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G2(MP2) and G2(MP2,SVP) Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of C_5 Hydrocarbons. 2. Substituted Cyclobutenes, Vinylcyclopropene, Spiropentane, and Methyltetrahedrane

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We report the ab initio G2(MP2) and G2(MP2,SVP) standard enthalpies of hydrogenation and isomerization ($\Delta_{\mathrm{hyd}}H$ and $\Delta_{\mathrm{isom}}H$) at 298 K of 23 C_5 cyclic hydrocarbons, including methyl- and methylenecyclobutane, spiropentane, and related unsaturated hydrocarbons, as well as methyltetrahedrane. $\Delta_{\mathrm{hyd}}H^{298}$ and $\Delta_{\mathrm{isom}}H^{298}$ are found from the differences in total energy (E_0) of the participants in the hydrogenation and isomerization reactions. Combination of calculated $\Delta_{\mathrm{hyd}}H^{298}$ and $\Delta_{\mathrm{isom}}H^{298}$ with one *experimental* enthalpy of formation ($\Delta_{\mathrm{f}}H^{298}$) in the set yields $\Delta_{\mathrm{f}}H^{298}$ of all the rest. In those few instances for which reliable experimental results can be found, agreement between experiment and calculation is within 1 kcal mol^{-1}.

The G2 family of ab initio calculations[1] enables one to determine, to a good approximation, the total energy (E_0) of a molecule at 0 K. The enthalpy of formation at 298 K can be obtained by some further calculations and minor approximations. A signal advantage of a G2 or similar method is that highly unstable molecules, indeed those whose existence now or ever is unlikely, can be examined by the same procedure as those that have a long history of classical thermochemistry and that provide secure thermodynamic benchmarks. Broader knowledge of the thermochemistry of small rings in particular leads to an increased understanding of the interaction of various kinds of strain and electron delocalization.[2] Parametrization of semiempirical methods benefits from energy data for strained molecules that may not be available experimentally. Although our special interest is in the thermochemistry of the ground state, Pople, Curtiss, and co-workers[1] applied their methods to ions and free radicals from the outset, making structural and thermodynamic information available on unstable intermediates in chemical reactions, flames, and explosions.

Recently, we carried out a study on the G2(MP2) and G2(MP2,SVP) enthalpies of hydrogenation, isomerization, and formation ($\Delta_{\mathrm{hyd}}H^{298}$, $\Delta_{\mathrm{isom}}H^{298}$, and $\Delta_{\mathrm{f}}H^{298}$) of disubstituted cyclopropenes, cyclopentene, bicyclopentane, and related three-membered and five-membered ring compounds.[3] This study extends that series of calculations to 23 new C_5 cyclic hydrocarbons by taking up the methyl-substituted cyclobutenes, methylenecyclobutane, ethyl-, vinyl-, and ethylidinecyclopropene, spiropentane, and related saturated and unsaturated hydrocarbons, as well as methyltetrahedrane. Where possible, calculated and experimental results for $\Delta_{\mathrm{f}}H^{298}$ are compared and discussed.

Theoretical and Computational.

An overview of G2(MP2) and G2(MP2,SVP) calculation of $\Delta_{\mathrm{hyd}}H^{298}$, $\Delta_{\mathrm{isom}}H^{298}$, and $\Delta_{\mathrm{f}}H^{298}$ of hydrocarbons was given in the first three papers in this series.[3] References in those papers give the theory in more detail.

Briefly, G2(MP2)[1d] is a three-point extrapolation using calculated energies at the MP2/6-311G(d,p), MP2/6-311+G(3df,2p), and QCISD(T)/6-311G(d,p) levels to estimate what the computed total energy E_0 of a molecule would be at the QCISD(T)/6-311+G(3d,2p) level had the last calculation been practical, which, in general, it is not. Computed zero-point energies are included in E_0.

The G2(MP2,SVP)[1d] method is similar to G2(MP2) except that the MP2/6-311G(d,p) point is replaced by an MP2/6-31G(d) calculation and the QCISD(T)/6-311G(d,p) point is replaced by a calculation at the QCISD(T)/6-31G(d) level. These simplifications result in a considerable saving of computer resources (amounting to 80−90% in some cases[1d]), thereby opening the field to calculations on larger molecules. Computational details were given in the previous papers in this series.[3b,c] The ab initio calculations described here were carried out using the program[4] Gaussian 94, revision C.2. The more resource-intensive calculations were carried out at the Pittsburgh Supercomputing Center.

Statistical thermodynamic corrections[5] to the total energy (E_0) obtained by the G2 family of calculations at 0 K lead to H^{298}, the total enthalpy at 298 K. Knowing H^{298} for a group of hydrocarbons related to each other by hydrogenation or isomerization (along with H^{298} for hydrogen), we calculate $\Delta_{\mathrm{hyd}}H^{298}$ and $\Delta_{\mathrm{isom}}H^{298}$ relating members of the group from differences in H^{298} for reactants and products in the hydrogenation or isomerization reaction. We then select one of the values obtained by either the G2(MP2) or G2(MP2,SVP) procedure, identify it with the *experimental* value of the enthalpy of formation, $\Delta_{\mathrm{f}}H^{298}$, of the selected hydrocarbon, and calculate $\Delta_{\mathrm{f}}H^{298}$ for all molecules in the set from $\Delta_{\mathrm{f}}H^{298}$ of the selected hydrocarbon and $\Delta_{\mathrm{hyd}}H^{298}$ and $\Delta_{\mathrm{isom}}H^{298}$ connecting the members of the set (see Schemes 1−3).

Results

The set of G2(MP2) and G2(MP2,SVP) results containing $\Delta_{\mathrm{hyd}}H^{298}$ and $\Delta_{\mathrm{isom}}H^{298}$ for 23 5-carbon hydrocarbons has been divided into three subsets, which are shown as Schemes 1−3. Italicized numbers are calculated by the G2(MP2,SVP) procedure. Enthalpies of reaction involving simultaneous hydrogenation and isomerization are not shown because they are evident

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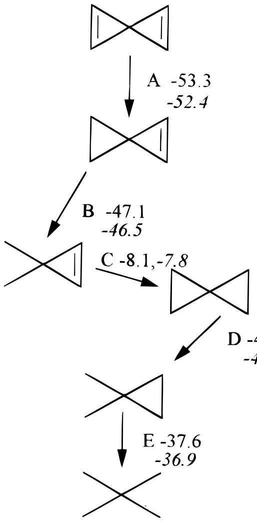
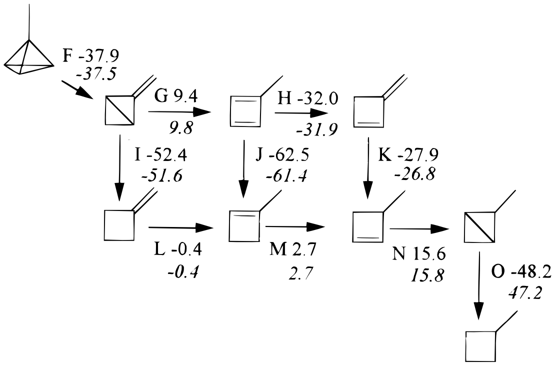
SCHEME 1



SCHEME 2



from Hess's law addition of the two concomitant reaction enthalpies. Energy E_0 and enthalpy H^{298} for the compounds studied in this work obtained by both computational methods are given in Table A of the Supporting Information. The G2(MP2,SVP) thermal correction to 298 K is the same as for the G2(MP2) calculations because the frequency calculation, from which the thermal correction is estimated, is at the HF/6-31G(d) level for both methods.

The three subsets in Schemes 1−3 are connected by *calculated* isomerization enthalpies. Sets 1 and 2 are connected by

$$\text{methylenecyclobutane} \rightarrow \text{spiropentane} \qquad \Delta_{\text{isom}}H^{298} = 15.04\ (\mathit{15.36})\ \text{kcal mol}^{-1}$$

and sets 2 and 3 are connected by

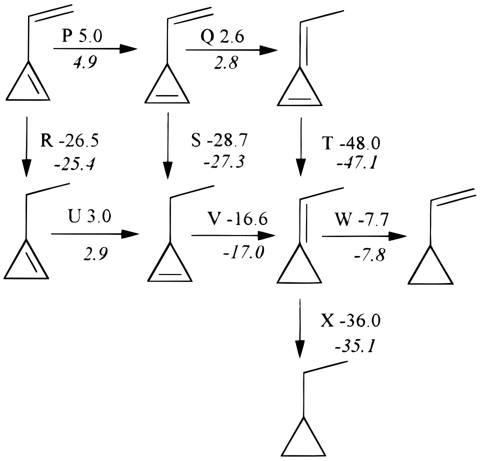
$$\text{methylenecyclobutane} \rightarrow \text{vinylcyclopropane} \qquad \Delta_{\text{isom}}H^{298} = 2.01\ (\mathit{1.87})\ \text{kcal mol}^{-1}$$

where the differences in H^{298} calculated by the G2(MP2,SVP) method and converted to kcal mol^{-1} are shown in italics.

The network of $\Delta_{\text{hyd}}H^{298}$ and $\Delta_{\text{isom}}H^{298}$ values in Schemes 1−3 yields Δ_fH^{298} for 22 of the 23 hydrocarbons if one Δ_fH^{298} in Table 1 is known. We have chosen the *experimental* result Δ_fH^{298}(methylenecyclobutane) [6] = 29.03 kcal mol^{-1}, indicated by an asterisk in Table 1, as the thermochemical reference point.

Thermal corrections of E_0 to H^{298}, which are essentially classical except for the contribution to the heat capacity from vibrational motion, average about 6.5 mhartrees = 4.1 kcal mol^{-1} within a range of 5.6 (spiropentadiene) to 8.1 mhartrees (2,2-dimethylpropane). Thermal corrections within any group of isomers are about the same; hence $\Delta_{\text{isom}}H^{298}$ results are about the same at 0 and 298 K. Exceptions are methyl → methylene isomerizations in Scheme 2, which are about 0.4 kcal mol^{-1} more exothermic at 298 K than at 0 K, and the 1,1-dimethylcyclopropene → spiropentane isomerization in Scheme 1, which is 0.7 kcal mol^{-1} more exothermic at 298 K than at 0 K. These differences, which are within the uncertainty of the method, appear to reflect the flexibility of the reactant molecule compared to the product.

SCHEME 3



With these exceptions in mind, the thermal correction of the hydrogenation products in Schemes 1−3 are about 0.1 or 0.2 kcal mol^{-1} larger than the reactants, leaving hydrogen as the dominant contributor to the thermal correction. $\Delta_{\text{hyd}}H$ values are about 1.9 kcal mol^{-1} less exothermic at 0 K than their 298 K values shown in Schemes 1−3. This consistency of the thermal correction to $\Delta_{\text{isom}}H^{298}$ and $\Delta_{\text{hyd}}H^{298}$ over a wide range of hydrocarbons has been discussed in detail.[3b]

The difference between E_0 calculated by the G2(MP2) method and the G2(MP2,SVP) procedure increases with the number of hydrogen atoms in a hydrocarbon, evidently owing to the lack of hydrogen p-orbital functions in G2(MP2,SVP). For example, the vinylcyclopropenes and ethylidine cyclopropene (C_5H_6) have G2(MP2) values that differ by less than 1 mhartree, while 2,2-dimethylpropane (C_5H_{12}) has a G2(MP2,SVP) value for E_0 that is almost 5 mhartrees higher than the G2(MP2) value. Error cancellation occurs as indicated by spiropentadiene (C_5H_4), which has a G2(MP2,SVP) value for E_0 that is *lower* than the G2(MP2) value. These differences are regular as shown in Figure 1.

This linear function, which has a slope of 0.84 mhartree per added hydrogen atom, affords a way of estimating the G2(MP2) (and by extension G2) values of E_0 from the result at the G2(MP2,SVP) level. The usefulness of such an estimate is questionable because Curtiss et al. have shown that the G2(MP2,SVP) method using the standard "atomization" method of obtaining Δ_fH produces better agreement than the G2(MP2) method when tested on their 148-compound G2 test set.[12] This superiority is especially noteworthy for the hydrocarbons among their test set. Indeed, for hydrocarbons, G2(MP2,SVP) does better than G2 by the ratio of 0.77 kcal mol^{-1} to 1.29 kcal mol^{-1}, respectively, in their average absolute differences.[12a] However, by use of a different empirical reference point, our results do not agree with those of Curtiss et al. in this respect; Δ_fH obtained

TABLE 1: $\Delta_f H^{298}$ from G2(MP2) ab Initio Calculations and from Experimental Measurements[a]

	G2(MP2)	G2(MP2,SVP)	exptl	Δ(exptl − calcd)
spiropentadiene	152.6	*151.1*		
spiropentene	99.3	*98.7*		
1,1-dimethylcyclopropene	52.2	*52.2*		
spiropentane	44.1	*44.4*	44.3 ± 0.2[7]	0.2, *−0.1*
1,1-dimethylcyclopropane	−2.1	*−1.2*	−2.0 ± 0.2[6]	0.1, *−0.8*
2,2-dimethylpropane	−39.7	*−38.1*	−40.2 ± 0.2[8]	−0.5, *−2.1*
methyltetrahedrane	119.3	*118.1*		
methylcyclobuta-1,3-diene	91.2	*90.0*		
methylenecyclobut−3-ene	59.2	*58.1*		
methylenebicyclobutane	81.4	*80.6*		
methylenecyclobutane	29.03*	*29.03**	29.03 ± 0.2[6]	0.0*, *0.0**
1-methylcyclobutene	28.6	*28.6*		
3-methylcyclobutene	31.3	*31.3*		
methylbicyclobutane	46.9	*46.9*		
methylcyclobutane	−1.3	*−0.3*	−4.0 ± 0.3 (?)[9]	−2.7, *−3.7*
1-vinylcyclopropene	79.1	*78.1*		
3-vinylcyclopropene	84.1	*83.0*		
ethylidinecyclopropene	86.7	*85.8*		
vinylcyclopropane	31.0	*30.9*	35.3 ± 1.0 (?)[10]	4.3, *4.4*
ethylidinecyclopropane	38.7	*38.7*		
3-ethylcyclopropene	55.4	*55.7*		
1-ethylcyclopropene	52.6	*52.8*		
ethylcyclopropane	2.7	*3.6*	0.1 ± 0.2[11]	2.6, *3.5*
			−3.0 ± 1.0 (?)[10]	5.7, *6.6*

[a] Units are kcal mol^{-1}

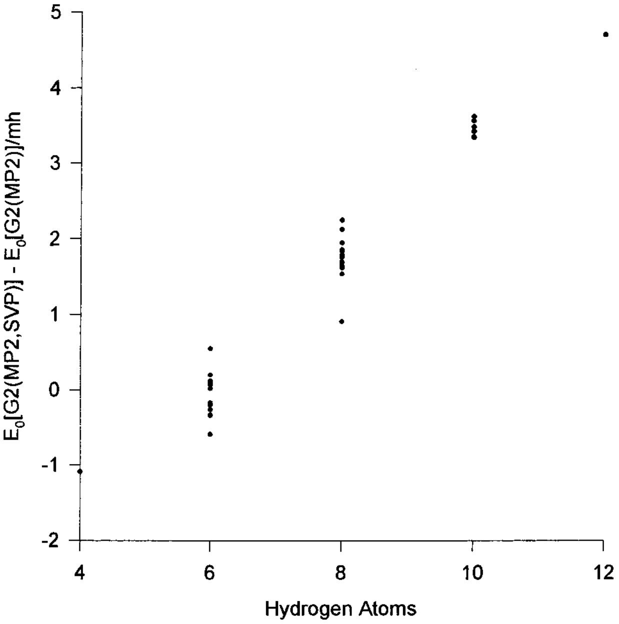


Figure 1. Differences (in mhartree) between E_0 calculated by the G2-(MP2) and G2(MP2,SVP) procedures as a function of the number of hydrogen atoms in C_5 hydrocarbons. The slope is 0.84 ± 0.06 mhartree/atom (95% confidence limits).

from G2(MP2,SVP) E_0 values agree less well with experimental results than G2(MP2) for the larger hydrocarbons that we have studied.

Discussion

In Scheme 1, addition of H_2 across one double bond in spiropentadiene, spiropentene, and 1,1-dimethylcyclopropene, i.e., saturation of a cyclopropene ring, is consistent in its exothermicity ($\Delta_{hyd}H^{298} = -53.3$ kcal mol^{-1} by reaction A, −55.2 kcal mol^{-1} by reaction B, and −54.3 kcal mol^{-1} by reactions C + D, respectively) at the G2(MP2) level and is consistent with cyclopropene itself ($\Delta_{hyd}H^{298} = -54.4$ kcal mol^{-1} by prior calculation[3] and $\Delta_f H^{298} = -53.5 \pm 0.6$ kcal mol^{-1} by experiment).[13]

In addition to the insensitivity of $\Delta_f H^{298}$ of the cyclopropene double bond to what is attached to the sp^3 carbon, we note the large exothermic isomerization enthalpy of 1,1-dimethylcyclopropene to spiropentane ($\Delta_{isom}H^{298} = -8.1$ (*−7.8*) kcal mol^{-1}). We have already seen that "escape" of the endocyclic double bond in 1,2-dimethylcyclopropene to methylmethylenecyclopropane is exothermic in the amount of 11.1 kcal mol^{-1} by G2-(MP2) calculation.[3b]

Addition of hydrogen to bring about ring opening seen in Scheme 1 is not self-consistent nor is it consistent with the $\Delta_{hyd}H^{298}$ observed in the cleavage of cyclopropane.[3a] Ring opening of spiropentene to produce 1,1-dimethylcyclopropene has $\Delta_{hyd}H^{298} = -47.1$ kcal mol^{-1} (G2MP2,SVP, *−46.5*), which is comparable to cleaving the cyclopropane ring in reaction B, Scheme 1, and reaction D, Scheme 1, but not to reaction E, Scheme 1, or to hydrogenation of cyclopropane to propane ($\Delta_{hyd}H^{298} = -38.6$ kcal mol^{-1} by G2).[3a] The cyclopropenyl or cyclopropanyl group opposite the C−C bond that is cleaved during hydrogenation causes an increase in magnitude of slightly less than 10 kcal mol^{-1} in $\Delta_{hyd}H^{298}$.

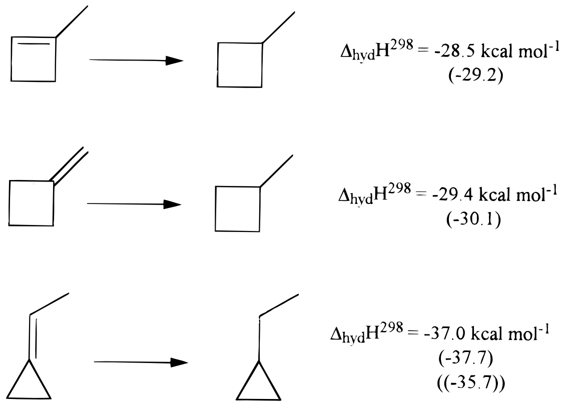
A strongly exothermic "escape" of a double bond is also seen in the isomerization of methylcyclobuta-1,3-diene to methylenecyclobutene in reaction H, Scheme 2, which can be viewed as a manifestation of the antiaromatic nature of cyclobutadiene. This remarkable isomerization enthalpy, the largest in the set, is as strongly exothermic as the hydrogenation enthalpy of ethene ($\Delta_{hyd}H^{298} = -32.4$ kcal mol^{-1}).[14a] Instability of methylbuta-1,3-diene is also reflected in hydrogenation J, which is more than twice as exothermic as the "normal" hydrogenation seen in reaction K. Escape of a lone double bond to the exocyclic location in reaction L is not energetically favored.

The energetically favored location of the double bond in cyclopropylethene is seen in reactions U, V, and W in Scheme 3. Hydrogenation of cyclopropylethene to cycloropylethane has a calculated $\Delta_{hyd}H^{298} = -28.9$ kcal mol^{-1}, which is slightly less than that of but-1-ene (−30.3 ± 0.1)[14b] but larger than the enthalpy of partial hydrogenation of buta-1,3-diene to but-1-ene,[14c] indicating weak stabilization of the terminal double bond analogous to hyperconjugative stabilization. Hydrogenation of the endocyclic double bond in reaction T, Scheme 3, is about 6 kcal mol^{-1} less exothermic than cyclopropene itself, suggesting conjugative stabilization of the reactant.

$\Delta_f H^{298}$. Calculated $\Delta_f H^{298}$ values are given in Table 1 along with experimental results where the latter can be found. In addition to the experimental values, Curtiss et al. have calculated $\Delta_{hyd}H^{298}$ by the G2, G2(MP2), and G2(MP2,SVP) methods using the standard "atomization" method to arrive at $\Delta_f H^{298}$ from the computed E_0 values.[12] Their results for spiropentane, the only compound appearing in both their paper and this, are 45.7, 46.7, and *45.4* kcal mol^{-1} for the three G2 procedures compared with our results of 44.1 and *44.4* and the experimental $\Delta_{hyd}H^{298}$ = 44.3 ± 0.2 kcal mol^{-1} measured by Frazer and Prosen.[7]

The same group has analyzed 10 C_3 and C_4 hydrocarbons by the "bond-separation" technique,[12b] which we have treated[3a,b] through $\Delta_{hyd}H^{298}$ and $\Delta_{isom}H^{298}$. Their average absolute deviation from experiment was 0.77 kcal mol^{-1} for G2(MP2,SVP) for a test set of 22 hydrocarbons compared with about 0.9 kcal mol^{-1} for obtaining $\Delta_f H^{298}$ through $\Delta_{hyd}H^{298}$ and $\Delta_{isom}H^{298}$ in a somewhat smaller hydrocarbon subset.[3a,b]

Agreement with Experimental Results. $\Delta_{hyd}H$. Three enthalpies of hydrogenation connecting compounds in Table 1 have been measured directly by hydrogen calorimetry.[15]



The parenthesized values are corrected by −0.7 kcal mol^{-1} to account for solvent effects concurrent with the hydrogenation reaction.[16] The second (double) parenthesized value for ethylidinecyclopropane has an added correction made by the original authors[15] to account for uptake of more than the quantitative amount of hydrogen, presumably in breaking the cyclopropane ring. The $\Delta_{hyd}H^{298}$ values obtained by summing the appropriate reaction sequences in Schemes 2 and 3 are −29.9, −30.3, and −36.0, respectively, leading to differences between experimental and computed $\Delta_{hyd}H^{298}$ of 0.7, 0.2, and 0.3 kcal mol^{-1}. G2(MP2,SVP) values are *−28.7*, *−29.1*, and *−35.1*, leading to differences from experimental values of *−0.5*, *−1.0*, and *−0.6* kcal mol^{-1}. The mean arithmetic unsigned differences for the G2(MP2) and G2(MP2,SVP) methods are 0.4 and 0.7 kcal mol^{-1}, respectively.

Beyond the hydrogenation results, it is difficult to assess agreement between experimental $\Delta_{hyd}H^{298}$ and computed results in Table 1 because of the sparse and scattered nature of the experimental data. The *overall* mean average differences between all experimental results in the standard reference sources[13,17] and calculation (excluding the reference compound, methylenecyclobutane) is poor. Mean average differences are 2.3 and *3.0* kcal mol^{-1} for unsigned differences and −1.0 and *−1.5* for signed differences, indicating both systematic and random discrepancies.

Table 1 shows that the most serious discrepancies come from methylcyclobutane, vinylcyclopropane, and ethylcyclopropane. Examination of the original papers shows that the experimental values of all three are open to serious question. Good[11] has observed that in a group of alkylcycloalkanes, the result for methylcyclobutane[9] is "an apparent misfit". If Humphrey and Spitzer's result for methylcyclobutane is corrected by 3.0 kcal mol^{-1} to conform with Good's results, the interpolated $\Delta_f H^{298}$ is −1.0 kcal mol^{-1}, in agreement with our calculation.

Two of the remaining three experimental results at the bottom of Table 1 are given in one reference source[13] as being by Fierens and Nasielski,[10] but a reading of the original paper shows that they did not carry out these experiments. Rather, they referred to unpublished National Bureau of Standards data as their source. Cox and Pilcher[17] also refer to "NBS measurements" but give neither a citation nor an experimental uncertainty, entering the values as "35.3 ± " and "−3.0 ± ", respectively. We were unable to locate either of these results in the Journal of the National Bureau of Standards.

If the three questionable results are ignored, only four results remain[6,7,8,11] (other than the reference point). For these few points the mean arithmetic unsigned differences between calculation and experiment are 0.9 and *1.6* kcal mol^{-1}. These means are comparable to our previous work, though it is difficult to rely on a comparison with such a depleted experimental data set. Whatever the reason, the G2(MP2) agreement is good in Schemes 1 and 2 (mean average deviation of 0.9) and poor in Scheme 3 (mean average deviation of ∼4 kcal mol^{-1}).

Conclusions

Results for 15 hydrocarbons in Schemes 1 and 2 support the semiempirical procedure of determining $\Delta_f H^{298}$ from differences in H^{298} and a single reference $\Delta_f H^{298}$, but in Scheme 3, agreement with experimental values is poor.

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Supporting Information Available: Table A, containing calculated enthalpies, and a listing of computational results for C_5 hydrocarbons (11 pages). Ordering information is given on any current masthead page.

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(5) H^{298} is the total energy E_0 corrected by statistical mechanics to the total enthalpy at 298 K. The calculation is carried out internally in Gaussian 94, activated by the g2 or g2mp2 keywords.

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