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AB-INITIO HEATS OF FORMATION OF MEDIUM-SIZED HYDROCARBONS. 4. PERHYDROTRIQUINACENE

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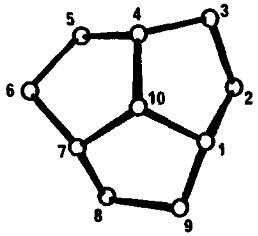
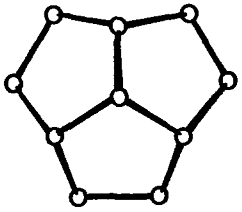
Summary: The ΔH_f of perhydrotriquinacene is obtained from that of adamantane and their enthalpy of isomerization computed by ab initio SCF methods, with corrections for zero-point and thermal effects.

As molecular mechanics is increasingly employed in the study of molecular energetics, it is desirable to examine cases in which its predictions differ from experiment. This note considers perhydrotriquinacene (I), tricyclo[5.2.1.$0^{4,10}$]decane, for which molecular mechanics gives heats of formation of -23.74 (EAS)[1a], -19.74 (MM1)[1a], -22.07 (MM2)[1b,1c] and -23.46 (WB)[2a] kcal/mol. The experimental value is -24.47±.86 kcal/mol[2].



Ia



Ib

We have recently reported ab initio calculation of ΔH_f for the perhydrotriquinacene isomer, adamantane[3]; here we calculate the energy difference between (I) and (II), and correct for zero-point energy differences and enthalpy changes in going from from 0 K to 298 K. This enthalpy of isomerization,when combined with the experimental ΔH_f of adamantane, furnishes that of perhydrotriquinacene, also of formula $(CH_2)_6(CH)_4$.

The geometry of perhydrotriquinacene was optimized in the STO-3G[4a] basis set for both C_3 (Ia) and C_{3v} (Ib) symmetries using gradient methods; their energies are -383.4994 and -383.4837 au, respectively (that of adamantane is -383.5155 au, slightly lower than reported previously[3] due to improved optimization). The geometric parameters for I are given in Table I. SCF calculations in the 6-31G* basis set[4b] at these geometries give: -388.0098 au, -387.9875 au, and -388.0259 au for (Ia), (Ib), and (II), respectively; the latter value is only 0.6 kcal/mol higher than that corresponding to the 6-31G*-optimized geometry.

The ab initio energy changes for the isomerization of (I) to (II) are:10.1 and 10.2 kcal-mol^{-1} at the STO-3G and 6-31G* levels, respectively (before rounding). To correct for differences in zero-point energies and to change ΔH from 0 K to 298 K, we computed the vibrational frequencies of (I) and (II) using the molecular mechanics method of Warshel and Lifson[5]. This yields zero-point energies for adamantane and perhydrotriquinacene of 149.6 and 147.4 kcal/mol, the former value comparing favorably with 148.9 and 148.6 kcal/mol calculated from the frequencies of adamantane given by Cyvin. et al.[6a] and by Snyder and Schactschneider[6b], respectively; Boyd, et al.[7] reported the zero-point energy of (II) to be 149.29 kcal/mol. In assessing the accuracy of the 2.2 kcal/mol difference in zero-point energies, it is noteworthy that Boyd, et al.[7] find that the zero-point energy of tetrahydrodicyclopentadiene (with two fused cyclopentanes rather than the present three) is 1.1 kcal/mol lower than that of adamantane. Also, our empirical formula for the zero-point energies of hydrocarbons gives 146.5 kcal/mol for $C_{10}H_{16}$[8], within 1 kcal/mol of the value for (I).

The frequencies also enable calculation of $H_{298\ K} - H_{0\ K}$ for each isomer in the harmonic oscillator and ideal gas approximations, giving 5.5 kcal/mol and 5.0 kcal/mol for (I) and (II), respectively. Thus, ΔH (298 K) for the transformation of (I) to (II) is computed as: $-10.2 + (149.6 - 147.4) + (5.0 - 5.5) = -8.5$ kcal/mol. Using the experimental value for adamantane, -32.51 kcal/mol[9], ΔH_f (298 K) of perhydrotriquinacene is -24.0 kcal/mol, in good agreement with the experimental value, -24.47±.86 kcal/mol[2].

The C_{3v} isomer is considerably higher in energy than (Ia). Osawa[1c] and Ermer[1d] report more than one conformational minimum for perhydrotriquinacene; the global minimum is of C_3

Table I. Geometrical Parameters of Perhydrotriquinacene in C_3 and C_{3v} Symmetry[a] Obtained from the STO-3G Basis Set

Ia (C_3)				Ib (C_{3v})			
Bond Length (A)							
C_1C_{10}	1.557	C_2H_{2n}	1.087	C_1C_{10}	1.555	C_2H_{2n}	1.086
C_1C_2	1.547	C_2H_{2x}	1.088	C_1C_2	1.557	C_2H_{2x}	1.087
C_2C_3	1.544	C_3H_{3n}	1.087	C_2C_3	1.552	$C_{10}H_{10}$	1.087
C_3C_4	1.552	C_3H_{3x}	1.087	C_1H_1	1.088		
Bond Angle (Degrees)							
$C_2C_1C_{10}$	105.3	$H_1C_1C_2$	110.9	$C_2C_1C_{10}$	107.4	$H_{2x}C_2C_1$	110.1
$C_3C_4C_{10}$	105.6	$H_1C_1H_{10}$	111.1	$H_1C_1C_{10}$	109.7	$H_{2x}C_2C_3$	110.3
$C_1C_{10}C_4$	107.3	$H_{3n}C_3C_4$	110.2	$C_1C_{10}C_4$	107.4	$H_{2n}C_2C_1$	110.8
$H_{2n}C_2C_1$	112.5	$H_{3n}C_3C_2$	109.8	$H_{10}C_{10}C_1$	110.2	$H_{2n}C_2C_3$	110.5
$H_{2n}C_2C_3$	112.4	$H_{3x}C_3C_4$	112.0				
$H_{2x}C_2C_1$	109.6	$H_{3x}C_3C_2$	112.3				
$H_{2x}C_2C_3$	109.8	$H_{10}C_{10}C_1$	111.6				
Torsion Angle (Degrees)							
$C_1C_2C_3C_4$	-35.5			$C_1C_2C_3C_4$	0.0		
$C_2C_3C_4C_{10}$	26.6			$C_{10}C_1C_2C_3$	-1.8		
$C_3C_4C_{10}C_1$	-7.7			$C_3C_4C_{10}C_1$	-2.9		
$C_4C_{10}C_1C_2$	-14.0						
$C_{10}C_1C_2C_3$	30.4						

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a. The hydrogens are numbered in the same manner as the carbons to which they are attached. The subscripts n and x refer to hydrogens pointing toward and away from the cup-shaped carbon cavity, respectively.

symmetry while the C_{3v} structure is found to be a maximum[1d]. The present 6-31G* ab initio energy difference between the C_3 and C_{3v} structures, 14.0 kcal/mol is in good agreement with the Ermer and Osawa molecular mechanics values, 12 and 13 kcal/mol, respectively.

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