Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 7. The [*n*]Prismanes[1]

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Abstract: Ab initio calculations on the [*n*]prismanes in D_{nh} symmetry have been performed at the STO-3G, 3-21G, and 6-31G* SCF levels, including geometry optimization and vibrational frequencies. The heats of formation of pentaprismane and hexaprismane are calculated from their 6-31G*(RMP2) energies in conjunction with homodesmic reactions. These provide an assessment of the accuracy of several methine group equivalent schemes and thereby furnish accurate heats of formation for heptaprismane, octaprismane, and nonaprismane.

I. Introduction

The [*n*]prismanes belong to that class of saturated hydrocarbons which are assemblies of even numbers of methine groups, i.e., have structural formula $(CH)_{2n}$. The class includes the well-known polyhedral hydrocarbons tetrahedrane, cubane (tetraprismane), and dodecahedrane, a number of semiregular polyhedral hydrocarbons other than prismanes, and many structures of lower symmetry. Indeed, Balaban has shown that for $n = 5$ and 6 there are respectively 9 and 32 members of this class.[2]

For each value of *n* there is only one prismatic graph, which must be nonseparable and limited to two *n*-membered rings and *n* four-membered rings. An indefinitely large number of configurations may have this graph, including a truly prismatic configuration of D_{nh} symmetry. Few hydrocarbons of this class, prismatic or otherwise, are known. Their syntheses continue to challenge the experimentalist, while they provide the theorist with a large testing ground for various levels of molecular structure calculation.

The purpose of this work is the ab initio theoretical study of the geometries and energetics of the smaller [*n*]prismanes. We have carried out geometry optimization constrained to D_{nh} symmetry at the SCF level in the STO-3G, 3-21G, and 6-31G* basis sets. We have also computed the 6-31G*(RMP2) energies of pentaprismane, the largest of the three known prismanes,[3-5] and hexaprismane.[6] RMP2 energies for triprismane and cubane were reported previously.[7,8] Finally, we have determined the force field of the D_{nh} structures at the STO-3G(SCF) level for $n = 5$–12 and at the 3-21G(SCF) level for $n = 6$ and 8.

The results reported here and recent developments in computational strategies for thermochemistry enable us to predict the heats of formation of the prismanes through $n = 9$ to high accuracy. A comparison with recent molecular orbital[9,10] and molecular mechanics studies[11] is made.

Table I. Geometric Parameters (in Å and deg) of the [*n*]Prismanes[a,b]

n	R_1	R_2	R_{CH}	HCC angle
3	1.549 (1.556)	1.507 (1.513)	1.074 (1.081)	132.5 (132.0)
4	1.559 (1.561)	1.559 (1.561)	1.081 (1.086)	125.3 (125.3)
5	1.558 (1.559)	1.552 (1.557)	1.082 (1.089)	123.3 (123.2)
6	1.553 (1.557)	1.551 (1.556)	1.083 (1.087)	121.5 (121.3)
7	1.553 (1.558)	1.553 (1.558)	1.084 (1.088)	119.8 (119.4)
8	1.551 (1.558)	1.556 (1.561)	1.084 (1.089)	118.7 (118.1)
9	1.550 (1.557)	1.561 (1.565)	1.084 (1.089)	117.8 (116.9)

[a] Geometries optimized at the 6-31G* and STO-3G SCF levels, with the latter values in parentheses. [b] R_1 and R_2 are the CC bond lengths between and within the *n*-membered rings, respectively. The HCC angles tabulated are ϕ_1, involving the CC bond parallel to the prism axis. Values for the other HCC angle, ϕ_2, are 129.7, 125.3, 119.4, 115.2, 112.1, 109.6, and 107.6°, for $n = 3$–9, respectively, in the 6-31G* basis.

Table II. Total Energies of the [*n*]Prismanes[a] (au) in D_{nh} Symmetry

	SCF			RMP2
n	STO-3G	3-21G	6-31G*	6-31G*
3	−227.7440	−229.1997	−230.5033	−231.2691
4	−303.7814	−305.6959	−307.3939	−308.4137
5	−379.8436	−382.2248	−384.3418[b]	−385.6262
6	−455.7951	−458.6351	−461.1957[c]	−462.7377
7	−531.6964	−534.9993	−538.0095	
8	−607.5735	−611.3481	−614.8029	
9	−683.4253[d]	−687.6758	−691.5732	

[a] SCF energies are for geometries optimized in that basis; the RMP2 values were computed at the 6-31G*(SCF) geometries. The RMP2 energy of cubane at the RMP2 geometry is −308.4147 au. [b] This energy at the STO-3G geometry is −384.3415 au. [c] The energy of the isomer in the form of a truncated tetrahedron is −461.2925 au. [d] The STO-3G energies for $n = 10$–14 are −759.2631, −835.0909, −910.9102, −986.7235, and −1062.5320 au, respectively.

II. Computational Methods

Geometries of the [*n*]prismanes were optimized at the SCF level in D_{nh} symmetry in the basis sets: STO-3G[12] for $n = 3$–14; 3-21G[13] for $n = 3$–9; and 6-31G*[14] for $n = 3$–9. The 6-31G*(RMP2) calculations were performed at the 6-31G*(SCF)-optimized geometries with the frozen-core approximation,[15] which excludes correlation contributions from the carbon 1s-like molecular orbitals. All ab initio calculations were carried out with optimized programs developed by us (The Queens College Quantum Chemistry Package).

III. Geometries

Table I contains the STO-3G and 6-31G* geometric parameters for the D_{nh} structures, $n = 3$–9. Here R_1 and R_2 are the CC bond lengths parallel to the prism axis and within the *n*-membered rings, respectively. The HCC angle ϕ_1 is formed from the CH bond and the CC bond parallel to the prism axis; the other HCC angle is denoted ϕ_2.

The calculated R_1 and R_2 values are fairly constant throughout the [*n*]prismane series beginning with $n = 4$: 1.550–1.561 and 1.556–1.565 Å in the 6-31G* and STO-3G basis sets, respectively.

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The only large differences are found for triprismane, where the 6-31G* R_1 and R_2 values are 1.549 and 1.507 Å, respectively. These bond lengths are similar to the 6-31G* values for cyclopropane and cyclobutane, 1.549 and 1.497 Å. The short CH bond length in triprismane, 1.081 and 1.074 Å in STO-3G and 6-31G*, respectively, is consistent with the 36.4% s-character ($sp^{1.75}$) in the carbon hybrid orbital of the CH bond, found in a semiempirical treatment.[16]

The [*n*]prismane R_1 and R_2 values are in reasonable agreement with the experimental values for substituted triprismanes,[17] cubane,[18] and prismanecarboxylic acid.[19] The X-ray-determined CC bond length of cubane, 1.551 Å,[18] is reasonably well reproduced at the SCF level: 1.559 Å (6-31G*),[20] 1.582 Å (3-21G), and 1.561 Å (STO-3G), although the 3-21G value is rather large. The geometry was also optimized at the 6-31G*(RMP2) level, yielding R_{CC} = 1.566 Å, R_{CH} = 1.095 Å, and an energy of −308.4147 au, which is only 0.6 kcal/mol lower than the value obtained at the 6-31G*(SCF) geometry. Note that the 6-31G*(RMP2) bond length is in slightly poorer agreement with experiment than the 6-31G*(SCF) value.

The [*n*]prismane HCC angle, ϕ_1, decreases monotonically from 132.5° for $n = 3$ to 117.8° for $n = 9$ in the 6-31G* basis; similar ϕ_1 values are found with the STO-3G and 3-21G basis sets. The decrease in ϕ_1 parallels the increase in the CCC angle of the *n*-membered rings which is required by symmetry to have the value $180-360/n$ deg. It is well known that an increase in an angle at a saturated carbon is accompanied by a decrease in the opposing angle.[21] The angle ϕ_1 also decreases with *n* so as to minimize the increase in eclipsing interactions between vicinal hydrogens of the same *n*-membered ring.[22] For hexaprismane the vicinal H–H distance is about 2.61 Å, whereas for octaprismane it is 2.28 Å.

For substituted triprismanes, ϕ_1 ranges from 125 to 127°[17] versus the 6-31G* value of 132.5° obtained here for the parent compound. Pentaprismanecarboxylic acid has a CCC angle involving the carboxyl carbon analogous to ϕ_1 of the parent compound; its value of 124.7°[19] is similar to that of ϕ_1, 123.3°. It is noteworthy that bicyclo[2.2.0]hexane contains fused four-membered rings in an otherwise acyclic structure. Ab initio calculations at the 4-31G level[23] show the analogues of angles ϕ_1 and CCC to be ca. 124° and 117°, respectively, which are close to their counterparts in pentaprismane.

The optimized geometries of the [*n*]prismanes produced by MM2[11] differ from the ab initio results. Anomalously small values of ϕ_1 are found for $n = 5–8$,[11,24] e.g., 116.6° in pentaprismane versus 123.3° obtained at the 6-31G* level. The AM1 and MNDO values[9,10] of ϕ_1 are in good agreement with the ab initio results. However, R_1 exceeds R_2 for larger *n* (as is also the case with MM2), in contrast to the ab initio results where they are similar for $n > 3$.

Force-field calculations at the SCF level through $n = 12$ (STO-3G) and for $n = 6$ and 8 (3-21G) furnish real vibrational frequencies for the D_{nh} structures. For $n = 6$, the lowest frequencies are 480 (STO-3G) and 431 cm^{-1} (3-21G), while for $n = 8$ they are 248 and 183 cm^{-1} in the same basis sets. Distortion of octaprismane according to the eigenvector of its 3-21G force-constant matrix having the lowest eigenvalue, of E_{2u} symmetry, leads to the structure depicted in Figure 1. Both the ab initio and the AM1 calculations reported previously[10] contradict the MM2 result that octaprismane prefers a crown-like D_{4d} structure.[11]

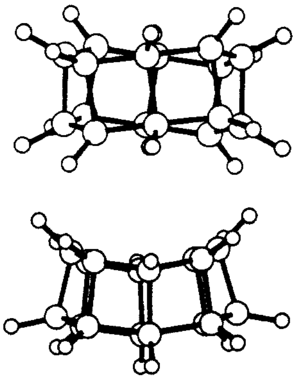

Figure 1. Two views of octaprismane distorted according to the eigenvector of its 3-21G force-constant matrix having the lowest eigenvalue. The symmetry is D_{2d}. The extent of the distortion has been exaggerated for clarity.

The question of how large *n* can be such that a truly prismatic configuration of D_{nh} symmetry is a minimum on the $(CH)_{2n}$ potential energy surface cannot be answered conclusively on the basis of the force-field analyses we have carried out thus far. In the STO-3G basis set, a minimum is obtained to $n = 12$, but the steady decrease in the lowest frequency from $n = 6–12$ suggests the approach of instability resulting from increasing angle strain in the carbon framework and eclipsing of vicinal hydrogens. The lowest frequencies obtained for $n = 10$, 11, and 12, viz., 149, 114, and 110 cm^{-1}, respectively, probably reflect over-stabilization of the prismatic configuration by the STO-3G basis. It seems unlikely that a kinetically stable structure of D_{nh} symmetry exists beyond $n = 9$ or 10.

The symmetry species of the vibrational modes of the D_{nh} prismanes are given in the Appendix.

IV. Energies

A. Pentaprismane. In previous studies we demonstrated the efficiency of using 6-31G*(RMP2) energies for the calculation of the heats of formation of hydrocarbons.[7] The ΔH for a homodesmic reaction[25,26] containing the molecule of interest is calculated by using ab initio energies, zero-point energies, and thermal corrections from 0 to 298 K. This presumably accurate heat of reaction is then used in conjunction with the known heats of formation of the other reactants and products to furnish the desired ΔH_f.

For the [*n*]prismanes, the simplest such reaction is

$$2n\,\text{isobutane} \rightarrow [n]\text{prismane} + 3n\,\text{ethane} \qquad (1)$$

When applied to cubane at the 6-31G*(RMP2) level, the calculated ΔH_f is found to be 148.5 kcal/mol, which is nearly identical with the experimental value, 148.7 ± 1.0 kcal/mol.[27] For triprismane, 6-31G*(RMP2) calculations give a ΔH_f of 136.4 kcal/mol.[7]

The pentaprismane ab initio 6-31G*(RMP2) energy at the SCF-optimized geometry is −385.6262 au. Its zero-point energy was determined from an empirical formula to be 103.8 kcal/mol,[28] while H(298 K) − H(0 K) was estimated to be 3.9 kcal/mol by interpolation from values for triprismane, cubane, and dodecahedrane. Use of reaction 1 for $n = 5$ with these data gives 119.6

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(20) These bond lengths are more accurate than those reported previously, due to improved optimization. The RMP2 energy based on the revised 6-31G* geometry is 0.0003 au lower than that given in ref 8.

(21) Such a result was found, for example, in an ab initio study of distorted methanes having C_{2v} symmetry (private communication from I. Shavitt).

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Table III. Heats of Formation and Strain Energies of the [*n*]Prismanes (kcal/mol)

n	from 6-31G*(RMP2) homodesmic cycles	from IS methine group equiv[a]	$\Delta H_f/2n$[b]	(SE)[e]
3	136.4	136.2	22.7	148.7
4	148.5[c]	146.3	18.6	164.9
5	119.6	120.5	12.0	140.1
6	153.1[d]	153.6	12.8	177.7
7		212.0	15.1	240.7
8		283.1	17.7	315.9
9		368.7	20.5	405.6

[a] See text for a discussion of the methine group equivalents. [b] Calculated from the 6-31G*(RMP2) values for $n = 3$–6 and the IS group equivalents for $n = 7$–9. [c] The experimental heat of formation is 148.7 kcal/mol. [d] Average of the two RMP2-derived values. [e] Calculated from eq 3.

kcal/mol as the heat of formation of pentaprismane.

Use of the homodesmic disproportionation reaction

$$2\,[4]\text{prismane} \rightarrow [3]\text{prismane} + [5]\text{prismane} \qquad (2)$$

at the RMP2 level also provides a ΔH_f of 119.6 kcal/mol, as expected, because the RMP2-derived and experimental values for the cubane ΔH_f are nearly identical and the calculated triprismane ΔH_f was employed.

B. Hexaprismane. The hexaprismane ab initio 6-31G*(RMP2) energy at the SCF-optimized geometry is −462,7377 au; its zero-point energy was determined to be 125.8 kcal/mol[28] and H(298 K) − H(0 K) was estimated to be 4.7 kcal/mol by extrapolation from the values of cubane and pentaprismane. Use of reaction 1 for $n = 6$ with these data gives 153.4 kcal/mol for the heat of formation of hexaprismane. Alternatively, the homodesmic disproportionation reaction

$$2\,[5]\text{prismane} \rightarrow [4]\text{prismane} + [6]\text{prismane} \qquad (2a)$$

at the RMP2 level provides a ΔH_f of 152.7 kcal/mol, in good agreement with the value obtained from reaction 1; the average of these two values is 153.1 kcal/mol.

C. Higher Prismanes. The homodesmic cycles with 6-31G*(SCF) energies underestimate the ΔH_f's of triprismane, cubane, pentaprismane, and hexaprismane by 11–15 kcal/mol. However, the ab initio 6-31G*(SCF) energy can be used to estimate the heats of formation of these and the higher prismanes by use of a group-equivalent scheme:[29a] the difference between the 6-31G*(SCF) total energy of the [*n*]prismane and 2*n* 6-31G* methine group equivalents provides an estimate of the heat of formation of the [*n*]prismane at 298 K. The method works well, often with an error of only a few kcal/mol, when zero-point energies, thermal corrections to heats of formation, and correlation energies are adequately provided for by group equivalents.

Methine group equivalents for the 6-31G* basis have been given by Wiberg, −38.45291 au (W1)[29a] and −38.45350 au (W2),[29b] and by Ibrahim and Schleyer (IS),[30] −38.45338 au. The pentaprismane ΔH_f values obtained from these group equivalents are the following: IS, 120.5 kcal/mol; W1, 121.2 kcal/mol; and W2, 117.5 kcal/mol. They are in reasonable agreement with the value of 119.6 kcal/mol obtained from the RMP2 energies. For hexaprismane, ΔH_f values obtained from these group equivalents are the following: IS, 153.6 kcal/mol; W1, 150.0 kcal/mol; and W2, 154.5 kcal/mol, which are, again, in reasonable agreement with the average RMP2-derived value of 153.1 kcal/mol. The IS group equivalent provides the best heat of formation for both pentaprismane and hexaprismane.

Table IV. Heats of Formation of the [*n*]Prismanes (kcal/mol)

n	ab initio[a]	AM1[b]	MNDO[b]	MM2[c]
3	136.4	165.0	121.9	
4	148.5	151.2	99.1	148.8
5	119.6	117.7	72.2	114.7
6	153.1	139.9	80.4	129.2
7	212.0	191.0	116.4	173.8
8	283.1	259.2	172.7	
9	368.7	340.6	243.8	

[a] Values for $n = 3$–6 were obtained from homodesmic cycles at the 6-31G*(RMP2) level; those for $n = 7$–9 were obtained from the 6-31G*(SCF) energies and the IS group equivalent. [b] Reference 9. [c] Reference 11.

The heats of formation of the [*n*]prismanes for $n = 3$–9 determined from the IS methine group equivalent are given in Table III, together with the 6-31G*(RMP2)-derived values. The latter are, of course, preferred for $n = 3$–6. The table also contains the heats of formation per two methine groups, which show that on this basis pentaprismane ($\Delta H_f/2n = 12.0$ kcal/mol) is the most stable of the [*n*]prismanes, with hexaprismane only slightly less stable ($\Delta H_f/2n = 12.8$ kcal/mol).

The strain energy, SE, of the [*n*]prismanes can be taken to be the enthalpy change for reaction 1. Since the ethane and isobutane heats of formation at 298 K are −20.0 and −32.1 kcal/mol, respectively,[8] it is easily shown that

$$\text{SE} = \Delta H_f([n]\text{prismane}) + 4.1n \text{ (kcal/mol)} \qquad (3)$$

(A similar relationship, with 2.18 replacing 4.1, is obtained by using Franklin's group equivalent for an unstrained methine, −1.09 kcal/mol.)[31] The SE values given in Table III show that pentaprismane has the smallest strain energy, 140 kcal/mol.

Since each [*n*]prismane contains 2*n* methine moieties and 3*n* CC bonds, one can compute the strain energy per methine as

$$\text{SE/CH} = \Delta H_f([n]\text{prismane})/2n + 2.1 \qquad (4a)$$

and the strain energy per CC bond as

$$\text{SE/CC} = \Delta H_f([n]\text{prismane})/3n + 1.4 \qquad (4b)$$

The values obtained from (4a) and (4b) show pentaprismane and hexaprismane to have very similar degrees of strain. Equally interesting, [9]prismane is slightly less strained by these criteria than triprismane, a known compound.

V. Discussion

Recently, an isomer of hexaprismane containing two double bonds and secohexaprismane have been synthesized.[6] The present results offer further encouragement in the quest for hexaprismane, in that (1) its stability is similar to that of pentaprismane on a per methine basis and (2) the vibrational frequencies of all 66 modes are real at the STO-3G and 3-21G(SCF) levels of computation. Using MNDO, Engelke et al.[10] obtained a high barrier for the dissociation of hexaprismane to *p,p'*-dibenzene and thence to two benzenes by a reaction coordinate of C_{2h} symmetry; their result is consistent with (2).

It is interesting to note that an isomer of hexaprismane, whose carbons form a truncated tetrahedron, has recently been discussed.[32] Its heat of formation is 93 kcal/mol, 60 kcal/mol lower than that of hexaprismane.

It is worthwhile to compare heats of formation obtained by the various computational methods (Table IV). The AM1 method gives good heats of formation for cubane and pentaprismane but is in error for triprismane and hexaprismane by 29 and −13 kcal/mol, respectively. MNDO values for all prismanes are poor due to its inability to treat the energetics of four-membered rings accurately. Heats of formation calculated with MINDO/3 are much better than the MNDO values, but slightly poorer than those of AM1.[33] The MM2 values for cubane and pentaprismane are in good and fair agreement, respectively, with the ab initio results, but the value for hexaprismane is in error by −24 kcal/mol; recall, also, the rather poor HCC angle produced by MM2.

We believe that the heats of formation obtained here are accurate and that this comparison demonstrates the value of ab initio

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calculations over less time-consuming molecular mechanics and semiempirical methods. The ab initio heats of formation could be of use in helping to reparametrize lower level computational methods such as molecular mechanics, which might yield accurate results with sufficient numbers of specialized parameters.

Since we have established that the IS methine group equivalent furnishes more accurate heats of formation for $(CH)_{2n}$ hydrocarbons than the W1 value, our previous ΔH_f of dodecahedrane should be revised slightly upward from 6.4 kcal/mol[8] (from W1) to 12.8 kcal/mol (from IS), although this value may be 1 to 2 kcal/mol too high.

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Appendix

The symmetry species of the vibrational modes of the D_{nh} prismanes are as follows. For odd n, there are 10 nondegenerate modes and $6n - 8$ degenerate pairs: $4A'_1 + A'_2 + 2A''_1 + 3A''_2 + 5E'_1 + 5E''_1 +$ (for $n > 3$) $6E'_2 + ... + 6E'_{(n-1)/2} + 6E''_2 + ... + 6E''_{(n-1)/2}$. For even n ($n > 4$), there are 22 nondegenerate modes and $6n - 14$ degenerate pairs: $4A_{1g} + A_{2g} + 2B_{1g} + 4B_{2g} + 2A_{1u} + 3A_{2u} + 4B_{1u} + 2B_{2u} + 5E_{1g} + 5E_{1u} + 6E_{2g} + ... + 6E_{(n/2-1)g} + 6E_{2u} + ... + 6E_{(n/2-1)u}$. Thus, all these prismanes have three nondegenerate and five twofold degenerate infrared active fundamentals. For $n = 4$ (cubane), octahedral symmetry leads to three threefold degenerate active fundamentals.

A Comparison of the Energies of Double Bonds of Second-Row Elements with Carbon and Silicon

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Abstract: Theoretical π-bond energies (E_π) are evaluated for the double bond systems $H_2Y{=}XH_n$ (Y = C, Si; X = B, C, N, O, Al, Si, P, S) employing the MP4SDTQ/6-31G*//6-31G* + ZPE level of theory. The difference in energy between two single bonds, X–Y, and a double bond, X=Y, is calculated by means of isodesmic equations. E_π is given by subtraction of this difference from the dissociation energies of the single bond system, $D_0°$. Si=X bonds are found to have significantly lower E_π energies than the corresponding C=X bonds; for each series, C=X and Si=X, the π-bond energies for both first- and second-row substituents correlate with the electronegativities of X. When electronegativity differences between carbon and silicon and among the X groups is taken into account, second- and first-row π-bond energies are similar. Families of linear correlations are also observed for E_π and Y=X bond lengths. Alternative procedures for estimating π bond energies (rotation barriers and diradical components) are criticized.

Until relatively recently, molecules with double bonds involving second-row elements were comparatively rare.[2] This was commonly attributed to the weakness of second-row π bonds due to poor p-orbital overlap.[3] This situation has changed drastically by the experimental realizations of one second-row double bond system after another.[2,4,5] Such molecules are persistent when isolated in a matrix or can be stabilized by bulky substituents. While it now seems clear that the earlier inability to observe such multiple bond systems was due primarily to their high reactivity, thermochemical factors also may contribute. The present state of affairs emphasizes the desirability of ascertaining the energies of double bonds involving second-row elements, particularly in comparison with their first-row counterparts. A survey of conventional double bond systems involving carbon ($H_2C{=}XH_n$, where XH_n = BH, CH_2, NH, O, AlH, SiH_2, PH, and S) as well as the silicon counterparts, $H_2Si{=}XH_n$, with the same XH_n groups is the subject of this paper.[5,6] Our results reveal unrecognized aspects of this problem.

Methods

Since experimental measurements on these molecules are difficult, ab initio molecular orbital theory affords an excellent source of data.[7] The level chosen for the thermochemical comparisons was MP4SDTQ/6-31G*//6-31G* + ZPE. All of the double bond systems and the single bond reference molecules were optimized by using the GAUSSIAN 82 program[7] with the 6-31G* basis set, which contains a set of d-functions on all non-hydrogen atoms. Electron correlation corrections, which have significant effects from about 5–12 kcal/mol on the relative energies, were estimated at the MP4SDTQ (complete fourth-order Møller–Plesset) level by using the frozen core approximation and the 6-31G* geometries. The latter also were used for frequency analyses to establish that all double bond structures were minima. Zero-point vibrational energies (ZPE) were estimated from our calculations or from the literature (Table I). Some of the data were taken from the CMU archive.[8] For those

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