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Stabilization in Ground-State Tropilidine and Tropone

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Thermochemical and structural evidence indicates that stabilization by 1,6-electronic interaction in ground-state 1,3,5-cycloheptatriene (tropilidine) is more important than presently thought. We believe that a stabilization energy of about 6 kcal/mol is due in significant part to homoaromatic delocalization across the sp^3 carbon. The stabilization energy of tropone is nearly twice as large as the stabilization energy of tropilidine. Comparisons are made with the larger stabilization energy of benzene and with the negligible stabilization energy of cyclooctatetraene, using experimental enthalpies of formation and enthalpies of formation calculated via homodesmic and thermoneutral reactions.

The idea of homoaromatic stabilization of ground-state cyclohepta-1,3,5-triene (tropilidine) has suffered declining fortunes during its lifetime. Early papers[1] suggested that 1–6 stabilization is a major influence on the energy of tropilidine. Homoaromaticity was scaled down to a minor influence by Conrow[2a] on the basis of chemical equilibration of 2,3,7,7-tetramethylcyclohepta-1,3,5-triene (tetramethyltropilidine) with its unstabilized exo-isomer, 1-methylene-2,6,6-trimethylcyclohepta-2,4-diene. Finding $K_{eq} < 10$ in favor of the stabilized isomer, he concluded that $\Delta G°_{isom}$ is not large and extrapolated to the same conclusion for $\Delta H°_{isom}$ on the reasonable assumption of small $\Delta S°_{isom}$. More recently, Williams, Kurtz, and Farley[2b] have entirely dismissed homoaromatic stabilization across the sp^3 carbon atom in tropilidine on the grounds of two-center energy partitioning terms appearing in MNDO and AM1 semiempirical molecular orbital calculations with partial configuration interaction.

A contrary view has been expressed by Herndon and Parkanyi[3] on the grounds of structure–resonance calculations. We find that thermochemical evidence also supports a significant homoaromatic stabilization of ground-state tropilidine.

Stabilization of the triene and the diene relative to the monoene is evident from the enthalpies of stepwise hydrogenation[1,4a,b] of tropilidine to cycloheptane (H_6trop). Enthalpies of stepwise hydrogenation are determined by difference; e.g., ΔH_h[tropilidine] − ΔH_h[cyclohepta-1,3-diene][1a] yields the top left entry in reaction 1. Experimental enthalpies of stepwise hydrogenation are above the arrows in reaction 1. The second hydrogenation step is more exothermic than the first by 3.16 ± 0.40 kcal/mol, and the third step is more exothermic than the second by 1.78 ± 0.30 kcal/mol. Experimental values are from the

$$\text{tropilidine} \xrightarrow[-20.2]{-21.58 \pm 0.33} H_2\text{trop-1,3} \xrightarrow[-25.0]{-24.74 \pm 0.15} H_4\text{trop} \xrightarrow[-30.1]{-26.52 \pm 0.15} H_6\text{trop} \quad (1)$$

data of Conn, Kistiakowsky, and Smith,[1a] obtained in the gas phase at 355 K. Corrections to standard conditions are small (about 0.2 kcal/mol) and are systematic, so that they largely cancel when enthalpies of partial reaction are determined by difference. Uncertainties are calculated from the summed variances of the original uncertainty estimates, i.e., the "sum in quadrature of the original absolute standard deviation[s]".[5]

More recent data,[4a] measured using glacial acetic acid as the calorimeter fluid, agree with those in reaction 1 to a high level of precision (−21.27 ± 0.40, −24.77 ± 0.12, −26.55 ± 0.26) when solvent corrections are taken into account.[6] The most recent ΔH_h[cycloheptatriene] = −72.8 ± 0.1 kcal/mol, by Roth et al.,[7] includes solvent correction for the calorimeter fluid (isooctane) and is precisely equal to that of Kistiakowsky.[1a] These are among the most precise data in the thermochemical literature.

When changes in strain energy, calculated by MM3,[8] are taken into account, strain-compensated ΔH_h values for stepwise hydrogenation can be calculated.[9] These are enthalpies of hydrogenation at constant strain energy, which are the same as would be observed upon hydrogenating strain-free reactants to strain-free products. The object of this procedure is to concentrate on electronic effects, uncomplicated by strain.

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(1) (a) Conn, J.; Kistiakowsky, G. B.; Smith, E. *J. Am. Chem. Soc.* **1939**, *61*, 1868. (b) Doering, W. von E.; Laber, G.; Vonderwahl, R.; Chamberlain, N. F. *J. Am. Chem. Soc.* **1956**, *78*, 5448. (c) Turner, R. B.; Meador, W. R.; Doering, W. von E.; Knox, L. H.; Mayer, J. R.; Wiley, D. W. *J. Am. Chem. Soc.* **1957**, *79*, 4127.

(2) (a) Conrow, K. *J. Am. Chem. Soc.* **1961**, *83*, 2958. (b) Williams, R. V.; Kurtz, H. A.; Farley, B. *Tetrahedron* **1988**, *44*, 7455.

(3) Herndon, W. C.; Parkanyi,C. *Tetrahedron* **1982**, *38*, 2551.

(4) (a) Turner, R. B.; Mallon, B. J.; Tichy, M.; Doering, W. von E.; Roth, W. R.; Schroeder, G. *J. Am. Chem. Soc.* **1973**, *95*, 8605. (b) Turner, R. B.; Meador, W. R.; Winkler, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 4116. (c) Fang, W.; Rogers, D. W. *J. Org. Chem.* **1992**, *57*, 2294. (d) Rogers, D. W.; Crooks, E. L. *J. Chem. Thermodynam.* **1983**, *15*, 1087. (e) Rogers, D. W. *J. Phys. Chem.* **1979**, *83*, 2430.

(5) Meyer, S. L. *Data Analysis for Scientists and Engineers*; J. Wiley & Sons: New York,1975; p 41.

(6) Enthalpies of hydrogenation taken from ref 4 have been corrected by 0.7 kcal mol^{-1} (exothermic) per double bond to correct for solvent effects. See: Allinger, N. L.; Dodziuk, H.; Rogers, D. W.; Naik, S. N. *Tetrahedron* **1982**, *11*, 1593.

(7) Roth, W. R.; Klarner, F.-G.; Grimme, W.; Koser, H.; Busch, R.; Muskulus, B.; Breuckmann, R.; Scholtz, B. P. Lennartz, H.-W. *Chem. Ber.* **1983**, *116*, 2717.

(8) MM392 available from Technical Utilization Corp., 235 Glen Village Court, Powell, OH 43065.

(9) Rogers, D. W.; Loggins, S. A.; Samuel, S. D.; Finnerty, F. M.; Liebman, J. F. *Struct. Chem.* **1990**, *1*,481.

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The strain-compensated ΔH_h values of partial hydrogenation are given below the arrows in reaction 1. They show the same trend as the uncompensated results, but there is a smoother progression—about 5 kcal/mol of stabilization for each double bond in the sequence. The incremental increase in strain-compensated ΔH_h of stepwise hydrogenation is larger than that of the uncompensated results, indicating that about half of the electronic influence on observed ΔH_h has been masked by concomitant strain changes during hydrogenation.

These values are in the pattern of normal conjugative stabilization. That is, they are in the same pattern (though not quantitatively the same) as the ΔH_h values for stepwise hydrogenation of the central double bond in (*Z*)-hexa-1,3,5-triene.[4,6]

$$(Z)\text{-hexa-1,3,5-triene} \xrightarrow[-19.9]{-20.7 \pm 0.7} \text{hexa-1,5-diene} \quad (2a)$$

$$(Z)\text{-hexa-1,3-diene} \xrightarrow[-23.1]{-23.7 \pm 0.4} \text{hex-1-ene} \quad (2b)$$

$$(Z)\text{-hex-3-ene} \xrightarrow[-28.0]{-28.9 \pm 0.2} \text{hexane} \quad (2c)$$

The middle double bond was selected for comparison to avoid terminal bond thermochemical effects not present in the cyclic compound.[10] (See reaction 3 below for the question of cyclohepta-1,4-diene.) Again, the measured enthalpies of stepwise hydrogenation are above the reaction arrows and strain-compensated enthalpies are below the arrows. Experimental uncertainties are somewhat larger for the acyclic hexenes, which are prone to polymerization, than they are for the cycloheptenes. Strain has little influence on the ΔH_h of the central double bond in the hexatriene series, and it produces no qualitative change in the pattern of stepwise hydrogenation in reaction set 2. The increment in exothermicity from the first step to the second step in reaction set 2 is 3.0 kcal/mol (uncompensated) and 3.2 kcal/mol (compensated). From the second step to the third, it is 5.2 kcal/mol (uncompensated) and 4.9 kcal/mol (compensated). By these thermochemical criteria, tropilidine is stabilized by only 1.6 kcal/mol more owing to electronic effects than (*Z*)-hexa-1,3,5-triene when changes in strain energy are taken into account.

The enthalpic similarities between these two serial hydrogenations have usually been thought to indicate normal triene conjugative stabilization over the double-bond system in tropilidine, with little or no homoconjugative interaction across the sp^3 carbon interval. Comparable trends in stepwise hydrogenation enthalpies were even used to argue in favor of a planar conformation of tropilidine involving all sp^2 carbon atoms,[1b,c] though this was later disproved by electron diffraction experiments.[11]

The two trienes are not really similar, however. In the tropilidine case, the 3,4 double bond is lifted out of the plane of the other two because the molecule assumes a boat conformation. Traetteberg's review[11] gives the rise angle of the middle double bond out of the plane of the ring in tropilidine, by gas-phase electron difraction, as 41 ± 2°, whereas in cyclohepta-1,3-diene it is 0°.

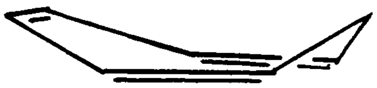

Figure 1. MM structure of tropilidine. Experimental results yield a larger departure from planarity than this diagram shows (refs 11 and 12).

An MMP2 calculation with no 1,6 interaction also shows that the 3,4 double bond is lifted out of the plane, though the rise angle is only about half the experimental value. MM3 also yields a nonplanar ring that is too flat and has too low an inversion barrier.[12] We have performed an MNDO calculation (MOPAC 5.0) which is in essential agreement with Williams, Kurtz, and Farley's calculation[3] and shows the same boat form for the triene.[13]

If the middle double bond is lifted out of the plane of the other two, stabilization is lost across that double bond, in the way that it is lost in cyclooctatetraene.[1c] Nevertheless, stabilization of the molecule as a whole is normal. *Stability lost by the departure of one stabilizing element in the molecule must have been gained by another.* In this case, about 5 kcal/mol of stabilization energy lost through nonplanarity at the stern of the boat appears to have been gained by homoaromaticity at the prow.

Cyclohepta-1,4-diene. Analogy between the energetics of hydrogenation of the middle double bond in hexa-1,3,5-triene is more closely approximated by stepwise hydrogenation of tropilidine through cyclohepta-1,4-diene than through the 1,3-isomer. Kistiakowsky's group did not publish data for cyclohepta-1,4-diene, but Turner's group did.[4a] Their results are shown in reaction 3, with solvent corrections (0.7 kcal/mol for each step).[6]

$$\text{tropilidine} \xrightarrow[-14.9]{-15.31 \pm 0.40} \text{H}_2\text{trop-1,4} \xrightarrow[-30.0]{-30.73 \pm 0.12} \text{H}_4\text{trop} \xrightarrow[-30.2]{-26.55 \pm 0.26} \text{H}_6\text{trop} \quad (3)$$

When the stabilizing influence of the 3,4 double bond is removed at one stroke, the result is dramatic: reduction in the magnitude of ΔH_h of the first step to one-half the value of the remaining two steps. A thermochemical effect of this size suggests the loss of both homoaromaticity at the first hydrogenation step and conjugative stabilization in the 1,4- relative to the 1,3-isomer. There is a masking effect of strain, but it is not the dominant factor.

MM2ERW Calculations

Roth et al. have described the use of their extension of Allinger's MM2 force field called the MM2ERW force field.[14] The MM2ERW force field does not combined SCF molecular orbital calculations for conjugated species with the classical results of the MM procedure but is parameterized to include conjugated species in the classical

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[10] For example, hydrogenation of the central double bond in (*Z*)-hexa-1,3,5-triene (reaction 2a) has ΔH_h[(*Z*)-hexa-1,3,5-triene] − ΔH_h[hexa-1,5-diene]: 41.1 − 20.4 = 20.7. This amounts to taking the central bond in (*Z*)-hexa-1,3,5-triene as a reference for a cyclic double bond. (Thermochemical closure is not quite achieved for cyclohepta-1,4-diene because data from two sources (refs 1a and 4a) are mixed.)

[11] Traetteberg, M. J. In Hargittai, I.; Hargittai, M. *Stereochemical Applications of Gas Phase Electron Diffraction*; VCH: New York, 1988; Part B.

[12] Allinger, N. L.; Li, F.; Yan, L.; Tai, J. C. *J. Comput. Chem.* **1990**, *11*, 868.

[13] A small difference in ΔH_h (0.3 kcal mol^{-1}) from the WKF calculation may be due to differences in MOPAC 5.0 relative to their earlier version

[14] (a) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boise, R. *Chem. Ber.* **1991**, *124*, 2499. (b) Roth, W. R.; Klärner, F.-G.; Siepert, G.; Lennartz, H.-W. *Chem. Ber.* **1992**, *125*, 217.

mechanical computation. At the expense of an extended parameter set, the authors have shown by numerous examples that, upon comparison of MM2ERW calculated ΔH_f with experimental results for conjugated (but not aromatic) systems, one obtains a null difference, within an uncertainty of about 0.5 kcal/mol.

Upon calculating the MM2ERW enthalpy of formation of an aromatic *or homoaromatic* molecule, and comparing the result to the experimental value, one obtains the aromatic or homoaromatic stabilization energy. By this method, Roth et al. have found that tropilidine is homoaromatically stabilized by 4.5 kcal/mol.

Homodesmic Reactions

Homodesmic reactions[15] are chemical reactions (hypothetical or real) that have been arranged so that the number and types of bonds on either side of the reaction are the same, as in the hypothetical reaction

$$\text{6 propane} \rightarrow \text{cyclohexane} + \text{6 ethane} \qquad (4)$$

in which the six $-CH_2-$ groups in propane are "converted" to cyclohexane, while 12 residual CH_3 groups form six molecules of ethane.

Benzene. For the prototypical example of aromaticity, consider the homodesmic reactions involving benzene and nonaromatic reactants and products

$$^3/_4(\text{cyclooctatetraene}) \rightarrow \textit{benzene} \qquad (5)$$

$$^3/_4(70.7 \pm 0.4) \rightarrow 53.0 \pm 0.3$$

$$^3/_2(\text{cyclopentadiene}) \rightarrow \textit{benzene} + {}^1/_4(\text{cyclohexane}) \qquad (6)$$

$$^3/_2(32.1 \pm 0.4) \rightarrow 55.5 \pm 0.6 + {}^1/_4(-29.5 \pm 0.2)$$

$$^3/_2(\text{butadiene} + \text{cyclopentadiene}) \rightarrow \textit{benzene} + {}^3/_2(\text{1,4-pentadiene}) \qquad (7)$$

$$^3/_2(26.3 \pm 0.3 + 32.1 \pm 0.4) \rightarrow 49.8 \pm 0.9 + {}^3/_2(25.2 \pm 0.3)$$

The numbers in the second line of reactions 4–7 are experimental ΔH_f values, in kcal/mol, from the standard thermochemical literature,[16] except for benzene, which is calculated by difference. These yield a mean heat of formation of benzene of 52 ± 3 kcal/mol by homodesmic reactions. Since its experimental heat of formation is 19.7 ± 0.2 kcal/mol,[16] we conclude that benzene is stabilized by some 32 ± 3 kcal/mol, a reasonable value for its somewhat ill-defined resonance energy. Roth's MM2ERW[14] method yields a resonance energy for benzene of 25.9 kcal/mol.

Tropilidine. The homodesmic reactions involving tropilidine[4]

$$^1/_2[\text{1,4-cyclohexadiene} + \text{cyclooctatetraene}] \rightarrow \textit{tropilidine} \qquad (8)$$

$$^1/_2[28.5 \pm 0.5 + 70.7 \pm 0.4] \rightarrow 49.6 \pm 0.3$$

$$^3/_2(\text{cyclopentadiene}) \rightarrow \textit{tropilidine}^{17} + {}^1/_{12}(\text{cyclohexane}) \qquad (9)$$

$$^3/_2(32.1 \pm 0.4) \rightarrow 50.6 \pm 0.6 + {}^1/_{12}(-29.5 \pm 0.2)$$

and

$$^1/_2[\text{1,3-butadiene} + \text{3 cyclopentadiene}] \rightarrow \textit{tropilidine} + {}^1/_2(\text{1,4-pentadiene}) \qquad (10)$$

$$^1/_2[26.3 \pm 0.3 + 3(32.1 \pm 0.4)] \rightarrow 48.7 \pm 0.8 + {}^1/_2(25.2 \pm 0.3)$$

lead to an enthalpy of formation of tropilidine of 49 ± 1 kcal/mol. The experimental value[18] is 43.2 ± 0.5 kcal/mol. Thus, "constructing" tropilidine from unstabilized parts yields a ΔH_f that is 6 ± 1 kcal/mol too large. The measured value must include about 6 kcal/mol stabilization energy.

It is well documented that MMP2 calculations do not give the correct enthalpy of formation without a 1,6 interaction computation.[19] MMP2 calculation without 1,6 interactions yields 49 kcal/mol, as do the homodesmic reactions just cited. Even with an extension of the calculation to include 1,6 interactions in tropilidine, only part of the discrepancy is removed in the MMP2 procedure.[19]

MM3 has been modified, through experience with MMP2, so that calculation of delocalization of electron densities on nonadjacent carbon atoms is automatically carried out.[20] The empirical necessity for this modification of the MM procedure is, by itself, an argument that nonadjacent electron delocalization is more important than previously believed.

Tropone. An important contrast may be made between reactions 8–10 and the homodesmic reaction forming cyclohepta-2,4,6-trien-1-one (tropone)

$$^1/_2[\text{1,4-benzoquinone} + \text{cyclooctatetraene}] \rightarrow \textit{tropone} \qquad (11)$$

$$-29.4 \pm 0.8 + 70.7 \pm 0.4 \rightarrow 20.6 \pm 0.4$$

The experimental value of ΔH_f of tropone in the gas phase is 10.5 ± 0.8 kcal/mol.[18] By this definition, tropone is stabilized by 10 kcal/mol, almost twice as much as tropilidine. Electron diffraction results show that the tropone ring is planar.[11]

Thermoneutral Reactions

The final comparison between tropilidine and tropone makes use of the near thermoneutrality of reactions[21] of

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(15) Miller, M. A.; Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 7681.

(16) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(17) Note that the right-hand side has two formally conjugated double bonds, the left-hand side has but $^3/_2$. Correcting this by $^1/_2$(1,3-butadiene vs 2(1-butene) – butane or $^1/_2$(2.3) kcal/mol = 1.2 kcal/mol, gives a revised value of 49.5 kcal/mol.

(18) Jackson, W.; Hung, T. S.; Hopkins, H. P., Jr. *J. Chem. Thermodyn.* **1971**, *3*, 347.

(19) Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985.

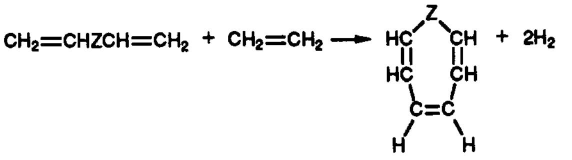
(20) Allinger, N. L. Operating Instructions for MM3, see ref 8.

(21) Liebman, J. F. *Struct. Chem.* **1992**, *3*, 449.

the type

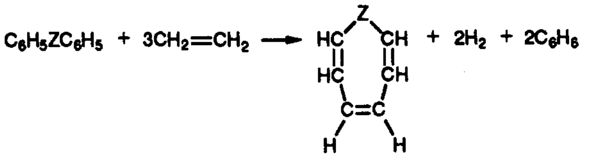
$$RCH{=}CH_2 + R'CH{=}CH_2 \rightarrow RCH{=}CHCH{=}CHR' + H_2 \quad (12)$$

In the absence of homoaromaticity, aromaticity, and strain, the following reaction would be nearly thermoneutral.


(13)

Experimental data on all component molecules would yield information on homoaromaticity, aromaticity, or strain or any combination thereof. Unfortunately, there are no thermochemical data for $CH_2{=}CHC(O)CH{=}CH_2$.

Using the phenyl–vinyl thermochemical equivalence,[22] $\Delta H_f(C_6H_5X) - \Delta H_f(C_2H_3X) \equiv \delta(x)$ is nearly independent of X, Thus, we may consider the alternative reaction


(14)

The new reactions are not expected to be thermoneutral since $\delta(X) \neq 0$. It is about 7 kcal/mol. Nonetheless, these results can be used in a way that parallels recent approaches to the aromaticity of heterocycles.[23] More precisely, the relative aromaticities may be determined by taking the difference of the sum of heats of formation of $(C_6H_5)_2Z$ and C_2H_4 on the left and the "real" heat of formation of the species on the right. We find[24] with Z = >CH$_2$ and >CO, there is stabilization of 6.3 and 15.2 kcal/mol, corresponding to a net stabilization of tropone over tropilidine of 9 kcal/mol. Letting Z = (*E*)-CH=CH—, the net stabilization is −2 kcal/mol, which means that tropilidine is stabilized over cyclooctatetraene by some 8 kcal/mol. Finally, letting Z = "–", i.e., letting biphenyl be one of our reference species, we find a net stabilization of 36 kcal/mol. Benzene is thus stabilized over tropilidine by 30 kcal/mol. The degree of stabilization of tropilidine is consonant with our prior knowledge, as is the order of stabilization: benzene > tropone > tropilidine > cyclooctatetraene.

It is noteworthy that Herndon and Parkanyi's application of structure–resonance theory[3] leads to a homoconjugative stabilization energy of tropilidine that is 21% of the resonance energy of benzene. If the resonance energy of benzene is taken as 36 kcal/mol, the stabilization of tropilidine should be about 7.5 kcal/mol as compared with the thermochemical values of 5–8 kcal/mol above.

Molecular Mechanics

Procedure. MM strain energies in Table I were obtained using MM392, ref 8. The stochastic search procedure[25] included in the MM392 package was used to locate the global potential energy minimum of each molecule studied.

Table I. Enthalpies of Formation, in kcal/mol, of Tropilidine and Related Compounds in Reactions 1–3

	ΔH_h (expl)	strain energy (MM3)[a]	ΔH_h strain compens
tropilidine	44.6 ± 0.5[b]	6.4	38.2
cyclohepta-1,3-diene	23.0 ± 0.3[b]	5.0	18.0
cyclohepta-1,4-diene	29.0 ± 0.3[c]	6.0	23.0
cycloheptene	−1.7 ± 0.3[b]	5.3	−7.0
cycloheptane	−28.2 ± 0.2[d]	8.9	−37.1
(*Z*)-hexa-1,3,5-triene	41.1 ± 0.6[e]	1.0	40.1
hexa-1,5-diene	20.4 ± 0.4[e]	0.2	20.2
(*Z*)-hexa-1,3-diene	14.0 ± 0.4[e]	0.6	13.4
(*Z*)-hex-3-ene	−11.0 ± 0.2[f]	0.9	−11.9
hex-1-ene	−9.7 ± 0.2[g]	0.0	−9.7
hexane	−39.9 ± 0.2[d]	0.0	−39.9

[a] Reference 8. [b] Reference 1a. [c] Reference 4a,b with solvent corrections. [d] Reference 16. [e] Reference 4c. [f] Reference 4d. [g] Reference 4e.

Conclusion

There are four (not entirely independent) ways of arriving at the conclusion of homoaromatic stabilization of approximately 5–8 kcal/mol in tropilidene from thermochemical evidence: (1) strain-compensated enthalpies of formation, (2) MM2ERW computation of resonance-free enthalpies of formation, (3) isodesmic reactions, and (4) thermoneutral reactions.

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[22] (a) Liebman, J. F. In *Molecular Structure and Energetics of Organic Molecules*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 3. (b) George, P.; Bock, C. W.; Trachtman, M. In *Molecular Structure and Energetics: Biophysical Aspects*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1987; Vol. 4. (c) Luo, Y. R.; Holmes, J. L. *J. Phys. Chem.* **1992**, *96*, 9568.

[23] (a) Hosmane, R. S.; Liebman, J. F. *Tetrahedron Lett.* **1991**, *32*, 3949. (b) Hosmane, R. S.; Liebman, J. F. *Tetrahedron Lett.* **1992**, *33*, 2303.

[24] The requisite ΔH_f was obtained by combining ΔH_f of solid diphenylmethane (ref 16) with $\Delta H_{\text{sublimation}}$ from: Chickos, J. S.; Annunziatta, R.; Ladon, L. H.; Hyman, A. S. Liebman, J. F. *J. Org. Chem.* **1986**, *51*, 4311.

[25] (a) Saunders, M.; Houk, K. N.; Wu, Y.-D.; Still, W. C.; Lipton, M.; Chang. G.; Guida, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 1419. (b) Ferguson, D. M.; Gould, I. R.; Glauser, W. A.; Schroeder, S.; Kollman, P. A. *J. Comput. Chem.* **1992**, *13*, 525.