endo/*exo* Preferences for Double Bonds in Three-Membered Rings Including Phosphorus Compounds

T. P. M. Goumans,[a] Andreas W. Ehlers,[a] Koop Lammertsma,*[a] and Ernst-Ulrich Würthwein*[b]

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Depending on the substituent and the heteroelements of an unsaturated three-membered ring system of the methylenecyclopropane/1-methylcyclopropene type, the double bond may be preferentially exo- or endocyclic. This preference may be considered as a combination of substituent and ring-strain effects. The substituent effect is a composite one, encompassing both exocyclic olefinic strain and tautomeric preference. The preference for exocyclic unsaturation increases in the order $=CH_2 < =NH < =PH < =O$ for the considered substituents. The higher the ring-strain, the higher the propensity for exocyclic unsaturation. The low-strain 2*H*-phosphirenes favor endocyclic unsaturation, except for the 3-OH-substituted species where the strong C=O double bond is the determining factor.

Introduction

Double bonds and three-membered rings, both reactive moieties, reveal, if combined, extraordinarily high chemical reactivity. Angle-strain exerted on the double bond, and ring-strain of the three-membered ring reinforce each other to a great extent. A typical example of such a combination is the tautomeric pair methylenecyclopropane and methylcyclopropene. It is not easy to predict relative chemical reactivity or the possible tautomeric preference for this, and for comparable heteroanalogous tautomeric pairs, from chemical intuition. Experimentally, and from quantum chemical calculations, it is known that methylenecyclopropane (**1**), with its exocyclic unsaturation, is much more stable than its endocyclically unsaturated isomer 1-methylcyclopropene (**2**).[1,2] The corresponding nitrogen system, however, shows a preference for an endocyclic double bond, thereby favoring 3-methyl-2*H*-azirine (**10**) over 2-methyleneaziridine (**9**).[1] This reversal of preference has been debated[1] to originate from the relatively low ring-strain in 2*H*-azirine.[3] The relative stability of the corresponding exo- and endocyclic unsaturated phosphorus compounds 2-methylenephosphirane (**17**) and 3-methyl-2*H*-phosphirene (**18**) has so far not been addressed. Since phosphirenes also have low ring-strain,[4] these heterocycles may similarly be anticipated to prefer endocyclic unsaturation when appropriately substituted.

Phosphiranes (**h**) have been known since 1963,[5] and have been extensively investigated.[6] Oxaphosphiranes[7] (**n**) and azaphosphiranes[8] (**k**) were discovered more recently. Even less is known about the unsaturated ring systems.[9] Following the synthesis in 1982 by Mathey of the first stable 1*H*-phosphirene (**i**), through addition of a phosphinidene to an alkyne,[10] the interest in phosphirene chemistry has surged.[6b,11] Remarkably, 2*H*-phosphirenes (**j**) are less easily accessible.[11c−11i] Rather recently, the chemistry of 2*H*-azaphosphirenes (**m**) was developed by Streubel's group.[9] However, 1*H*-azaphosphirenes (**l**) have only been claimed as reactive intermediates,[12] and to the best of our knowledge, no oxaphosphirenes have yet been reported in the literature.

The preference of endo- vs. exocyclic unsaturation in heterocyclic three-membered rings is likely to depend on the nature of the heteroatom, and also on the ring substituent, although these relationships are not well understood. In this study, we extend a previous analysis on carbon and nitrogen three-membered ring systems to the phosphorus analogues and present highly accurate G3 calculations[13] on phosphirenes, azaphosphirenes, oxaphosphirenes and their respective tautomers. We also report on the effect of phosphane-substitution compared to that by methyl, amino, and hydroxyl groups.

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[a] Department of Organic and Inorganic Chemistry, Faculty of Sciences, Vrije Universiteit,
De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands
Fax: (internat.) +31-20/444-7488
E-mail: lammert@chem.vu.nl
[b] Institut für Organische Chemie, University of Münster,
Corrensstraße 40, 48149 Münster, Germany
Fax: (internat.) +49-251/833-9772
E-mail: wurthwe@uni-muenster.de

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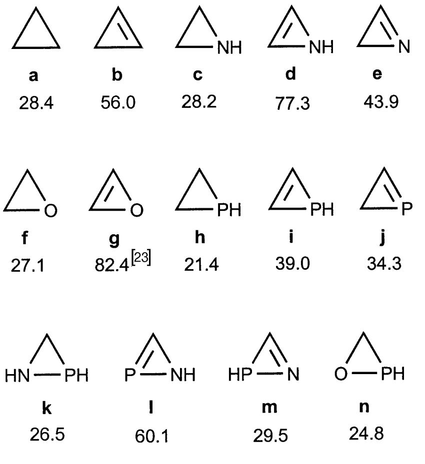
Results and Discussion

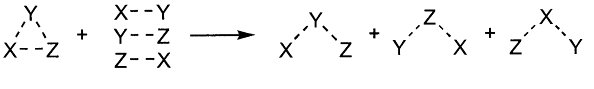
Strain and strain-energies are useful concepts that facilitate the discussion of structural and chemical properties, especially in small ring chemistry.[14,15] From a theoretical point of view, Cremer and Kraka[16] have treated this subject quite thoroughly, highlighting the scope and limitations of various theoretical treatments, including σ-aromaticity. The semiquantitative evaluation of strain has been achieved successfully by use of isodesmic and homodesmotic equations, which try to quantify strain-energy by comparing the molecules with appropriately choosen "strain-free" model compounds. We start by discussing the strain-energy of the unsubstituted rings, i.e. the hydrocarbons cyclopropane (**a**) and cyclopropene (**b**), and their nitrogen (**c-e**), oxygen (**f**,**g**), and phosphorus (**h-j**) analogues, as well as the azaphosphira/enes (**k-m**), and oxaphosphirane (**n**).[17] We address the effect of the heteroatom on the strain-energy of the three-membered rings. Subsequently, we discuss the effect of phosphorus ($-PH_2$, $=PH$) and other substituents on the preference for endo- vs. exocyclic unsaturation for cyclopropenes (**7**,**8**) and 2*H*-azirines (**15**,**16**), and their tautomers. This is followed by an analysis of the tautomers of substituted phosphirenes (**17−24**) and their respective tautomers. Finally, we study briefly methyl-substituted azaphosphirenes and oxaphosphirenes and their tautomeric preference.

Ring-Strain

The strain-energies of the various unsubstituted ring systems were calculated at G3(MP2) using homodesmotic Equation (1)[18,19] and are summarized in Scheme 1. The dotted lines in Equation (1) represent either a single or a double bond, and X, Y, and Z refer to CH, CH_2, CH_3, N, NH, NH_2, O, OH, P or PH. Negative homodesmotic reaction-energies are reported as strain-energies.



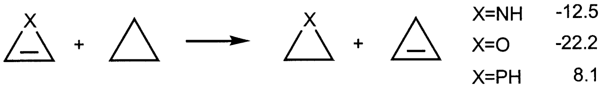
Scheme 1. Calculated homodesmotic strain-energies G3(MP2), according to Equation (1) (kcal/mol)

 (1)

The G3(MP2) method calculates similar strain-energies for the saturated systems cyclopropane (**a**), aziridine (**c**), and oxirane (**f**) of 28.4, 28.2, and 27.1 kcal/mol, respectively, in agreement with earlier reported theoretical[19,20] and experimental[21] values. Phosphirane (**h**) has a much lower strain-energy of 21.4 kcal/mol.[22] Aza- and oxaphosphiranes (**k**) and (**n**) show strain-energies of 26.5 and 24.8 kcal/mol.

Effect of Heteroelements on the Strain in Cyclopropene Analogues

Unsaturated three-membered rings are much more strained than the saturated systems. For cyclopropene (**b**), 1*H*-azirine (**d**), and oxirene (**g**),[23] the calculated strain-energies are 56.0, 77.3, and 82.4, respectively, and for 1*H*-phosphirene (**i**) 39.0 kcal/mol. The effect of introducing a heteroatom on the strain-energy of cyclopropene can be illustrated by exchanging the double bond [Equation (2)]. Likewise this shows 1*H*-azirine and oxirene to be more strained than cyclopropene and 1*H*-phosphirene to be less strained by respectively 12.5, 22.2, and −8.1 kcal/mol.

 (2)

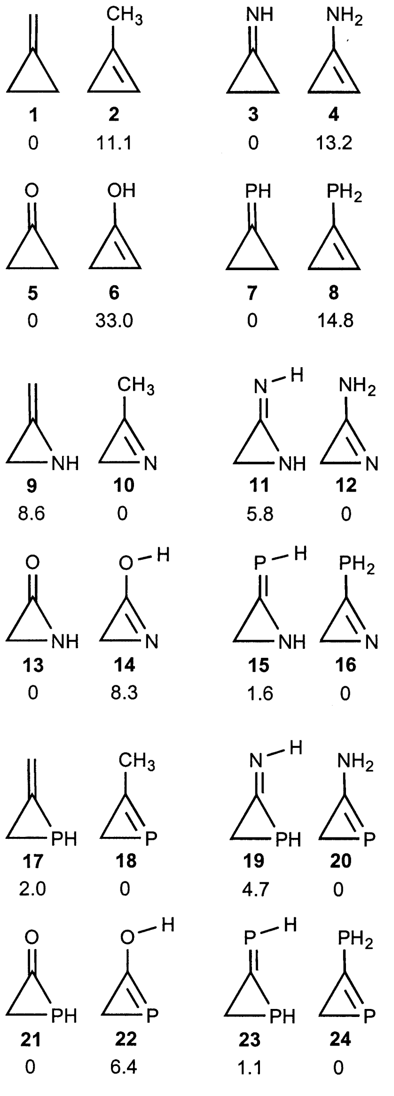
Thus, compared to cyclopropene (**b**), the strain increases on replacing the methylene group by NH (**d**) or O (**g**), whereas it decreases for replacement by PH (**i**). This contrasting behavior may originate from two effects: Firstly, the force constant of the hard-to-bend C=C−X bond angle increases as X becomes more electronegative (angle-bending force constant: C=C−C < C=C−NH2 < C=C-OH).[24] However, bonds with heavier, second row atoms (such as P) are generally easier to bend. This is reflected in the Baeyer (angle-bending) strain for C=C−X rings, which is larger for X = O and NH and smaller for X = PH, as more acute C=C−X angles are needed for the first row elements. Secondly, the unfavorable Pauli repulsive interaction between the olefinic bond and the lone pair on the heteroatom (Hückel anti-aromaticity) has been argued to be much less prominent in 1*H*-phosphirene than in 1*H*-azirine, if indeed it is present at all.[25]

Interestingly, 2*H*-azirine (**e**) is much less strained than the 1*H* isomer (**d**) (by, 33.4 kcal/mol), whereas the corresponding energy difference is only 5.7 kcal/mol for the phosphorus analogues (**i**,**j**). These features are also evident in 1*H*-azaphosphirene (**l**) and 2*H*-azaphosphirene (**m**), of which the former is 30.6 kcal/mol more strained. 1*H*-Azirine (**d**) and oxirene (**g**) have been discussed in terms of Hückel anti-aromaticity.[25] The relatively low strain-energy of 1*H*-phosphirene (**i**) and 2*H*-azaphosphirene (**m**) may be related to the absence of anti-aromaticity in the phosphorus compounds.[25b,26]

Endocyclic versus Exocyclic Unsaturation

Methylenecyclopropane (**1**) is 11.1 kcal/mol more stable than 1-methylcyclopropene (**2**) (Scheme 2).[1] For the imino/

amino-substituted rings (**3** and **4**), the preference for exocyclic unsaturation (**3**) increases to 13.2 kcal/mol. A similar energy difference of 14.8 kcal/mol is found for the phosphorus-substituted rings (**7** and **8**), again favoring an exocyclic double bond (**7**). By far the largest difference (33.0 kcal/mol) is obtained for the oxo-substituted rings (**5** over **6**).[1]



Scheme 2. Relative energies of pairs of tautomers (G3) (kcal/mol)

Heteroatom substitution within the three-membered ring has a significant impact on the preference for endo- vs. exocyclic unsaturation. For example, 3-methyl-2*H*-azirine (**10**), with its endocyclic double bond, is favored over methylene aziridine **9** by as much as 8.6 kcal/mol. Likewise, for the imine/amine derivatives **11** and **12** the energy difference remains in favor of the amino azirine **12** (5.8 kcal/mol),[1] and this is also the case for the P-substituted derivatives, although the preference for the azirine **16** over **15** is reduced to only 1.6 kcal/mol. Only the α-lactam **13**, with its exocyclic C=O bond, is favored over the hydroxyazirine **14** by 8.3 kcal/mol.

Whereas the CCC ring systems strongly prefer exocyclic double bonds and the CCN rings endocyclic ones, the effect of the substituent on the relative stability of the tautomers is similar for both. That this is also the case for the CCP rings is illustrated in Figure 1, in which the energy differences between the endo- and exocyclic species are plotted as a function of the substituent for the three types of rings. Figure 1 also shows that the strongest preference for an exocyclic (C=O) double bond occurs for the oxygen substituent, and that this is in fact the only such preference among the C, N, O and P substituents for the CCN and CCP ring systems.

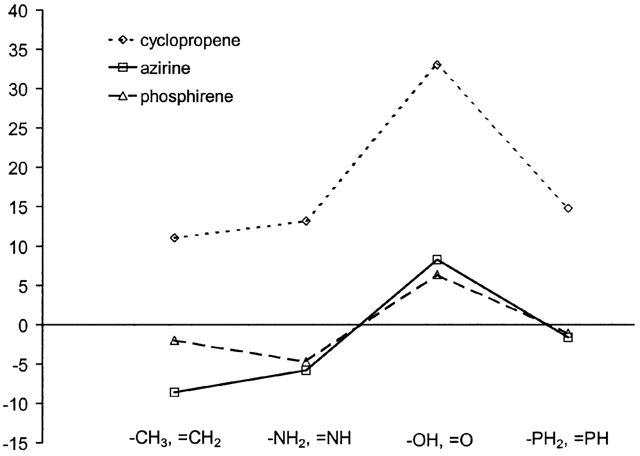
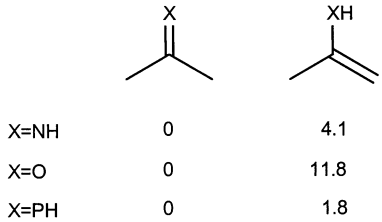


Figure 1. Relative energies of endocyclic tautomers of substituted cyclopropenes, azirines and phosphirenes for different substituents with respect to the exocyclic tautomers (G3) (kcal/mol)

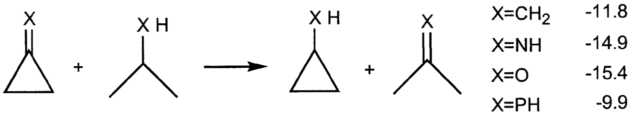
The preference of the other substituted nitrogen heterocycles for endocyclic unsaturation (as compared to that of the cyclopropane/cyclopropene pair) is due to the reduced olefinic strain, which can be attributed to the effect of the nitrogen lone pair. The same applies to the substituted phosphorus rings, even though the tautomerization energy of 2.0 kcal/mol for the methyl-substituted derivatives **17** and **18** is much smaller than the 8.6 kcal/mol for the CCN rings **9** and **10**. The exocyclic CCN ring system **9** is relatively destabilized since the nitrogen atom is pyramidalized. This results in a loss of conjugation, analogous to that present in, for example, vinylamine.[27] In contrast, vinylphosphirane prefers a bisected conformation in which the phosphorus lone pair is oriented orthogonal to the π-system bond.[28] Consequently, there is no such loss of conjugation in the CCP ring **17**. Experimentally, substituted derivatives of **17** have been observed.[29] They are, however, not able to undergo tautomerism due to their substitution pattern.

The propensity for exo- or endocyclic unsaturation depends on ring-strain, but is also related to the nature of the substituent (Figure 1). The substituent determines, to a large degree, the strength of the tautomeric preference, which is of the order C=O > C=N > C=P > C=C, as determined by the energy difference of the tautomers shown in Scheme 3.[30]



Scheme 3. Relative energies of tautomers (G3) (kcal/mol)

This suggests that the nitrogen substituent would support exocyclic unsaturation more than the corresponding phosphorus substituent. However, the energy difference of the acyclic tautomers does not take into account the extra strain that the exocyclic double bond introduces into the ring system. This extra olefinic strain[31] can be estimated from the following homodesmotic equation [Equation (3)]:

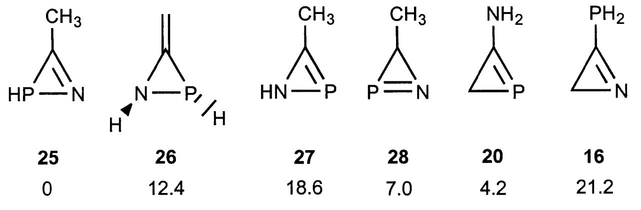


(3)

Evidently, the C=P bond imposes the least extra strain on the ring structure, whereas the strain resulting from both the imido and oxo groups is larger than that caused by the methylidene group. Thus, of these four types of C=X bonds, the phosphaalkene most easily adopts a tight R−C(=X)−R angle. Thus, although an ordinary C=P bond is weaker than the C=N bond, for exocyclic bonds the opposite is true. Combining the exocyclic olefinic strain from Equation (3) with the tautomeric preference from Scheme 3 gives the following propensity for exocyclic unsaturation for the substituents: $CH_2 < NH < PH << O$, which is in agreement with the calculated tautomeric preferences shown in Scheme 2 and Figure 1.

Unsaturated three Membered Rings with Two Heteroatoms

The influence of a second heteroatom in the three-membered ring on the exo/endo tautomerism can be evaluated for the C_2H_4PN structures shown in Scheme 4. Of these, 3-methyl-2*H*-azaphosphirene (**25**) is energetically favored over its tautomers 3-methylene-azaphosphiridine (**26**), 3-methyl-1*H*-azaphosphirene (**27**), and 3-methyl-3*H*-azaphosphirene (**28**) by as much as 12.4, 18.6, and 7.0 kcal/mol, respectively. 3*H*-Phosphiren-2-yl amine (**20**) and 3-phosphanyl-2*H*-azirine (**16**) are also less stable than **25** by 4.2 and 21.2 kcal/mol.[32]

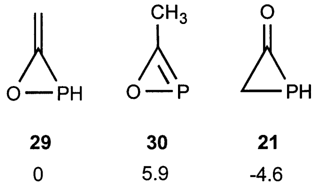


Scheme 4. Relative energies of pairs of tautomers (G3) (kcal/mol)

Apparently, on replacing a methylene group in the CCN ring by a PH group, the preference for endo- over exocyclic unsaturation increases by 3.8 kcal/mol (compare **25−26** with **9−10**). In contrast, replacing a CH_2 group in a CCP ring by an NH unit results instead in 8.2 kcal/mol stabilization of the exocyclic olefin (compare **26−27** with **17−18**).

This contrasting effect on the endo- vs. exocyclic unsaturation by nitrogen and phosphorus as second heteroatoms is directly related to the influence on the strain of the unsaturated three-membered ring, which is increased by nitrogen in 1*H*-azirine and reduced by phosphorus in 1*H*-phosphirene. As noted above, **27** suffers more from antiaromaticity (Pauli repulsion) than **25** does.

Also, extra strain is introduced into the unsaturated ring when oxygen is introduced as a second heteroatom. This is evident from the energetic preference of exocyclic **29** over **30** (Scheme 5). However, 2-oxo-phosphirane (**21**) is the most stable C_2H_3PO three-membered ring structure in analogy to the α-lactam (**13**).[33]



Scheme 5. Relative energies of isomeric O,P systems (G3) (kcal/mol)

Conclusion

Relative ring-strain is one of the two major factors that determine whether a substituted three-membered heterocyclic ring structure prefers exo- or endocyclic unsaturation. The other factor is the particular substituent enabling tautomerism. Of the four substituents, the preference for endocyclic unsaturation decreases in the order $CH_3 < NH_2 < PH_2 < OH$. This is determined by the relative strength of the double bond ($C{=}C < C{=}P < C{=}N << C{=}O$) and the exocyclic olefinic strain ($C{=}P < C{=}C < C{=}N \approx C{=}O$).

The parent cyclopropene, which has a ring-strain of 56.0 kcal/mol, prefers exocyclic unsaturation for each of the substituents. The less-strained 2*H*-azirine (43.9 kcal/mol) and 2*H*-phosphirene (34.3 kcal/mol) both prefer endocyclic unsaturation, except for the oxo-substituent where the strong exocyclic C=O bond prevails. Incorporating an electronegative element (NH, O) into the 2*H*-phosphirene ring increases the ring-strain significantly and thereby enhances the propensity for exocyclic unsaturation in the substituted 1*H*-azaphosphirenes and oxaphosphirenes. However, C=N endocyclic unsaturation is possible in 2*H*-azaphosphirene, the parent of which has a modest strain energy of 29.5 kcal/

mol. Such "in-ring" tautomerism is not possible for oxophosphirene, which therefore prefers exocyclic unsaturation.

Computational Methods

All calculations were performed with the Gaussian 98 suite of programs.[34] Ring-strain energies are based on homodesmotic reactions,[18] and calculated at G3(MP2)[35] at 298 K, whereas relative energies are reported at G3[13] at 0 K. All energies are given in kcal/mol. Relative energies of different tautomers of the numbered structures are reported in parentheses. Where different isomers are possible (*E*/*Z*, *syn*/anti), we report only the lowest energy isomer and provide the structural and energetic data of the others in the Supporting Information.

Supporting information(see also footnote on the first page of this article): G3 total energies of all molecules and Gaussian archive entries of the numbered compounds.

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[33] Other possible isomers such as 2-hydroxy-2*H*-phosphirene and 2-hydroxy-1*H*-phosphirene are respectively 8.9 and 15.7 kcal/mol higher in energy than **22**. See Supporting Information for chemical drawings.

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