Ab Initio Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of Cyclic C_6 Hydrocarbons. Benzene Isomers

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We have calculated the standard enthalpies of formation $\Delta_f H^{298}$ of benzene, 8 benzene isomers, and 15 of their mono-, di-, and trihydrogenation products by the G2(MP2) and G2(MP2,SVP) ab initio methods. The ab initio results are used in conjunction with isodesmic "bond separation" reactions to obtain enthalpies of isomerization and hydrogenation, $\Delta_{isom}H^{298}$ and $\Delta_{hyd}H,^{298}$ which follow directly from the calculated total enthalpies at 298 K. G2(MP2,SVP) calculations are not, insofar as can be determined from the scattered experimental data, inferior to G2(MP2) calculations within the usual target uncertainty range of ±2 kcal mol^{-1}.

Chemists' fascination with the isomers of benzene is more than a century old[1] but the actual synthesis and detection of some of them is so difficult as to have been achieved only in the past decade.[2] Still today, some benzene isomers exist in theory only.[3]

We have been pursuing the G2 family of calculations on the thermochemistry of hydrocarbons of increasing complexity, starting with C_2, C_3, and C_4 hydrocarbons[4] and including, recently, C_5 hydrocarbons such as spiropentane and methyltetrahedrane.[5] This paper is an extension of those studies into G2-(MP2) and G2(MP2,SVP) calculations of the enthalpies of formation of benzene, which has been thoroughly studied both experimentally and theoretically,[6] and of its isomers and hydrogenation products, which have been the subject of more limited theoretical and experimental work. We have calculated the structures at the MP2(full)/6-31G(d) level, the total energies at 0 K (E_0) and the total enthalpies at 298 K (H^{298}) of 8 isomers of benzene, 10 monohydrogenation products of benzene and its isomers, 4 dihydrogenation products, and a trihydrogenation product (cyclohexane) by the G2(MP2) and G2(MP2,SVP) ab initio molecular orbital methods. A knowledge of H^{298} for any of these compounds leads to its enthalpy of formation $\Delta_f H^{298}$ by Curtis' "bond separation" method and to many enthalpies of hydrogenation and isomerization, $\Delta_{hyd}H^{298}$ and $\Delta_{isom}H,^{298}$ from benzene to related compounds. Even among this group of unusual molecules, benzene is, by virtue of its aromaticity, unique.

The obvious question as one carries out calculations on larger molecules is whether the G2 family of ab initio methods retains its validity for the larger species. We present evidence that it does, at least for the restricted group of benzene isomers and their mono-, di-, and trihydrogenation products.

Theory

G2 Methods. G2 computational methods[7,8] have been discussed in this series of papers[4,5] and in references therein.

Atomization Method. The most important molecular energetic result of the G2 family of computations is the total energy, E_0, of the gaseous species in the ground state at 0 K, corrected for the zero-point energy. The energy of formation at 0 K from the gaseous atoms of a target molecule, for example, methane,

$$C(g) + 4H(g) \rightarrow CH_4(g) \qquad (1)$$

can be calculated from the E_0 values in Table 1. In this example, $\Delta_f E_0(CH_4, 0\ K) = -0.62654$ hartree (h) $= -393.2$ kcal mol^{-1} as shown by Curtiss *et al.*[7]

The reverse of reaction 1 is the energy of atomization; hence the name of this procedure is the "atomization method". To find the energy of formation of methane from the elements in the *standard state* at 0 K, we add the *experimental* energies of atomization[9] of hydrogen (51.63 ± 0.001 kcal mol^{-1}) and carbon (169.98 ± 0.1 kcal mol^{-1}), multiplied by the appropriate stoichiometric coefficients, to the energy of formation at 0 K to obtain $\Delta_f E_0 = -393.2 + 376.5 = -16.7$ kcal mol^{-1}.

At 298 K, the enthalpy of formation of C and H atoms from the elements in the standard state increases[9] to 52.64 and 170.23 kcal mol^{-1}, respectively. The total increase in enthalpy change from standard state elements to atoms from 0 to 298 K is $0.25 + 4(1.01) = 4.3$ kcal mol^{-1}. The enthalpy of methane relative to the atoms increases by the difference between columns 2 and 3 in Table 1, i.e., 0.003 82 hartree = 2.4 kcal mol^{-1}. Thus, methane has decreased by 1.9 kcal mol^{-1} relative to the elements in their standard state and $\Delta_f H^{298}(CH_4, \text{calc}) = -16.7 - 1.9 = -18.6$ kcal mol^{-1} as compared to the experimental value of -17.9 ± 0.1 kcal mol^{-1}.

Bond Separation Method.[10] Because the $\Delta_f H^{298}$ values of many small molecules are known[11] to within 0.1 or 0.2 kcal mol^{-1}, one need not start with atoms in the hypothetical formation reaction 1. One can build up the target molecule by a hypothetical reaction at 298 K from smaller *molecules* rather than from atoms, for example, for benzene

$$3C_2H_4 + 3C_2H_6 \rightarrow C_6H_6 + 6CH_4 \qquad (2)$$

Working from H^{298} values in Table 1 and taking H^{298}(benzene)[12]

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TABLE 1: G2 Values of $\Delta_f H^{298}$ of Methane and C_2 Hydrocarbons Calculated by the Atomization Method[7]

	ZPE (scaled)	E_0	H^{298}	$\Delta_f H^{298}$ calc	$\Delta_f H^{298}$ expt
H		−0.500 00[a]			
C		−37.784 32			
H_2	0.009 45	−1.166 36	−1.163 06	−1.1	0.0
methane	0.042 70	−40.410 86	−40.407 04	−18.6	−17.90 ± 0.1
acetylene	0.026 29	−77.185 73	−77.182 33	55.6	54.20 ± 0.1
ethene	0.048 90	−78.415 93	−78.411 93	12.8	12.54 ± 0.1
ethane	0.071 22	−79.630 89	−79.626 40	-20.6	−20.08 ± 0.1

[a] E_0 of the hydrogen atom is from the exact solution of the Schroedinger equation.

$= -231.775\,08$ (circumventing the E_0 calculation),

$$\Delta_r H^{298} = \sum \nu_i H^{298}(\text{products}) - \sum \nu_j H^{298}(\text{reactants}) \quad (3)$$

$$= -0.10233 \text{ hartree} = -64.21 \text{ kcal mol}^{-1}$$

where $\Delta_r H^{298}$ is the enthalpy change of reaction for the formation of benzene from ethene and ethane, and ν_i and ν_j are the appropriate stoichiometric coefficients. Now systematic computational errors may cancel between the right and left sides of isodesmic reaction 2, giving a more accurate estimate of $\Delta_r H^{298}$ than one obtains by mixing calculated molecular H^{298} values with atomic H^{298} values as in the atomization method. Indeed this has been found to be true by Raghavachari, Stefanov, and Curtiss[10b] for G2 and G2(MP2) calculations of $\Delta_f H^{298}$ of the molecules in the G2-2 test set.[9,10b] The calculated $\Delta_r H^{298}$ above and the *experimental* $\Delta_f H^{298}$ for CH_4(g), $CH_2{=}CH_2$(g), and $CH_3{-}CH_3$(g) which are −17.90, 12.54, and −20.08 kcal mol^{-1}, respectively,[10b] leave only $\Delta_f H^{298}$(benzene) as an unknown in the equation

$$\Delta_r H^{298} = \sum \nu_i \Delta_f H^{298}(\text{products}) - \sum \nu_j \Delta_f H^{298}(\text{reactants}) \quad (4)$$

For example, for benzene,

$$-64.21 = \Delta_f H^{298}(\text{benzene}) + (-107.4) - [37.62 + (-60.24)]$$

$$\Delta_f H^{298}(\text{benzene}) = 20.6 \text{ kcal mol}^{-1}$$

where the experimental value is 19.74 ± 0.1.[11] We note that the "higher level correction" (HLC) of G2-family E_0 calculations[7] drops out when one calculates $\Delta_{\text{isom}} H^{298}$ or $\Delta_{\text{hyd}} H$,[298] albeit at the expense of including a considerable amount of other empirical information in what was originally an ab initio method.

Results

Geometry. Geometries of benzene and 23 of its isomers and isomeric hydrogenation products were calculated at the MP2-(full)/6-31G(d) level. A summary table of salient bond lengths and angles optimized at this level is given as Table S1 in the Supporting Information.

Noteworthy geometric features include the surprisingly small distortion brought about by normally linear allylic double bonds or by triple bonds in the cyclohexanyl structure. Also unusual is the long central bond in dewarbenzene (1.570 A) and the "roof" angle of dewarbenzene, which decreases from about 116.9 to 114.2° upon mono- and dihydrogenation to bicyclo-[2.2.0]hexane. (The "roof" in tetrahydrodewarbenzene twists to a 2−1−4−3 dihedral angle of slightly less than 10°.) The three-membered rings in cyclopropenyl compounds seem to be independent of one another both geometrically and energetically (see below).

Enthalpy. Values of H^{298} calculated by the G2(MP2) method are given in Scheme 1 along with H^{298} calculated by G2(MP2,-SVP) results, which are shown in italics. Zero-point energies and E_0 values are given in the Supporting Information. The enthalpy correction from 0 to 298 K is given by the difference between H^{298} and E_0 in the Supporting Information. This correction is the same for both G2(MP2) and G2(MP2,SVP) results because both sets of harmonic frequencies are computed from the same geometry. Harmonic frequencies are scaled by 0.8929.[13]

If one wishes to calculate $\Delta_f H^{298}$ for any compound in Scheme 1, the G2(MP2) values for H^{298} should be used in conjunction with the G2(MP2) values for methane, ethyne, ethene, and ethane in Table 2. G2(MP2, SVP) calculations should be carried out with the small-molecule values in Table 3.

Calculated G2(MP2,SVP) H^{298} values for trienes (top line, Scheme 1) are very close to those from G2(MP2) calculations, being 1.14 ± 0.43 millihartrees or 0.72 ± 0.27 kcal mol^{-1} *lower* in enthalpy than the G2(MP2) results. G2(MP2,SVP) results for isomers of cyclohexadiene (second line, Scheme 1) are also very close to the G2(MP2) values, but they are 0.71 ± 0.32 mhartree (0.42 ± 0.20 kcal mol^{-1}) *higher* than the G2(MP2) results. G2(MP2,SVP) calculated values of isomers of cyclohexene are higher than G2(MP2), by 2.43 ± 0.41 mhartrees (1.52 ± 0.26 kcal mol^{-1}). In agreement with the atomization-type calculations of Nicolaidis and Radom,[14] the G2(MP2,SVP) result for cyclohexane is a little more than 4 mh higher than G2(MP2). A roughly linear dependence of the difference between G2(MP2) results and G2(MP2,SVP) results on the number of hydrogen atoms in the target molecule, and a reversal in the sign of the difference for highly unsaturated molecules has been previously noted for smaller cyclic hydrocarbons.[5]

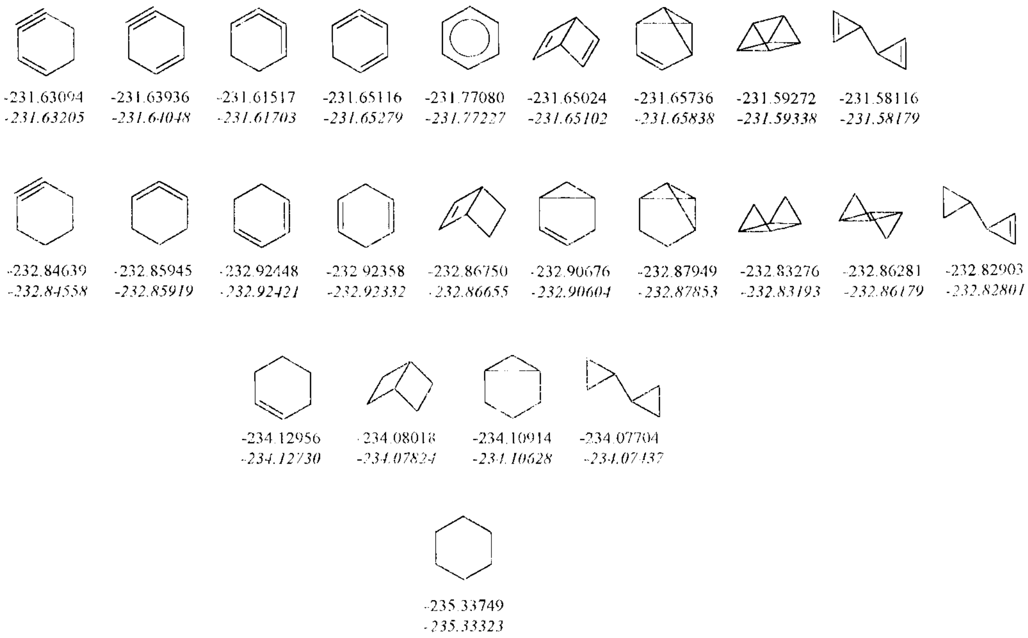
$\Delta_f H^{298}$. Enthalpies of formation of benzene and 23 compounds related to benzene by isomerization or hydrogenation, calculated by the bond separation method, are given in Table 4. The unsigned mean deviation from experimental results is 1.2 kcal mol^{-1} if the experimental result for benzvalene (which may be an outlier) is left out and 1.6 kcal mol^{-1} if it is not left out. The signed and unsigned mean deviations are the same, indicating a systematic error of between 1 and 2 kcal mol^{-1} toward calculated $\Delta_f H^{298}$ that are higher than experimental results.

These results confirm the early values of Schulman and Disch,[22] who obtained 94.0, 90.4, 136.4, and 137.6 kcal mol^{-1} for dewarbenzene, benzvalene, prismane, and 3,3′-bicyclopropenyl, respectively, using isodesmic reactions (not bond separation reactions) with MP2/6-31(d) energies calculated at 6-31G(d) optimized geometries. With the exception of prismane, our results are about 2.5 kcal mol^{-1} higher than theirs.

Isomerization enthalpies can be obtained as $\Delta_{\text{isom}} H^{298} = 627.51\{H^{298}(\text{isomer}) - H^{298}(\text{benzene})\}$ from Scheme 1. The consistent standard deviations for the differences between G2-(MP2) results and those of G2(MP2,SVP) mentioned above show that the differences cancel between isomers so that both methods give essentially the same answers for $\Delta_f H$.[298] The worst case discrepancy between G2(MP2) and G2(MP2,SVP) in Scheme 1 is 1.23 mhartrees = 0.77 kcal mol^{-1}.

$\Delta_{\text{hyd}} H^{298}$. Selecting the literature values for 1,3 and 1,4 dienes presents some difficulties. Kistiakowsky[23] found $\Delta_{\text{hyd}} H^{298}$-(cyclohexa-1,3-diene) = −55.4 ± 0.1 kcal mol^{-1} in the gas

SCHEME 1: G2(MP2) and G2(MP2,SVP) Total Enthalpies, H^{298}, of Benzene, Benzene Isomers, and Isomers of Benzene Hydrogenation Products[a]



[a] G2(MP2,SVP) values are in italics and the units are hartrees.

TABLE 2: G2(MP2) Values of H^{298} and $\Delta_f H^{298}$(expt) of Methane and C_2 Hydrocarbons[a]

	ZPE (scaled)	E_0	H^{298}	$\Delta_f H^{298}$(expt)
H		−0.500 00[a]		
C		−37.784 32		
H2	0.009 45	−1.166 36	−1.163 06	0.0
methane	0.042 70	−40.409 63	−40.405 81	−17.90 ± 0.1
acetylene	0.026 29	−77.184 07	−77.180 38	54.20 ± 0.1
ethene	0.048 90	−78.414 30	−78.410 29	12.54 ± 0.1
ethane	0.071 22	−79.628 93	−79.624 45	−20.08 ± 0.1

[a] E_0 of hydrogen is from the exact solution of the Schroedinger equation.

TABLE 3: G2(MP2,SVP) Values of H^{298} and $\Delta_f H^{298}$(expt) of Methane and C_2 Hydrocarbons

	ZPE (scaled)	E_0	H^{298}	$\Delta_f H^{298}$(expt)
H		−0.500 00[a]		
C		−37.784 32		
H2	0.009 45	−1.166 36	−1.163 06	0.0
methane	0.042 70	−40.407 64	−40.403 83	−17.90 ± 0.1
acetylene	0.026 29	−77.184 45	−77.180 75	54.20 ± 0.1
ethene	0.048 90	−78.413 43	−78.409 43	12.54 ± 0.1
ethane	0.071 22	−79.626 08	−79.621 59	−20.08 ± 0.1

[a] E_0 of hydrogen is from the exact solution of the Schroedinger equation.

TABLE 4: G2(MP2) Results for $\Delta_f H^{298}$ of Benzene Isomers and Products of Mono-, Di-, and Trihydrogenation by the Bond-Separation Method (See Text) (Units kcal mol^{-1})

compound[a]	$\Delta_f H^{298}$(b-sep)	$\Delta_f H^{298}$(expt)
1. cyclohexene-3-yne	108.5	
2. cyclohexene-4-yne	102.8	
3. cyclohexa-1,2,3-triene	118.8	
4. cyclohexa-1,2,4-triene	96.2	
5. benzene	21.1	19.7 ± 0.2[11]
6. dewarbenzene	96.8	
7. benzvalene	92.4	87.2[19]
8. prismane	133.0	
9. 3,3′-bicyclopropenyl	140.2	
10. cyclohexyne	74.6	
11. cyclohexa-1,2-diene	67.3	
12. cyclohexa-1,3-diene	26.5	25.4 ± 0.2[11]
13. cyclohexa-1,4-diene	27.0	26.0 ± 0.2[16]
14. bicyclo[2.2.0]hex-2-ene	62.2	61.5 ± 0.2[17]
15. bicyclo[3.1.0]hex-2-ene	37.6	
16. tricyclo[3.1.0.0^{2,6}]hexane	54.8	
17. *cis*-dihydroprismane	84.1	
18. *trans*-dihydroprismane	65.2	
19. 3,3′-cyclopropylcyclopropene	86.4	
20. cyclohexene	−0.5	−1.2 ± 0.2[11,18]
21. bicyclo[2.2.0]hexane	30.6	29.8 ± 0.2[17]
22. bicyclo[3.1.0] hexane	12.4	9.2 ± 0.2[11,19]
23. 3,3′-bicyclopropyl	32.5	30.9 ± 0.9[11,20]
24. cyclohexane	−29.2	−29.5 ± 0.2[11,21]

[a] (**6**) Bicyclo[2.2.0]hexa-2,5-diene, (**7**) tricyclo[3.1.0.0^{2,6}]hex-3-ene, (**8**) tetracyclo[2.2.0.^{2,6}0^{3,5}]hexane, (**14**) bicyclo[2.2.0]hex-2-ene, (**15**) bicyclo[3.1.0]hex-2-ene, (**16**) tricyclo[3.1.0.0^{2,6}]hexane, (**17**) *anti*-tricyclo[3.1.0.0^{2,4}]hexane, (**23**) 3,3′-cyclopropylcyclopropane.

phase at 355 K with cyclohexane as the reaction product. From statistical thermodynamic arguments, one can find a small thermal correction to get −54.6 kcal mol^{-1} at 298 K. Turner's group[24] measured $\Delta_{hyd}H^{298}$ of both the 1,3 and 1,4 isomers in glacial acetic acid solution and found them to be −53.6 ± 0.3 and −53.9 ± 0.3 kcal mol^{-1}, respectively, at 298 K. Corrections for the significant solvent effect of glacial acetic acid were not made in this work. Roth's group[25] found $\Delta_{hyd}H^{298}$(cyclohexa-1,4-diene) = −55.6 kcal mol^{-1}. Solvent effects were taken into account in this work but only one measurement was made, and hence no experimental uncertainty was given.[25] Our attempts at experimental determination of the $\Delta_{hyd}H^{298}$ of the isomeric cyclohexadienes were unsuccessful, presumably due to our inability to avoid polymerization during microdistillation. We were hesitant to accept any previous hydrogenation work uncritically because prior experiments may have been limited by the same polymerization problem.

Nevertheless, computed $\Delta_{hyd}H^{298}$ values below give strong support for both Kistiakowsky's and Roth's experiments on cyclohexa-1,3-diene and cyclohexa-1,4-diene, respectively. The only C_6H_8 isomer listed in Pedley's compendium[11] is $\Delta_f H^{298}$(cyclohexa-1,3-diene) = 25.38 ± 0.22 kcal mol^{-1} in the gas phase, which comes from Kistiakowsky's $\Delta_{hyd}H^{298}$(cyclohexa-

1,3-diene) = 54.88 kcal mol^{-1} with a temperature correction (slightly different from ours).

Hydrogenation of benzene (**5**) to cyclohexa-1,3-diene (**12**) gives $\Delta_{hyd}H^{298}$ = 5.33 kcal mol^{-1}, confirming the well-known (but nonetheless remarkable) endothermicity of the first step in hydrogenation of benzene to cyclohexane (**24**).

$$\begin{tikzcd} & 12 \arrow[dr] & & \\ 5 \arrow[ur] \arrow[dr] & & 20 \arrow[r] & 24 \\ & 13 \arrow[ur] & & \end{tikzcd}$$

Hydrogenation to the 1,4 isomer (**13**) yields $\Delta_{hyd}H^{298}$ = 5.90 kcal mol^{-1}, which is consistent with the isomerization enthalpy $\Delta_{isom}H^{298}$(**12**→**13**) = 0.6 kcal mol^{-1} in Scheme 1. Subtracting the calculated $\Delta_{hyd}H^{298}$ for (**5**→**12**) from $\Delta_{hyd}H^{298}$(benzene)[23] = −49.1 ± 0.2 kcal mol^{-1} yields $\Delta_{hyd}H^{298}$(**12**→**24**) = −54.5 kcal mol^{-1} in good agreement with Kistiakowsky's finding[23] of −54.6 kcal mol^{-1} for $\Delta_{hyd}H^{298}$(**12**). The same subtraction for **13** gives $\Delta_{hyd}H^{298}$(**13**) = −55.0 kcal mol^{-1}, in good agreement with Roth's measurement[16] of −55.6 kcal mol^{-1}. The isomerization **12** → **13** is found to be <1 kcal mol^{-1} and endothermic by all three assessments (two experimental and one calculation) in agreement with Turner's finding[24] of $\Delta_{isom}H^{298}$(**12**→**13**)= 0.3 kcal mol^{-1}. A solvent effect of slightly less than 1.4 kcal mol^{-1} is consistent with hydrogenation of two double bonds[25] in **12** or **13** and would account for the difference between Turner's measurement and those of Kistiakowsky and of Roth. Although Turner's $\Delta_{hyd}H^{298}$ measurements also disagree with calculations by about 1 kcal mol^{-1}, the solvent effect cancels in the $\Delta_{isom}H^{298}$ calculation,[25] removing the inconsistency.

The sequential hydrogenation of dewarbenzene (**6**) through dihydro- and tetrahydrodewarbenzene (**14** and **21**) to cyclohexane (**24**)

$$\mathbf{6} \xrightarrow[-34.6]{} \mathbf{14} \xrightarrow[-31.6]{} \mathbf{21} \xrightarrow[-59.8]{} \mathbf{24} \tag{5}$$

has the calculated stepwise $\Delta_{hyd}H^{298}$ values, shown in reaction 5, which are obtained Δ_fH^{298} differences between the appropriate reactants and products in Table 4. We found experimentally[26] that $\Delta_{hyd}H^{298}$(hexamethyldewarbenzene) = −31.4 ± 0.7 kcal mol^{-1}. The methyl groups, which may stabilize the molecule through hyperconjugation or destabilize it because of crowding (or both), prevent direct comparison of the hexamethyl case with the unencumbered parent compound, but there is, at least, reasonable agreement with the first step in reaction 5.

Roth et al. found[17] that dihydrodewarbenzene is hydrogenated to cyclohexane with the evolution of −91.0 ± 0.2 kcal mol^{-1} of heat, which compares with the sum of the calculated $\Delta_{hyd}H^{298}$ for steps 2 and 3 in reaction 5, i.e., −91.4 kcal mol^{-1}. For the third step in the sequence, $\Delta_{hyd}H^{298}$(tetrahydrodewarbenzene) is calculated to be −59.8 kcal mol^{-1} and was measured as −59.3 ± 0.2 kcal mol^{-1} by Roth et al.[17] These $\Delta_{hyd}H^{298}$ values were used to obtain the experimental Δ_fH^{298}(**14** and **21**) in Table 4.

From Table 4, the sequence

$$\mathbf{9} \xrightarrow[-53.8]{} \mathbf{19} \xrightarrow[-53.9]{} \mathbf{23} \tag{6}$$

gives the $\Delta_{hyd}H^{298}$ values shown below the arrows in reaction 6. These results show that there is little mutual energetic influence between cyclopropene rings in 3,3′-bicyclopropyl (**9**), or between cyclopropene and cyclopropane rings in (**19**). Comparison with the experimental value[11] (from Δ_fH^{298}) for cyclopropene, −53.5 ± 0.6 kcal mol^{-1} shows that, energetically at least, 3,3′-bicyclopropyl is essentially two cyclopropene molecules loosely linked together by the single bond. In the calculations above, G2(MP2) and G2(MP2,SVP) results differ by a negligible amount (∼0.2 kcal mol^{-1}).

Table 4 G2(MP2) results lead to the enthalpy of hydrogenation of **20** → **24** $\Delta_{hyd}H^{298}$(cyclohexene) = −28.7 kcal mol^{-1}. G2(MP2,SVP) also yields −28.7 kcal mol^{-1} as contrasted to the experimental value[27] of −28.4 ± 0.1 kcal mol^{-1}.

Other experimental comparisons are with Δ_fH^{298}(bicyclo-[3.1.0]hexane) = 9.2 ± 0.2 kcal mol^{-1} and Δ_fH^{298}(bicyclopropyl) 30.9 ± 0.9 kcal mol^{-1}. The calculated values for these two quantities are 12.4 and 32.5 kcal mol^{-1} as shown in Table 4.

Measurement of the isomerization enthalpy of benzvalene to benzene **7** → **5** has been made by Turro,[15] who found $\Delta_{isom}H^{298}$ = −67.5 kcal mol^{-1}. The calculated value from Scheme 1 is −71.2 kcal mol^{-1} by G2(MP2) and −71.8 by G2(MP2,SVP).

Note Added in Proof. Our results are consistent with those of a very recent paper[28] on compounds **5**−**9**.

Conclusion

Although experimental results are too scattered to provide a rigorous arithmetic mean difference between calculation and experiment (AMD = 1.2 kcal mol^{-1}), G2(MP2) and G2(MP2,-SVP) calculations using the bond dissociation method appear to be within the 1−2 kcal mol^{-1} uncertainty limits associated with the G2 family calculations of Δ_fH^{298} for hydrocarbons.

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Supporting Information Available: Table of bond lengths and angles optimized at MP2(full)/6-31G(d) level, and zero-point energies and E_0 values. This information is available free of charge via the Internet at http://pubs.acs.org.

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