1 H; $J = 19.9$ Hz). **9**: ^{1}H NMR (CDCl$_3$) δ 3.26 (br s, 1 H), 2.81 (d, 1 H; $J = 18.8$ Hz), 2.67 (d, 1 H; $J = 18.9$ Hz), 2.44 (d, 1 H; $J = 19.7$ Hz), 2.25 (d, 1 H; $J = 19.5$ Hz).

The ^{11}B NMR spectra were recorded on a Bruker WM 250 spectrometer (80 mHz for ^{11}B), and signals were referenced to external boron trifluoride etherate. Chemical shifts were measured on decoupled spectra and multiplicities on coupled spectra. **7**: ^{11}B NMR (CDCl$_3$) δ 3.6 (s, 1 B), -8.7 (d, 3 B), -9.6 (d, 2 B), -10.5 (d, 2 B), -13.4 (d, 2 B). **8**: ^{11}B NMR (CDCl$_3$) δ -2.1 (d, 2 B), -2.5 (s, 1 B), -10.8 (d, 2 B), -13.4 (d, 2 B), -15.2 (d, 2 B). **9**: ^{11}B NMR (CDCl$_3$) δ -3.3 (d, 1 B), -5.5 (s, 1 B), -8.3 (d, 2 B), -10.4 (d, 2 B), -12.2 (d, 3 B), -13.5 (d, 1 B).

Supplementary Material Available: A complete map of the 80 possible transformations for all 10 pairs of triangles and a scheme illustrating the five different "pure DSD" transformations (11 pages). Ordering information is given on any current masthead page.

Is Triquinacene Homoaromatic? A Computational Study

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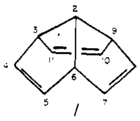
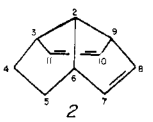
Abstract: AM1, ab initio, and MM2 calculations indicate triquinacene shows no significant homoaromatic stabilization, in contrast to conclusions drawn by Liebman et al. from thermochemical measurements. The discrepancy is attributed to the fact that the five-membered rings in di-, tetra-, and hexahydrotriquinacene are twisted and it can be accounted for quantitatively in this way. A discrepancy between a recent ab initio study by Miller et al. and experiment is attributed to computational errors.

Ever since the concept of homoaromaticity was first introduced by Adams and Winstein[1] some 40 years ago, it has been the subject of much interest to both experimentalists and theoreticians.[2] A variety of criteria have been suggested and applied as evidence for its presence or absence in given systems, the most direct being the observation of a ring current by ^{1}H NMR spectroscopy.[3] The others involve molecular properties whose values differ from those expected for "normal" molecules, the properties in question including molecular geometries,[4] values of overlap integrals between the "nonbonded" atoms,[5] ionization energies measured by photoelectron spectroscopy,[6] and heats of hydrogenation.[7] This work has indicated that homoaromatic stabilization is mainly a property of ionic systems, the stabilization energies of neutral ones usually being very small, and convincing theoretical explanations have been given[2] for this difference.



1



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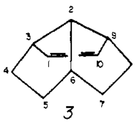

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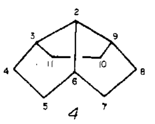

4

However, Liebman, Paquette, Peterson, and Rogers[7] (cited here as LPPR) have recently claimed that triquinacene (**1**, tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene) is a homoaromatic species with a small (4.5 kcal/mol) stabilization energy on the basis of measurements of the heats of hydrogenation of **1** and its dihydro (**2**) and tetrahydro (**3**) derivatives to hexahydrotriquinacene (**4**). This result seems very surprizing, given that **1** is a neutral hydrocarbon and that aromaticity in it would involve cyclic conjugation in a ring containing *three* weak homoconjugative interactions. We therefore decided to investigate the matter further, by carrying out AM1, ab initio, and MM2 calculations for **1–4**.

After the paper reporting our results had been submitted, two papers reporting geometry-optimized ab initio calculations for **1–4** appeared in print.[8] According to these, the heats of hydrogenation for the individual steps in the series **1** → **2** → **3** → **4** should all be equal, implying that **1** is not significantly stabilized and hence that one or more of the experimental heats of hydrogenation must have been in error by amounts well outside the expected limits. We have therefore revised our paper to take this additional information into account, arriving at a possible explanation for the experimental results.

Theoretical Procedure

Our studies involved use both the AM1[9] semiempirical model, as implemented in the AMPAC program[10] and the ab initio SCF MO procedures embodied in the GAUSSIAN82[11] program. All geometries were fully optimized, using the methods included in AMPAC and GAUSSIAN82. The AM1 geometries were used as starting geometries in the ab initio

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Table I. Difference in Energy[a] between Twisted (C_3) and Untwisted (C_{3v}) Forms of Perhydrotriquinacene (**4**)

method	energy difference
MM2	13.0[b]
AM1	1.0
6-31G*//STO-3G	14.0[c]

[a] Kilocalories/mole. [b] Reference 14. [c] Reference 15.

Table II. AM1 Heats of Formation[a] for Triquinacene and Its Reduction Products

molecule	expl ΔH_f[b]	AM1 ΔH_f
triquinacene (**1**)	53.5	56.27
dihydrotriquinacene (**2**)	30.5	23.71
tetrahydrotriquinacene (**3**)	3.0	−8.26
perhydrotriquinacene (**4**)	−24.5	−40.33 (−39.33)[e]

[a] Kilocalories/mole. [b] Calculated from the heat of formation of **3**[c] and heats of hydrogenation of **2**.[d] [c] Clark, T.; Knox, T. McO.; McKervey, M. A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404. [d] Reference 7. [e] ΔH_f for C_{3v} structure.

calculations. The AM1 minima were characterized as such by calculating force constants.[12]

The ab initio geometry optimizations for **1** and its analogues required use of the slower but more reliable Murtagh–Sargent optimization protocol, due to failure of the default BERNY optimizer.[11] Our experience shows that this is often the case for cyclic systems. Geometries were optimized using the 3-21G basis set and single point energy calculations were then carried out at the 6-31G* level.

Molecular mechanics geometry optimizations and calculations were carried out using standard procedures present in the MM2 program.[13]

Results

All three procedures predicted **1** to have C_{3v} symmetry, the five-membered rings being, as expected, planar. However, all three procedures predict **4** to have a C_3 structure (**4t**) in which the rings are twisted, the twisting leading to a decrease in the eclipsing interactions between the saturated carbon atoms in the C_{3v} structure. The latter corresponds to a stationary point on the potential surface, with three imaginary frequencies. The two possible geometries are not illustrated by a figure because a variety of plots failed to show the difference between them adequately. Similar results were found in earlier MM2[14] and ab initio[15] studies where the figures intended to illustrate the twisted structures are similarly obscure.

Our MM2 calculations, in agreement with previous ones[14] and the recent ab initio calculation[8a] noted above, predicted similar pairs of isomers (**2** and **2t**; **3** and **3t**) for **2** and **3**. Since the symmetries involved are different from those for **4**, we will refer to the structures as *untwisted* or *twisted*, depending on whether or not the saturated five-membered rings have planes of symmetry.

While AM1 agreed with the other procedures in predicting **1** to be untwisted and **4** to be twisted, it predicted **2** and **3** to be untwisted. Furthermore, the AM1 estimate of the difference in energy between the two structures for **4** was far smaller than the others; see Table I. The discrepancy is clearly due to the known[9] underestimation of eclipsing interactions by AM1. As Table II shows, the errors in the AM1 heats of formation for **1–4** increase progressively, the results indicating that the eclipsing strain in each saturated ring is underestimated by ca. +6 kcal/mol. The bond lengths in **1–4** are similar to those in cyclopentane and cyclopentene.[9]

Table III. AM1, 3-21G, and Experimental Geometries (Å) of Triquinacene

parameter	AM1	3-21G	expl[a]	6-31G*[b]
$C_{11}\cdot\cdot C_4$, $C_5\cdot\cdot C_7$, $C_8\cdot\cdot C_{10}$	2.5094	2.5170	2.533	
$C_2–C_3$	1.5585	1.5671	1.558	1.554
$C_5–C_6$, $C_3–C_4$, $C_6–C_7$, $C_9–C_8$, $C_{10}–C_9$	1.5024	1.5194	1.512	1.514
$C_4–C_5$, $C_8–C_7$, $C_{11}–C_{10}$	1.3444	1.3160	1.319	1.318
$C_2–H_1$	1.1093	1.0790	0.974	1.082
$C_3–H_{12}$, $C_6–H_{13}$, $C_9–H_{14}$	1.1184	1.0846	0.982	1.088
$C_4–H_{15}$, $C_5–H_{16}$, $C_7–H_{17}$, $C_8–H_{18}$, $C_{10}–H_{19}$, $C_{11}–H_{20}$	1.0913	1.0720	0.943	1.076
$C_3C_2H_1$	112.64^0	112.51^0	–	112.1^0
$C_4C_3C_2$, $C_7C_6C_2$, $C_{10}C_9C_2$	104.41	103.76	103.9^0	103.7
$C_5C_4C_3$, $C_8C_7C_6$, $C_{11}C_{10}C_9$	112.49	113.09	112.8	
$C_6C_5C_4$, $C_9C_8C_7$	112.39	113.08	112.8	112.8
$H_{12}C_3C_2$, $H_{13}C_6C_2$, $H_{14}C_9C_2$	112.20	113.10	112.8	112.9
$H_{15}C_4C_3$, $H_{17}C_7C_6$, $H_{19}C_{10}C_9$	120.39	121.81	–	
$H_{16}C_5C_4$, $H_{18}C_8C_7$, $H_{20}C_{11}C_{10}$	127.18	125.09	–	124.9
$C_4C_3C_2H_1$, $C_7C_6C_2H_1$, $C_{10}C_9C_2H_1$	120.37	121.49	–	
$C_5C_4C_3C_2$, $C_8C_7C_6C_2$, $C_{11}C_{10}C_9C_2$	2.26	1.33	–	1.9
$C_6C_5C_4C_3$, $C_9C_8C_7C_6$	−0.16	0.02	–	0.0
$H_{12}C_3C_2H_1$, $H_{13}C_6C_2H_1$, $H_{14}C_9C_2H_1$	−0.04	0.00	–	
$H_{15}C_4C_3C_2$, $H_{17}C_7C_6C_2$, $H_{19}C_{10}C_9C_2$	−177.90	−180.08	–	
$H_{16}C_5C_4H_{15}$, $H_{18}C_8C_7H_{17}$, $H_{20}C_{11}C_{10}H_{19}$	−0.11	−0.03	–	

[a] Reference 4g. [b] Reference 8b.

Table IV. AM1 and 3-21G Geometries (Å) of Dihydrotriquinacene

parameter	AM1	3-21G
$C_2–C_3$	1.5464	1.5634
$C_5–C_6$, $C_3–C_4$	1.5257	1.5634
$C_9–C_8$, $C_{10}–C_9$, $C_7–C_6$	1.5014	1.5161
$C_5–C_4$	1.5240	1.5572
$C_8–C_7$, $C_{11}–C_{10}$	1.3442	1.3158
$C_2–H_1$	1.1122	1.0826
$C_3–H_{12}$, $C_6–H_{13}$, $C_9–H_{14}$	1.1195	1.0826
$C_4–H_{15}$, $C_5–H_{16}$	1.1193	1.0847
$C_8–H_{18}$, $C_7–H_{17}$, $C_{11}–H_{20}$, $C_{10}–H_{19}$	1.0912	1.0722
$H_{21}–C_4$, $H_{22}–C_5$	1.1195	1.0826
$C_3C_2H_1$	112.02^0	112.17^0
$C_4C_3C_2$	107.24	107.68
$C_7C_6C_2$, $C_{10}C_9C_2$	104.31	103.76
$C_5C_4C_3$	108.77	108.14
$C_8C_7C_6$, $C_{11}C_{10}C_9$	112.58	113.13
$C_6C_5C_4$	108.52	108.14
$C_9C_8C_7$	112.32	113.12
$H_{12}C_3C_2$, $H_{13}C_6C_2$	111.12	111.58
$H_{14}C_9C_2$	112.28	112.93
$H_{15}C_4C_3$	110.53	110.12
$H_{17}C_7C_6$, $H_{19}C_{10}C_9$	120.34	121.67
$H_{16}C_5C_4$	110.40	110.46
$H_{18}C_8C_7$, $H_{20}C_{11}C_{10}$	127.30	125.21
$H_{21}C_4C_3$	109.92	110.39
$H_{22}C_5C_4$	110.18	110.14
$C_4C_3C_2H_1$	120.69	120.83
$C_{10}C_9C_2H_1$, $C_7C_6C_2H_1$	119.80	120.53
$C_5C_4C_3C_2$	2.26	2.30
$C_{11}C_{10}C_9C_2$, $C_8C_7C_6C_2$	1.21	0.92
$C_6C_5C_4C_3$	0.35	0.37
$C_9C_8C_7C_6$	0.36	−0.28
$H_{12}C_3C_2H_1$, $H_{13}C_6C_2H_1$	0.48	0.40
$H_{14}C_9C_2H_1$	−0.51	−0.80
$H_{17}C_7C_6C_2$, $H_{19}C_{10}C_9C_2$	−178.76	−180.34
$H_{15}C_4C_3C_2$	123.58	123.18
$H_{16}C_5C_4H_{15}$	0.16	0.19
$H_{20}C_{11}C_{10}H_{19}$, $H_{18}C_8C_7H_{17}$	−0.04	−0.01
$H_{21}C_4C_3C_2$	−118.34	−118.21
$H_{22}C_5C_4H_{21}$	0.32	0.16

Tables III–VI compare the ab initio (3-21G) and AM1 geometries for untwisted **1–3** and for twisted **4**. The agreement between the different values for the various untwisted species is very good, as is also the agreement between them and the results of an earlier ab initio calculation[15] and experiment.[4g] The agreement for twisted **4** is also good except for the dihedral angles in the bridges, where the AM1 values are much smaller, as would be expected in view of the underestimation of eclipsing interactions by AM1.

Table VII compares our ab initio (6-31G*//3-21G) total energies for **1**, untwisted **2** and **3**, and twisted **4** with those given

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Table V. AM1 and 3-21G Geometries (Å) of Tetrahydrotriquinacene

parameter	AM1	3-21G
C_2–C_3	1.5510	1.5681
C_5–C_6, C_3–C_4, C_6–C_7, C_9–C_8	1.5261	1.5579
C_{10}–C_9	1.5017	1.5136
C_4–C_5, C_8–C_7	1.5232	1.5555
C_{11}–C_{10}	1.3437	1.3161
C_2–H_1	1.1147	1.0812
C_3–H_{12}, C_9–H_{14}	1.1196	1.0829
C_6–H_{13}	1.1215	1.0829
C_4–H_{15}, C_4–H_{21}, C_7–H_{17}, C_7–H_{23}, C_8–H_{18}, C_8–H_{24}, C_5–H_{16}, C_5–H_{22}	1.1194	1.0829
H_{19}–C_{10}, H_{20}–C_{11}	1.0910	1.0724
$C_3C_2H_1$	110.81^0	109.82^0
$C_4C_3C_2$, $C_7C_6C_2$	107.26	107.55
$C_{10}C_9C_2$	104.81	103.77
$C_5C_4C_3$, $C_8C_7C_6$	108.51	108.17
$C_6C_5C_4$, $C_9C_8C_7$	108.60	108.17
$C_{11}C_{10}C_9$	112.18	113.13
$H_{12}C_3C_2$, $H_{14}C_9C_2$	111.06	111.47
$H_{13}C_6C_2$	109.85	109.70
$H_{15}C_4C_3$, $H_{17}C_7C_6$	110.89	110.20
$H_{19}C_{10}C_9$	120.47	121.58
$H_{16}C_5C_4$, $H_{18}C_8C_7$	110.28	110.57
$H_{20}C_{11}C_{10}$	127.63	125.19
$H_{21}C_4C_3$, $H_{23}C_7C_6$	109.94	110.46
$H_{22}C_5C_4$, $H_{24}C_8C_7$	110.18	110.14
$C_4C_3C_2H_1$, $C_7C_6C_2H_1$	119.29	119.77
$C_{10}C_9C_2H_1$	119.49	120.03
$C_5C_4C_3C_2$, $C_8C_7C_6C_2$	1.8	1.38
$C_6C_5C_4C_3$, $C_9C_8C_7C_6$	0.84	1.38
$C_{11}C_{10}C_9C_2$	0.92	−0.59
$H_{12}C_3C_2H_1$, $H_{14}C_9C_2H_1$	−0.26	−0.23
$H_{13}C_6C_2H_1$	0.78	1.49
$H_{15}C_4C_3C_2$, $H_{17}C_7C_6C_2$	123.05	122.16
$H_{19}C_{10}C_9C_2$	−179.27	−181.27
$H_{16}C_5C_4H_{15}$, $H_{18}C_8C_7H_{17}$	0.88	1.68
$H_{20}C_{11}C_{10}H_{19}$	−0.17	−0.27
$H_{21}C_4C_3C_2$, $H_{23}C_7C_6C_2$	−118.76	−119.39
$H_{22}C_5C_4H_{21}$, $H_{24}C_8C_7H_{23}$	0.85	1.71

Table VI. AM1 and 3-21G Geometries (Å) of Perhydrotriquinacene

parameter	AM1	3-21G	STO-3G[a]
C_2–C_3	1.5374	1.5617	1.557
C_5–C_6, C_3–C_4, C_6–C_7, C_9–C_8, C_{10}–C_9	1.5261	1.5460	1.547
C_4–C_5, C_8–C_7, C_{11}–C_{10}	1.5233	1.5444	1.544
C_2–H_1	1.1164	1.0812	
C_3–H_{12}, C_6–H_{13}, C_9–H_{14}	1.1207	1.0839	
C_4–H_{15}, C_{10}–H_{19}, C_7–H_{17}	1.1200	1.0839	1.087
C_8–H_{18}, C_5–H_{16}, C_{11}–H_{20}	1.1179	1.0839	
H_{21}–C_4, H_{23}–C_7, H_{25}–C_{10}	1.1178	1.0839	1.088
H_{22}–C_5, H_{24}–C_8, H_{26}–C_{11}	1.1197	1.0839	
$C_3C_2H_1$	110.96^0	111.96^0	111.6^0
$C_4C_3C_2$, $C_7C_6C_2$, $C_{10}C_9C_2$	106.70	104.72	105.3
$C_5C_4C_3$, $C_8C_7C_6$, $C_{11}C_{10}C_9$	107.44	104.12	
$C_6C_5C_4$, $C_9C_8C_7$	107.44	104.12	
$H_{12}C_3C_2$, $H_{13}C_6C_2$, $H_{14}C_9C_2$	110.26	111.42	110.9
$H_{15}C_4C_3$, $H_{17}C_7C_6$, $H_{19}C_{10}C_9$	109.64	109.75	109.6
$H_{16}C_5C_4$, $H_{18}C_8C_7$, $H_{20}C_{11}C_{10}$	110.83	112.48	
$H_{21}C_4C_3$, $H_{23}C_7C_6$, $H_{25}C_{10}C_9$	111.49	112.44	112.5
$H_{22}C_5C_4$, $H_{24}C_8C_7$, $H_{26}C_{11}C_{10}$	109.88	109.89	
$C_4C_3C_2H_1$, $C_7C_6C_2H_1$, $C_{10}C_9C_2H_1$	−113.06	−107.99	
$C_5C_4C_3C_2$, $C_8C_7C_6C_2$, $C_{11}C_{10}C_9C_2$	−17.24	−33.15	−26.6
$C_6C_5C_4C_3$, $C_9C_8C_7C_6$	19.24	39.06	35.5
$H_{12}C_3C_2H_1$, $H_{13}C_6C_2H_1$, $H_{14}C_9C_2H_1$	−6.07	12.95	
$H_{15}C_4C_3H_2$, $H_{17}C_7C_6C_2$, $H_{19}C_{10}C_9C_2$	102.24	83.84	
$H_{16}C_5C_4H_{15}$, $H_{18}C_8C_7H_{17}$, $H_{20}C_{11}C_{10}H_{19}$	21.14	43.47	
$H_{21}C_4C_3C_2$, $H_{23}C_7C_6C_2$, $H_{25}C_{10}C_9C_2$	−139.04	−155.68	
$H_{22}C_5C_4H_{21}$, $H_{24}C_8C_7H_{23}$, $H_{26}C_{11}C_{10}H_{25}$	21.07	43.24	

[a] Reference 15.

Table VII. Ab Initio Total Energies[a] of Triquinacene and Its Reduction Products

molecule	6-31G*//3-21G[b]	6-31$^+$G*//6-31G*[c]
triquinacene (**1**)	−384.45015	−384.4609
dihydrotriquinacene (**2**)	−385.63212	−385.6458
tetrahydrotriquinacene (**3**)	−386.81102	−386.8302
perhydrotriquinacene (**4**)	−388.00950	−388.0138

[a] Hartrees. [b] Present work. [c] Reference 8a.

Table VIII. Energy[a] Steps between Hydrogenation Processes on Triquinacene and Its Reduction Products

molecule	6-31G*//3-21G	AM1	MM2
triquinacene (**1**)			
dihydrotriquinacene (**2**)	741.7	32.56	27.65
tetrahydrotriquinacene (**3**)	739.8	31.97	26.83
perhydrotriquinacene[b] (**4**)	738.0	31.65	27.41

[a] Kilocalories/mole. [b] Untwisted, C_{3v} form.

by Miller et. al,[8a] using a higher level procedure (6-31$^+$G*//6-31G*). The agreement between the two sets of values is very close, indicating that the 3-21G geometries do not differ significantly from those obtained by using the 6-31G* basis set. The ab initio geometries listed in Tables III–VI are therefore likely to be reliable.

Discussion

The heat of hydrogenation for each step in the series, **1** → **2t** → **3t** → **4t**, can be divided into two parts, one corresponding to the heat of hydrogenation under conditions where the rings are kept untwisted throughout and the other being the relief of strain energy due to twisting. If **1** is not aromatic, the "untwisted" heats of hydrogenation should be equal, because any change in strain energy should be the same in each step. If **1** is homoaromatic, the value for **1** → **2** should be correspondingly smaller than that for **2** → **3** or **3** → **4**.

The relief of strain by twisting would not be expected to be the same for each step because the twist angles need not vary regularly along the series. The twist angles are different, being determined by the opposed tendencies of unsaturated rings to be untwisted and of saturated ones to be twisted. Any attempt to determine the degree of aromatic stabilization of **1** should therefore be based on the "untwisted" heats of hydrogenation.

Table VIII shows the heats of reaction calculated by AM1 and MM2 for successive steps in the hydrogenation of **1** to untwisted **4**, via untwisted **2** and **3**. The corresponding ab initio differences in total energy are also listed for comparison, with a combination of our results and those from Miller et al.[8a] In each case, the values for the three steps agree closely. There is no indication of any special stabilization of **1**.

These results indicate unequivocally that **1** is *not* significantly stabilized by homoaromaticity. The fact that three quite different procedures all lead to the same conclusion leaves very little doubt concerning its correctness.

In view of these considerations, it is surprizing that the recent ab initio calculation by Miller et. al.[8a] led to approximately equal heats of hydrogenation for each step, implying that the contributions by twisting are the same in each case. Furthermore, while the experimental values[7] for the second and third are equal, that for the first (**1** → **2**) is less by 4.5 kcal/mol. Before considering possible explanations of the discrepancy, we need first to see whether the experimental results can be explained in terms of contributions by the twisting energies.

If the heats of hydrogenation for each of the three steps (**1** → **2** → **3** → **4**)are all equal (h, kcal/mol), as our calculations imply, the corresponding experimental heats of hydrogenation (h_{ij} for $i \rightarrow j$) will be

$$\begin{aligned} h_{12} &= h + t_2 \\ h_{23} &= h - t_2 + t_3 \qquad (1) \\ h_{34} &= h - t_3 + t_4 \end{aligned}$$

where t_2, t_3, and t_4 are the twisting energies (kcal/mol) of **2**–**4**, respectively, i.e. the differences in energy between corresponding untwisted and twisted isomers.

The experimental results[7] indicate that

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$$h_{23} + h_{34} = 2h_{34}$$

$$h_{12} + h_{23} + h_{34} = 3h_{34} - 4.5$$

i.e.

$$h_{23} = h_{34}$$

$$h_{12} = h_{34} - 4.5 \qquad (2)$$

Equations 1 and 2 are consistent if

$$t_3 = 0.5(t_2 + t_4)$$

$$t_4 - t_2 - t_3 = 4.5 \qquad (3)$$

The close agreement between the estimates of t_4 given by the ab initio[15] (14 kcal/mol) and MM2[14] (13 kcal/mol) calculations indicate that the true value must be close to 13.5 kcal/mol. If so, then

$$t_2 = 1.5;\ t_3 = 7.5 \text{ kcal/mol} \qquad (4)$$

The small value for t_2 seems very reasonable because two of the bridges in **2t** favor the untwisted geometry. The corresponding saturated bridge should relax further in **3t**, and the two saturated bridges in **3t** should relax further in **4t**. The values for the twisting energies in eq 4 also agree with our MM2 estimates (4.0, 7.9, and 13.0 kcal/mol, respectively) within the combined error limits of experiment and MM2. Thus the results reported by LPPR[7] can be interpreted satisfactorily in terms of a model where **1** is *not* stabilized by homoaromaticity, the difference between the heat of hydrogenation of **1** to **2t** and that of **2t** to **3t** or of **3t** to **4t** being due to differences in the twisting energies.

Conclusions

The calculations and arguments presented here strongly imply that triquinacene (**1**) is *not* an aromatic species, the effects of homoconjugation on its energy being very small. This is satisfactory because it is very difficult to see how homoconjugative interactions could lead to significant stabilization in a neutral cyclic conjugated hydrocarbon with an even numbered ring and three "long" (2.51 Å) CC bonds. LPPR[7] arrived at an erroneous conclusion in this connection because they failed to consider the effects of twisting in **2**–**4**. Their results can be explained quantitatively in this way.

Note that this conclusion is not inconsistent with evidence[6] from UPE spectroscopy, showing that interactions between the π MO's of **2** leads to significant changes in orbital energies. The interactions that lead to these changes correspond[16] to first-order perturbations involving mutual interaction between the three degenerate π MO's. While such first-order interactions can lead to signficant changes in the MO energies, they do *not* lead to overall stabilization.[16]

While Miller et al.[8] have also concluded that **1** is not homoaromatic, their ab initio calculations disagree with experiment in predicting the heats of hydrogenation for each of the four steps in the conversion of **1** to **4t** to be the same. Discrepancies of this kind are nearly always due to errors in the calculated values and the work reported above makes it seem almost certain that this is the case here. Errors of this magnitude in heats of formation calculated by the procedures used by Miller et al.[8] are by no means unknown.

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Sesquibicyclic Hydrazines: Oxidation Thermodynamics and Cation Radical Nitrogen ESR Splittings and UV Absorption Maxima

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Abstract: Diels–Alder addition of 1,3-cyclohexadiene to protonated 3,4-diazatricyclo[4.2.1.0^{2,5}]non-3-ene (**3**), 2,3-diazabicyclo[2.1.1]hex-2-ene (**4**), and 6,7-diazabicyclo[3.2.2]non-6-ene (**5**) gave **8**, **6**, and **9**, respectively, and addition of 1,3-cycloheptadiene to **5** gave **10**. The saturated compounds **7**, **11**, and **12** were prepared by hydrogenating **6**, **9**, and **10**. Comparisons of $E°'$, vIP, cation radical ESR nitrogen splitting constants [a(N)], and UV absorption maxima with values for other sesquibicyclic hydrazines and with AM1 semiempirical calculations are discussed. The double nitrogen inversion barrier of $\mathbf{7}^{\bullet+}$ was determined by ESR to be 4.6 kcal/mol, within experimental error of that previously measured for $\mathbf{16}\text{-}d_{12}{}^{\bullet+}$. Changing bicyclic ring size in sesquibicyclic hydrazines greatly affects the ease of oxidation and cation radical properties. Changes in $\Delta G°$ for first electron loss are usefully described as one dimensional in nitrogen pyramidality caused by the rings present regardless of their identity (using α(av) calculated by AM1). Calculation of nitrogen ESR splitting constants for the cation radicals requires averaging over the energy surface for bending at nitrogen. This problem is less well described as one dimensional in α(av) as the ring sizes are enlarged, and a(N) is calculated to be modestly sensitive to the identity of the bicyclic rings. Cation radical UV absorption spectra are not calculated usefully by semiempirical methods. The identity of the rings and not simply nitrogen pyramidality is clearly of importance, and this is not handled accurately enough by available calculations.

Protonated bicyclic azo compounds **1** and **2** undergo Diels–Alder addition to cyclic 1,3-dienes to give protonated bis-N,N'-bicyclic ("sesquibicyclic") hydrazines.[1] The neutral adducts are thermally unstable to retro-Diels–Alder cleavage, and no adduct

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