,[2a] including hydrogenations and isomerizations,[6] because the HLC contains the number of spins (or spin pairs in restricted Hartree−Fock ground-state thermochemical calculations). Raghavachari et al. refer to their bond separation calculations as "nonempirical" because of HLC cancellation, but it should be clear that the scheme is not a pure ab initio method because of the error cancellation that motivates all isodesmic reaction schemes, and because of the infusion of empirical $\Delta_f H^{298}$ values for the reference molecules, methane, ethene, ethane, and others.

It is likely that a reason for the accuracy of bond separation calculations relative to the original atomization method in G2 calculations[2] is that they involve only molecular orbital results at the same level of approximation (see Table 1) while the atomization method mixes approximate atomic orbital and molecular orbital results, and even uses one energy obtained by exact solution of the Schroedinger equation, E_0(atomic hydrogen) = 0.50000 hartrees. In the G3 and G3(MP2) procedures, the atomization method is modified by including an HLC for atoms as well as for molecules to take into account deficiencies in the energy calculations.[4]

DFT. Density functional theory has been summarized,[12b,18] and detailed treatments are available.[19,20] Briefly, the ground-state energy *E* is a *functional*[18] of electron probability density, which obeys a set of equations, the Kohn−Sham equations,

$$\mathbf{K}\Psi = \epsilon_i\Psi \tag{1}$$

that is similar in form to the Hartree−Fock equations. The **K** operator in eq 1 differs from the Hamiltonian operator in the Hartree−Fock equations because it does not contain a nonlocal exchange operator (though exchange does enter via a term in the HF part of the B3LYP expression). The **K** operator contains an exchange-correlation potential energy V^{XC} instead. This difference reduces the computation (after certain ancillary calculations have been made) to a one-electron, single-point calculation, reducing demands on computer resources.

The potential V^{XC} can be approximated in a number of ways, but an empirical 3-parameter formulation due in part to Becke[21] and Lee, Yang, and Parr,[22] dubbed B3LYP, appears to be the best in current use for thermochemical purposes.[11] Having decided to use eq 1 with the B3LYP approximation, the next question is which basis set to use. Because DFT calculations make modest demands on computer resources, we were able to choose a high-level basis set, the 6-311+G(3df,2p) set, in combination with an MP2(full)/6-31G(d) optimized geometry and an HF/6-31G(d) zero point energy. Combining these nomenclatural conventions, the method used here is called the B3LYP/6-311+G(3df,2p) procedure.

Computation

G2 and G2(MP2). The computational procedure for G2 or G2(MP2) has been described.[6a,b] Briefly, we construct the target molecule using the draw function of PCMODEL[23] and minimize the energy using MMX, followed by a PM3 optimization in MOPAC6.0.[24] The resulting geometries are used as the starting point for the G2 calculations.[25,26]

G2(MP2,SVP). For the G2(MP2,SVP) calculation, the QCISD(T)/6-31G(d) component can be run at the MP2(full)/6-31G(d) geometry directly from the checkpoint file or from an optimized MP2(full)/6-31G(d).GJF file.[25] Curtiss et al. have made optimized .GJF files readily available for molecules in the G2-2 test set.[16a]

If a prior G2 or G2(MP2) calculation has been made with establishment of a checkpoint file, the zero point energy, *E*(ZPE), and thermal correction, THC, to the enthalpy can be taken from the output. Both the MP2 and QCISD(T) points for the G2(MP2,SVP) extrapolation can be read from the QCISD(T) run, leaving only the MP2/6-311+G(3df,2p) point, which is already known from the prior G2 or G2(MP2) calculation.

B3LYP. Once having the MP2(full)/6-31G(d) geometry, *E*(ZPE), and THC, the B3LYP calculation can be run at the MP2(full) geometry with 6-311+G(3df,2p) B3LYP in the route section of the input file to the GAUSSIAN 94 or GAUSSIAN98 package.

G3(MP2). G3(MP2) was run just as G2(MP2) is except for inclusion of a new basis set called G3MP2Large, which was not in either the GAUSSIAN94 or -98 packages at this writing but is readily available via anonymous ftp.[4b] After establishing *E*(ZPE) and TCH at the HF/6-31(d) level, the geometry was optimized at the MP2(full)/6-31G(d) level as before. Since the G3MP2Large basis set was not available as part of a linked suite at this writing, we had the choice of using the NEWZMAT utility to obtain the optimized *z*-matrix or working from a checkpoint file with the - -Link1- - option.[25]

A run at the QCISD(T)/6-31G(d) level yields both *E*[MP2/6-31G(d)] and *E*[QCISD(T)/6-31G(d)]. The G3MP2Large basis set is now appended to the optimized *z*-matrix and run with MP2/gen in the route section to obtain *E*[MP2/G3MP2Large]. Corrections to *E*[QCISD(T)/6-31G(d)] are *E*(ZPE) which is already known from a prior G2 calculation or can be obtained independently[25] and

$$\Delta E_{MP2} = E[\mathrm{MP2/G3MP2Large}] - E[\mathrm{MP2/6\text{-}31G(d)}]$$

$$E(\mathrm{HLC}) = n(-0.009279)$$

where *n* is the number of paired *valence* electrons. These corrections are added to *E*[QCISD(T)/6-31G(d)] to obtain E_0. E_0 is treated as described under “the atomization method” above, using G3 atomization energies[4] for C and H to obtain $\Delta E°$ (0 K). Adding *E*(TCH) to E_0 gives H^{298} which leads to $\Delta_f H^{298}$ as described.

There is a small spin−orbit coupling term, but it is not used in molecular calculations.[4] Although atomic spin−orbit coupling has an influence on the energy of atomization of a molecule, it does not appear in the final result for $\Delta_f H^{298}$(molecule). There are numerous numerical results available via anonymous ftp to verify the procedure or to debug any computer programs one may wish to write to facilitate routine summations.[4b]

Results

G2(MP2), G2(MP2,SVP), G3(MP2), and B3LYP/6-311+G(3df,2p) values for H^{298} of the molecules in Scheme 1 are given in Table 1. Systematic nomenclature is given in Table 3.

The mean absolute deviation (MAD) between G2 and G2(MP2) calculated H^{298} values in Table 1 is 5.1 mh = 3.2 kcal mol^{-1} and relatively constant (standard deviation with 4 degrees of freedom = 0.1 mh). As expected, G2 values are lower than G2(MP2). The MAD between G2(MP2) and G2(MP2,SVP) for H^{298} is 1.4 mh = 0.88 kcal mol^{-1}. The pattern for the G2(MP2) and G2(MP2,SVP) results is similar to what we have seen before[4c] in that the largest difference is found in the compound with the most hydrogen atoms (NBA: 3.34 mh). The G2(MP2) and G2(MP2,SVP) results for QC are essentially the same, while the most unsaturated compound, NBD, actually has an H^{298} calculated by G2(MP2,SVP) that is lower than that calculated by G2(MP2).

G3(MP2) results are also lower in energy than either G2 or G2(MP2), the difference being quite substantial, 67.0 ± 2.8 mh = 42.0 ± 1.8 kcal mol^{-1} and 61.9 ± 2.7 mh (38.8 ± 1.7 kcal mol^{-1}), respectively. The 4.4% variation among these enthalpy differences is about twice the percent variation in the differences between G2 and G2(MP2), but the pattern is the same, increasing in the order C_7H_8, C_7H_{10}, C_7H_{12}.

The B3LYP results differ from the G2(MP2) and G2(MP2,SVP) results by more than half a hartree (∼300 kcal mol^{-1}). The MAD between B3LYP/6-311+G(3df,2p) and G2(MP2,SVP) results is 0.51188 h with a standard deviation of 3.6 mh, the difference for NBA being greatest while that for QC is least. The B3LYP results are uniformly lower than the Gaussian results, but the post Hartree−Fock extensions used here are not variational procedures so one cannot say that a lower result is ipso facto a “better” result.

$\Delta_f H^{298}$. Energies and enthalpies of the reference molecules to be used in the bond separation calculations are shown in Table 2. Bond separation calculations must be internally consistent; energies of methane, ethene, and ethane used to obtain $\Delta_f H^{298}$ by G2 must be G2 values, G2(MP2) energies must be used in G2(MP2) calculations, and so on. Small differences in experimental $\Delta_f H^{298}$ selected for the reference molecules (from different compilations, for example) have a cumulative effect on the target $\Delta_f H^{298}$ for larger molecules, such as benzene, and can be responsible for discrepancies of a kcal mol^{-1} or more.[4d,27]

The H^{298} values in Table 2 lead to the enthalpies of formation given in Table 3. Results for the G2 family and B3LYP were obtained by the bond separation method. The G3(MP2) energies were converted to $\Delta_f H^{298}$ by the atomization method. Experimental values of $\Delta_f H^{298}$ shown in Table 3 were obtained by combustion calorimetry[14] and hydrogenation calorimetry. Two sources[13,15a] of hydrogenation data give essentially the same results when corrected for solvent effects, hence the (italicized) entries in Table 3 for NBD, NBE, and QC are results from ref 13 only. The $\Delta_{hyd} H^{298}$ value for NTC was taken from a more recent study by Roth’s group.[15c]

The range of calculated $\Delta_f H^{298}$ on the same molecule by different Gaussian-*n* methods is less than 1 kcal mol^{-1} except for nortricyclane, which has a range of 1.4 kcal mol^{-1}. Standard deviations from the mean calculated values for the five target molecules are 0.5, 0.5, 0.6, 0.7, and 0.5 kcal mol^{-1}.

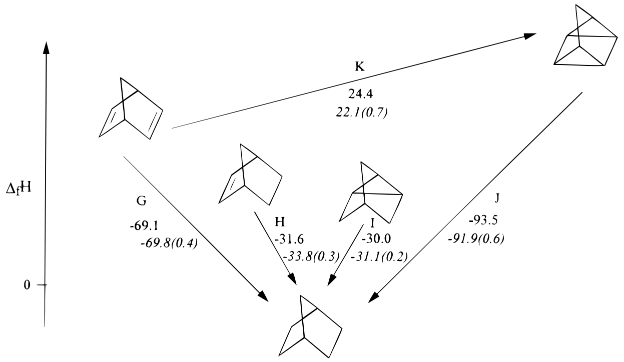
Arithmetic mean differences from combustion data are likewise consistent at 2.9, 3.3, 0.9, 3.3, and 1.1 kcal mol^{-1}. The signed mean of the arithmetic mean differences is 2.3 kcal mol^{-1}, the same as the unsigned mean, that is, combustion results for $\Delta_f H^{298}$ are *systematically* higher than the Gaussian-*n* calculated results reported here by about 2.3 kcal mol^{-1}.

The signed arithmetic mean differences between Gaussian-*n* calculations and hydrogenation data $\Delta_f H^{298}$ are 0.4, 2.2, 1.6, and -1.2 kcal mol^{-1} for the C_7H_8 and C_7H_{10} isomers. Experimental values were obtained by subtracting the experimental $\Delta_{hyd} H^{298}$ from the combustion result for $\Delta_f H^{298}$ of NBA The signed arithmetic mean of “exp − calcd” over the four compounds is 0.8 kcal mol^{-1}. The unsigned mean is 1.4 kcal mol^{-1}. Agreement between experiment and Gaussian-*n* theory is somewhat better for the set of results from hydrogenation calorimetry than it is for combustion, and the deviation is not systematic. The largest single deviation (2.7 kcal mol^{-1}) in this set is that for NBE. Experimental uncertainties of the $\Delta_f H^{298}$ values taken from hydrogenation data are the uncertainties in $\Delta_{hyd} H^{298}$ of NBD, NBE, NTC, and QC combined with the uncertainty of NBA, expressed as the square root of the summed variances. In each case, the major contributor to the final uncertainty is NBA.

Results in Table 3 indicate that B3LYP is not the method of choice for calculating $\Delta_f H^{298}$ of molecules in the norbornadiene cycle. This method will not be discussed further.

$\Delta_{isom} H^{298}$ and $\Delta_{hyd} H^{298}$. Numerous enthalpies of isomerization, hydrogenation, and partial hydrogenation are easily obtained from the data in Table 3, some of which are shown in Scheme 2. A comparison between calculated and experimental results for hydrogenation to NBA is shown in Scheme 2. Values of $\Delta_{hyd} H^{298}$ for reactions in Scheme 2 were calculated by G3(MP2), the newest of the Gaussian-*n* procedures, using the atomization method. We are especially interested in the hydrogenation reactions G, H, I, and J which have been measured by direct means,[13,15] and in the isomerization K, which, in part, motivates this work. The signed mean difference between experiment and theory in Scheme 2 is 0.9 kcal mol^{-1} and the MAD is 1.6 kcal mol^{-1}.

SCHEME 2. G3(MP2) Calculated and Experimental $\Delta_{hyd} H^{298}$ and $\Delta_{isom} H^{298}$ in the Norbornadiene Cycle[a]



[a] Italicized ΔH^{298} were obtained by direct hydrogenation. Experimental uncertainties are parenthesized.

Discussion

The geometry of the norbornadiene cycle is regular and symmetrical, distorted only slightly from the simple schematic structures given in Schemes 1 and 2. Double bonds are about at about the textbook value for ethene and single bonds deviate by less than 2% from the textbook value for ethane. The ridgepole angle in NBD, NBE, and NBA are within a degree of 112°, and the internal angle of the cyclopropane rings in NBE and QC are within a degree of 60°. The planes of the cyclopropane rings lean away from each other in QC so as to make an angle of 107° from the floor of the structure.

Calculated values of $\Delta_f H^{298}$ are closely grouped but the experimental values are not.[30] In particular, $\Delta_f H^{298}$(NBA) has been reported as -12.4 ± 1.1 kcal mol^{-1},[31] -13.1 ± 0.3 kcal mol^{-1},[29] and -14.7 ± 0.8 kcal mol^{-1}.[14] This latter value has been revised by Pedley et al.[28] and is supported by a more recent measurement of $\Delta_f H^{298}$(NBA) $= -13.1 \pm 0.3$ kcal mol^{-1}.[29] Of these three experimental results for $\Delta_f H^{298}$(NBA), only the revised Pedley value has been retained for the NIST database[30] and we have used it for the NBA entry in Table 3.

There is, of course, no way to determine $\Delta_f H^{298}$(NBA) by hydrogen calorimetry, hence there are only four italicized entries in Table 3. Hydrogenation results in Table 3 for $\Delta_f H^{298}$ of NBD, NBE, NTC, and QC were obtained by subtracting the experimental $\Delta_{hyd} H^{298}$ from the Pedley revised experimental $\Delta_f H^{298}$(NBA).

Close grouping of the points on either the right or the left in Figure 1 shows that the Gaussian-*n* family give very similar results for this problem. The combustion curves on the left show that the combustion results are self-consistent but more than 2 kcal mol^{-1} higher than calculated results for NBD, NBE, and NTC. The $\Delta_f H^{298}$ values determined from hydrogenation thermochemistry on the right are not as self-consistent as the combustion results, but agreement with theory is better. Both curves show a sharp drop on going from NTC to QC, possibly showing that the calculation breaks down for the tetracyclic QC. We speculate, on the basis of these curves, that the hydrogenation thermochemical results are the more accurate of the two experimental sets.

Scheme 2 shows that the bond separation technique in combination with G2(MP2) calculations of $\Delta_{hyd} H^{298}$ can be extended to the seven heavy atom members of the norbornadiene cycle with a discrepancy between calculation and selected

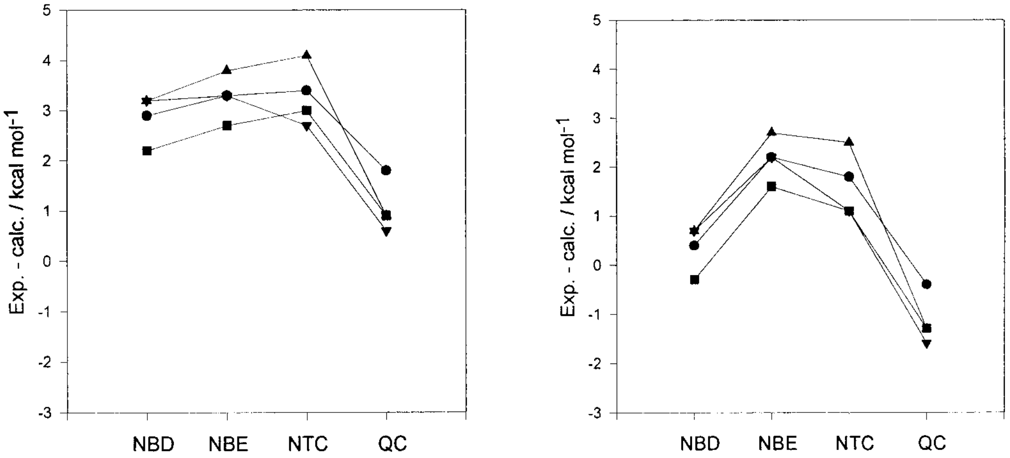


Figure 1. Differences between experimental and computed values of $\Delta_f H^{298}$ by the Gaussian-*n* family of procedures. Comparison with combustion data are shown on the left and with hydrogenation data on the right. Symbols are: ● G2, ■ G2MP2, ▲ G2(MP2,SVP), ▼ G3(MP2).

experimental results of <2 kcal mol^{-1}. Calculating $\Delta_{\mathrm{hyd}}H^{298}$ of reactions G, H, I, and J using G3(MP2) results with $H^{298}(H_2) = -1.16682$ h from ref 4 yields $\Delta_{\mathrm{hyd}}H^{298}$ values that are less exothermic than experimental measurements and have MAD = 1.6 kcal mol^{-1}. Part of this difference is due to the G3(MP2) value of -1.1 kcal mol^{-1} for $\Delta_f H^{298}(H_2)$.

Conclusion

Correspondence between Gaussian-*n* calculations and thermochemical results for $\Delta_f H^{298}$ and $\Delta_{\mathrm{hyd}}H^{298}$ from three independent but self-consistent sources show that the G-*n* methods can be extended to the C_7 compounds in the norbornadiene cycle without diminution in the 1−2 kcal mol^{-1} agreement found for smaller cyclic alkenes and alkanes.

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