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A Comparison of the Cope Rearrangements of *cis*-1,2-Divinylcyclopropane, *cis*-2,3-Divinylaziridine, *cis*-2,3-Divinyloxirane, *cis*-2,3-Divinylphosphirane, and *cis*-2,3-Divinylthiirane: A DFT Study

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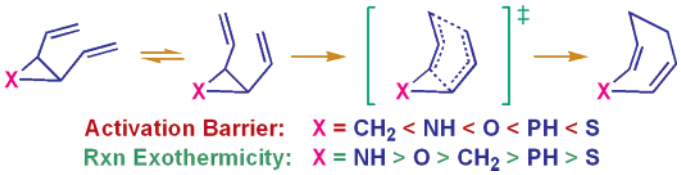
Received April 9, 2005

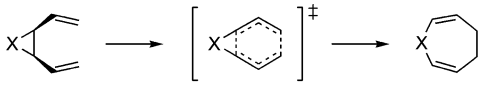


Transition structures, energetics, and nucleus-independent chemical shifts (NICS) for Cope rearrangements of *cis*-2,3-divinylaziridine (**1N**), *cis*-2,3-divinyloxirane (**1O**), *cis*-2,3-divinylphosphirane (**1P**), and *cis*-2,3-divinylthiirane (**1S**), leading to 4,5-dihydro-1*H*-azepine (**3N**), 4,5-dihydrooxepine (**3O**), 4,5-dihydro-1*H*-phosphepine (**3P**), and 4,5-dihydrothiepine (**3S**), respectively, are reported at the (U)B3LYP/6-31G* level and compared to those of *cis*-1,2-divinylcyclopropane (**1C**). The minimum energy path for all rearrangements proceeds through an *endo*-boatlike, aromatic transition structure. The predicted activation barriers increase in the order of **1C** < **1N** < **1O** < **1P** < **1S**, which agrees qualitatively with the decreasing ring strain order of reference compounds (cyclopropane > aziridine > oxirane > phosphirane > thiirane). The exothermicities for these rearrangements decrease in the order of **1N** > **1O** > **1C** > **1P** > **1S**. If the place of **1C** in this sequence is ignored, the decreasing reaction exothermicity order correlates well with the increasing activation barrier order and with decreasing strain order of reference compounds. NICS values calculated for transition structures are typical of highly aromatic transition structures of thermally allowed pericyclic reactions.

Introduction

Cope rearrangement of *cis*-1,2-alkenylcycloalkanes represents a very rapid entry into *cis*,*cis*-cycloalkadienes.[1] In this regard, divinylcyclopropane-to-cycloheptadiene (**1C** to **3C**) rearrangement is one of the most known and studied examples of these types of reactions (Scheme 1).[2] Vogel[3] first reported this rearrangement in 1960, and since then, it has been studied quite extensively from a mechanistic point of view. In his experiments, Vogel did not isolate **1C** since, under the conditions of its formation, it converts rapidly to **3C**.[3] However, more than a decade later, divinylcyclopropane **1C** was isolated and shown to rearrange to cycloheptadiene **3C** with a half-life of approximately 90 s at 35 °C and 25 min at 11 °C.[4] The energy of activation for this rearrangement was reported to be about 19.0−20.0 kcal/mol.[4,5] Cope rearrangement of divinylcyclopropane **1C** has also been theoretically

SCHEME 1



X = CH_2	**1C**	**2C**	**3C**
X = NH	**1N**	**2N**	**3N**
X = NCH_3	**1NMe**	**2NMe**	**3NMe**
X = NCH_2CH_3	**1NEt**	**2NEt**	**3NEt**
X = O	**1O**	**2O**	**3O**
X = PH	**1P**	**2P**	**3P**
X = S	**1S**	**2S**	**3S**

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10.1021/jo0507111 CCC: $30.25
Published on Web 06/04/2005

studied at the levels of RHF/6-31G* and MP2(full)/6-31G*//RHF/6-31G*[6] and B3LYP/6-31G*.[7] The calculated activation barrier of 19.7 kcal/mol[7] at the B3LYP/6-31G* level is in good agreement with the experimentally derived value of 19−20 kcal/mol.[4,5] It is well-known that the rearrangement of divinylcyclopropane **1C** proceeds in a concerted manner via a boatlike transition structure (TS);[2,7] in contrast, the parent [3,3]-sigmatropic rearrangement of 1,5-hexadiene operates via a chairlike TS.[8] Particularly since 1980, synthetic applications of these reactions have been explored and these rearrangements have proved to be a versatile, effective method for the construction of functionalized cyclic compounds.[2]

Thermal rearrangements of the heteroanalogues of divinylcyclopropane **1C** have been studied with considerable interest as well since they can easily provide the corresponding seven-membered ring heterocycles (Scheme 1). In this regard, Cope rearrangements of *cis*-2,3-divinyloxirane (**1O**),[9−12] *N*-methyl-*cis*-2,3-divinylaziridine (**1NMe**),[12b] *N*-ethyl-*cis*-2,3-divinylaziridine (**1NEt**),[13] and *cis*-2,3-divinylthiirane (**1S**)[14] have been investigated as well as their substituted and *trans* derivatives.[15,16] The rearrangements of *cis* heteroanalogues proceed by analogy with *cis*-divinylcyclopropane (**1C**) reorganization, but most take place at relatively higher temperatures. The rearrangement of divinyloxirane **1O** to 4,5-dihydrooxepine (**3O**) is the most studied reaction among the heteroanalogues of **1C** since the oxepin nucleus is presented in a number of natural products of biological interest.[17] Divinyloxirane **1O** is stable at room temperature, but it starts to rearrange to dihydrooxepine **3O** over 60 °C.[10,16] The mechanism of this rearrangement has since been studied on a number of occasions, and it is generally agreed that concerted, electrocyclic closure of divinyloxirane **1O** is operating in the formation of dihydrooxepine **3O**. The activation enthalpy for this rearrangement has been found to be 24.6 kcal/mol by Vogel[11] and 22.7 kcal/mol by Pommelet and Chuche,[12b] both of which are relatively higher than that (19−20 kcal/mol)[4,5] for divinylcyclopropane **1C**. To the best of our knowledge, *cis*-2,3-divinylaziridine (**1N**) is not known, but its *N*-alkyl derivatives such as **1NMe** and **1NEt** have been prepared and their subsequent transformations to the corresponding dihydroazepines **3NMe** and **3NEt** have been reported (Scheme 1).[12b,13] Divinylaziridine **1NMe** was prepared and isolated at −15 °C,[12b] which rearranged quickly to **3NMe** and completely at 40 °C. The activation enthalpy for this rearrangement was found to be 18.5 kcal/mol,[12b] which is relatively lower than that (19−20 kcal/mol)[4,5] for divinylcyclopropane **1C**. Similarly, under the conditions of its formation, divinylaziridine **1NEt** was found to convert to dihydroazepine **3NEt**.[13] On the other hand, *cis*-2,3-divinylthiirane (**1S**), if kept under nitrogen, is stable at room temperature and does not give any significant reaction below 80 °C.[14] However, it rearranges smoothly at 90 °C to afford 4,5-dihydrothiepine (**3S**) (Scheme 1), along with the formation of 2,7-dihydrothiepine[18] and polymerization of the so produced *cis*- and *trans*-1,3,5-hexatrienes, resulting from cheletropic sulfur elimination.[14] Interestingly, in control experiments, dihydrothiepine **3S** did not convert to 2,7-dihydrothiepine at 130 °C, indicating that **3S** is not a precursor for 2,7-dihydrothiepine. Thus, 2,7-dihydrothiepine must have arisen via a different pathway, presumably via a radical mechanism as suggested by the authors of this study.[14] It should be noted that the dissociation of sulfur from thiirane (ethylene sulfide), or vice versa, has received considerable attention from the experimental and theoretical points of view.[19] The experimental activation energy for the dissociation of thiirane to form S(^{3}P) and $C_2H_4(^1A_g)$ is about 63 ± 2 kcal/mol while it is 88 ± 1 kcal/mol for that to form S(^{1}D) and $C_2H_4(^1A_g)$, both of which are consistent with the calculated activation barriers of 59.5 and 85.1 kcal/mol, respectively, at the Gaussian-3 (G3) level.[19a] Apparently, the channel leading to ground-state sulfur and ethylene is energetically more favorable. The experimental activation barrier for the reverse reaction, however, is only 1.6 kcal/mol,[20] consistent with its calculated value (1.5 kcal/mol) at the G3 level.[19a] To the best of our knowledge, *cis*-2,3-divinylphosphirane (**1P**) and its subsequent transformation to 4,5-dihydro-1*H*-phosphepine (**3P**) are not known.

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TABLE 1. Experimental and Theoretical Ring-Strain Energies (kcal/mol) for Cyclopropane (4C), Aziridine (4N), Oxirane (4O), Phosphirane (4P), and Thiirane (4S)

	4C	**4N**	**4O**	**4P**	 **4S**	Ref.
Experimental	27.5	26.7	26.3			21a, 26
	27.5	27.1	27.2			27
	27.6	27.7	26.9			28
	28.1					29
			27.3		19.8	21b
	27.5		25.1		19.6	30
HF/6-31G*		26.8		20.1		31
HF/6-31+G*	27.6	28.0	28.9			32
MP2/6-31+G*	27.7	27.7	26.6			32
MP2(Full)/6-31+G*			26.1		26.3	24
B3LYP/6-31+G*			31.2		28.8	24
G2	27.4[a]	27.0[a]	26.4[a]	19.7[b]	17.8[b]	[a]33, [b]This study
G2(MP2)	28.0			21.3		34
G2(MP2)	27.8		25.2		18.6	30
G3	28.1		25.6		19.0	30
G3(MP2)	28.4	28.2	27.1	21.4		35

Ring strain is clearly a very important factor in reactivity differences.[21] Actually, strain is a relative quantity, and commonly defined as the energy excess between the molecule and an appropriately chosen strain-free counterpart. Experimentally, the ring strain energy of a cyclic molecule is obtained as an energy difference between the actual heat of formation (ΔH_f) observed for the ring compound and the hypothetical strain-free heat of formation (ΔH_f) calculated for the same molecule by employing the group-increment or bond-energy additivity schemes. On the other hand, the theoretical ring strain energy of a cyclic molecule is derived as the negative of the energy change associated with the related isodesmic or homodesmotic reaction since the conversion of calculated energy to the enthalpy of formation normally requires the use of such equation to cancel the correlation energy.[22] If the closely related molecules are used in these equations the cancellation will be most effective. The relief of ring strain in the TS is commonly noted as the sole or primary source of the increased reactivity but the ring strain alone is insufficient to account entirely for the observed rate enhancement since the connection between strain energies and activation energies could not be, always, made in a definite manner. For this reason, additional factors,[23] disjoined effects,[24] and orbital interactions through bonds[25] have been defined to explain the large rate differences shown by the different size ring systems with the nearly identical ring strain. The study of the ring strain of three-membered rings has been a subject of considerable interest for chemists from both the experimental and theoretical points of view. Table 1 summarizes the ring strain energies for cyclopropane (**4C**), aziridine (**4N**), oxirane (**4O**), phosphirane (**4P**) and thiirane (**4S**). Although there are some discrepancies among the strain energy data reported for these molecules, the following reasoning can be extracted from Table 1: the ring strain energies, particularly on the basis of high level of ab initio calculations, show a decreasing trend in the order of **4C** > **4N** > **4O** > **4P** > **4S**. In addition, the rings containing a heteroatom within the same row denote more closely related strain energies.

The mechanisms and activation barriers of pericyclic reactions are a subject of long-standing and continuing interest.[36] In this regard, the [3,3]-sigmatropic shifts of *cis*-2,3-divinyl-1-heterocyclopropanes (**1N**, **1O**, **1P**, and

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1S) present a challenge to understand the rate effects caused by nitrogen, oxygen, phosphorus, and sulfur atoms, which have not been previously studied from the theoretical point of view in contrast to that of *cis*-1,2-divinylcyclopropane (**1C**). The aim of this study is to contribute to a better understanding of such processes. Reported herein is a detailed study of these rearrangements at the density functional theory level and an exploration of the properties of the transition structures involved, particularly via nucleus-independent chemical shift (NICS) values.[37]

Computational Methods

All calculations were performed at the density functional theory (DFT) level by using the Gaussian 98 program package.[38] Becke's three-parameter exchange functional (B3)[39] in conjunction with the Lee−Yang−Parr correlation functional (LYP)[40] was employed as implemented in Gaussian 98.[38] In all geometry optimizations, Pople's 6-31G* split valence basis set was used.[41] In all regions of the potential energy surfaces investigated in this study, the spin-restricted DFT was stable with respect to spin-symmetry breaking (i.e., $\langle S^2 \rangle = 0$ with UB3LYP using "guess = (mix,always)" option). Geometries were optimized without constraint. Vibrational frequencies were computed to characterize each stationary structure as a minimum or TS, via the number of imaginary frequencies (zero for minima and one for TSs, respectively). After locating a TS, an intrinsic reaction coordinate (IRC) calculation[42] was carried out to identify its respective reactant and product. All results reported in this work refer to such completely verified reactant−TS−product triples. Note that (U)B3LYP/6-31G*-optimized Cartesian coordinates, all energy values including zero-point vibrational energies (ZPE), and imaginary vibrational frequencies (IMF) for all structures, as well as those for related inversion processes and reference compounds, and G2 energies[43] for calculation of ring strain energies are given in the Supporting Information.

It should be noted that Houk and co-workers have explored in detail the advantages and disadvantages of (U)B3LYP/6-31G* method for potentially pericyclic reactions and concluded that the (U)B3LYP/6-31G* method is an effective and inexpensive way to compute the structures and energetics for such reactions.[8f,44] Very recently, (U)B3LYP/6-31G* calculations have been successfully used in the calculation of TSs and reaction parameters for the Cope rearrangements of divinylcyclopropanes,[7] divinylcyclobutanes,[7] divinylcyclobutenes,[45] and fickle hexadienes.[46] Notably, the calculated activation barriers of 19.7[7] and 25.0[7] kcal/mol for Cope rearrangements of *cis*-divinylcyclopropane and *cis*-divinylcyclobutane are in good agreement with their experimentally derived values of 19.0−20.0[4,5] and 24.0[47] kcal/mol, respectively.

Absolute NMR shielding values were calculated using the gauge-independent atomic orbital (GIAO) method[48] in the restricted Hartree−Fock (RHF) formalism employing the 6-31+G* basis set[41] at the B3LYP/6-31G*-optimized geometries. NICS values, pioneered by Schleyer,[37] are effective probes of aromaticity in transition states of pericyclic reactions.[49] Note that negative NICS values denote aromaticity (−11.5 for benzene, −11.4 for naphthalene) and positive NICS values show antiaromaticity (28.8 for cyclobutadiene, 21.7 for heptalene) while small NICS values indicate nonaromaticity (−2.1 for cyclohexane, −1.1 for adamantane).[37]

Results and Discussion

The relative energies for the species studied are illustrated in Scheme 2. Although divinylcyclopropane-to-cycloheptadiene rearrangement (**1Cxx** to **3Ccc**) was previously studied in detail,[7a] it has been included in Scheme 2 for comparison purposes. Note that the capital letters **C**, **N**, **O**, **P**, and **S** indicate the corresponding carbon, nitrogen, phosphorus, and sulfur analogues of the system studied. The small letter **n** denotes a vinyl group in the *endo* orientation, relative to the three-membered ring, while **x** indicates that in *exo* orientation. In addition, **a** shows the hydrogen atom of the heteroatom which is *trans* to vinyl substituents while **s** denotes the one that is *cis*. Similarly, **c** indicates a *cis* double bond while **t** denotes a *trans* double bond. On the other hand, **i** refers to heteroatom inversion, the hydrogen atom of the heteroatom being coplanar with the other two substituents of the heteroatom. The computed geometries of TSs are depicted in Figure 1 along with the selected bond distances and bond angles.

As shown previously,[7a] three distinct conformations were located for *cis*-1,2-divinylcyclopropane (**1C**), and the conformer **1Cxx** is more stable than other conformers **1Cnx** and **1Cnn** by 0.8 and 2.9 kcal/mol, respectively (Scheme 2). Similarly, *cis*-2,3-divinyl-1-heterocyclopropanes have been found to exist in three distinct conformations, which are differentiated by the orientation of vinyl groups. As expected, heterocyclopropanes with two *exo*-vinyl groups are relatively more stable than other conformers by 0.1−5.3 kcal/mol (Scheme 2). However, as shown for similar systems,[7a,45] these conformers are easily interconvertible isomers due to low activation barriers.

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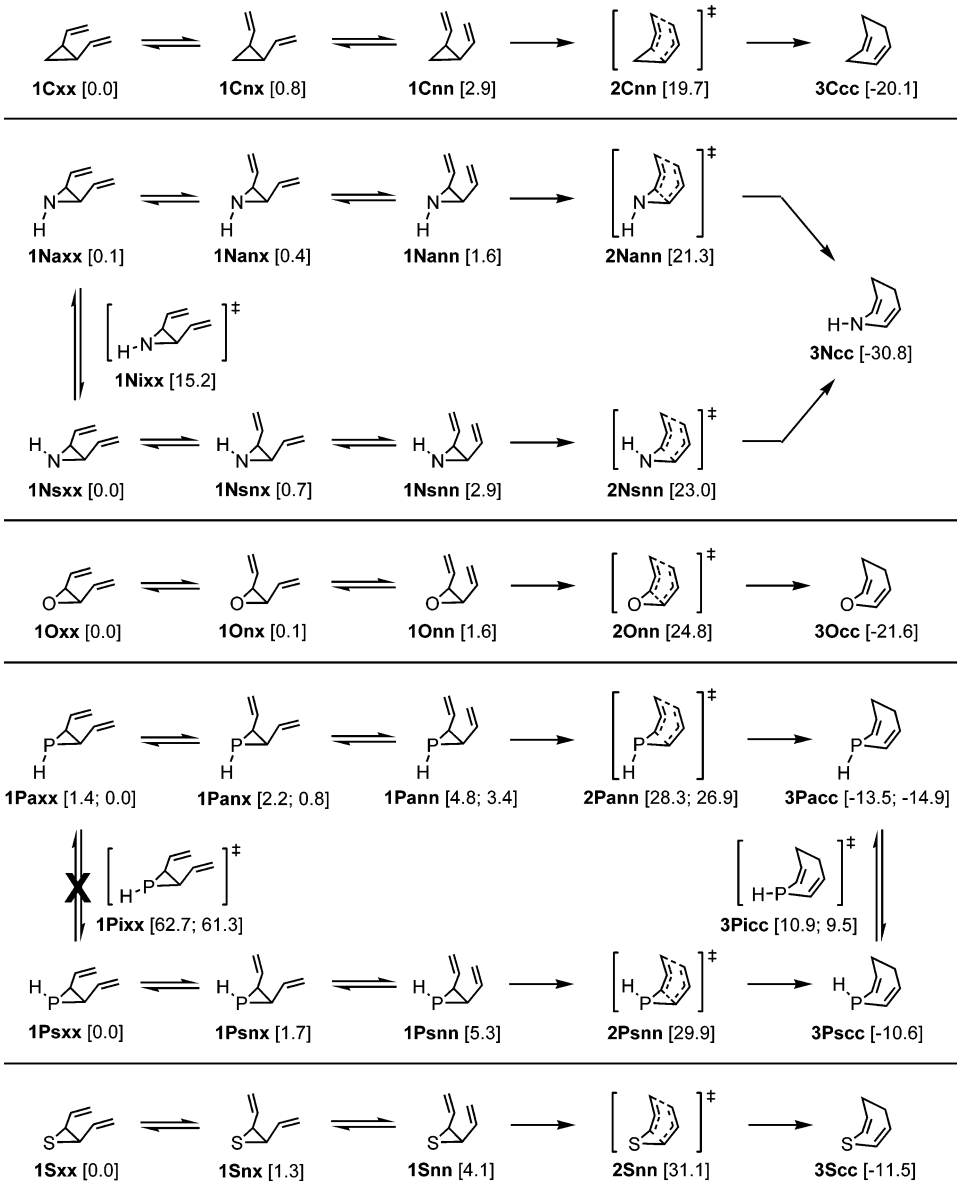
SCHEME 2[a]



[a] Energies including ZPE (kcal/mol) are in brackets and relative to those of **1Cxx**, **1Nsxx**, **1Oxx**, **1Psxx,** and **1Sxx**, respectively. If given, second energy values for phosphorus compounds are relative to that of **1Paxx**.

Interestingly, under experimental conditions, **1Nsxx** can easily invert to **1Naxx**, or vice versa, via TS **1Nixx** (Figure 1), similar to a classical *vertex* TS.[50] The activation barrier to this nitrogen inversion is 15.2 kcal/mol. In fact, the barriers to nitrogen and phosphorus inversions in three-membered rings have attracted a great deal of attention from both the experimental and theoretical points of view since the effect of angular constraint in these systems leads to considerably high inversion barriers. Table 2 summarizes the experimental and theoretical barriers to nitrogen and phosphorus inversions in related compounds, as well as those calculated in this study. The inversion barriers in NH_3 and $(CH_3)_2$-NH are 5.5 and 4.2 kcal/mol at the B3LYP/6-31G* level, respectively, consistent with the experimental values of 5.8[55] and 4.4[56] kcal/mol. Apparently, alkyl substitution slightly decreases the activation barrier for nitrogen inversion. The inversion barrier in aziridine (**4N**), however, is 16.4 kcal/mol at the same level of theory, which is compared to 18.3[57] and 19.1[58] kcal/mol, obtained by experiments. The relatively higher inversion barriers in

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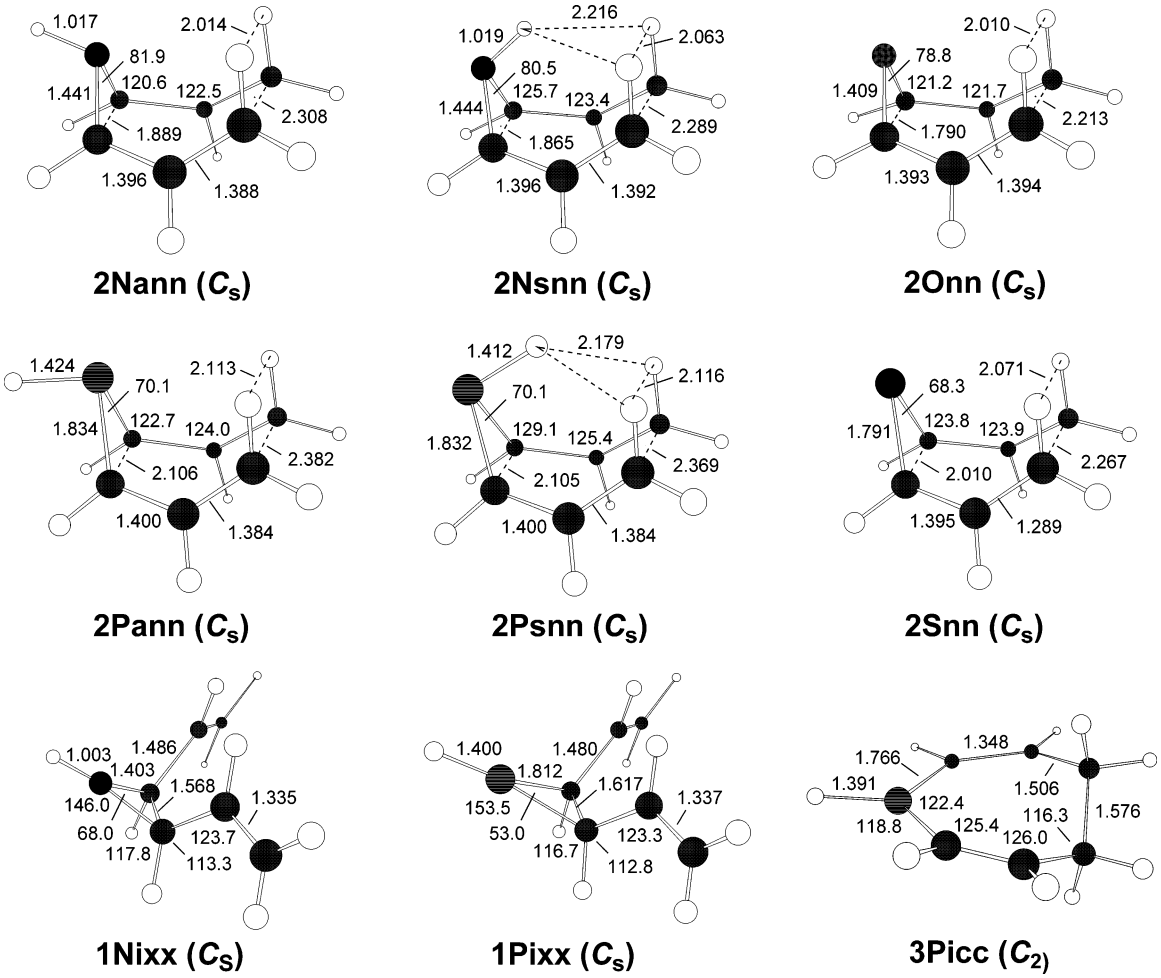

FIGURE 1. B3LYP/6-31G*-optimized geometries of transition structures, shown in Scheme 2, along with selected bond distances (Å) and bond angles (deg).

TABLE 2. Inversion Barriers (kcal/mol) in Some Nitrogen and Phosphorus Compounds

	NH_3	$(CH_3)_2NH$	aziridine (**4N**)	PH_3	$(CH_3)_2PH$	phosphirane (**4P**)	ref
AM1	4.2	4.1	15.7	32.8	35.7	36.4	this study
HF/6-31G*//HF/6-31G* + ZPE (3-21G(*))					41.5	72.1	51
HF/6-31G*			19.4[a]			73.2[b]	[a]52, [b]51
HF/6-31G** + ZPE	5.5		18.7				53
MP2/6-31G*//HF/6-31G* + ZPE (3-21G(*))					38.3	68.3	52
MP2/6-31G*//HF/6-31G*			19.9[c]			69.4[d]	[c]52, [d]51
MP2/6-31G*	6.1		19.6				53
MP3/6-31G*//3-21G*	5.4			35.6			54
MP3/6-31G** + ZPE	5.3		18.7				53
B3LYP/6-31G* + ZPE	5.5	4.2	16.4	34.7	36.8	65.3	this study
B3LYP/6-311+G(2df,p) + ZPE				33.1	35.5		50
QCISD(T)/6-311+G(2df,p) + ZPE (MP2)				33.8			50
Experimental	5.8[e]	4.4[f]	18.3,[g] 19.1[h]	32.3,[i] 37.2[j]			[e]55, [f]56, [g]57, [h]58, [i]59, [j]60

4N, **1Nsxx** and **1Naxx**, compared to that in $(CH_3)_2NH$, are clearly due to the geometric restrictions imposed by the ring. Moreover, as a result of vinyl substitution, the inversion barriers of 15.2 and 15.1 kcal/mol for **1Nsxx** and **1Naxx**, respectively, are slightly less than that (16.4 kcal/mol) for aziridine (**4N**).

Similarly, as seen in Scheme 2, **1Psxx** and **1Paxx** can be expected to convert to each other via a phosphorus inversion through TS **1Pixx** (Figure 1), but this does not seem to be possible under the experimental conditions since the inversion barrier from **1Psxx** to **1Paxx** has been calculated to be 62.7 kcal/mol while it is 61.3 kcal/mol from **1Paxx** to **1Psxx**, both of which are approximately twice of the activation barriers required for their Cope rearrangements. Notably, the inversion barriers in phosphorus compounds are much higher than those in corresponding nitrogen compounds. For instance, the inversion barriers in PH_3 and $(CH_3)_2PH$ are 34.7 and 36.8 kcal/mol, respectively, as compared to 5.5 and 4.2 kcal/mol in NH_3 and $(CH_3)_2NH$ at the same level of theory

(Table 2). Similarly, the inversion barrier (65.3 kcal/mol) in phosphirane (**4P**) is much higher than that (16.4 kcal/mol) in aziridine (**4N**). Clearly, the experimental and calculated values suggest that geometric restrictions imposed by a phosphirane ring are much more pronounced in the inversion barriers than those by an aziridine ring.

In principle, each conformer of a particular reactant might give rise to an isomer of the corresponding seven-membered ring through an initial-conformer-specific TS. The lowest activation barrier for a peculiar *cis*-2,3-divinyl-1-heterocyclopropane has been obtained from the conformer with two *endo*-vinyl groups via an *endo*-boatlike TS, providing the corresponding *cis*,*cis*-3-hetero-1,4-cycloheptadiene (Scheme 2), which has been the case in the Cope rearrangements of *cis*-1,2-divinylcyclopropane,[7a] *cis*-1,2-divinylcyclobutane[7a] and *cis*-3,4-divinylcyclobutene.[45] It should be noted that other conformers bearing *endo*- and *exo*-vinyl groups or two *exo*-vinyl groups can give rise to formation of more strained *cis*,*trans*- and *trans*,*trans*-3-hetero-1,4-cycloheptadienes via chairlike and *exo*-boatlike TSs, respectively, which are energetically less or unfavored as compared to formation of the *cis*,*cis* analogue, as shown previously for the rearrangements of the related conformers of *cis*-1,2-divinylcyclopropane,[7a] *cis*-1,2-divinylcyclobutane,[7a] and *cis*-3,4-divinylcyclobutene.[45]

For the Cope rearrangement of *cis*-2,3-divinylaziridine (**1N**), two *endo*-boatlike TSs, **2Nann** and **2Nsnn**, have been located (Scheme 2, Figure 1), the latter of which is 1.7 kcal/mol less stable than the former, presumably due to transannular interaction between heteroatom hydrogen and inward terminal vinylic hydrogens in **2Nsnn**, which are 2.216 Å apart. The forming bonds in TSs **2Nann** and **2Nsnn** are 2.308 and 2.289 Å while the breaking bonds are 1.889 and 1.865 Å, respectively. In fact, forming and breaking bonds in these TSs are eclipsed, thus appearing to suffer from the slightly worse eclipsing interactions. An interesting feature for TSs **2Nann** and **2Nsnn** is the close interaction distances (2.014 and 2.063 Å, respectively) between inward hydrogens of terminal vinylic carbons, which are 0.294 and 0.226 Å shorter than corresponding forming bonds. If these interactions were a serious steric interference to rearrangement, then the relatively longer forming bond distances to decrease the repulsive interactions and/or higher activation energies to overcome such interactions would be expected. This is not the case here since the forming bond lengths are very similar to those for pericyclic reactions and activation energies are less than typical activation barrier for pericyclic reactions (32 ± 3 kcal/mol).[36a] Such close interaction distances were also observed in the 6π cyclizations of hexatrienes[61] and dienylketenes.[62] Interestingly, the formation of 4,5-dihydro-1*H*-azepine (**3Ncc**) has been predicted to be the most exothermic process by 30.8 kcal/mol among the systems studied (Scheme 2). Dihydroazepine **3Ncc** is twisted in such a manner as to bring the adjacent methylene carbons into a staggered conformation, which relieves the eclipsing strains. More importantly, as in the case of divinylamine, nitrogen atom in **3Ncc** has a trigonal planar structure with the C−N−C and C−N−H bond angles of 129.0 and 115.5°, respectively, which complements the conjugation between double bonds. As a result of this conjugation, N−C bond lengths (1.390 Å) in **3Ncc** get shorter as compared to that in dimethylamine (1.457 Å) while C=C bond lengths (1.344 Å) become slightly longer when compared to those (1.336 Å) in **3Ccc**. It should be noted that both channels through TSs **2Nann** and **2Nsnn** lead to the same product, **3Ncc**, and the C_s symmetries of TSs change to C_2 in product, which closely relates to both change in hybridization of nitrogen atom from sp^3 to sp^2 and conformational change of neighboring methylene carbons from eclipsed to staggered. In summary, it is predicted that *cis*-2,3-divinylaziridine (**1N**) rearranges via TS **2Nann** due to a low activation barrier.

Cope rearrangement of *cis*-2,3-divinyloxirane (**1O**) proceeds via *endo*-boatlike TS **2Onn** (Scheme 2, Figure 1). The forming and breaking bonds in TS **2Onn** are eclipsed and 2.213 and 1.790 Å, respectively. TS **2Onn** has also a close interaction distance (2.010 Å) between inward hydrogens at bonding termini, which is 0.203 Å shorter than the forming bond. The calculated activation barrier of 24.8 kcal/mol is in very good agreement with the experimentally derived value of 24.6 kcal/mol by Vogel[11] while it is 2.1 kcal/mol higher than that (22.7 kcal/mol) by Pommelet and Chuche.[12b] Formation of 4,5-dihydrooxepine, **3Occ**, is exothermic by 21.6 kcal/mol, which is 1.5 kcal/mol more exothermic than that of cycloheptadiene **3Ccc** but it is 9.2 kcal/mol less exothermic than that of dihydroazepine **3Ncc**. Neighboring methylene carbons in **3Occ** are staggered, i.e., free of eclipsing strains, and C−O−C bond angle is 125.3°. In fact, the oxygen atom in **3Occ** is almost coplanar with double bonds, and it improves the conjugation between them, as concluded from the O−C bond lengths (1.369 Å) that are shorter than those (1.410 Å) in dimethyl ether, showing some double bond character. C=C bond distances in **3Occ**, however, are 1.337 Å, which are almost the same with those (1.336 Å) in **3Ccc** but slightly shorter than those (1.344 Å) in **3Ncc**.

For the Cope rearrangement of *cis*-2,3-divinylphosphirane (**1P**), two *endo*-boatlike TSs, **2Pann** and **2Psnn**, have been located (Scheme 2, Figure 1), the geometrical features of which are quite similar to those found for *cis*-2,3-divinylaziridine (**1N**). The forming bonds in TSs **2Pann** and **2Psnn** are 2.382 and 2.369 Å, while the breaking bonds are 2.106 and 2.105 Å, respectively. It is interesting to note that the forming and breaking bonds in **2Pann** are the longest when compared with those in other TSs studied. Furthermore, forming and breaking bonds in TSs **2Pann** and **2Psnn** are eclipsed, which might suffer from the eclipsing strains to some extent. Moreover, TSs **2Pann** and **2Psnn** experience close interaction distances (2.113 and 2.116 Å, respectively) between inward hydrogens of terminal vinylic carbons, which are 0.269 and 0.253 Å shorter than corresponding forming bonds. TS **2Psnn** is 1.6 kcal/mol less stable than **2Pann**, possibly due to transannular interaction between heteroatom hydrogen and inward terminal vinylic hydrogens, which are 2.179 Å apart. Two reaction channels

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TABLE 3. GIAO-HF/6-31+G*//B3LYP/6-31G*-Calculated NICS Values (ppm) for Transition Structures of Cope Rearrangements of *cis*-1,2-Divinylcyclopropane (1C), *cis*-2,3-Divinylaziridine (1N), *cis*-2,3-Divinyloxirane (1O), *cis*-2,3-Divinylphosphirane (1P), and *cis*-2,3-Divinylthiirane (1S), as Well as for Reference Compounds

	NICS(0)[a]			NICS(1)$_{out}$ (NICS(1)$_{in}$)[a]		
structure (point group)	3MR	6MR	ΣNICS(0)[b]	3MR	6MR	ΣNICS(1)$_{out}$ (ΣNICS(1)$_{in}$)[b]
2Cnn (C_s)	−42.2[c]	−23.2[c]	−65.4[c]	−4.8[c] (−18.3)	−16.9 (−13.2)	−21.7 (−31.5)
2Nann (C_s)	−48.0	−23.9	−71.9	−4.9 (−19.6)	−17.2 (−13.5)	−22.1 (−33.1)
2Nsnn (C_s)	−50.4	−23.7	−74.1	−3.9 (−18.5)	−17.2 (−13.6)	−21.1 (−32.1)
2Onn (C_s)	−52.5	−23.8	−76.3	−3.9 (−18.9)	−17.2 (−13.0)	−21.1 (−31.9)
2Pann (C_s)	−34.7	−23.3	−58.0	−5.9 (−18.2)	−16.6 (−14.0)	−22.5 (−32.2)
2Psnn (C_s)	−35.0	−23.0	−58.0	−5.5 (−17.3)	−16.4 (−13.1)	−21.9 (−30.4)
2Snn (C_s)	−45.0	−24.4	−69.4	−5.5 (−19.1)	−17.1 (−14.3)	−22.6 (−33.4)
4C (D_{3h})	−43.2[c,d]			−9.4[c]		
4N (C_s)	−45.6			−7.6 (−8.4)		
4O (C_{2v})	−46.2			−6.5		
4P (C_s)	−39.2			−9.9 (−10.5)		
4S (C_{2v})	−47.3			−9.2		
1,5-hexadiene (C_{2h}) (Cope chairlike TS)		−25.1[c,e]			−16.5	
1,5-hexadiene (C_{2v}) (Cope boatlike TS)		−23.1[c,f]			−16.6 (−11.8)	

[a] 3MR and 6MR denote three- and six-membered rings, respectively. [b] Sum of NICS values of rings in compound. [c] From ref. 65. [d] −42.8 ppm at PW91/IGLO-III//B3LYP/6-311+G** level (ref 66). [e] −25.4 ppm atGIAO-HF/6-31G*//B3LYP/6-311+G** level (ref 49b). [f] −22.7 ppm at GIAO-HF/6-31G*//B3LYP/6-311+G** level (ref 49b).

involving TSs **2Pann** and **2Psnn** lead to 4,5-dihydro-1*H*-phosphepines **3Pacc** and **3Pscc**, respectively. In fact, the rearrangements of divinylphosphiranes **1Paxx** and **1Psxx** can be considered as separate systems since, as mentioned before, the interconversion of **1Paxx** and **1Psxx** via phosphorus inversion is not possible under the conditions of Cope rearrangement. The calculated activation barrier for the rearrangement of **1Paxx** to **3Pacc** via TS **2Pann** is 3.0 kcal/mol lower than that for the conversion of **1Psxx** to **3Pscc** via TS **2Psnn**. In addition, the formation of dihydrophosphepine **3Pacc** from **1Paxx** is 4.3 kcal/mol more exothermic as compared to that of **3Pscc** from **1Psxx** (Scheme 2). In fact, **3Pacc** is more stable than **3Pscc** by 2.9 kcal/mol. In both dihydrophosphepines **3Pacc** and **3Pscc**, adjacent methylene carbons are staggered, thus relieving the eclipsing strains. In **3Pacc**, C−P−C and C−P−H bond angles are 104.0 and 97.4°, respectively, while they are 105.2 and 98.7° in **3Pscc**, both of which are indicative of a trigonal pyramidal structure for phosphorus atom in these compounds. Interestingly, via a phosphorus inversion, dihydrophosphepines **3Pacc** and **3Pscc** could be expected to convert into each other (Scheme 2). The calculated inversion barrier from **3Pacc** to **3Pscc**, via TS **3Picc** (Figure 1), is 24.4 kcal/mol while it is 21.5 kcal/mol from **3Pscc** to **3Pacc**, both of which are lower than those of corresponding Cope rearrangements. Since the latter inversion (**3Pscc** to **3Pacc**) appears to be more feasible, **3Pscc** is expected to invert to **3Pacc** to some extent under the experimental conditions of the rearrangement.

Cope rearrangement of *cis*-2,3-divinylthiirane (**1S**) operates via *endo*-boatlike TS **2Snn** (Scheme 2, Figure 1). It is interesting to note that calculated activation barrier (31.1 kcal/mol) has been found to be the highest among the barriers investigated. The forming and breaking bonds in TS **2Snn** are eclipsed, and 2.267 and 2.010 Å, respectively. TS **2Snn** has also a close interaction distance (2.071 Å) between inward hydrogens at bonding termini, which is 0.196 Å shorter than the forming bond. The formation of 4,5-dihydrothiepine (**3Scc**) is exothermic by 11.5 kcal/mol, but it is the least exothermic process among those studied. Neighboring methylene carbons in **3Scc** are staggered, i.e., free of eclipsing strains. The C−S−C bond angle is 110.0°, and the sulfur atom is nearly coplanar with double bonds, improving the conjugation between them.

To summarize, the activation barriers predicted for the Cope rearrangements for *cis*-1,2-divinylcyclopropane (**1C**) and *cis*-2,3-divinyl-1-heterocyclopropanes (**1N**, **1O**, **1P**, and **1S**) increase in the order of **1C** < **1N** < **1O** < **1P** < **1S**. This increase in the activation barriers correlates well with the decreasing ring strain of the related reference compounds in the order of **4C** > **4N** > **4O** > **4P** > **4S**. Compared to the Cope rearrangement of parent 1,5-hexadiene (barriers of 34.0 kcal/mol for chairlike rearrangement and 42.0 kcal/mol for boatlike rearrangement at the same level of theory),[8f,63] lower activation barriers have been calculated for these rearrangements. These rate accelerations are no doubt due to three-membered rings' strain. Another point for consideration is the relative exothermicity of these rearrangements. The exothermicities for these rearrangements decrease in the order of **1N** > **1O** > **1C** > **1P** > **1S**. In general, the lower activation barrier is the more exothermic reaction is, or vice versa, expected. Interestingly, the rearrangement of **1C** is less exothermic than those of **1N** and **1O**. In fact, the exothermicity of a reaction could be in part due to the product stability. As concluded from the related C=C bond (1.336 Å) and C−C bond (1.508 Å) distances, the presence of an sp^3-hybridized carbon between double bonds in **3Ccc** interrupts the conjugation, thus possibly making the product less stable and the rearrangement less exothermic as compared to those of **1N** and **1O**. If the place of **1C** in this sequence is ignored, the decreasing reaction exothermicity order correlates well with the increasing activation barrier order (**4C** < **1N** < **1O** < **1P** < **1S**) and with the decreasing strain order of the reference compounds (**4C** > **4N** > **4O** > **4P** > **4S**).

We have also calculated NICS values for TSs and reference compounds, which are shown in Table 3 along with some literature values. NICS(0) values were obtained by calculating absolute NMR shielding at ring centers (nonweighted mean of the heavy atom coordinates). NICS(1) values were calculated at 1 Å above and below the ring centers. Note that for six-membered rings, which are not planar, 1 Å distance from the ring center

was obtained perpendicular to an imaginary plane containing the carbon atoms of forming and breaking bonds. The notations $NICS(1)_{out}$ and $NICS(1)_{in}$ were used to refer to NICS(1) values calculated at outside and inside faces of the rings, respectively. When compared to NICS(0), NICS(1) values are less affected by the paratropic contributions of the neighboring C−H and C−C σ bonds and give a more reliable indication of aromaticity.[64] Between $NICS(1)_{out}$ and $NICS(1)_{in}$, the first is, however, more appropriate to evaluate the aromaticity since the paratropic effects are better minimized in $NICS(1)_{out}$. That's why, for discussion, we have analyzed only the $NICS(1)_{out}$ values.

Six-membered rings in all TSs show considerable aromaticity since $NICS(1)_{out}$ values vary from −16.4 to −17.2 ppm (Table 3). Moreover, these values are comparable with those in chairlike and boatlike TSs (−16.5 and −16.6 ppm, respectively) for Cope rearrangement of 1,5-hexadiene. Three-membered rings in TSs, however, are weakly or slightly aromatic since $NICS(1)_{out}$ values alter between −3.9 and −5.9 ppm. Interestingly, as compared to those in reference compounds (**4C**, **4N**, **4O**, **4P**, and **4S**), their aromaticity is approximately 35−50% reduced. It should be noted that the overall aromaticity of a TS is better indicated by its $\Sigma NICS(1)_{out}$ value. Boatlike TSs we studied are quite aromatic, typical of highly aromatic TSs of thermally allowed pericyclic reactions.[25,49b] Moreover, these TSs show similar aromaticity on the basis of $\Sigma NICS(1)_{out}$ values, varying between −21.1 and −22.6 ppm. It should be noted that when rearrangements are compared with each other in terms of $\Sigma NICS(1)_{out}$ values versus activation barriers or reaction exothermicities, there is no such a clear qualitative trend between them.

Conclusion

In summary, we have theoretically explored Cope rearrangements of *cis*-2,3-divinylaziridine (**1N**), *cis*-2,3-divinyloxirane (**1O**), *cis*-2,3-divinylphosphirane (**1P**), and *cis*-2,3-divinylthiirane (**1S**), two of which (**1N** and **1P**) are previously unknown prototype reactions. We have also compared these rearrangements with that of *cis*-1,2-divinylcyclopropane (**1C**). Our DFT results reveal that the lowest energy path for these rearrangements proceeds through an *endo*-boatlike, aromatic TS, as has been the case in divinylcyclopropane **1C**. All TSs experience a close interaction distance between inward hydrogens of terminal vinylic carbons, which is 0.196−0.294 Å shorter than corresponding forming bonds. However, this is not a significant steric obstruction to rearrangements as concluded by corresponding activation barriers and forming bond distances. The increasing ring strain in reactants, as evidenced from reference compounds, lower the activation barrier for rearrangements. In other words, the increasing activation barrier order (**1C** < **1N** < **1O** < **1P** < **1S**) agrees qualitatively with the decreasing ring strain order of the reference compounds (**4C** > **4N** > **4O** > **4P** > **4S**). Apparently, the ring strain has a predominant effect in determining the activation barriers for the rearrangements of divinylcyclopropane and divinylheterocyclopropanes, all of which involves the release of a three-membered ring's strain. The exothermicities for these rearrangements, however, decrease in the order of **1N** > **1O** > **1C** > **1P** > **1S**. If the place of **1C** in this sequence is ignored, the decreasing reaction exothermicity order correlates well with the increasing activation barrier order and with the decreasing strain order of the related reference compounds. The lower exothermicity of the rearrangement of **1C**, as compared to those of **1N** and **1O**, may be attributed to the interrupted conjugation in the corresponding product, **3Ccc**, although it is not clear to exactly what extent the product stability affects the reaction exothermicity. NICS values calculated for TSs are typical of highly aromatic TSs of thermally allowed pericyclic reactions.

Acknowledgment. We thank the Scientific and Technical Research Council of Turkey (TBAG-104T202), the State Planning Organization of Turkey (DPT-2000K-120390), and the Research Board of Middle East Technical University (BAP-2005-01-03-04 and BAP-2005-08-16-05) for support of this research.

Supporting Information Available: (U)B3LYP/6-31G*-optimized Cartesian coordinates and all energy values for all structures and G2 energies for calculation of ring strain energies. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050711L

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