dissolved in deuterated acetone. NMR spectra showed the mixture contained the minor (**37**) and major (**39**) adducts as well as benzopyranone (**36**) in 13, 68, and 19%, respectively, together with a small amount of starting material. The solution was then diluted with benzene. The major adduct **39** was obtained as white crystals, mp 250–253 °C dec, only slightly soluble in benzene at room temperature: ^{1}H NMR (360 MHz, CD_3COCD_3) **39** δ 7.50–7.29 (m, 9 H), 4.52 (d, J = 6.3 Hz, 1 H), 3.51–3.39 (m, 2 H), 3.22 (d, d, J = 7, 14.5 Hz, 1 H), 3.04 (d, d, J = 10, 14.5 Hz, 1 H). ^{1}H NMR (360 MHz, CD_3COCD_3) **37** δ 7.50–7.29 (m, 9 H), 4.36 (d, J = 2 Hz, 1 H), 4.03 (d, d, J = 2, 9 Hz, 1 H), 3.66 (d, d, d, J = 2.4, 7, 9 Hz, 1 H), 3.18 (d, d, J = 2.4, 15 Hz, 1 H), 3.06 (d, d, J = 7, 15 Hz, 1 H). Pure **39** (2 mg) was placed in an NMR tube with benzene and was heated at 140 °C for 15 h. After cooling, the solvent was replaced with deuterated acetone. No trace of **37** was detected.

Benzocyclobutene-7-carboxaldehyde (40). Oxidation of benzocyclobutene-7-methanol[43] with PDC at 0 °C or reduction of **4** with DIBAL[44] gave **40**: ^{1}H NMR (360 MHz, C_6D_6) δ 9.30 (d, J = 3 Hz, 1 H), 7.02–6.96 (m, 2 H), 6.83–6.77 (m, 2 H), 3.68 (m, 1 H), 2.94 (d, d, J = 2.4, 14.4 Hz, 1 H), 2.76 (d, d, J = 5.4, 14.4 Hz, 1 H); ^{13}C NMR (90 MHz, C_6D_6) δ 197.90, 144.56, 141.43, 128.51, 127.65, 123.18, 123.03, 53.99, 30.59. A solution of **40** (12 mg, 0.09 mmol) in C_6D_6 (0.5 mL) was heated at 130 °C. After 2 h, 95% conversion to a single product, (1*H*)-2-benzopyran (**42**), had occurred: ^{1}H NMR (360 MHz, C_6D_6) δ 7.01–6.86 (m, 2 H), 6.73 (d, J = 7.4 Hz, 1 H), 6.53 (d, J = 7 Hz, 1 H), 6.37 (d, J = 5.7 Hz, 1 H), 5.55 (d, J = 5.7 Hz, 1 H), 4.75 (s, 2 H).[45] In another experiment, **40** (10 mg, 0.076 mmol) was heated at 130 °C in C_6D_6 (0.5 mL) with **9** (38 mg, 0.39 mmol), **42** was formed in >98% yield together with ~2% of an unknown product as revealed by NMR.

7-Methylbenzocyclobutene-7-carbonitrile (50) in the Presence of 9. A solution of **4** (200 mg, 1.55 mol) in THF (0.5 mL) was added to LDA, prepared from diisopropylamine (196 mg, 1.94 mmol) and BuLi (1.94 mmol, 1.6 M in hexane, Aldrich) in THF (7 mL) at 0 °C, at −78 °C. After 1 h, MeI (382 mg, 2.7 mmol) was added, and the reaction mixture was stirred overnight at room temperature. Workup gave **50** (204 mg) in 92% yield after chromatography.[40]

A solution of **50** (18 mg, 0.13 mmol) and **9** (28 mg, 0.29 mmol) in C_6D_6 containing 2 crystals of hydroquinone was heated at 140 °C for 5 days. A single adduct formed (**52**). A crystal suitable for X-ray analysis was obtained by recrystallization of **52** from benzene and hexane, mp 139–140 °C: ^{1}H NMR (360 MHz, C_6D_6) δ 6.94–6.80 (m, 3 H), 6.66 (m, 1 H), 3.10 (d, d, J = 8.5, 16.5 Hz, 1 H), 2.76 (d, d, J = 3, 16.5 Hz, 1 H), 2.74 (d, d, d, J = 3, 8.5, 10 Hz, 1 H), 2.57 (d, J = 10 Hz, 1 H), 1.56 (s, 3 H).

7-Methylbenzocyclobutene-7-carbonitrile (50) in the Presence of 10. A solution of **50** (20 mg, 0.14 mmol) and **10** (63 mg, 0.35 mmol) in C_6D_6 (0.5 mL) was heated for 6 days and 18 h at 140 °C until the reaction was complete. Only one adduct (**53**) was formed: ^{1}H NMR (360 MHz, C_6D_6) δ 7.33–6.77 (m, 9 H), 3.35 (d, d, J = 15.5 Hz, 1 H), 3.01 (d, d, J = 3, 15.5 Hz, 1 H), 2.83 (d, d, d, J = 3, 8, 10 Hz, 1 H), 2.75 (d, J = 10 Hz, 1 H), 1.75 (s, 3 H).

Methyl 7-Methylbenzocyclobutene-7-carboxylate (54) in the Presence of 9. A solution of **54** (10 mg, 0.06 mmol) and **9** (15 mg, 0.15 mmol) in C_6D_6 (0.5 mL) containing 3 crystals of hydroquinone was heated at 130 °C for 10 days. Only one adduct (**56**) formed: ^{1}H NMR (360 MHz, C_6D_6) δ 7.14 (d, J = 7.5 Hz, 1 H), 7.00 (t, J = 7.5 Hz, 1 H), 6.92 (t, J = 7.5 Hz, 1 H), 6.81 (d, J = 7.5 Hz, 1 H), 3.61 (d, J = 10 Hz, 1 H), 3.17 (d, d, d, J = 2, 8, 10 Hz, 1 H), 3.07 (s, 3 H), 2.92 (d, d, J = 2, 15.5 Hz, 1 H), 2.45 (d, d, J = 8, 15.5 Hz, 1 H), 1.81 (s, 3 H). In a control experiment, the same amount of sample was heated for the same period without dienophile. After 10 days reaction only 10% conversion to methyl 2-(2′-methylphenyl)acrylate (**58**) had occurred. On further heating at 185 °C for 36 h conversion to **58** was complete: ^{1}H NMR (360 MHz, C_6D_6) δ 7.10–6.95 (m, 4 H), 6.43 (d, J = 2 Hz, 1 H), 5.32 (d, J = 2 Hz, 1 H), 3.28 (s, 3 H), 2.12 (s, 3 H). In another experiment **58** was obtained when the reaction was conducted at 190 °C for 2 days in the presence of hydroquinone.

3-((Dimethyl-*tert*-butyl)siloxy)-4-methyl-(1*H*)-2-benzopyran (61). A solution of **61** (35 mg, 0.12 mmol) in benzene (0.7 ml) was heated at 170 °C for 17 h. A mixture of **61**, 7-((dimethyl-*tert*-butyl)siloxy)-7-methylbenzocyclobutene (**62**) and dimethyl-*tert*-butylsily 2-(2′-methylphenyl)acrylate (**63**) was formed in a 9:5:1 ratio. On continued heating for 5 days, conversion of **61** to **63** was complete: ^{1}H NMR (360 MHz, C_6D_6) **62** δ 7.15–6.85 (m, 4 H), 3.76 (d, J = 7 Hz, 1 H), 2.80 (d, J = 7 Hz, 1 H), 1.60 (s, 3 H), 0.95 (s, 9 H), 0.20 (s, 6 H). ^{1}H NMR (360 MHz, C_6D_6) **63** 7.20–6.90 (m, 4 H), 6.47 (s, 1 H), 5.38 (s, 1 H), 2.23 (s, 3 H), 0.90 (s, 9 H), 0.29 (s, 6 H).

Crystallographic Data for Compounds 12, 28, and 52. Cell parameters and reflection intensities were measured at room temperature on Nonius CAD-4 (**12** and **28**) and Philips PW100 (**52**) diffractometers with graphite monochromated Mo Kα radiation. The structures were solved by direct methods (MULTAN-80) and refined by least-square analysis with the XTAL program (Table VI).

Acknowledgment. We are grateful to the U.S. and Swiss National Science Foundations (Grant No. 20-5380.87) for financial support of this research.

Supplementary Material Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, and bond distances and angles for **12**, **28**, and **52** (21 pages); tables of observed and calculated structure factors for **28** and **52** (20 pages). Ordering information is given on any current masthead page.

(42) Horner, L.; Kirmse, W.; Muth, K. *Chem. Ber.* **1958**, *91*, 430.
(43) Cava, M. P.; Mitchell, M. J. *J. Org. Chem.* **1962**, *27*, 631.
(44) O'Leary, M. A.; Wege, D. *Tetrahedron* **1981**, *37*, 801.
(45) Normant-Chefnay, C.; Thibault, J.; Maitte, P. C. *R. Acad. Sci. Paris (C)* **1968**, *267*, 547.

Is Triquinacene Homoaromatic? An MM3 Study of Triquinacene and Its Hydrogenation Products

Joey W. Storer and K. N. Houk*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024. *Received August 21, 1991*

Abstract: MM3 energies of triquinacene and di-, tetra-, and perhydrotriquinacene are in reasonable accord with the thermochemical measurements reported by Liebman, Paquette, Peterson, and Rogers (*J. Am. Chem. Soc.* **1986**, *108*, 8267). An analysis of the optimized structures shows the origin of the "differential relaxation" postulated for this series by Dewar and Holder (*J. Am. Chem. Soc.* **1989**, *111*, 5384). The anomalously low heat of hydrogenation of triquinacene can be explained without invoking homoaromaticity.

Introduction

Liebman, Paquette, Peterson, and Rogers have measured the heats of hydrogenation of triquinacene (**1**), dihydrotriquinacene (**2**), and tetrahydrotriquinacene (**3**) to the fully saturated perhydrotriquinacene (**4**). The reported values are shown in Figure 1.[1] The heat of hydrogenation of triquinacene to dihydrotriquinacene (**1** → **2**) is 4.5 ± 2 kcal/mol smaller than for **2** → **3**

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

0002-7863/92/1514-1165$03.00/0

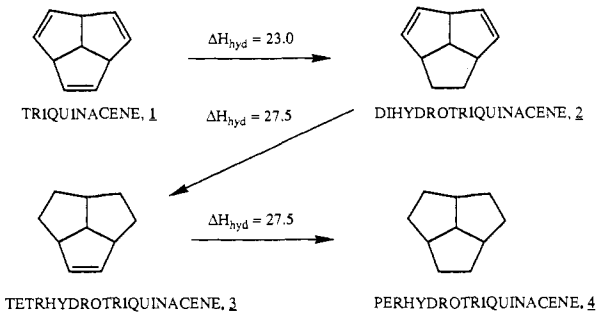


Figure 1. Triquinacene, its hydrogenation products, and heats of hydrogenation (kcal/mol).

and **3** → **4**. This discrepancy was attributed to extra stabilization in triquinacene arising from homoaromaticity, caused by overlap of its three π orbitals.[2,3] This conclusion was suprising for several reasons. For example, no spectroscopic evidence such as ring current has been observed in support of homoconjugation or homoaromaticity in this or related systems.[3] X-ray crystallography of triquinacene showed no internal distortion indicative of bonding interactions between the π systems.[4] Photoelectron spectroscopy did indicate some interaction between the π orbitals, but the through-bond interaction was found to be larger than the through-space interaction.[5]

Houk, Paquette, and co-workers have argued that the interaction between π orbitals in triquinacene is predominantly a destabilizing interaction between the doubly occupied π orbitals.[6] Indeed, it was claimed that no neutral homoaromaticity would ever be observed in hydrocarbons, since closed-shell repulsion between filled orbitals would overwhelm stabilizing π–π^* interactions.[6a]

Theoretical work by Miller et al. using ab initio molecular orbital theory was unable to reproduce experimental trends in ΔH_h at the MP2/6-31G*//RHF/6-31G* level of theory.[7] MM2 force field calculations also failed to reproduce experimental trends and instead supported the ab initio results.[6b-8] The results imply that either the experiments or the calculations are wrong.

Recently, Dewar and Holder suggested that the anomaly in the experimental heats of formation could arise from the differing tendency of **2**–**4** to relieve strain by twisting.[9] This proposal provides an explanation of the heats of hydrogenation without requiring homoaromaticity or any special stability in triquinacene. However, when subjected to scrutiny, the MM2, AM1, and ab initio results presented by Dewar and Holder provide no support to the hypothesis, as will be described below. Because we were convinced of the validity of Dewar's qualitative arguments, we undertook further computational studies of **1**–**4** to try to find computational support for it. In this paper we report MM3 calculations which verify the experimental trends and allow us to identify the structural cause of the unusually small heat of hydrogenation of triquinacene.

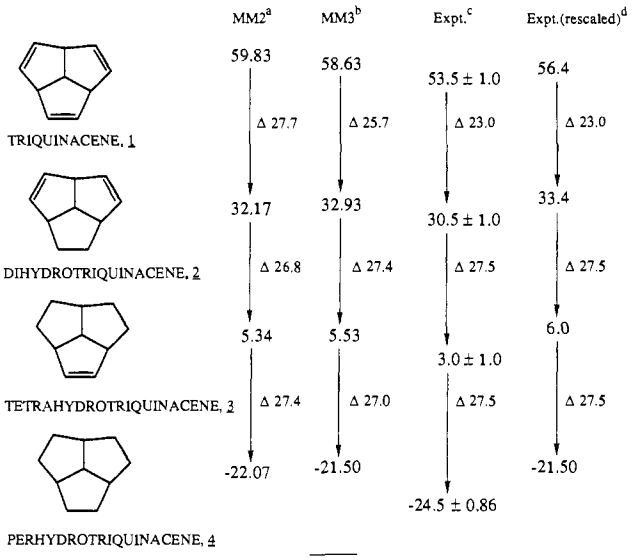


Figure 2. Comparison of MM2 and MM3 calculations with experimental heats of formation (kcal/mol): (a) MM2 results for fully optimized structures; (b) MM3 results for fully optimized structures; (c) from refs 1 and 13; (d) combining the MM3 result for perhydrotriquinacene with the experimental heats of hydrogenation.

Dewar and Holder proposed that the heat of hydrogenation of triquinacene (**1** → **2**) is unusually low because the strain energy in dihydrotriquinacene cannot be fully relieved by twisting of the saturated ring. That is, triquinacene is not unusually stable, but its hydrogenation product **2** is unusually unstable. Hydrogenation of **2** → **3**, or **3** → **4** is accompanied by relaxation because the carbon skeleton becomes more flexible with each saturation. Dewar and Holder analyzed these effects by calculating heats of hydrogenation without allowing torsional relaxation. Heats of formation were calculated for four high-symmetry structures: triquinacene (C_{3v}), dihydrotriquinacene (C_s), tetrahydrotriquinacene (C_s), and perhydrotriquinacene (C_{3v}). No stabilization arising from twisting can occur in three symmetry-constrained structures. The energy differences reported by Dewar's and Holder's Table VIII[9] corresponding to hydrogenation without structure relaxation are similar. MM2, AM1, and 6-31G*//3-21G calculations predict relatively constant differences of 27.3 ± 0.4, 32.1 ± 0.5, and 739.8 ± 1.8 kcal/mol, respectively, and the first difference (**1** → **2**) is larger, rather than smaller as found experimentally.

Unfortunately, there are some problems and inconsistencies to be noted in the Dewar–Holder analysis. The MM2 energy differences for the high-symmetry structures in Dewar's Table VIII[9] are actually 23.6, 23.1, and 22.4 kcal/mol for hydrogenations **1** → **2**, **2** → **3**, and **3** → **4**, rather than the 27.65, 26.83, and 27.41 kcal/mol that they report. The MM2 energy differences for the *fully optimized* structures were inadvertently reported by Dewar and Holder. Also the structures of **2**(C_s) and **3**(C_s), Dewar's Table VIII[9], were actually found to be minima by AM1 due to its well-known underestimation of eclipsing interactions.

Most damaging to this analysis is that none of these methods reproduces the experimental results: when the fully optimized structures are used, the calculated heats of hydrogenation do not give the trend that is being explained! We have sought first to find a computational technique which gives results in accord with experiment, and then to determine if numerical support for the very attractive Dewar–Holder hypothesis could be found.

Results and Dicussion

We first attempted, as have others before, to study these hydrocarbons with MM2.[10] Many of the shortcomings of MM2 come to the fore in triquinacene. These involve van der Waals

(2) a) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524. b) Doering, W. v. E.; Laber, G.; Vanderwahl, R.; Chamberlain, N. F.; Williams, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 5448. c) Reviews include Winstein, S. *Q. Rev.* **1969**, *23*, 141. Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.

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

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

(5) a) Bunzli, J. C.; Frost, D. C.; Weiler, L. *Tetrahedron Lett.* **1973**, *14*, 1159. b) Bischof, P.; Bosse, D.; Gleiter, R.; Kukla, M.; de Meijere, A.; Paquette, L. A. *Chem. Ber.* **1975**, *108*, 1218. c) Christoph, G. G.; Muthard, J. L.; Paquette, L. A.; Bohm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1978**, *100*, 7782.

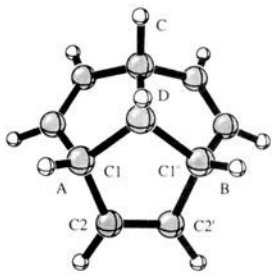
(6) a) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797. b) McEwen, A. B.; Schleyer, P. v. R. *J. Org. Chem.* **1986**, *51*, 4357.

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

(8) a) Osawa, E. *J. Am. Chem. Soc.* **1979**, *101*, 5523. b) Schulman, J. M.; Miller, M. A.; Disch, R. L. *J. Mol. Struct: THEOCHEM* **1988**, *169*, 563.

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

(10) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington DC, 1982.



	X-ray[a]	MM_3[b]
A–D	2.89	2.39
B–D	2.89	2.39
C–D	2.89	2.39
A–C1–C2	112.8	110.6
B–C1′–C2′	113.8	110.6

[a] Reference 4. [b] This work.

Figure 3. Low-temperature X-ray crystallographic and MM3 structural data for triquinacene.

1,4-interactions as well as the parameterization of cyclopentane and cyclopentene rings.[11] These problems have been largely corrected in MM3.[12]

The MM3 force field proved more successful.[13] The MM2, MM3, and experimental heats of formation are presented in Figure 2. The heats of formation of triquinacene and dihydro- and tetrahydrotriquinacene in the third column are based on the experimental ΔH_f of perhydrotriquinacene[14] and the respective heats of hydrogenation of **1**–**3**. Allinger has questioned the experimental ΔH_f for perhydrotriquinacene.[11e,14] Taking Allinger's MM3 ΔH_f for perhydrotriquinacene as a new reference, the rescaled heats of formation in the last column of Figure 2 are obtained. The result is a better matchup of MM3 with experiment.

MM3 does not predict the 4.5 kcal/mol lower heat of hydrogenation for **1** → **2** as compared to **2** → **3** and **3** → **4**, but it does give a value for the first hydrogenation that is nearly 2 kcal/mol lower than the other two, and is almost within experimental error of the measured value. There are also some discrepancies between the MM3 and X-ray crystallographic structures of triquinacene. A comparison of the low-temperature X-ray structure of triquinacene[14] with the MM3 structure shows a large systematic error in the calculated positions of hydrogens A, B, and C, as shown in Figure 3. MM3 places the hydrogens A, B, and C all 0.50 Å closer to D than in the X-ray structure. The discrepancy in these three atom positions is very large, but it should be present to a similar or smaller extent in MM3 structures of **1**–**4**.

Since MM3 better reproduces experimental trends for this system than other computational methods, we have analyzed the MM3 optimized structures to determine why the heat of hydrogenation of triquinacene is anomalously low. Adopting Dewar's approach, we have separated relaxation due to overall twisting from the other processes occurring during hydrogenation, Figure 4. The left column gives heats of formation and reaction for the constrained high-symmetry structures. Energy differences between the high-symmetry structures are hydrogenation energies without relaxation. Energy differences between high- and low-symmetry structures are defined as relaxation energies. Both the heats of hydrogenation without relaxation and the relaxation energies

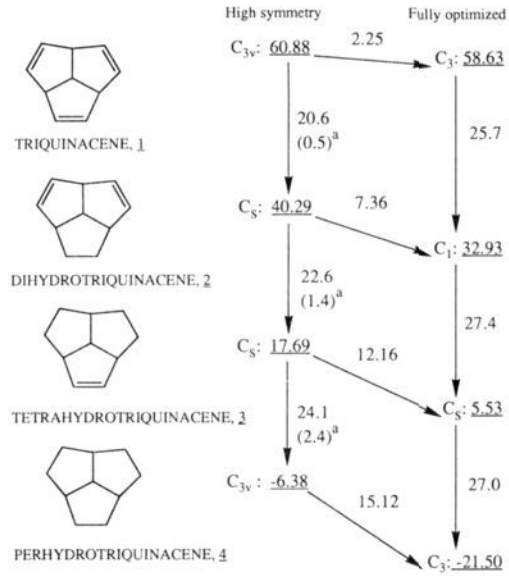
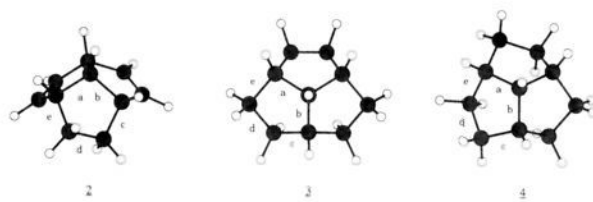


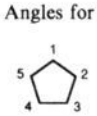
Figure 4. MM3 analysis of differential relaxation proposed by Dewar and Holder, ΔH_f (kcal/mol): (a) the MM3 calculated change in dipole–dipole interaction.



torsion angle (deg)	**2**	**3**	**4**
e–a–b	14	26	9
a–b–c	11	4	15
b–c–d	32	19	33
e–d–c	42	36	39
d–e–a	34	39	29

Figure 5. MM3 optimized structures of **2**–**4**. Torsional angles are shown for a cyclopentane ring in each molecule.

Table I. Calculated Torsion Angles for Cyclopentane[15]



	Pitzer and Donath		Hendrickson		MM3	
torsion angle	C_s	C_2	C_s	C_2	C_s	C_2
$\Phi_{12} = \Phi_{51}$	46.1	15.2	41.7	13.7	40.4	12.3
$\Phi_{23} = \Phi_{45}$	28.6	39.4	25.9	35.5	25.0	32.3
Φ_{34}	0.0	48.1	0.0	44.0	2.0	40.0

increase along the series. This is expected since the number of saturated rings relaxing also increases. The high-symmetry heats of formation differ by an additional 2 kcal/mol. This difference arises primarily from a change in the dipole-dipole interaction term which is substantial for **3** but zero for **4**. This is an additional feature contributing to the heats of hydrogenation not recognized by Dewar and Holder. With the dipole correction the heat of hydrogenation of each double bond then becomes roughly equivalent, forming the reference for this analysis.

We have analyzed ring strain relaxation from the distribution of torsional angles in the saturated rings. We first present some notes on cyclopentane. The envelope (C_s) and half-chair (C_2) conformers of cyclopentane are equal in energy even though the dihedral angles present in each structure are quite different. The envelope conformer in cyclopentane is characterized by one small

(11) a) Broeker, J. L.; Hoffman, R. W.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5006. b) Allinger, N. L.; Tribble, M. T.; Miller, M. A. Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1637. c) Allinger, N. L.; Dodzuik, H.; Rogers, D. W.; Naik, S. N. *Tetrahedron* **1982**, *38*, 1593. d) Allinger, N. L.; Geise, H. J.; Pyckhout, W.; Paquette, L. A. Gallucci, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1106. e) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551. f) Allinger, N. L.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8566.

(12) Allinger, N. L.; Li, F.; Yan, L. *J. Comput. Chem.* **1990**, *11*, 848.

(13) MM3 was obtained from the Technical Utilization Corp., 235 Glen Village Ct., Powell, OH 43065.

(14) Clark, T.; Mc O. Knox, T.; McKervey, M. A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404.

dihedral near 0°, while the half-chair is characterized by one large torsional angle near 48°. Table I shows the calculated torsional angles for cyclopentane from the literature and from MM3 for comparison.[15]

The presence of the two cyclopentene rings in **2** makes the envelope conformer in the saturated ring unattainable. In order for the saturated ring in dihydrotriquinacene to achieve the envelope conformation, one torsion angle running along the backbone would have to be zero and the neighboring torsion angle would have to be at least 25°. Geometrical constraints therefore enforce a half-chair conformation on the saturated portion of dihydrotriquinacene. This is the major difference between **2** and **3** or **4**. Thus, the saturated ring in dihydrotriquinacene (**2**) has the half-chair conformation, and the saturated rings in tetrahydrotriquinacene (**3**) and perhydrotriquinacene (**4**) are in envelope conformations (Figure 5). The consequence of the enforced half-chair in **2** is larger nonbonded 1,4-interactions relative to those in compounds **3** and **4**. A detailed analysis of the MM3 energy components revealed that the increase in steric energy between triquinacene and the optimized dihydrotriquinacene is mainly due to nonbonded 1,4-interactions such as those involving endo hydrogens on the saturated cyclopentane and carbons attached to the cyclopentane ring. The cyclopentanes in **3** and **4** can have envelope conformations because of increased backbone flexibility, not found in **2**. These envelope conformations are preferred because 1,4-interactions are reduced by the more even distribution of saturated ring dihedrals. The hydrogenation energies of **2** and **3** are larger than **1** primarily for this reason.

This simple analysis shows that geometrical constraints of dihydrotriquinacene prevent it from relaxing in the same way that **3**, **4**, or cyclopentane does relative to unsaturated analogues. There is still a small discrepancy between the MM3 calculated heat of hydrogenation of **1** (25.7 kcal/mol) and that found experimentally (21–25 kcal/mol).[16] The calculated heat of formation is 0.7 kcal/mol above the experimental range, but computations or experiment could easily be in error by this amount. Homoaromaticity in triquinacene, and in other neutral hydrocarbon systems, is vanishingly small.[17]

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research. We would also like to thank Professor N. L. Allinger for helpful comments.

Registry No. 1, 6053-74-3; **2**, 31678-74-7; **3**, 57595-39-8; **4**, 17760-91-7.

(15) Fuchs, B. In *Tropics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds; John Wiley & Sons: New York, 1978; Vol. 10, p 1.

(16) There are no major differences in MM3 entropies (85.4, 85.9, 86.2, and 82.7 cal/(mol·K), respectively) calculated from vibrational analysis of **1–4**.

(17) N. L. Allinger, private communication, reports the MM3 π-stabilization energy for triquinacene to be 0.52 kcal/mol versus the calculation with no π energy included. This corroborates our conclusion that homoaromatic stabilization is very small.

Effects of Geminate Recombination in Measurements of Rate Constants in Perturbation/Relaxation and NMR Line-Shape Experiments on Fast Bimolecular Reactions in Solution

John F. Garst

Contribution from the Department of Chemistry, The University of Georgia, Athens, Georgia 30602. *Received November 21, 1990*

Abstract: Geminate recombination plays an important role in the kinetics of a reversible bimolecular association A + B $\rightleftarrows$ C in solution. Since geminate pairs usually have mean lifetimes of 10^{-10} s or less, a pseudo-steady flux through geminate pairs is closely approached within about 10^{-9} s, after which the rate of geminate recombination is first order in C. Thus, geminate pairs behave as if they were sparsely populated subspecies of C, not independent molecules A and B. As a consequence, when reaction relaxation times longer than 10^{-9} s are measured, as in classical perturbation/relaxation or NMR line-shape experiments, geminate recombination is not detected, and the rate constants determined are those for the global forward and backward reactions, which consist, respectively, of nongeminate combination of A and B and of those bond cleavages in C that are followed by escape to independent A and B molecules. The global rate constants are the diffusion-influenced constants that are measured in many conventional kinetic experiments. These conclusions do not support the recent suggestion that perturbation/relaxation and NMR line-shape experiments measure the diffusion-independent, activation-control rate constants (Keizer, J. *J. Am. Chem. Soc.* **1990**, *112*, 7952).

The rate of a fast bimolecular reaction in solution, such as an association

$$A + B \rightleftarrows C \qquad (1)$$

is often determined through a perturbation/relaxation experiment on a system that is at equilibrium initially. In "classical" methods of this type, e.g., T-jump, E-jump, ultrasonic relaxation, etc., the measured relaxation times are greater than 10^{-9} s (and usually greater than 10^{-7} s).[1]

According to Eigen and others,[1,2] the value so determined is that of the diffusion-influenced or global rate constant k_G, which is analogous to the long-time, steady-state rate constant k_{SCK} of the theory of Smoluchowski, Collins, and Kimball (SCK) or Noyes.[3,4] Keizer proposes instead that it is the value of the

(1) See, for example: Cauldin, E. F. *Fast Reactions in Solution*; Wiley: New York, 1964.

(2) (a) Eigen, M. *Angew. Chem.* **1964**, *3*, 1. (b) Eigen, M.; Kruse, W.; Maass, G.; De Maeyer, L. *Prog. React. Kinet.* **1964**, *2*, 286. (c) Eigen, M. *Z. Phys. Chem. (Munich)* **1954**, *1*, 176.

(3) For a recent review, see: Rice, S. A. *Comprehensive Chemical Kinetics. Diffusion-Limited Reactions* Vol. 25. Bamford, C. H., Tipper, C. F. H., Compton, R. G., Eds.; Elsevier: Amsterdam, 1985.

(4) (a) Noyes, R. M. *J. Chem. Phys.* **1954**, *22*, 1349. (b) Noyes, R. M. *Prog. React. Kinet.* **1961**, 129.

0002-7863/92/1514-1168$03.00/0