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An Experimental Thermochemical and Theoretical Study of Triquinacene: Definitive Disproof of Its Neutral Homoaromaticity

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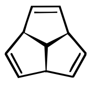
Abstract: The enthalpy of formation ($\Delta H_f^\circ(g) = 57.51 \pm 0.70$ kcal/mol) of triquinacene (**1**), newly determined by measuring its energy of combustion in a microcalorimeter, is about 4 kcal/mol higher than that previously reported and corresponds to ab initio and density functional theory computational results. As a consequence, the previously derived homoaromatic stabilization energy (claimed to be 4.5 kcal/mol) from enthalpy of hydrogenation measurements is not present in **1**. The lack of homoaromaticity in **1** is supported by evaluation of geometric, energetic, and magnetic criteria. In contrast, the isomerization transition state from diademane (**5**) to **1** is highly aromatic on the basis of the same criteria. The enthalpy of isomerization of **5** to **1** was experimentally determined by differential scanning calorimetry (DSC) to be -29.4 ± 0.3 kcal/mol (measured at 368.2 K). The enthalpy of activation for this rearrangement as determined from the DSC measurements (28.4 ± 0.2 kcal/mol) is 2.5 kcal/mol higher than the value computed at B3LYP/6-311+G**+ZPE.

Introduction

In 1964, Woodward, Fukunaga, and Kelly[1] conceived the tantalizing possibility that the three double bonds of triquinacene (**1**), although separated, might still interact in benzene-like fashion. Indeed, a 1986 experimental determination by Liebman et al.[2] found a significantly lower (4.5 kcal/mol) enthalpy of hydrogenation of **1** to dihydrotriquinacene (**2**) than that of the subsequent steps, **2** to **3** and **3** to **4**. However, an extensive ab initio study by Schulman et al.[3] both questioned the experimental heats of hydrogenation and estimated the enthalpy of formation of **1** to be 56.6−57.0 kcal/mol rather than the experimental 53.5 ± 1 kcal/mol. Several other theoretical investigations[4−9] also failed to find evidence of substantial homoaromatic stabilization in **1**. In particular, the computed stepwise heats of hydrogenation of **1**, **2**, and **3** were nearly the same with various molecular mechanics and semiempirical methods and at various ab initio levels (Table 1). This contradiction between theory and experiment has been interpreted in various ways. For example, Dewar and Holder[5] ascribed the unusually small differences in enthalpy of formation between **1** and **2** [$\Delta\Delta H_f^\circ(\mathbf{1})$] to a decreased stability of **2** rather than an increased stability of **1**, and the discrepancy between theory and experiment to computational errors.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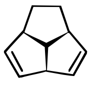
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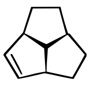
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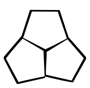
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Holder[9] applied atoms in molecules (AIM) theory to analyze the bonding pattern in **1** but was unable to locate any bond critical points among the supposedly homoaromatically bonded atoms. This finding was declared as "another (and hopefully the final) nail to the coffin of neutral homoaromaticity" of **1**. The present study was undertaken to obtain new experimental information.

Results and Discussion

While homoaromaticity clearly is present in ionic systems, such stabilization, if at all detectable, is often considered to be very small in neutral hydrocarbons.[2,6] Spectroscopic (IR,[10]

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(1) Woodward, R. B.; Fukunaga, T.; Kelly, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 3162−3164.

(2) Liebman, J. F.; Paquette, L. A.; Peterson, J. R.; Rogers, D. W. *J. Am. Chem. Soc.* **1986**, *108*, 8267−8268.

(3) Miller, M. A.; Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 7681−7684.

(4) Spanget-Larsen, J.; Gleiter, R. *Angew. Chem.* **1978**, *90*, 471−472; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 441−442.

(5) Dewar, M. J. S.; Holder, A. J. *J. Am. Chem. Soc*. **1989**, *111*, 5384−5387.

(6) Storer, J. W.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1165−1168.

(7) Schulman, J. M.; Miller, M. A.; Disch, R. L. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 563−568.

(8) McEwen, A. B.; R. Schleyer, P. v. R. *J. Org. Chem.* **1986**, *51*, 4357−4368.

(9) Holder, A. *J. Comput. Chem.* **1993**, *14*, 251.

(10) Childs, R. F. *Acc. Chem. Res.* **1984**, *17*, 347−352.

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Table 1. Calculated and Experimentally Determined Enthalpies of Formation for Triquinacene (**1**) and Heats of Hydrogenation for Hydrocarbons **1**−**3** (All Values in kcal/mol)

method	$\Delta\Delta H_f^\circ$(g) **1**	$\Delta\Delta H_f^\circ$(g) **2**−**1**	**3**−**2**	**4**−**3**	ref
MINDO/3	78.7				4
MM2	59.8	−27.7	−26.8	−27.4	5−7
MM3	58.6	−25.7	−27.4	−27.0	6
MMP2	61.5, 60.2				8
AM1	56.3	−32.6	−32.0	−31.7	5
HF/STO-3G		−26.0	−26.3	−26.4	3
HF/6-31G*	53.0, 57.0[b]	−27.0	−26.4	−26.3	3, 7
HF/6-31+G*		−27.0	−26.6	−26.4	3
MP2/6-31G*	56.6[b]	−27.2	−25.8	−26.3	3
B3LYP/6-31G* [a]	57.2	−27.7	−27.3	−26.7	
B3LYP/6-311+G** [a]	57.2	−27.6	−27.3	−26.8	
expt	53.5 ± 1,[c] 56.4[d]	−23.0 ± 0.9	−27.5 ± 0.7	−27.5 ± 0.3	2, 6
expt[a]	57.51 ± 0.70				

[a] This work. [b] Derived from calculated enthalpies of hydrogenation and experimentally determined ΔH_f°(g) of perhydrotriquinacene (**4**, −24.47 ± 0.86 kcal/mol[17]). [c] Derived from experimentally determined enthalpies of hydrogenation. [d] Derived from calculated ΔH_f°(g) of perhydrotriquinacene and experimentally determined enthalpies of hydrogenation.

Table 2. Calculated Zero-Point Energies (ZPE, kcal/mol), Thermal Energies (E_{th}, kcal/mol) at 298 K, Number of Imaginary Frequencies (NImag), and Magnetic Susceptibilities (χ_{tot}, ppm cgs)

	ZPE (NImag)[a]	E_{th}[b]	χ_{tot}[c]
1 ($C_{10}H_{10}$, C_{3v})	106.9 (0)	111.1	−66.2
2 ($C_{10}H_{12}$, C_1)	122.1 (0)	126.5	
3 ($C_{10}H_{14}$, C_1)	137.2 (0)	141.9	
4 ($C_{10}H_{16}$, C_3)	152.5 (0)	157.3	−83.6
C_5H_{10} (C_2)	88.8 (0)	92.0	−44.5
C_5H_8 (C_s)	73.6 (0)	76.5	−38.5
5 ($C_{10}H_{10}$, C_{3v})	107.7 (0)	112.2	−83.7
6 ($C_{10}H_{10}$, C_{3v})	105.2 (1)	109.0	−101.5
adamantane	154.1 (0)	158.3	

[a] B3LYP/6-31G*. [b] B3LYP/6-311+G**. [c] CSGT-B3LYP/6-31G*//B3LYP/6-311+G**.

UV,[10] CD,[11] PES[12]) and structural[13] data, as well as the calculated overlap integral of nonbonded interaction,[14] offer no evidence of homoaromatic character in **1**. We determined ΔH_f°(g) for triquinacene (**1**) for the first time by measuring its energy of combustion.

The hydrocarbon **1** was prepared by using the established procedure of Deslongchamps et al.[15] and purified thoroughly (see Experimental Section). The energy of combustion measurements, performed as described previously,[16] gave ΔH_f°(g) = 57.51 ± 0.70 kcal/mol for triquinacene (**1**). This value agrees well with the computed estimate of Schulman et al.[3] at the RMP2/6-31G* level of theory and with AM1 semiempirical calculations (also see Table 1).

In contrast, the previously reported ΔH_f°(g) = 53.5 ± 1.0 kcal/mol for **1**, derived from the experimental enthalpy of hydrogenation of **1** to **4**, −78.0 ± 0.5 kcal/mol, and ΔH_f°(g) of **4** (−24.47 ± 0.86 kcal/mol[17]), is 4.0 kcal/mol lower. This difference is practically the same as the 4.5 kcal/mol previously claimed to be the homoaromatic stabilization for **1**. We do not presume to explain the observed anomalously low value for the ΔH_f°(g) of **1** to **2**, but the new experimental enthalpy of formation is, at least, in line with the most reliable computational results. The only logical conclusion is that **1** is not homoaromatic.

To support the new experimental finding, we carried out high-level density functional theory (DFT) computations using the Gaussian 94 program.[18] In contrast to the earlier calculations, the electron-correlated DFT method (B3LYP) and a larger basis set (6-311+G**) were used. All the structures are energy minima, as shown by the B3LYP/6-31G* frequency calculations. The computed total energies, zero-point energies, thermal corrections, and number of imaginary frequencies are given in Table 2. Magnetic susceptibilities (χ) were calculated at the B3LYP/6-31G*//B3LYP/6-311+G** level with the CSGT[19] method, and nucleus-independent chemical shift (NICS) at B3LYP/6-31G*/6-31G*//B3LYP/6-311+G** with the GIAO[20] method as implemented in Gaussian 94.

The optimized structural parameters of **1** (C_{3v}), e.g., the C=C double bond length (1.333 Å, the same as in cyclopentene) and the nonbonded distance (2.549 Å), agree with the X-ray data (1.319, questionably too short, and 2.533 Å[13]). Thus, there are no geometric changes which might be caused by homoconjugation in **1**. On the other hand, **2** and **3** have C_1 symmetry, and the ethene unit of the five-membered ring in **2** is twisted by 36.2°, 38.2°, and 31.9° in **3** as compared with the value for cyclopentene (41.1°). Perhydrotriquinacene (**4**) has C_3 symmetry; the three ethene units are twisted by 37.9°. All these results agree well with Schulman et al.'s calculations.[3]

We have employed Schulman et al.'s[3] method to derive the enthalpies of hydrogenation, the ΔH_f°(g) of **1**−**3**, and the

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(11) Paquette, L. A.; Kearney, F. R.; Drake, A. F.; Mason, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 5064−5069.

(12) (a) Bischof, P.; Bosse, D.; Gleiter, R.; Kukla, M. J.; de Meijere, A.; Paquette, L. A. *Chem. Ber.* **1975**, *108*, 1218−1223. (b) Christoph, G. G.; Muthard, J. L.; Paquette, L. A.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1978**, *100*, 7782−7784.

(13) Stevens, E. D.; Kramer, J. D.; Paquette, L. A. *J. Org. Chem.* **1976**, *41*, 2266−2269.

(14) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1979**, *101*, 6991−6996.

(15) Deslongchamps, P.; Cheriyan, U. O.; Lambert, Y.; Mercier, J.-C.; Ruest, L.; Russo, R.; Soucy, P. *Can. J. Chem.* **1978**, *56*, 1687−1704.

(16) Beckhaus, H.-D.; Rüchardt, C.; Kozhushkov, S. I.; Belov, V. N.; Verevkin, S. P.; de Meijere, A. *J. Am. Chem. Soc.* **1995**, *117*, 11854−11860.

(17) Clark, T.; Knox, T. M.; McKervey, M. A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404−2410.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(19) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1993**, *210*, 223−231.

(20) (a) Dichtfield, R. *Mol. Phys.* **1974**, *27*, 789−807. (b) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260.

Table 3. Estimated Enthalpies of Formation (kcal/mol) for **1**−**4**

	1	**2**	**3**	**4**
expt[a]	53.5 ± 1.0 (57.45 ± 0.68)[c]	30.5 ± 1.0	3.0 ± 1.0	−24.47 ± 0.86[d]
HF/6-31G* [b]	57.0	30.0	3.6	−22.7
MP2/6-31G* [b]	56.6	29.4	3.6	
B3LYP/6-31G* [c]	57.2	29.5	2.2	−23.8
B3LYP/6-311+G** [c]	57.2	29.6	2.3	−24.7

[a] Reference 2. [b] Reference 3. [c] This work. [d] Reference 17.

stabilization energy of **1**. Thus, the enthalpies of hydrogenation of **1**, **2**, and **3** are obtained from the homodesmotic eqs 1−3, in which cyclopentane (C_5H_{10}) and cyclopentene (C_5H_8) are used as reference molecules.

$$\mathbf{1} + C_5H_{10} = \mathbf{2} + C_5H_8 \qquad \Delta H_r(\mathbf{1}) = -0.6\ \text{kcal/mol} \quad (1)$$

$$\mathbf{2} + C_5H_{10} = \mathbf{3} + C_5H_8 \qquad \Delta H_r(\mathbf{2}) = -0.4\ \text{kcal/mol} \quad (2)$$

$$\mathbf{3} + C_5H_{10} = \mathbf{4} + C_5H_8 \qquad \Delta H_r(\mathbf{3}) = +0.2\ \text{kcal/mol} \quad (3)$$

Using the experimental hydrogenation enthalpy of cyclopentene to cyclopentane (which corresponds to the difference in the enthalpies of formation, −26.94 ± 0.13 kcal/mol)[2] and the enthalpies of reaction, the calculated stepwise enthalpies of hydrogenation (in kcal/mol) are −27.6 for **1**, −27.3 for **2**, and −26.8 for **3** (Table 1). In agreement with other theoretical values, the B3LYP results indicate that all three double bonds in **1** are essentially independent and do not interact. The enthalpy of hydrogenation for the first C═C double bond, −27.6 kcal/mol, is 4.6 kcal/mol larger than the experimental value reported by Liebman et al.[2]

$$\mathbf{1} + \mathbf{4} = \mathbf{2} + \mathbf{3} \qquad \Delta H_{\mathbf{r}} = -0.8\ \text{kcal/mol} \quad (4)$$

$$\mathbf{1} + \mathbf{3} = 2\times\mathbf{2} \qquad \Delta H_r = -0.3\ \text{kcal/mol} \quad (5)$$

$$\mathbf{1} + 3C_5H_{10} = \mathbf{4} + 3C_5H_8 \qquad \Delta H_r = -0.8\ \text{kcal/mol} \quad (6)$$

Although **1** is a normal hydrocarbon as deduced from eq 1, we can calculate the "stabilization energy" for **1** using the homodesmotic eqs 4 and 5, in which not only the number of double bonds but also the strain effects can be balanced to a large extent. Clearly, the quite small reaction enthalpies of eqs 4 (−0.8 kcal/mol) and 5 (−0.3 kcal/mol) also show that there is no homoaromatic interaction among the three double bonds in **1**. Thus, **1** is not homoaromatic energetically.

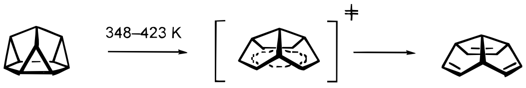
Using the calculated enthalpy of reaction (eq 6) and the enthalpies of formation of cyclopentane,[21] cyclopentene,[21] and **4**,[17] the enthalpy of formation of **1** is estimated to be 57.2 kcal/mol. This is larger than the value reported by Liebman et al.[2] but close to the MP2/6-31G* result and, in particular, to the new experimental value (57.51 ± 0.70 kcal/mol). The same procedure gives the enthalpies of formation of **2** and **3** as 29.6 and 2.3 kcal/mol, respectively, close to the other theoretical and experimental results (Table 3). Using the enthalpy of isomerization from **4** to adamantane, corrected to 298.15 K, and the experimental $\Delta H_f^\circ(g)$ of adamantane (32.2 ± 0.55 kcal/mol[21]), the $\Delta H_f^\circ(g)$ of **4** is computed to be 24.7 kcal/mol,[22] in agreement with the experimental value (24.47 ± 0.86 kcal/mol).

In addition to this energetic evidence, we have also computed the magnetic properties to characterize the homoaromaticity of **1**. If **1** were homoaromatic, it should have significant diamagnetic susceptibility exaltation[23] and NICS values.[24] Homodesmotic equations are appropriate not only to estimate aromatic stabilization energies but also to evaluate magnetic susceptibility exaltations.[25]

The calculated (via eq 6) magnetic susceptibility exaltation of **1**, −0.6 ppm cgs, is negligible for a system with six π-electrons and a large ring perimeter.[25] The benzene exaltation is −16.7.[26] In addition, the calculated NICS value at the geometrical center of the three double bonds, −1.6 ppm, may be comparable with those of the nonaromatic perhydrotriquinacene **4** (−4.6), cyclopentane (−4.2), cyclopentene (−2.3) as well as cyclohexane (−2.0). Hence, **1** is also not homoaromatic magnetically.

Can Neutral Trishomoaromatic Systems Exist?

Triquinacene (**1**) is not homoaromatic, but can neutral trishomoaromatic systems exist?[6,23a] This question was discussed recently. Semibullvalenes, if annelated appropriately, can result in homoaromatic ground states.[27] What would happen if the three C═C double bonds in **1** were to approach more closely? During the isomerization of diademane (**5**)[28] into **1**, the three cyclopropyl σ bonds in **5** are converted into three separated double bonds as in **1** simultaneously. Such isomerization can be induced thermally[28,29] as well as carried out under



5 **6** **1**

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

[22] Recent MM4 calculations also gave an enthalpy of formation for perhydrotriquinacene (**4**), $\Delta H_f^\circ(g) = 24.01$ kcal/mol: Allinger, N. L.; Chen, K.; Liu, J.-H. *J. Comput. Chem.* **1996**, *17*, 642−668.

[23] (a) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209−218. (b) Schleyer, P. v. R.; Freemann, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem.* **1995**, *107*, 332−335; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337−340. (c) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. II, pp 167−206. (d) Zywietz, T. K.; Jiao, H.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1998**, *63*, 3417−3422.

[24] Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van E. Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.

[25] (a) Jiao, H.; van E. Hommes, N. J. R.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1996**, *61*, 2826−2828. (b) Jiao, H.; Schleyer, P. v. R. *Angew. Chem.* **1996**, *108*, 2548−2551; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2383−2386.

[26] Jiao, H.; Schleyer, P. v. R.; Beno, B. R.; Houk, K. N.; Warmuth, R. *Angew. Chem.* **1997**, *109*, 2929−2933; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2761−2764.

[27] Jiao, H.; Nagelkerke, R.; Kurtz, H. A.; Williams, R. V.; Borden, W. T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 5921−5929.

[28] IUPAC name: hexacyclo[4.4.0.0.^{2,10}0.^{3,5}0.^{4,8}0^{7,9}]decane. Preparation: (a) de Meijere, A.; Kaufmann, D.; Schallner, O. *Angew. Chem.* **1971**, *83*, 404−405; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 417−418. (b) Kaufmann, D.; Fick, H.-H.; Schallner, O.; Spielmann, W.; Meyer, L.-U.; Gölitz, P.; de Meijere, A. *Chem. Ber.* **1983**, *116*, 587−609.

[29] (a) de Meijere, A.; Kaufmann, D.; Schallner, O. *Tetrahedron Lett.* **1973**, 553−556. (b) Spielmann, W.; Fick, H.-H.; Meyer, L.-U.; de Meijere, A. *Tetrahedron Lett.* **1976**, 4057−4060. (c) Meyer, L.-U.; de Meijere, A. *Chem. Ber.* **1977**, *110*, 2545−2560.

Table 4. Calculated and Experimentally Determined ΔH_f°(g) for Diademane (**5**) (All Values in kcal/mol)

method	MINDO/3	MM2	MM3	6-31G*	exptl[b]
ΔH_f°(g)	106.3	86.3	70.7	89	86.90 ± 0.33
SE[a]	127.9	107.9	92.3	107	108.6
ref	4	this work	this work	7	this work

[a] Calculated using an increment of −2.16 kcal/mol per CH group for an unstrained molecule.[40] [b] Derived from experimentally determined ΔH_f°(g) for triquinacene and experimentally determined ΔH_r° for diademane → triquinacene isomerization.

Table 5. Results from the Measurements of the Enthalpy of Reaction ΔH_r° and Eyring Parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the Isomerization Diademane (**5**) → Triquinacene (**1**) at $T = 368.2$ K in the Liquid Phase by DSC[38]

medium	mass of sample, mg	$-\Delta H_r^\circ$, kcal/mol	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
tetradecane	1.44	29.5	28.8	3.0
tetradecane	4.12	28.8	28.1	1.6
tetradecane	1.85	29.0	28.5	2.4
tetradecane	3.95	30.1	28.7	2.7
tetradecane	2.25	28.0	28.7	2.6
tetradecane	1.95	28.7	28.8	3.1
di-*n*-butylphthalate	1.75	30.2	28.1	1.9
N-methylacetamide	2.60	30.8	27.5	0.4
mean values		29.39 ± 0.33	28.40 ± 0.16	2.21 ± 0.32

transition metal or acid catalysis.[30] This reaction is allowed according to the rules of orbital symmetry conservation and has a relatively low Arrhenius activation energy in solution (E_a = 31.7 ± 0.7 kcal/mol)[28b] as well as in the gas phase (E_a = 28.3 ± 1.0 kcal/mol).[29a] Calculated as well as experimentally determined values of ΔH_f°(g) and strain energy (SE) for **5** are presented in Table 4. Experimental values for the enthalpy of isomerization **5** → **1** and the enthalpy of activation for this process as derived from DSC measurements are compiled in Table 5.

The concerted and synchronous pathway of this isomerization **5** → **1** is also indicated by the calculated energy surface along the RHF/6-31G* intrinsic reaction coordinate (IRC) descending from both sides of the transition state.[31] Moreover, the change of magnetic susceptibility ($\Delta\chi$) and the change in NICS (ΔNICS) at each of the discrete points along the IRC can be plotted as shown in Figure 1. The calculated relative magnetic susceptibility ($\Delta\chi$), the relative NICS values (ΔNICS), and the relative energy (E_{rel}) have maxima in magnitude at the transition-state geometry (IRC = 0, and the delocalized C−C bond separations of 1.924 and 1.376 Å at RHF/6-31G*). Thus, this transition state is to be aromatic.[31]

At B3LYP/6-311+G**, the transition state **6** C−C bond separations of 1.867 and 1.414 Å are highly delocalized as compared with the corresponding distances in **5** (1.523 vs 1.508 Å) and in **1** (2.549 vs 1.333 Å). On this basis, this transition state is aromatic geometrically. This conclusion is supported by the computed magnetic susceptibility exaltation of −35.3 ppm cgs (difference between the transition state and **1**) and the calculated NICS value (−24.7 ppm) at the geometric center of the six active carbons and is in agreement with our preliminary Hartree−Fock computations.[31]

As discussed above, triquinacene (**1**) is not aromatic, but diademane (**5**) has relatively more negative magnetic susceptibility than **1** (Table 2). Does **5** have some aromatic character? Note that **5** has three three-membered rings, and the enhancement of magnetic susceptibility exaltation (−17.5 ppm cgs) and NICS (−9.4 ppm) values over those of nonaromatic **1** is due to contributions from these three-membered rings.[27,32] For example, *cis*,*cis*-1,2,3-trimethylcyclopropane has a small magnetic susceptibility exaltation of −5.7 ppm cgs, the NICS value at a distance of 1.5 Å (nearly the same distance as the central point of the six active carbons to the three-membered ring in diademane) over the ring center is −3.6 ppm, and the sum of these values is close to that of diademane. Thus, **5** is not aromatic.

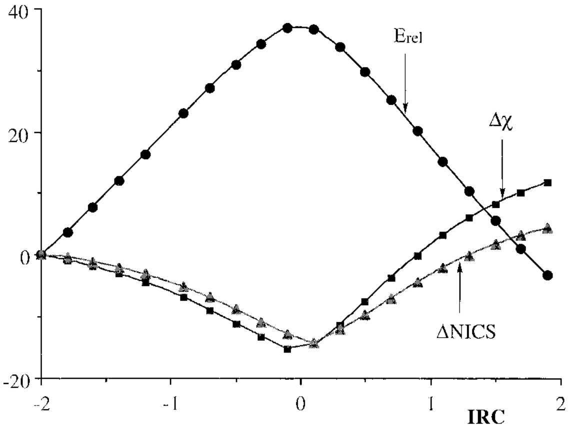

Figure 1. Relative energies (RHF/6-31G*) and magnetic susceptibilities as well as NICS values (RHF-GSGT/6-31G*//RHF/6-31G*) for discrete points along the RHF/6-31G* intrinsic reaction coordinate (IRC) with IRC = 0 for the transition state **6**, IRC = 2 for triquinacene (**1**), and IRC = −2 for diademane (**5**).

However, we cannot reproduce the experimental activation barrier of the isomerization from **5** to **1** at B3LYP/6-311+G**+ZPE (B3LYP/6-31G*). The calculated barrier of 25.9 kcal/mol is 2.5 kcal/mol lower than the experimental value of 28.4 ± 0.2 kcal/mol, determined here by differential scanning calorimetry (DSC), which in turn is in good agreement with the value of 28.3 ± 1.0 kcal/mol reported before for the isomerization in solution.[29a]

Conclusion

The experimental enthalpy of formation of triquinacene (**1**) has been revised by measuring its energy of combustion in a microcalorimeter and by high-level density functional theory computations. The new experimental value (ΔH_f°(g) = 57.51 ± 0.70 kcal/mol) agrees with various ab initio and density functional theory calculations but is about 4 kcal/mol higher than the previously reported value derived from an enthalpy of hydrogenation measurement. This revised enthalpy refutes the claimed stabilization due to homoaromatic interaction. Whatever the reasons for the discrepancy between the conclusion from the heat of hydrogenation (ΔH_H) measurements and our current results may be, this is not the first case in which ΔH_H measurements pointed toward homoconjugative stabilizations which could not be confirmed by computational or other experimental methods.[25a] That **1** is not homoaromatic also is shown by the negligible calculated stabilization energy (−0.8 kcal/mol), diamagnetic susceptibility exaltation (−0.6 ppm cgs), and NICS (−1.6 ppm), as well as the quite normal C═C bond lengths. This situation changes when the three double bonds, too far apart to interact in **1**, are brought together. The concerted and synchronous transition state of the isomerization from diademane (**5**) to **1** is highly aromatic on the basis of the same

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(30) de Meijere, A. *Tetrahedron Lett.* **1974**, 1845−1848.

(31) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.*, in press.

(32) Sauers, R. R. *Tetrahedron* **1998**, *54,* 337−348.

Table 6. Results from Typical Combustion Experiments of Triquinacene (**1**) at $T = 298.15$ K[a]

	run			
	1	2	3	4
$m_{(\text{substance})}/\text{g}^b$	0.042 532	0.034 211	0.028 466	0.030 375
$m'_{(\text{Mylar})}/\text{g}^b$	0.014 696	0.014 604	0.015 072	0.014 901
$m''_{(\text{cotton})}/\text{g}^b$	0.000 644	0.000 705	0.000 543	0.000 642
$\Delta T_c/\text{K}^c$	1.467 91	1.227 61	1.067 17	1.117 83
$-\epsilon_{\text{calor}}\Delta T_c$/cal	−515.69	−431.27	−374.91	−392.70
$-\epsilon_{\text{cont}}\Delta T_c$/cal	−0.96	−0.77	−0.68	−0.71
$\Delta E_{\text{corr}}/\text{cal}^d$	0.29	0.24	0.21	0.22
$-m'\Delta u_c^{\circ\prime}$/cal	80.22	79.72	82.37	81.34
$-m''\Delta u_c^{\circ\prime\prime}$/cal	2.61	2.86	2.20	2.60
$\Delta u_c^\circ(\text{sub})/\text{cal g}^{-1}$	−10 184.4	−10 197.2	−10 206.4	−10 184.2

[a] For the definition of the symbols, see ref 35; $T_h = 298.15$ K; $V_{\text{bomb}} = 0.0460$ dm^3; $p^i_{\text{gas}} = 3.04$ MPa; $m^i_{\text{water}} = 0.23$ g; $E_{\text{ignition}} = 0.35$ cal; $m_{\text{platin}} = 2.883$ g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{\text{corr}}$; $\epsilon_{\text{calor}} = 351.31 \pm 0.05$ cal K^{-1}; $-\epsilon_{\text{cont}}\Delta T_c = \epsilon^i_{\text{cont}}(T^i - 298.15\text{ K}) + \epsilon^f_{\text{cont}}(298.15\text{ K} - T^f + \Delta T_{\text{corr}})$. [d] ΔE_{corr} is the sum of items 81−85, 87−90, 93, and 94 in ref 35.

Table 7. Densities ρ (293 K), Specific Heat Capacities c_p (298.15 K), Enthalpy of Fusion $\Delta H^\circ_{\text{fus}}$, Temperature of Fusion T_{fus}, and Expansion Coefficients of the Materials

	ρ,[a] g cm^{-3}	C_p,[b] cal K^{-1} g^{-1}	$\Delta H^\circ_{\text{fus}}$,[b] kcal/mol	T_{fus},[b] K	$10^{-6}(\delta V/\delta T)_p$,[c] dm^{-3} K^{-1}
triquinacene (**1**)	1.06	0.390	3.54 ± 0.05	289.0	1.0
diademane (**5**)		0.359		365.2	
cotton[d]	1.500	0.399			0.1
Mylar[e]	1.380	0.315			0.1

[a] Measured with a pycnometer. [b] From DSC measurements. [c] Estimated. [d] Cotton $\Delta u_c^\circ(\text{CH}_{1.774}\text{O}_{0.887}) = -4050.0 \pm 1.0$ cal g^{-1}. [e] Mylar: $\Delta u_c^\circ(\text{C}_{10}\text{H}_8\text{O}_4) = -5458.6 \pm 1.1$ cal g^{-1}, $m_{(\text{Mylar})} = m_{\text{moist}}\,[1 - (4.64 \times 10^{-5})$ (relative moisture of air in %)].

Table 8. Enthalpies of Combustion ΔH°_c at $T = 298.15$ K from All Combustion Experiments and Their Mean Value $\langle -\Delta H^\circ_c \rangle$ in kcal/mol for Triquinacene (**1**)

ΔH°_c	$\langle -\Delta H^\circ_c \rangle$
1330.27	1328.14 ± 0.67
1329.07	
1327.41	
1327.38	
1326.57	

criteria. While neutral trishomoaromaticity does not exist in triquinacene, other more promising systems have been proposed.[8,23a]

Experimental Section

The hydrocarbons **1**[15] and **5**[28b] were prepared following the previously published procedures. Triquinacene (**1**) was purified by a sequence of column chromatography on silica gel, then repeated (two times) preparative gas chromatography (20% SE 30 on Chromosorb W-AW-DMCS, 1000 mm × 8.2 mm column, 90 °C), and finally distillation over 4-Å molecular sieves. Analysis of **1** by gas chromatography failed to show any impurity peaks (greater than 0.01%). For this compound, a purity of 99.99% (mp 288.9 K) was additionally established by DSC measurements of the melting process.[33] Diademane (**5**) was purified by working up the mixture with snoutene through oxidation with dimethyldioxirane, separating it from snoutene epoxide by column chromatography on silica gel, then repeatedly (two times) subliming under vacuum, 0.01 Torr at 303 K. **5** is not stable enough thermally to test its purity by gas chromatography.

Thermochemical Measurements. (i) Combustion Calorimetry. For measurements of the energy of combustion of **1**, an isoperibolic aneroid microcalorimeter with stirred water bath was used. The substance was placed in Mylar bags, which were burned in oxygen at a pressure of 3.04 MPa with a mass of 0.23 g of water added to the bomb. The detailed procedure has been described previously.[34] The energy equivalent of the calorimeter, ϵ_{calor} (see Table 6), was determined with a standard reference sample of benzoic acid (sample SRM 39i, U.S. NIST). The summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass measured in air to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states[35] is given in Table 7. Some typical combustion experiments for triquinacene are given in Table 6. The individual values of the enthalpies of combustion ΔH°_f together with the mean value and its standard deviation, are given in Table 8. The given standard deviations of the mean include the uncertainties from calibration and the combustion energies of the auxiliary materials.

(ii) Transpiration Method. The enthalpy of vaporization of **1** was determined with the method of transference in a saturated N_2 stream[36] using the Clausius−Clapeyron equation. About 0.2 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube, and the transported amount of material was collected in a cooled trap. The flow rate, 0.28−0.56 cm^3 s^{-1}, of the nitrogen stream was optimized in order to reach the equilibrium of saturation of transporting gas at each temperature of the investigation. The amount of condensed substance was determined by GC analysis using an internal standard. The vapor pressure p at each saturation temperature was calculated from the amount of product collected within a definite time period with the help of the ideal gas equation $p = mRT/V(\text{N}_2)M$, in which $R = 8.31451$ J K^{-1} mol^{-1}, m is the mass of transported compound, $V(\text{N}_2)$ is the volume of transporting gas, M is the molar mass of compound, and T is the saturation temperature. The vapor pressure p was corrected for the residual vapor pressure at the condensation temperature. The latter was calculated from a linear correlation between ln p and T^{-1} obtained by iteration. The molar enthalpy of vaporization was calculated from the slope of the linear Clausius−Clapeyron correlation: $\Delta H^\circ_{\text{vap}} = -R(\text{d ln } p/\text{d}T)$. The observed enthalpy of vaporization, $\Delta H^\circ_{\text{vap}}(T)$, at the temperature T obtained by this procedure is given in Table 9. Because of the deviations from $T = 298.15$ K of the average temperature ($T = 308.9$ K) of measurement by the transpiration method, the observed value of the enthalpy of vaporization of **1** (Table 9) was extrapolated (see Table 10) to this reference temperature using the "Sidgwick correction":[37]

$$\{\Delta H^\circ_{\text{vap}}(T) - \Delta H^\circ_{\text{vap}}(298.15\text{ K})\}/\text{kcal/mol} = -0.014(T - 298.15)/\text{K}$$

(iii) DSC Measurements.[38] The first experiments on **5** were carried out with pure **5** without addition of any solvent. In these experiments, two signals were observed simultaneously (the summarized enthalpy of transformations was −26.0 kcal/mol). It was not possible to separate the signals from the melting process and the process of interconversion of the diademane (even in a wide range of variations of the heating rates). Therefore, further experiments were carried out as follows: 1−4 mg of diademane together with a solvent (see Table 5) was placed in small screwable high-pressure steel pans. The sample and the reference pan with pure solvent (10 μL) were heated in a differential scanning calorimeter (DSC-2, Perkin-Elmer, calibrated with indium) at a constant

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(33) Hemminger, W. F.; Cammenga, H. K. *Methoden der Thermischen Analyse*; Springer: Berlin, 1989; pp 268−277.

(34) Beckhaus, H.-D.; Rüchardt, C.; Smisek, M. *Thermochim. Acta* **1984**, *79*, 149−159.

(35) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; pp 75−128.

(36) (a) Beckhaus, H.-D.; Kratt, G.; Lay, K.; Geiselmann, J.; Rüchardt, C.; Kitschke, B.; Lindner, H. J. *Chem. Ber.* **1980**, *113*, 3441−3455. (b) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York; 1970.

(37) Chickos, J. S.; Hesse, D. G.; Panshin, S. Y.; Rogers, D. W.; Saunders, M.; Uffer, P. M.; Liebman, J. F. *J. Org. Chem.* **1992**, *57*, 1897−1899.

(38) Peyman, A.; Hickl, E.; Beckhaus, H.-D. *Chem. Ber.* **1987**, *120*, 713−725.

Table 9. Results from Measurements of the Vapor Pressure p of Triquinacene (**1**)

T, K[a]	m, mg[b]	$V(N_2)$, dm^3 [c]	p, Pa[d]
291.3	4.09	0.747	119.2
296.4	3.48	0.390	172.6
301.5	3.31	0.259	246.0
306.5	3.39	0.195	333.4
311.9	3.77	0.162	445.4
316.5	3.96	0.129	586.7
321.5	3.79	0.098	738.3
326.5	5.29	0.098	1030.0
	$\Delta H^\circ_{vap,T} = 11.31 \pm 0.16$ kcal/mol		

[a] Temperature of saturation, N_2 gas stream 0.26−0.52 cm^3 s^{-1}. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at $T = 243$ K.

Table 10. Thermochemical Results at $T = 298.15$ K in kcal/mol for Triquinacene (**1**) and Diademane (**5**)

compound	ΔH°_f(liq)	ΔH°_{vap}	ΔH°_f(g) (expt)	ΔH°_f(g) (calcd)[f]	H_S[g]
triquinacene (**1**)	46.05[a] (±0.68)	11.46[b] (±0.16)	57.51 (±0.70)	43.0	14.5
diademane (**5**)	75.56[e] (±0.85)	11.34[c] (±0.37)	86.90[d] (±0.77)	−21.7	108.6

[a] Calculated from the specific energies of combustion. [b] From the measurements of vapor pressures at different temperatures from Table 9 using the Clausius−Clapeyron equation. [c] Calculated from the equation for the solvent-accessible areas (see text). [d] From the measurements of enthalpy of isomerization from Table 5 and ΔH°_f(liq) of triquinacene. [e] Calculated from the values for diademane from this table: $\Delta H^\circ_f(\text{liq}) = \Delta H^\circ_f(\text{g}) - \Delta H^\circ_{ap}$. [f] Calculated as the sum of increments for a strain-free model:[40,41] [CH] = −2.16; [HC═] = 8.6 kcal/mol. [g] Strain enthalpy: $H_S = \Delta H^\circ_f(\text{g,expt}) - \Delta H^\circ_f(\text{g,calcd})$.

heating rate of 5 K min^{-1} from 308 to 473 K. All experiments showed an exothermic peak between 348 and 423 K as a result of interconversion of **5** into **1**. For details about the calculation of the area of the signal which was interpreted as enthalpy of reaction, see ref 38. The results of the DSC measurements are given in Table 5. The activation parameters of the thermal interconversion of diademane were obtained by simulation of the signals.[38] The acceptable deviation of the activation enthalpy $\Delta H^\ddagger$ from the measured enthalpy of reaction is evidence that the studied reaction proceeds according to a rate law of first-order reactions. No significant difference was found for the value of the enthalpy of reaction investigated in rather polar solvents (di-*n*-butyl phthalate and *N*-methylacetamide) and in a nonpolar solvent (tetradecane). This fact was a reason to admit the very similar change of enthalpy of interconversion of diademane into triquinacene in the gaseous phase, too. Therefore, the average value of enthalpy of reaction, measured in solution, was suggested to be equal for the gaseous state. The temperature dependence of the enthalpy of reaction was expected to be negligible within the limits of the experimental uncertainties. Therefore, the enthalpy of reaction (−29.39 ± 0.33 kcal/mol), measured at 368.2 K, was accepted without extrapolation to the reference temperature, 298.15 K.

Estimation of the ΔH°_{vap} of Diademane (5). Due to the thermal lability of **5**, the transpiration method failed to provide reliable results. A good approximation for the magnitude of ΔH°_{vap} of hydrocarbons can be obtained from correlation with the solvent-accessible surface area F:[39]

$$\Delta H^\circ_{vap}(298.15\ \text{K})/\text{kcal/mol} = (0.0793 \pm 0.0029)(F/\text{Å}^2) + (1.25 \pm 1.60)$$

The value of $\Delta H^\circ_{vap} = 11.85 \pm 0.38$ kcal/mol calculated by this equation for **1** ($F = 133.5$ Å^2) is in good agreement with the experimental value (Table 10). Therefore, this equation could also be used to calculate the $\Delta H^\circ_{vap} = 11.34 \pm 0.37$ kcal/mol for **5** (see Table 10).

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Supporting Information Available: Cartesian coordinates and total energies computed at the B3LYP/6-311+G** level for compounds **1**−**6**, cyclopentane, cyclopentene, and adamantane (5 pages, print/PDF; available in ASCII format on the Web). See any current masthead page for ordering information and Web access instruction.

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(39) Chickos, J. S.; Hesse, D. G.; Hosseini, S.; Liebman, J. F.; Mendenhall, G. D.; Verevkin, S. P.; Rakus, K.; Beckhaus, H.-D.; Rüchardt, C. *J. Chem. Thermodyn.* **1995**, *27*, 693−705.

(40) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377−2386.

(41) Benson, S. W. *Thermochemical Kinetics*; Wiley-Interscience: New York, 1976; p 272.