to that of a hydrogen atom. Thus, it may be that no "rules" are violated in interpreting the greater cleavage of P–Cl bonds by an inversion route compared to cleavage of P–F bonds.

That the two forms, B and C, might arise in competition with each other in the first place most likely rests with a balance of relief of a certain degree of ring strain for the six-membered form favoring intermediate C. As Marsi[41,42] has shown in the alkaline cleavage of cyclic phosphonium salts varying in ring size from five to seven membered, the stereochemistry goes from 100% retention for reaction of a five-membered ring *cis*-phosphonium salt, to about 50% retention for reaction of the corresponding six-membered ring *cis*-phosphonium salt, and to 0% retention for reaction of the seven-membered ring salt, all with cleavage of the poor leaving group, benzyl.

Activated-state E may result as a kinetically favored initial intermediate if we assume that the α-naphthyl group is of sufficient size to sterically block the approach of the nucleophile opposite the endocyclic Si–O bond undergoing cleavage. Pseudorotation then brings the Si–O bond to a departing apical position. Intermediate D may gain relative stability to E with the use of a softer nucleophile. In addition to the relief of ring strain, hydrogen bonding may assist in the cleavage process as indicated in D.

Conclusion

The results of the calculations support the main proposals that have been used in phosphorus chemistry as expressed by Westheimer[4] and others.[43] It is felt that the treatment of apicophilicity presented in this paper shows variations that aid in interpreting nucleophilic displacement reactions of phosphorus and silicon. These interpretations are meant to serve as working hypotheses. The extent of their usefulness will only be known as future work in the area unfolds.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 8504737) is gratefully acknowledged. A major portion of this work was carried out at the San Diego Supercomputer Center where we were located on leave. We thank the National Science Foundation and San Diego Supercomputer Center for generous allocation of computer time and the staff at SDSC for their advice and encouragement.

Supplementary Material Available: Total energies (au) for trigonal bipyramids with H, F, and Cl substituents for (a) phosphorus and anionic silicon species computed with the 3-21G(*) and 3-21+G* basis sets, respectively (Table S1), (b) phosphorus species computed with the 6-31G* and 6-31G** basis sets (Table S2), and (c) anionic silicon species computed with the 6-31+G* basis set (Table S3) and bond lengths and charge densities for (d) phosphorus species computed with the 3-21G(*) and 6-31G* basis sets (Table S4) and (e) anionic silicon species computed with the 3-21+G* and 6-31+G* basis sets (Table S5) (13 pages). Ordering information is given on any current masthead page.

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Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 8. On the Homoaromatic Character of Triquinacene[1]

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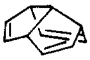
Contribution from the Department of Chemistry, City University of New York, Queens College, Flushing, New York 11367. *Received April 14, 1988*

Abstract: An ab initio molecular orbital study of the energetics of the successive hydrogenations of triquinacene provides no indication of homoaromatic stabilization of this system, a conclusion at variance with a recent thermochemical study. The absence of this effect persists even when energies are computed in the 6-31G* basis set to second order in electron correlation, and the contributions of zero-point energies and thermal corrections to enthalpies are taken into account.

I. Introduction

A recent investigation[2] of the heats of hydrogenation of triquinacene (**1**), dihydrotriquinacene (**2**), and tetrahydrotriquinacene (**3**) to hexahydrotriquinacene (**4**) found evidence of homoaromatic stabilization[3] in **1** to the extent of 4.5 kcal/mol. This result is surprising, as the authors observe, because spectroscopic (IR,[4a] UV,[4a] CD,[4b] PES[4c]) and structural[4d] data offer no evidence whatever of homoaromatic character in triquinacene. The rarity of homoaromatic character in neutral cyclic polyolefins such as **1**, together with considerations of electronic structure, leads to the observation that when three proximal π bonds interact the result is, in fact, destabilization rather than stabilization.[5]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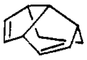
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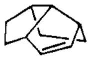
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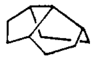
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The case for homoaromatic character in triquinacene is based solely upon thermochemical data; in view of this, we have carried

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Table I. Total Energies (au), Zero-Point Energies (kcal/mol) and Thermal Enthalpy Corrections (kcal/mol)[a]

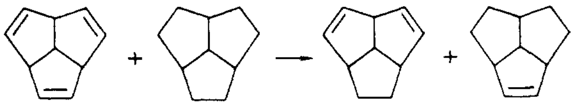
molecule	STO-3G	6-31G* SCF	6-31+G* SCF	6-31G* RMP2	zero-pt energy	H(298 K) H(0 K)
triquinacene	-379.8427	-384.4515	-384.4609	-385.7198	105.4	5.0
dihydrotriquinacene	-381.0612	-385.6386	-385.6458	-386.9198	119.5	5.3
tetrahydrotriquinacene	-382.2805	-386.8250	-386.8302	-388.1178	133.7	5.7
hexahydrotriquinacene	-383.4994	-388.0105	-388.0138	-389.3160	148.1	5.5
adamantane	-383.5153	-388.0265		-389.3336	149.3	5.0
cyclopentane	-192.8931	-195.1636	-195.1653	-195.8154	85.3[b]	3.60[c]
cyclopentene	-191.6736	-193.9772	-193.9811	-194.6164	71.1	3.46[c]

[a] Zero-point energies and values of H(298 K) − H(0 K) were calculated by the method of Boyd, ref 11. The 6-31+G* SCF and 6-31G* RMP2 energies were calculated at the 6-31G* SCF geometries. [b] Experimental value, see ref 16. [c] Rossini, F. D.; Pitzer, K. S.; Arnett, R. C.; Braun, R. M.; Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; Carnegie Press: Pittsburgh, 1953.

out a computational study of the thermochemistry of the hydrogenation reactions by means of accurate ab initio molecular orbital calculations and estimation of zero-point energies and thermal effects. In contrast to the experimental results, these calculations indicate no special stability for **1**.

II. Method

Consider homodesmic reactions I and II,[6] where triquinacene, dihydrotriquinacene, tetrahydrotriquinacene, and hexahydrotriquinacene are combined in I so as to balance the number of double bonds and, to a very good approximation, the extent of ring strain. Reaction II, which does not involve triquinacene, serves as a control. A computational test of the homoaromatic stabilization of triquinacene can be made by comparing the enthalpy changes for I and II derived from the experimental heats of hydrogenation[2] 4.5 ± 1.2 and 0.0 ± 1.0 kcal/mol, respectively, with values obtained by ab initio calculation.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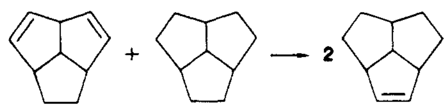
(II)

The enthalpy changes of I and II were calculated from the differences of total energies at the 6-31G*[7a] SCF and RMP2[8] levels using programs developed by us. Geometries were optimized at the STO-3G[7b] and 6-31G* SCF levels. The RMP2 energies (in the frozen-core approximation) were calculated at the 6-31G* SCF geometries and, in several cases, at STO-3G geometries as well. The molecules were also studied using the MM2[9] and AM1[10] methods. Differences in zero-point energies and changes in ΔH from 0 to 298 K were estimated by the molecular mechanics method of Boyd.[11]

The perspective drawings were obtained with Chem-X, developed and distributed by Chemical Design Ltd., Oxford, England.

III. Results

Geometry optimization of triquinacene in C_{3v} symmetry at the STO-3G and 6-31G* SCF levels has been reported previously.[12] The geometric parameters are in good agreement with those of the X-ray structure[4d] of triquinacene and with the corresponding parameters of cyclopentene calculated in the same basis sets. The 6-31G* distance between nonbonded π centers is 2.533 Å; the X-ray value is 2.546 Å. It has been suggested[13] that a distance less than 2.2 Å between nonbonded π carbons is required for homoaromatic stabilization.

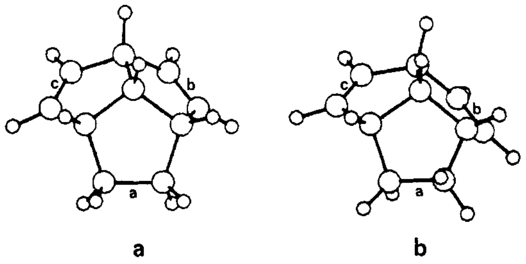

Figure 1. Perspective drawing of dihydrotriquinacene. The C_s and C_1 forms are depicted in (a) and (b), respectively.

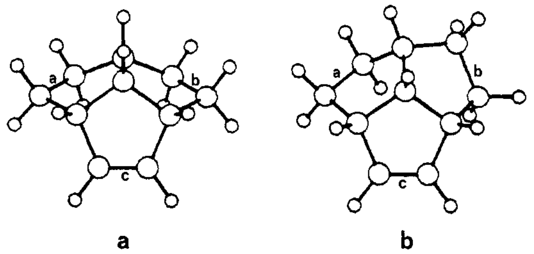

Figure 2. Perspective drawing of tetrahydrotriquinacene. The C_s and C_1 forms are depicted in (a) and (b), respectively.

An STO-3G study[14] and the present work show hexahydrotriquinacene (**4**) to have C_3 symmetry, in agreement with the results of molecular mechanics calculations.[15]

The lowest energy conformer of dihydrotriquinacene (**2**), depicted in Figure 1b, is devoid of symmetry; a C_s form, shown in Figure 1a, is found to be 3.3 kcal/mol higher at the 6-31G* SCF level, using STO-3G geometries, and 4.0 kcal/mol higher in MM2. The CCCC dihedral angles of **2** in the C_1 form, viewed along bonds labeled a, b, and c in Figure 1, are −37.5, −1.3, and −1.1°, respectively, at the 6-31G* SCF level; these angles in the C_s form are 0.0, −0.7, and 0.7°, respectively, in the STO-3G basis. The corresponding CCCC angles in hexahydrotriquinacene and triquinacene are −36.5 and 0.0°.

Tetrahydrotriquinacene (**3**) has two low-energy conformers, Figure 2, of which the most stable has no symmetry; a C_s form lies 0.9 kcal/mol higher at the 6-31G*//STO-3G level and 0.2

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kcal/mol higher according to MM2. The C_1 structure has dihedral angles of −37.0, −30.7, and −1.3°, for a, b, and c, respectively; the corresponding angles in the C_s form are −28.8, 28.8, and 0.0°.

The ab initio energies of the most stable conformers of **1**–**4** are given in Table I, together with values for cyclopentane and cyclopentene. The table also contains zero-point energies and thermal effects on the enthalpy. The zero-point energy differences for reactions I and II, computed by Boyd's method, are only −0.3 and −0.2 kcal/mol, respectively. The zero-point energy differences obtained from the AM1 frequencies are 0.0 kcal/mol in each case, as are those given by an empirical formula.[16] For hydrocarbons, zero-point energies and thermal effects are closely related to stoichiometry. It is therefore not surprising that the combined zero-point energy and thermal enthalpy corrections for the isomerization reactions I and II are only 0.2 and 0.4 kcal/mol.

The computed enthalpy change of reaction I is −0.8 and −0.9 kcal/mol at the 6-31G* SCF and RMP2 levels; these values differ significantly from the experimental value of +4.5 ± 1.2 kcal/mol. In contrast, the calculated ΔH's for II are −0.2 and 0.5 kcal/mol at the SCF and RMP2 levels, in good agreement with experiment, 0.0 ± 1.0 kcal/mol. That both I and II are essentially thermoneutral is due to the nearly identical differences in total energies **1**–**2**, **2**–**3**, and **3**–**4** 1.1863 ± 0.0008 and 1.1990 ± 0.001 au at the two levels. These values are essentially the same as the energy differences between cyclopentene and cyclopentane, 1.1864 and 1.1990 au at the 6-31G* SCF and RMP2 levels.

We have also calculated the SCF energies of **1**, **2**, **3**, **4**, cyclopentane and cyclopentene in the 6-31+G* basis[7c] using the 6-31G* geometries; the energies are given in Table I. It is possible that π interactions between nonbonded carbons 2.533 Å apart are not treated adequately in the 6-31G* basis, but the 6-31+G* basis, which contains a diffuse sp shell of exponent 0.0438 on carbon, should be sufficient; the diffuse atomic orbitals have maxima at ca. 1.8 Å from their atomic centers. The 6-31+G* ΔH values obtained for I and II are −0.6 and −0.1 kcal/mol, respectively, virtually the same as the 6-31G* SCF values. The differences in total energies of **1**–**2**, **2**–**3**, and **3**–**4** are 1.1843 ± 0.0007 au with that of **1**–**2**, 1.1849 au, the largest; the difference in total energies of cyclopentene and cyclopentane is 1.1842 au.

Note that I may be combined with various multiples of II to yield homodesmic reactions (e.g., I + II) from which either **2**, **3**, or **4** is absent; the enthalpy changes for all of these are nearly zero by calculation and +4.5 kcal/mol according to experiment. This is the principal result of the present work.

The AM1 method leads to heats of reaction almost identical with the ab initio values, namely, −0.5 and −0.1 kcal/mol for I and II, respectively. Thermoneutrality of I and II is also predicted by the molecular mechanics method of Boyd, and by MM2 and MMP2.[13] Thus, none of the theoretical models applied here indicates special stability for **1**.

While there is a conflict between experiment and theory, we cannot say where the problem lies. It is possible that inclusion of higher orders in the perturbation expansion of the correlation energy and/or use of larger basis sets would furnish a ΔH for I closer to the experimental value while retaining the good agreement for II. An important reason for considering the role of correlation effects here is the error in the calculated heat of the reaction (including zero-point energies and thermal effects)

benzene + (3)ethylene → (3)butadiene

3.7 and 7.9 kcal/mol at the 6-31G* SCF and RMP2 levels, respectively.[6d] (The error at the RMP4 level can be estimated to be 3.3 kcal/mol.[17]) Note, however, that both levels err in overestimating the stability of the aromatic system, while reconciliation of the calculated heat of reaction I with experiment requires an error of underestimation. Moreover, the errors for benzene apply to an aromatic system; smaller errors would reasonably be expected for a homoaromatic system. Finally, whereas for benzene there is a large disparity in the heat of reaction at the SCF and RMP2 levels, suggestive of additional correlation effects, these two levels of theory furnish almost identical values of ΔH for reaction I.

Table II. Enthalpies of Reaction (kcal/mol)[a]

reaction[b]	STO-3G	6-31G* SCF	6-31+G* SCF	6-31G* RMP2	expt[c]
I	0.5	−0.8	−0.6	−0.9	4.5 ± 1.2
II	0.2	−0.2	−0.1	0.5	0.0 ± 1.0
1 → **4**	−78.7	−79.7	−80.0	−79.3	−78.0 ± 0.5
2 → **4**	−52.7	−52.7	−53.0	−52.1	−55.0 ± 0.4
3 → **4**	−26.4	−26.3	−26.4	−26.3	−27.5 ± 0.3

[a] Zero-point energies and thermal corrections are included. [b] These reactions are not all independent. [c] Reference 2.

IV. Discussion

The heats of homodesmic reactions I and II can be calculated with greater accuracy than the heats of hydrogenation of **1**, **2** and **3** to **4**, which require reference molecules outside the series. With this caveat, we turn to a brief discussion of the heats of hydrogenation in the 6-31G* basis. (All energies are in kcal/mol, with the RMP2-derived values in parentheses.)

The heat of hydrogenation of triquinacene to hexahydrotriquinacene can be estimated from the homodesmic reaction

triquinacene + (3)cyclopentane →
hexahydrotriquinacene + (3)cyclopentene (III)

The 6-31G* ab initio enthalpy change for this reaction, when combined with the zero-point energy and thermal effects on ΔH, is 0.3 (0.7). The heat of hydrogenation of cyclopentene to cyclopentane, measured in the vapor phase at 355 K[18a] and corrected, as an ideal gas, to 298 K is −26.67 kcal/mol.[18b] (A value of −26.94 for the heat of hydrogenation of cyclopentene in hexane is reported in ref 2.) From these data the enthalpy difference between hexahydrotriquinacene and triquinacene at the 6-31G* level is −79.7 (−79.3), in fair agreement with the experimental value, −78.0 ± 0.5.

Using a reaction analogous to III for dihydrotriquinancene,

dihydrotriquinacene + (2)cyclopentane →
hexahydrotriquinacene + (2)cyclopentene (IV)

we find the heat of reaction to be 0.7 (1.3), which leads to a calculated heat of hydrogenation for **2** → **4** of −52.7 (−52.1); the experimental value is −55.0 ± 0.4. Finally, for

tetrahydrotriquinacene + cyclopentane →
hexahydrotriquinacene + cyclopentene (V)

the 6-31G* heat of reaction is 0.4 (0.4), leading to a calculated heat of hydrogenation for **3** → **4** of −26.3 (−26.3). The experimental value is −27.5 ± 0.3.

Comparison of the three heats of hydrogenation with their experimental counterparts (Table II) exhibits the disagreement, especially for **2** → **4**. More important, for the successive hydrogenations **1** → **2**, **2** → **3**, and **3** → **4**, the computed values are −27.0 (−27.2), −26.4 (−25.8), and −26.3 (−26.3), compared with the experimental values of −23.0, −27.5, and −27.5. The experimentally derived result for **1** → **2** indicates the special stability of triquinacene attributed to homoaromatic character. We find no theoretical confirmation of this result; indeed, this reaction is predicted to be the most exothermic of the three. Moreover, the thermoneutrality of II (as well as of I) argues against the presence even of (linear) homoconjugation, as distinct from (cyclic) homoaromatic conjugation.

An experimental value of ΔH_f of hexahydrotriquinacene (**4**) is −24.47 ± 0.86.[19] We have previously reported[14] a calculated ΔH_f of −24.0 for **4** based upon the ab initio ΔH of isomerization of **4** to adamantane at the 6-31G* SCF level (−10.2), the experimental ΔH_f of adamantane (−32.51[6c]), and a zero-point energy

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Table III. Derived Heats of Formation (kcal/mol)[a]

molecule	6-31G* SCF (RMP2)	expt
1	57.0 (56.6)	53.5[b]
2	30.0 (29.4)	30.5[b]
3	3.6 (3.6)	3.0[b]
4	−22.7	−24.47 ± 0.86[c]

[a] The heat of formation of **4**, calculated as described in the text, and the heats of formation of **1**, **2**, and **3** derived from that of **4** and the 6-31G* SCF (RMP2) heats of hydrogenation, Table II. [b] Calculated from the experimental heat of formation of **4** and the experimental heat of hydrogenation, ref 2. [c] Reference 19.

difference (2.2) between **4** and adamantane obtained using the molecular mechanics method of Warshel.[20] In the present work we have computed the 6-31G* RMP2 isomerization energy of **4** → adamantane to be −11.0 and the zero-point energy difference to be 1.2 using the Boyd molecular mechanics method (0.9 in AM1). Given the differences in the ab initio isomerization energies and the uncertainties in the zero-point energy and experimental heat of formation of adamantane, we revise our earlier estimate of the ΔH_f of hexahydrotriquinacene to −22.7 ± 1.0. Although this value is in slight disagreement with experiment, it does encompass the values of −23.1, −22.6, and −22.1 obtained with the group equivalent methods of Wiberg[21] and Ibrahim et al.,[22] and with MM2.[9]

Using −79.7 (−79.3) for the enthalpy change of **1** → **4** and −22.7 for the heat of formation of hexahydrotriquinacene, we predict ΔH_f of triquinacene to be ca. 57.0 (56.6). For comparison, the empirical method of Ibrahim et al.[22] (with our 6-31G* SCF energy) gives a ΔH_f of 53.0; its value for the ΔH_f of cyclopentene is too low by 1.4. Using −22.7 and the heats of hydrogenation (Table II), the heats of formation of **2** and **3** are estimated to be 30.0 (29.4) and 3.6 (3.6), respectively. These results are collected in Table III. The respective MM2 energies of **1**, **2**, **3**, and **4** are 59.8, 32.2, 5.3, and −22.1 kcal/mol, in reasonable agreement with the ab initio results.

Acknowledgment. This research was supported, in part, by grants 663228, 665218, 666356, and 667253 of the PSC-CUNY Research Award Program and a grant of computing time from the City University Committee on Research Computing. We thank Professor Paul v. R. Schleyer for interesting us in this problem and for sharing his AM1 and MNDO results with us. We acknowledge several interesting discussions with Professor Donald W. Rogers. We thank Dr. Robert Haddon for a copy of his program.

Registry No. 1, 6053-74-3; **2**, 31678-74-7; **3**, 57595-39-8; **4**, 17760-91-7; adamantane, 281-23-2; cyclopentane, 287-92-3; cyclopentene, 142-29-0.

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Chemical Hardness and Bond Dissociation Energies

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Abstract: An empirical method is proposed to rank order Lewis acids and bases in terms of their local hardness, $\bar{\eta}$, at their reaction sites. The method uses bond energy differences between two acids (or bases) of different chemical hardness. The assumption is made that in an exchange reaction, A:B′ + A′:B = A:B + A′:B′, the most stable pair will match the softest acid with the softest base, and the hardest acid with the hardest base. The relative values of $\bar{\eta}$ obtained in this way for many cations and anions are both consistent and logical for the most part. The few exceptions have simple explanations.

Recently two new chemical concepts have been derived from density functional theory.[1,2] These are the absolute electronegativity, χ, and the absolute hardness, η. The exact and approximate definitions of these quantities are $\chi = (\partial E/\partial N)_v \simeq (I + A)/2$, and $\eta = -{}^1/_2(\partial\chi/\partial N)_v \simeq (I - A)/2$. E is the electronic energy, N the number of electrons, v the potential of the nuclei, I the (vertical) ionization potential, and A the (vertical) electron affinity. The relationships apply to any isolated chemical system, atom, ion, molecule, or radical. A number of values of χ and η have been calculated for various system, using experimental values of I and A.[3]

χ must be a constant, the same at every point in a chemical system. The hardness, however, allows for local values, $\bar{\eta}$;[4] η is the global, or average, value. The softness, σ, is simply the reciprocal of η.

If two chemical systems, X and Y, are brought into contact, electrons will flow from the one of lower χ to that of higher χ until the electronegativities become equalized. An approximate value for ΔN, the number of electrons transferred, is given by

$$\Delta N = (\chi_X - \chi_Y)/2(\eta_X + \eta_Y) \quad (1)$$

Equation 1 has been found useful for a number of reactions between neutral species.[3,5] A large value of ΔN gives rise to strong bonds, or to low energy barriers. However, it is far from a complete prescription for bonding.

The concept of chemical hardness was first introduced to describe Lewis acids and bases.[6] The definitions used were only qualitative, essentially emphasizing polarizability as the major factor. In simple MO theory, the quantity 2η is the energy gap

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