G3(MP2) Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of Bi- and Tricyclic C_8 and C_{10} Hydrocarbons. The Bicyclo[3.3.0]octenes and Triquinacenes

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We have calculated the enthalpies of hydrogenation, isomerization, and formation in the gaseous state ($\Delta_{\mathrm{hyd}}H$,^{298} $\Delta_{\mathrm{isom}}H$,^{298} and $\Delta_{\mathrm{f}}H^{298}$) of cyclopentenes, bicyclo[3.3.0]octenes, and triquinacenes by the G3(MP2) procedure. Comparison with combustion and hydrogenation thermochemical results shows that agreement between G3-(MP2) calculations and experiment remains well within the target interval of 1 to 2 kcal mol^{-1} for those cases in which experimental results exist. The sole exception is our earlier study on the hydrogenation of triquinacene to perhydrotriquinacene, which deviates from both calculation and a more recent combustion study.

In the previous paper in this series,[1] we found that the G3-(MP2) molecular orbital method produces results for the enthalpies of formation, hydrogenation, and isomerization ($\Delta_{\mathrm{f}}H$,^{298} $\Delta_{\mathrm{hyd}}H$,^{298} and $\Delta_{\mathrm{isom}}H^{298}$) of five C_7 hydrocarbons related to norbornadiene that are in substantial agreement with experimental results.[1f] Recently, Curtiss et al. have extended G*n* calculations, (G1, G2, G3, and modifications),[2] to the C_{10} hydrocarbon naphthalene.[2h] Along with an arithmetic mean accuracy that is well within the target range of ±2 kcal mol^{-1} set for the G*n* series of procedures,[2a] G3(MP2) is conservative of computer time and disk space relative to other G*n* procedures of comparable accuracy. These economies encourage investigation of the thermochemistry of large (~C_{10}) molecules.

Because of the rigidity and structural simplicity of cyclic hydrocarbons and because we have relevant experimental thermochemical information on some of them, we have chosen cyclic C_5, C_8, and C_{10} hydrocarbons to extend our work in computational thermochemistry.[1] We are especially interested in the fused five-membered ring systems related to bicyclo-[3.3.0]octa-1,3,5,7-tetraene (pentalene) and its various hydrogenation and partial hydrogenation products. We have also carried out G3(MP2) calculations on the C_{10} systems, tricyclo-[5.2.1.0^{4,10}]deca-2,5,8-triene (triquinacene) and its hydrogenation and partial hydrogenation products. Triquinacene offers the interesting possibility of neutral homoaromaticity (vide infra) and has been the subject of several papers on that topic.[3] For comparison purposes, we have repeated G2(MP2) calculations[2c] on five C_5 cyclic hydrocarbons[1c] related to cyclopentene using the newer G3(MP2) method.

Theory

The primary difference between the G2(MP2)[2c] and G3(MP2) methods[2g] for hydrocarbons is the substitution of a new basis set, called G3MP2large, for the 6-311G(3d,2p) set previously used. The details of the new basis set are given in the original publication,[2f,g] and it is available on the web.[2g,ref10] Having made the change in basis set, the computational strategy is similar to that of the G2(MP2) method.

The G3(MP2) method uses three calculated points in a basis set-correlation level space to extrapolate a fourth point, the QCISD(T)/G3MP2large result, which is inaccessible for the molecule of interest because of limitations on computer time and storage space. The extrapolation is made in two steps. First the MP2/6-31G(d) calculation is "corrected" for basis set inadequacy by carrying out a more rigorous calculation using the MP2/G3MP2large basis set, taking note of the difference in energy, $\Delta E_{\mathrm{MP2}} = [E(\mathrm{MP2/G3MP2large})] - [E(\mathrm{MP2/6\text{-}31G(d)})]$, brought about by the calculation at the higher level basis set relative to the lower one. A similar decrement in energy, $[E(\mathrm{QCISD(T)/6\text{-}31G(d)})] - [E(\mathrm{MP2/6\text{-}31G(d)})]$, is found upon imposing the post-Hartree−Fock treatment QCISD(T) upon the 6-31G(d) basis set relative to the MP2 energy obtained from the same basis set. Subject to the assumption that the two energy differences are additive, the first correction plus E(QCISD(T)/6-31G(d)) gives the desired energy at the QCISD(T)/G3(MP2)-large level of approximation.

A second difference between G2(MP2) and G3(MP2) calculations is the inclusion of an atomic spin−orbit coupling energy (E(SO)) in the total molecular energy. Only atomic ΔE(SO) corrections (C: 0.14 mh, H: 0.0 mh) are included in the G3(MP2) method.[2g] A "higher level correction" (HLC) and a zero-point energy (E(ZPE)) are used as in G2(MP2). The HLC (9.279 mh per pair of valence electrons) is purely an empirical factor, reparametrized in the newer method so as to give the minimum discrepancy between the G2/97 test set of experimental energies[2d,g] and the calculated energies. The sum of these five energies is E_0[G3(MP2)]

$$E_0[\mathrm{G3(MP2)}] = E(\mathrm{QCISD(T)/6{-}31G(d)}) + \Delta E_{\mathrm{MP2}} + \Delta E(\mathrm{SO}) + E(\mathrm{HLC}) + E(\mathrm{ZPE}) \quad (1)$$

The geometry is at the MP2(full)/6-31G(d) level, and the zero-point energy is from the scaled (0.8929) HF/6-31G(d) harmonic oscillator frequencies.[4] Other calculations are carried out on valence electrons only (the "frozen core" approximation).

E_0[G3(MP2)] is the energy of the molecule in the gas phase at 0 K relative to isolated nuclei and electrons. This energy is converted to the ground-state enthalpy (H^{298}) at 298 K, by adding a thermal correction to the enthalpy (TCH) over the temperature range from 0 to 298 K. The TCH is a composite of classical statistical thermodynamic enthalpy changes with a

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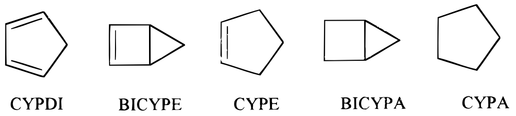
SCHEME 1. Cyclic and Bicyclic C_5 Hydrocarbons



quantum harmonic oscillator term for vibrational energy.[5,6] Having obtained E_0[G3(MP2)] and H,^{298} there are several ways of converting either to the thermodynamically desired datum, Δ_fH.^{298} All are in some degree empirical.

The Atomization Method. In the "atomization method", E_0[G3(MP2)] of each atom in the molecule is calculated (C; −37.78934, H; −0.50184 hartrees).[2d] The *experimental* enthalpy of atomization of each element in the standard state (C: 169.73, H: 50.62 kcal mol^{-1} at 298 K) is subtracted from E_0[G3(MP2)] of the elements to find H^{298} of the elements in the standard state and thus to obtain Δ_fH^{298}(hydrocarbon) from H^{298}(hydrocarbon) via the reaction

$$C_m(s,gr) + \frac{n}{2}H_2(g) = C_mH_n(g) \qquad (2)$$

where all components are in the standard state. An analogous treatment using energies of atomization at 0 K and E_0[G3(MP2)] leads to $\Delta_fE°$, the energy of formation in the standard state at 0 K.

Bond Separation and Hydrogenation. Two other methods, the "bond separation" method[2e] and a method involving isomerization or hydrogenation[1b] to a product of known Δ_fH^{298}, have been used to obtain accurate Δ_fH^{298} values. They are not used here and will not be discussed further.

Computational

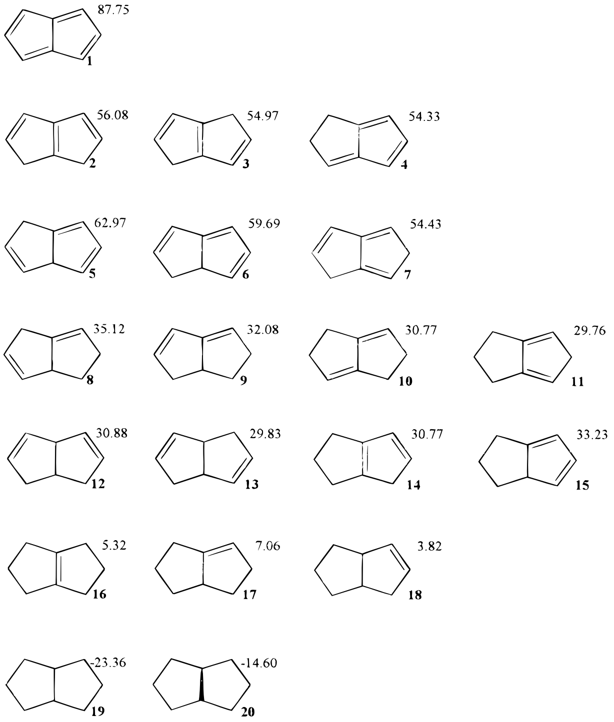
Although recent versions of GAUSSIAN98[6] contain linked single-point calculations and ancillary calculations that provide E_0 and H^{298} directly, the same results can be obtained using older versions of GAUSSIAN98 or GAUSSIAN94 by a stepwise process. We used this stepwise process to obtain the results given below: 1. Obtain an input geometry by molecular mechanics, e.g., MM2 as implemented in PCMODEL.[7] The step that we previously used[1c] to generate an input z-matrix using a PM3 semiempirical optimization can be eliminated by working directly from the geometry in Cartesian coordinates. 2. Use the input geometry to obtain an initial geometry at the Hartree−Fock level. Refine the HF geometry to the MP2(full)/6-31G(d) level. This geometry will be used in subsequent steps. Obtain E(ZPE). The TCH can be obtained using the **opt freq = readisotopes** keyword at the HF level with 298.15, 1.0, and 0.8929 as the temperature, pressure, and harmonic scale factor.[8] 3. Run the QCISD(T) and G3(MP2)large calculations either individually or linked.[8] E(MP2/6-31G(d)) is generated along with E(QCISD(T)/6-31G(d)). 4. Calculate Δ_fH^{298} from eqs 1 and 2.

Further information on the G*n* series of methods is in the literature.[2] A short BASIC program containing all of the necessary parameters for carrying out ancillary calculations for hydrocarbons is available.[9]

Results

Nomenclature. The various C_5 compounds are given abbreviations related to their common names as shown in Scheme 1. The more numerous bicyclo[3.3.0]octenes are given numbered names BICY**1** through BICY**20** as shown in Scheme 2. The hydrogenation products of triquinacene are named as derivatives of the parent compound, e. g., H_2TRIQ etc.

SCHEME 2. G3(MP2) Enthalpies of Formation of Pentalene, the Bicyclo[3.3.0]octatrienes, -octadienes, -octenes, and -octanes, BICY1 − BICY20



Cyclopentenes. The MP2(full)/6-31G(d) geometries of the molecules in Scheme 1 are unexceptional and have been discussed.[1c]

G3(MP2) and G2(MP2) Δ_fH^{298} results for the cyclopentenes differ from one another by a mean absolute deviation (MAD) of 2.8 kcal mol^{-1} when both are calculated by the atomization procedure. G3(MP2) values of Δ_fH^{298} calculated by the atomization method have a MAD from experimental values (exp − calc) of 0.5 kcal mol^{-1}, which is a marked improvement over G2(MP2). The mean signed deviation (MSD) is 0.2 kcal mol^{-1}, showing no significant systematic difference. By contrast, for the G2(MP2) results, both the MAD and MSD for the hydrocarbons in Table 1 are −2.6 kcal mol^{-1}, indicating bias in favor of higher calculated Δ_fH^{298} values than those indicated by the experimental results.

Bicyclooctenes. Results for pentalene, the bicyclo[3.3.0]-octatrienes, -octadienes, -octenes, and -octanes in Scheme 2, BICY**1** − BICY**20**, are given in Table 2. G3(MP2) calculated Δ_fH^{298} values are also shown in Scheme 2.

Pentalene consists of two coplanar irregular pentagons. (The double bonds are 1.361 **Å** and the single bonds are 1.488 **Å** in the MP2(full)/6-31G(d) geometry.) Its symmetry point group is C_{2h}. There is only one stable conformer at 298.15 K. Bicyclooctenes **2**, **3**, and **4** in Scheme 2 are coplanar irregular pentagons with C_{2v}, C_{2h}, and C_s symmetry. None of the bicyclo[3.3.1]octatrienes has more than one stable conformer at 298.15 K.

Only compounds **5** and **6** in Scheme 2 have nonplanar structures as found by searching their several dihedral angles via MM3. The symmetry point groups of compounds **5** − **7** in Scheme 2 are C_1, C_1, and C_s respectively, also found by MM3.

Of the remaining 13 bicyclo[3.3.0]octadienes, -octenes, and -octanes, only **10** and **14** are planar. The symmetry point groups of the bicyclo[3.3.0]octadienes **8** − **15** are C_1, C_1, C_{2h}, C_s, C_1, C_2, C_1, and C_1 respectively. The symmetry of several of the compounds is lower than might be anticipated from the structural

TABLE 1: Energy and Enthalpy Calculations for Cyclopentadiene and Its Hydrogenation and Isomerization Products. Units Are Hartrees and kcal mol^{-1}

	CYPDI	BICYPE	CYPE	BICYPA	CYPA
E^0	−193.749 14^a	−193.673 85	−194.951 72	−194.904 24	−196.158 82
H^{298}	−193.743 96^a	−193.668 74	−194.946 01	−194.898 80	−196.152 49
E(ZPE)	0.089 05^a	0.088 61	0.112 05	0.111 73	0.134 34
TCH	0.005 18^a	0.005 11	0.005 71	0.005 44	0.006 33
$\Delta_f E^0$	35.56^b	82.81	14.01	43.81	−10.38
$\Delta_f H^{298}$	31.50^c	78.71	8.27	37.89	−17.76
G2(MP2)	35.95^b	81.49	11.38	39.73	−15.93
$\Delta_f H^{298}$(exp)	32.10 ± 0.36^{b,d}	79.7 ± 0.5^{b,e}	8.10 ± 0.33^{b,d}	37.8± 0.5^{b,e}	−18.26 ± 0.19^{b,d}

[a] hartrees. [b] kcal mol^{-1}. [c] G3(MP2), kcal mol^{-1}. [d] ref 10. [e] ref 11.

TABLE 2: H^{298} for Bicyclooctenes, Their Isomers and Hydrogenation Products. Units Are Hartrees and kcal mol^{-1}

	BICY**1**	BICY**2**	BICY**3**	BICY**4**	BICY**5**
E^0	−307.840 54	−309.056 54	−309.058 31	−309.059 35	−309.045 36
H^{298}	−307.833 79	−309.049 27	−309.051 04	−309.052 07	−309.038 30
E(ZPE)	0.106 40	0.127 91	0.127 90	0.128 82	0.128 61
TCH	0.006 75	0.007 26	0.007 27	0.007 28	0.007 06
$\Delta_f E^0$	91.57	61.61	60.49	59.84	68.62
$\Delta_f H^{298}$	87.75	56.08	54.97	54.33	62.97
$\Delta_f H^{298}$(exp)					

	BICY**6**	BICY**7**	BICY**8**	BICY**9**	BICY**10**
E^0	−309.050 56	−309.059 07	−310.255 20	−310.260 01	−310.262 62
H^{298}	−309.043 53	−309.051 91	−310.247 70	−310.252 54	−310.254 63
E(ZPE)	0.128 83	0.128 32	0.151 30	0.151 52	0.151 01
TCH	0.007 03	0.007 16	0.007 50	0.007 47	0.007 99
$\Delta_f E^0$	65.35	60.01	42.51	39.49	37.85
$\Delta_f H^{298}$	59.69	54.43	35.12	32.08	30.77
$\Delta_f H^{298}$(exp)					

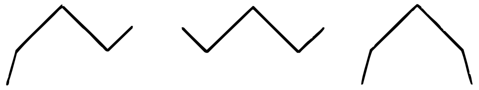
	BICY**11**	BICY**12**	BICY**13**	BICY**14**	BICY**15**
E^0	−310.263 88	−310.261 51	−310.263 58	−310.262 44	−310.258 30
H^{298}	−310.256 23	−310.254 02	−310.256 12	−310.254 63	−310.250 73
E(ZPE)	0.150 74	0.151 55	0.151 55	0.150 89	0.151 24
TCH	0.007 65	0.007 49	0.007 46	0.007 81	0.007 57
ΔE^0	37.06	38.55	37.25	37.97	40.57
$\Delta_f H^{298}$	29.76	31.15	29.83	30.77	33.22
$\Delta_f H^{298}$(exp)		32.0 ± **0.6**^{a}			

	BICY**16**	BICY**17**	BICY**18**	BICY**19**	BICY **20**
E^0	−311.468 53	−311.465 47	−311.470 45	−312.679 05	−312.665 44
H^{298}	−311.460 20	−311.457 43	−311.462 59	−312.670 93	−312.656 97
E(ZPE)	0.173 80	0.173 83	0.174 23	0.197 02	0.196 67
TCH	0.008 33	0.008 04	0.007 86	0.008 12	0.008 47
ΔE^0	14.21	16.13	13.01	−12.32	−3.78
$\Delta_f H^{298}$	5.32	7.06	3.82	−23.36	−14.60
$\Delta_f H^{298}$(exp)			4.6 ± 0.5^a	−22.20 ± 0.36^b	−15.92 ± 0.45^b

[a] combination of $\Delta_{hyd}H^{298}$ (ref 12) with $\Delta_f H^{298}$ of BICY**19**, [b]ref 10, 13.

formulas given in Scheme 2 because of skewing about the bond fusing the two rings. Skewing also reduces symmetry in the remaining bicyclo[3.3.0]alkenes and -alkanes BICY**16**−**20**, which have the point groups C_{2v}, C_1, C_1, C_2, and C_{2h} respectively, as found by MM3. Point groups determined by different minimization procedures are not necessarily the same, possibly due to small displacements of atoms at shallow potential energy minima.

None of the compounds BICY**16** − **20** is planar. Among the bicyclo[3.3.0]octenes and -octanes, only BICY**13**, **16**, **18**, and **19** exist at 298 K as conformational mixtures. BICY**19**, a "worst-case" example of conformational mixing, has three conformers with "wings" down−up, up−up, and down−down, looking down the C−C bond at the ring fusion.

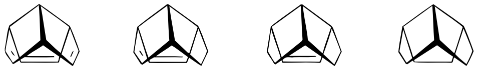


The $\Delta_f H^{298}$ values are −22.25, −21.84, and −21.59 kcal mol^{-1}, respectively, by MM3. The weighted average $\Delta_f H^{298}$ of the conformational mixture of Bicy**19** is only 0.19 kcal mol^{-1} above its ground state. Consequently, energy values in Scheme 2 and Table 2 were not corrected for conformational mixing. The MAD between the calculated $\Delta_f H^{298}$ and the four experimental results in Table 2 is 1.1 kcal mol^{-1} (uncorrected), or 1.0 kcal mol^{-1} if calculated values of BICY**18** and **19** are corrected to account for a conformational mixture at 298 K. The MSD (exp − calc) are 0.4 kcal mol^{-1}, uncorrected, and 0.3 kcal mol^{-1}, corrected.

The 6 trienes show significant enthalpic differences, having a range of almost 8 kcal mol^{-1} in $\Delta_f H$.^{298} The 8 dienes have a range of 5.4 kcal mol^{-1}, an arithmetic mean $\Delta_f H^{298}$ = 31.6 kcal mol^{-1}, and a standard deviation from the mean of 1.8 kcal mol^{-1}.

Triquinacenes. Triquinacene and its hydrogenation products are shown in Scheme 3. Their geometry and physical properties

SCHEME 3. Triquinacene and Its Hydrogenation Products



TRIQ H_2TRIQ H_4TRIQ H_6TRIQ

have been discussed recently.[3i] Energy information calculated by G3(MP2) for the triquinacenes is given in Table 3. The MAD between calculated $\Delta_f H^{298}$ values and $\Delta_f H^{298}$ obtained by combustion calorimetry for TRIQ and H_6TRIQ[14] and by hydrogenation thermochemistry[3b] for H_2TRIQ and H_4TRIQ is 1.1 kcal mol^{-1}. The MSD is -0.2 kcal mol^{-1} for the same four computed and experimental results. The noteworthy exception in the data set is $\Delta_f H^{298}$ of TRIQ itself from hydrogenation calorimetry ($\Delta_{hyd}H^{298}$(TRIQ) $= -78.0 \pm 0.5$ kcal mol^{-1}) which leads to $\Delta_f H^{298}$(TRIQ) $= 53.5 \pm 1.0$ kcal mol^{-1} relative to $\Delta_f H^{298}$(H_6TRIQ) $= -24.47 \pm 0.86$ kcal mol^{-1} determined by combustion calorimetry. The uncertainty of the values obtained by hydrogenation is the square root of the sum of squares of the two experimental uncertainties. H_4TRIQ and H_6TRIQ have conformers within 3 kcal mol^{-1} of the ground state as determined by the conformational search subprogram in MM3[15] but neither contributes more than 0.1 kcal mol^{-1} to the ground-state enthalpy, and corrections for conformational mixing have not been made.

Discussion

Cyclopentenes. There is some choice as to how one arrives at $\Delta_f H^{298}$ from a knowledge of H.[298] Among the options are the atomization,[2b,e] bond separation,[2d] hydrogenation, and isomerization[1c] methods. The latter two methods were devised to improve upon the accuracy of the first, accuracy being defined as the difference between calculated and experimental results.

Intuitively, at least, the atomization method comes closer than the other methods to the definition of an enthalpy of formation, i.e., the enthalpy change that accompanies the formation of a molecule from its elements in the standard state (eq 2). In G3[2f] and G3(MP2)[2g], a return has been made to the atomization method, with impressive results. In the present work, the atomization procedure produced agreement with experiment (MAD $= 0.5$ kcal mol^{-1}), for the compounds in Scheme 1, that is well within the limits of accuracy (± 2.0 kcal mol^{-1}) expected from the G-*n* family.[2a] Hence, the second and third methods were not used. It should be noted that the atomization procedures are not the same for G2(MP2) and G3(MP2).

A disappointing feature of G2(MP2) calculations, the failure to provide accurate $\Delta_{hyd}H^{298}$ for cyclopentene, CYPE, is alleviated in the data in Table 1. CYPE offers no special stumbling blocks to molecular orbital calculations; it is not a highly strained molecule, and intramolecular crowding encountered upon insertion of two hydrogen atoms into the ring to obtain cyclopentane, CYPA, is not especially severe. Experimentally, hydrogenation of CYPE to CYPA offers no special difficulties either. Over the years, several groups have measured $\Delta_{hyd}H^{298}$ by different techniques, and the results have always come out the same. Nevertheless, agreement between calculation and experiment[9,10] is poor in the G2(MP2) calculation on this simple molecule (exp $-$ calc $= -3.3$ kcal mol^{-1}). Table 1 shows that this discrepancy is largely removed by the G3(MP2) calculation.

Reliable values of $\Delta_{hyd}H^{298}$ for all of the compounds in Table 1 and Figure 1 are in the literature.[9,10] The MAD between 6 experimental and 4 calculated results shown in Figure 1 is 1.2 kcal mol^{-1} and the signed average deviation (calc $-$ exp) is 1.0 kcal mol^{-1}, showing slight bias in favor of more positive calculated values of $\Delta_{hyd}H^{298}$. Bias is outside of experimental error.

Roth points out[17] that one would expect some antiaromatic character in bicyclopentene, BICYPE, by analogy to cyclobutadiene, with the cyclopropane ring playing the role of pseudo-double bond. Indeed, $\Delta_{hyd}H^{298}$(BICYPE) $= -96.5$ kcal mol^{-1} is very large, amounting to triple the value of ethene, -32.6 ± 0.1 kcal mol^{-1}. Not all of this excess enthalpy can be attributed to antiaromaticity, however, there being a substantial decrease in bond bending upon breaking the transannular bond in BICYPE. Indeed, the driving enthalpy for hydrogenation of BICYPA is entirely due to strain release during ring opening. Hydrogenation of BICYPE and BICYPA entails the opening of both a four- and a three-membered ring.

The reactions in Figure 2 constitute a thermochemical cycle with reaction enthalpies $\Delta_r H^{298}(A + B + C + D) = 0$. (Hydrogen is not shown because it does not contribute to $\Delta_r H$.[298])

Reaction A involves ring opening and destruction of antiaromaticity (if any). Reaction C involves ring closing but does not involve antiaromaticity. The (negative) sum $\Delta_r H^{298}(A + C) = 14.9$ kcal mol^{-1} is our estimate of the (rather large) antiaromatic destabilization of BICYPE. A comparison of the “normal” ring hydrogenation reaction B with the reverse of reaction D shows that BICYPE is destabilized by exactly the same amount, as it must by nature of the thermochemical cycle.

Bicyclopentenes. Pentalene (BICY**1**) has long been of interest with respect to the aromaticity or antiaromaticity of its conjugated system of double bonds.[18] Accumulated evidence indicates that BICY**1** is planar with significant bond length alternation, suggesting that it is either nonaromatic or antiaromatic.

The computed enthalpy of hydrogenation of pentalene to the more stable cis isomer of perhydropentalene (BICY**19**) is -111.11 kcal mol^{-1}, that is, -27.8 kcal mol^{-1} per double bond. This result, compared to $\Delta_{hyd}H^{298}$(CYPE) $= -27.5$ kcal mol^{-1}, indicates neither strong stabilization nor destabilization for the molecule as a whole. However, a null result for $\Delta_{hyd}H^{298}$ does not prove the absence of either electronic stabilization or strain destabilization because both can influence the hydrogenation enthalpy simultaneously, perhaps in opposition to one another. Electronic stabilization in the reactant can be nullified by strain release concomitant with the hydrogenation reaction.

Of the six trienes, BICY**2** $-$ BICY**7**, four are planar with $\Delta_f H^{298} = 55.0 \pm 0.8$ kcal mol^{-1}, whereas the two nonplanar trienes, BICY**5** and BICY**6** have $\Delta_f H^{298}$ values that are more than 5 kcal mol^{-1} above the arithmetic mean of the other four. We believe that loss of planarity interferes with transannular conjugation in BICY**5** and BICY**6**, destabilizing them relative to the other trienes. If transannular conjugation (aromaticity) is important in the planar trienes, it is reasonable to suppose that it is important in pentalene as well, though its enthalpic effects are masked by strain. Dewar calculates a null resonance energy as distinct from intra- and interannular conjugation energy.[19]

The addition of G3(MP2) values for $\Delta_{hyd}H^{298}$ of cyclopentadiene and cyclopentene leads one to expect $\Delta_{hyd}H^{298} = -75.3$ kcal mol^{-1} for the bicyclooctatrienes in the absence of interannular interactions. The range of calculated $\Delta_{hyd}H^{298}$ for the trienes is -77.7 kcal mol^{-1} to -86.4 kcal mol^{-1} indicating interannular destabilizing interactions in all cases, especially those of BICY**5** and BICY**6**. The heat capacities of the trienes from 0 to 298 K are virtually identical, as seen from comparison

TABLE 3: H^{298} for Triquinacene and Its Hydrogenation Products. Units Are Hartrees and kcal mol^{-1}

	TRIQ	H_2TRIQ	H_4TRIQ	H_6TRIQ
E^0	−386.340 68	−387.549 59	−388.756 80	−389.965 83
H^{298}	−386.332 70	−387.541 26	−388.748 05	−389.956 84
E(ZPE)	0.163 77	0.186 47	0.209 08	0.231 88
TCH	0.007 97	0.008 33	0.008 75	0.008 99
ΔE^0	64.46	38.94	14.47	−11.13
$\Delta_f H^{298}$	56.86	29.54	3.32	−24.15
$\Delta_f H^{298}$(exp)	53.53± 1.00[a]	30.53± 0.95[a]	3.03± 0.91[a]	
$\Delta_f H^{298}$(exp)	57.51± 0.70[b]			−24.47± 0.86[c]

[a] Combination of $\Delta_{hyd}H^{298}$ (ref 3b) with $\Delta_f H^{298}$of H_6TRIQ, [b]ref 3i, [c]ref 14

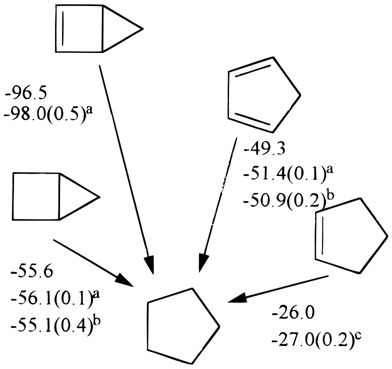


Figure 1. $\Delta_{hyd}H^{298}$ of Cyclopentenes and Bicyclopentenes. G3(MP2) values are at the top of each group. Numbers in parentheses are experimental uncertainties. a, ref 16(a); b, ref 16(b); c, ref 16(c).

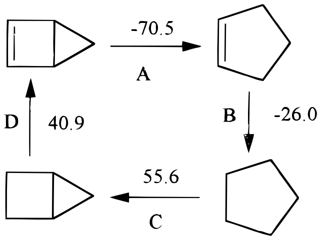


Figure 2. Thermochemical Cycle Involving Cyclic C_5 Compounds.

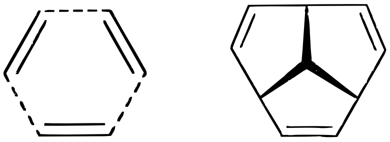
of the TCH values. BICY**5** and BICY**6** have heat capacities that are slightly different from the remaining four trienes.

The eight dienes have a mean $\Delta_f H^{298}$ of 31.56 kcal mol^{-1} with a standard deviation from the mean of only 1.84 kcal mol^{-1}. The outlier is BICY**8**, which deviates by 4.1 kcal mol^{-1} from the mean of the remaining 7 dienes ($\Delta_f H^{298}$(7 dienes) = 31.1 ± 1.2 kcal mol^{-1}). BICY**8** is unique among the dienes in having a "bridgehead" double bond that is not in conjugative juxtaposition to any other double bond in the molecule. In the monoenes, some destabilization of the bridgehead (1,2) double bond is evident in BICY**17**.

Correspondence between $\Delta_{hyd}H^{298}$(exper) and $\Delta_f H^{298}$(calcd) values obtained by the G3(MP2) method is shown in Figure 3 where the calculated values are in kcal mol^{-1}, and the experimental values are below them.[12]

Triquinacenes.

Long ago, it was suggested[3a] that the unusual juxtaposition of double bonds around the "bottom" of the triquinacene molecule, where the broken lines represent not a single bond



but the −C− link, might lead to stabilization *like* the aromatic

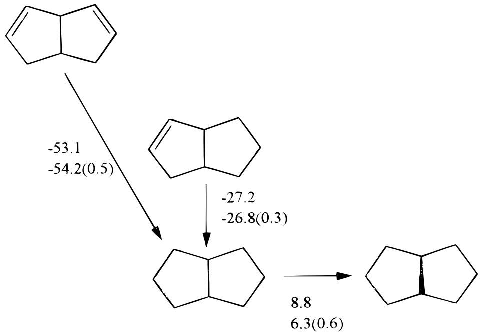


Figure 3. Calculated and Experimental $\Delta_{hyd}H^{298}$ and $\Delta_{isom}H^{298}$ of Bicyclopentenes. Experimental values[12] are shown with the uncertainty in parentheses.

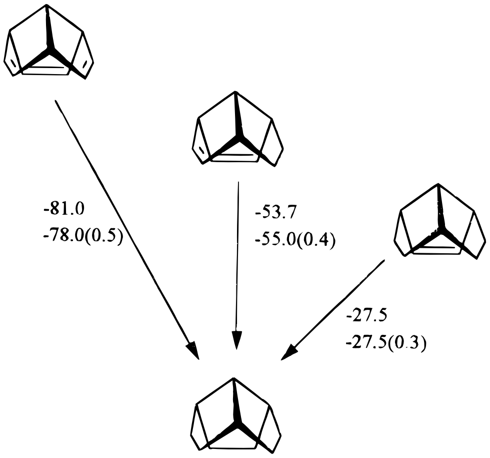


Figure 4. Enthalpies of Hydrogenation and Partial Hydrogenation of Triquinacene, Dihydrotriquinacene, and Tetrahydrotriquinacene.

stabilization of benzene, i.e., *neutral homoaromaticity*. In 1986, we found[3b] experimental evidence to support homoaromaticity in TRIQ in the form of a $\Delta_{hyd}H^{298}$ that is about 4 kcal mol^{-1} less exothermic than expected by extrapolation of $\Delta_{hyd}H^{298}$ for H_2TRIQ and H_4TRIQ to H_6TRIQ (Figure 4). Since then, several papers have appeared[3c,f,i] showing that evidence for homoaromaticity of TRIQ is not found in a variety of calculations, or in indirect experimental observations. We have no wish to be the last to desert the barricades of triquinacene homoaromaticity, but we felt that (1) most of the instruments used to detect neutral homoaromaticity (both experimental and theoretical) have been too blunt, and (2) the thermochemical record (which, in matters of stability, is the only one that counts) is incomplete. Accreted evidence against neutral homoaromaticity of TRIQ is now very strong, but a final judgment should not be reached until the case is airtight, which it is not.

Homoaromaticity of TRIQ, if it exists, is a minute perturbation on the energy of the whole molecule. A homoaromatic stabilization energy of 4 kcal mol^{-1} relative to the total energy of TRIQ, −386.333 66 hartrees by G3(MP2), would be 1.6 ×

10^{-3} % of the total. Use of the term “blunt instrument” in the preceding paragraph is not meant to denigrate either experimental or theoretical methods now in use, but only to indicate the difficulty of the problem. This difficulty is made greater by the distance over which homoaromaticity would need to operate. One is not seeking to detect electron exchange within substantially overlapping orbitals, but at their utmost extremity.

New experimental information presented by Verevkin et al.,[3i] along with an existing value by Clark et al.,[14] place a top and a bottom on the enthalpy of the TRIQ series in Figure 4, but they do not provide values in between. Even granting that $\Delta_f H^{298}$(TRIQ) $= 57.5 \pm 0.7$ kcal mol^{-1},[3i] it is the difference between $\Delta_f H^{298}$(TRIQ) and $\Delta_f H^{298}$(H_2TRIQ) that matters, an experimental quantity not given in that paper.

Accordingly, we have recalculated $\Delta_f H^{298}$ of the triquinacene series using G3(MP2), which we believe yields the most reliable results of all the G-*n* family of molecular orbital calculations for hydrocarbons. The agreement between G3(MP2) calculated values and experiment for $\Delta_f H^{298}$ in Tables 1−3 is excellent for all cases in which the experimental data exist, *with the exception of TRIQ*. Our conclusion is that the accumulated evidence,[3i] including the present G3(MP2) calculation, argues that the experimental determination of $\Delta_f H^{298}$(TRIQ) is wrong.

This leaves the question of how an experimental procedure that yields the correct values of $\Delta_{hyd} H^{298}$(H_2TRIQ) and $\Delta_{hyd} H^{298}$(H_4TRIQ) can fail in the third and most critical case, that of $\Delta_{hyd} H^{298}$(TRIQ). Recently,[20] we observed low values of $\Delta_f H^{298}$(for [5]- and [6]metacyclophanes due to kinetic lag. Although there are great dissimilarities between the metacyclophane and triquinacene molecules (geometry, strain, etc.), our 1986 experiments on triquinacene might have suffered a similar systematic error owing to local depletion of adsorbed hydrogen by three juxtaposed double bonds not encountered by only two or one. In this case, the reaction could be slow enough to give low results but fast enough to elude detection by GLC analysis of the product. New experiments under more severe hydrogenation conditions are needed.

Conclusion

The G3(MP2) method has been extended to calculations of $\Delta_f H,^{298}$ $\Delta_{hyd} H,^{298}$ and $\Delta_{isom} H^{298}$ of C_5, C_8, and C_{10} hydrocarbons. Comparison with experimental hydrogenation and combustion data in all cases except that of triquinacene shows no diminution in accuracy relative to calculations on smaller hydrocarbons. G3(MP2) calculations suggest that pentalene is stabilized but they do not indicate homoaromatic stabilization of the neutral molecule, triquinacene.

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