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Four-Membered Heterocycles with a Carbon−Heteroatom Exocyclic Double Bond at the 3-Position: Puckering Potential and Thermodynamic Properties

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Despite the specific importance of four-membered heterocycles with a carbon−heteroatom double bond at the 3-position in organic and medicinal chemistry, little attention has been given up to now to theoretical computational studies on these molecules. However, the overall geometry, and degree of ring puckering especially, could significantly influence the reactivity and biological properties of these four-membered ring compounds. In this paper, focus is made on the influence of different substituents on the equilibrium geometry, ring puckering potential, and thermodynamic quantities. It was found that these properties are mainly affected by the heteroatom (oxygen, nitrogen, sulfur, phosphorus) contained in the ring skeleton. Moreover, the correct description of the puckering potential with the hindered rotor treatment leads to substantial corrections on the thermodynamic properties in the harmonic oscillator approximation.

1. Introduction

Four-membered heterocycles occupy a prominent place in organic and medicinal chemistry due to their synthetic potential in numerous ring transformation reactions and important biological properties, respectively.[1−4] Their specific reactivity is a result of the high ring strain of the four-membered ring skeleton, promoting various ring opening and ring expansion reactions. In addition, the forces that induce this high ring strain also have impact on the conformational properties of these compounds. In that respect, it is known that numerous four-membered rings adopt a puckered (butterfly-like) conformation.[5] This structural feature results in the occurrence of pseudoaxial and pseudo-equatorial positions, which may affect reaction rates in elimination reactions or induce stereoselectivity in various ring transformations. Also, the geometry of the ring skeleton is of importance in medicinal chemistry because many biological activities depend on the conformational properties of the active compound (e.g., key−lock interactions with enzymes).

As an important class of four-membered heterocycles, azetidin-2-ones have received immense attention as antibiotic compounds, e.g., monobactams, penicillins, cefalosporins, etc.[2] Compared to these β-lactams, azetidin-3-ones are much less widespread in the literature despite their potential in synthetic and pharmaceutical chemistry. Even less attention has been devoted to the various heterocyclic analogues, i.e., oxetan-3-ones, thietan-3-ones, and phosphetan-3-ones. In addition, only very few data are available concerning the corresponding heterocyclic imines, phosphines, and thiones. For the majority of these molecules, neither experimental data nor previous theoretical studies are available. Little experimental work is available in the literature on azetidin-3-one **2**, oxetane-3-one **6**, and thietane-3-one **14**, where information is given on the geometry of these compounds.[6−9]

In this paper, the puckering potential and thermodynamic properties of a variety of sixteen four-membered ring compounds is studied (Chart 1). These four-membered heterocycles have a carbon−heteroatom double bond at the 3-position: azetidine-3-imine **1**, azetidine-3-one **2**, azetidine-3-ylidenephosphine **3**, azetidine-3-thione **4**, oxetane-3-imine **5**, oxetane-3-one **6**, oxetan-3-ylidenephosphine **7**, oxetane-3-thione **8**, phosphetane-3-imine **9**, phosphetane-3-one **10**, phosphetan-3-ylidenephosphine **11**, phosphetane-3-thione **12**, thietane-3-imine **13**, thietane-3-one **14**, thietan-3-ylidenephosphine **15**, and thietane-3-thione **16**. The ring puckering angle is defined as the angle between the planes 4−1−2 (CXC) and 2−3−4 (CCC), as shown in the figure. The sign of the angle is only important for the species where the symmetry is broken by an out-of-plane NH or PH group on the 1-position. The negative sign is given to the geometries with the ring folding toward the out-of-plane hydrogen.

All these molecules with a four-membered ring moiety have potential applications in heterocyclic chemistry.[1] They are strained cyclic species, characterized by one ring vibration, the so-called puckering mode, which can exhibit various minima. For the description of this vibration, the standard harmonic oscillator (HO) approximation is no longer viable because, in this approach, only one minimum is considered. In a previous paper of the presenting authors, the one-dimensional hindered rotor (1D-HR) scheme was extended to and tested on a variety of four-membered rings in which only one CH_2 fragment of the cyclobutane ring was substituted.[5] This 1D-HR method has the merit of incorporating the true puckering potential into the calculation of thermodynamic properties, resulting in more accurate predictions.[5,10,11]

The primary goal of this paper is to unravel the effect of the various heteroatoms at the 3-position of the cyclobutane ring on the structure, on the puckering potentials, and finally, on the thermodynamic properties such as entropy and heat capacity.

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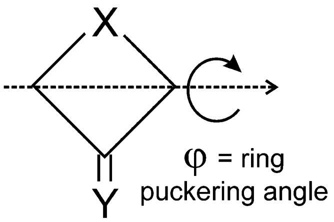
CHART 1



	X = NH	X = O
Y = NH	**(1)** azetidine-3-imine	**(5)** oxetane-3-imine
Y = O	**(2)** azetidine-3-one	**(6)** oxetane-3-one
Y = PH	**(3)** azetidin-3-ylidenephosphine	**(7)** oxetan-3-ylidenephosphine
Y = S	**(4)** azetidine-3-thione	**(8)** oxetane-3-thione

	X = PH	X = S
Y = NH	**(9)** phosphetane-3-imine	**(13)** thietane-3-imine
Y = O	**(10)** phosphetane-3-one	**(14)** thietane-3-one
Y = PH	**(11)** phosphetan-3-ylidenephosphine	**(15)** thietan-3-ylidenephosphine
Y = S	**(12)** phosphetane-3-thione	**(16)** thietane-3-thione

The standard ab initio procedures systematically predict estimates for the latter properties in the HO approach. The nature of the ring puckering potentials suggests some substantial corrections of the partition functions with regard to the HO values when the real potential shape is taken into account. This methodology (of the 1D-HR scheme) is outlined in ref 5.

All ab initio calculations were performed with Gaussian03[12] at the mPW1B95/6-31+G(d,p)[13] level of theory. This level is expected to be a reliable method for reproducing accurate geometries and energy values of molecules with heteroelements.[14] Moreover, it was found to be the most appropriate level to describe simple four-membered rings.[5]

2. Equilibrium Geometries and Puckering Potential

The shape of the potential function associated with the ring puckering depends on the structural features inhibiting the ring vibration. This function is calculated by pointwise geometry optimizations at fixed out-of-plane angles and thereby relaxing all other degrees of freedom. The resulting ring puckering potentials are shown in Figure 1 (black lines) for all molecules. It is readily clear that the shape of the potential energy function is determined by the heteroatom contained within the ring: for each row of plots, almost identical shapes are found.

(i) For X = NH (**1**−**4**), an asymmetric azetidine-like shape is found, and the equilibrium geometry has an average puckering angle of 15° (equatorial position). This is in good agreement with the equilibrium puckering angle of 15° found in 1-*p*-toluenesulfonyl-2-ethylazetidine-3-one, the closest related molecule for which experimental data are found.[7]

(ii) For X = O (**5**−**8**), a nearly quadratic energy behavior is obtained for each of these heterocycles. This is not surprising because the "parent" molecule, i.e., oxetane, already exhibits a very small puckering angle and barrier to planarity. The additional exo double bond at the 3-position forces the equilibrium geometry of the ring to be entirely planar.

(iii) For X = PH (**9**−**12**), the equilibrium geometry is strongly puckered, with the angle ranging from −30.8° to −39.9°. Contrary to the azetidines, the hydrogen of the PH group contained in the ring is oriented toward the carbon atom at the 3-position, and the resulting puckering angle is therefore in the axial position. Apparently, the lone pairs of the phosphorus atom, which are more spread out than the nitrogen lone pairs, cause more steric hindrance and prefer to be oriented away from the ring. Still, for phosphetan-3-ylidenephosphine **11** and phosphetane-3-thione **12**, a second energy minimum (equatorial conformer) is found at $\varphi = 38.24°$ and $\varphi = 34.77°$, respectively, with a relative energy of 8.88 kJ/mol and 13.32 kJ/mol.

(iv) Finally, for X = S (**13**−**16**), the thione compounds are characterized by a widespread low-energy plateau. The width of this plateau (energy smaller than 2 kJ/mol), spans a range of about 44° [φ: $-22° \rightarrow +22°$] for thietane-3-one **14**, 50° for thietane-3-imine **13**, 64° for thietane-3-thione **16**, and up to 72° for thietan-3-ylidenephosphine **15**.

Thietane has an equilibrium puckering angle of ±25.8°.[5] As for the oxetanes (X = O), an additional exo double bond forces the ring to a planar configuration and removes the energy barrier between the original thietane minima. The width of the low-energy plateau is therefore approximately the difference of the two equilibrium puckering angles ($\approx 2 \times 25.8°$). The only (slight) exception to this rule is thietan-3-ylidenephosphine (**15**). This molecule does not have a planar equilibrium geometry but has its ring puckered by 24.0°. The barrier to planarity is a mere 1.32 kJ/mol, allowing to state that the shape of all thietane puckering potentials is very similar.

The nature of the exo substituent determines only the height/width of the potential energy plot without affecting its shape. An important parameter for the influence of the heteroelement on the ring puckering is the C=Y double bond length. It has approximate values of 1.474, 1.434, 1.891, and 1.834 Å for $|CN|$, $|CO|$, $|CP|$, and $|CS|$, respectively. For large C=Y bond lengths, the potential energy variation will be limited. The carbonyl and imino bond lengths are about the same, but the NH-group induces additional ring strain because of the presence of a hydrogen atom and the lone pair of nitrogen, which is much more spread out than the oxygen lone pairs. The latter can a fortiori be said about the PH group. However, its long double bond length with the carbon atom reduces its steric hindrance to the same order of magnitude of the carbonyl group. The combination of both effects leads to the curves of Figure 1, where the largest energy variations are observed in the imino compounds, while the thione species exhibit the smaller variations.

As the heteroatom within the ring only determines the shape of the puckering potential, one may expect that the equilibrium geometry is also mainly determined by that substituent. This is indeed true (except for thietan-3-ylidenephosphine (**15**)), as can be seen in Tables 1 and 2. The imino substituent is oriented in plane with the ring structure and causes a slight asymmetry. Therefore, averaged values for the $|CX|$, $|CC|$, and $\widehat{XCC}$ geometric parameters are presented. The same applies to Y=PH.

Changing the Y substituent leaves the ring nearly unaffected. Change of the X substituent leads to large variations of $|CX|$ bond lengths *and* affects the $\widehat{CXC}$ and $\widehat{CCC}$ bond angles. It is interesting to note that the influences exerted by Y and X are nearly independent of each other. This is also reflected in the bond lengths $|CX|$ and $|CY|$ of the single heterosubstituted four-membered rings studied in ref 5, also shown in Table 1 in the "no exo-substitution" column (azetidine, oxetane, phosphetane, and thietane) and the "no endo-substitution" row (cyclobutylideneamine, cyclobutanone, cyclobutylidenephosphine, and cyclobutanethione).

Comparison with experiment is only possible for oxetane-3-one **6**[8] and 3-thietane-3-one **14**[9] and is also presented in Tables 1 and 2 (values between brackets). The calculated and experimental data are in good agreement.

3. Thermodynamic Properties

In this section, we discuss the thermodynamic properties of all four-membered compounds taken into consideration. More precisely, we investigate the influence of the ring puckering

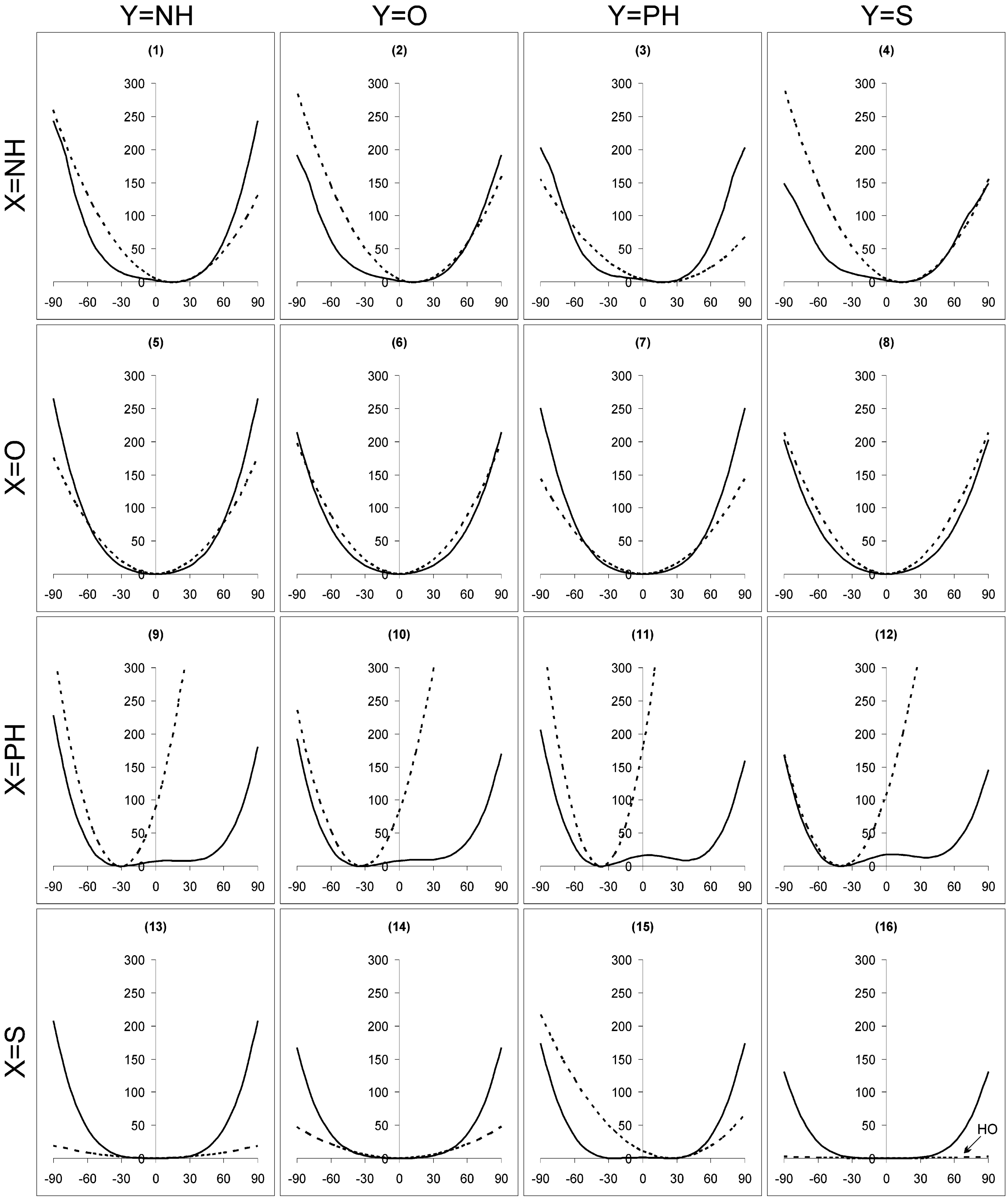


Figure 1. Ring puckering potential for all investigated compounds (full lines). The dotted lines are the quadratic (HO) energy variations calculated from the second derivative at the equilibrium. Energy values in kJ/mol, angle values in degrees.

potential on these properties with regard to the HO approach. It has already been reported that the harmonic oscillator potential (dotted line in Figure 1) can significantly differ from the true puckering potential. Hence, it can be expected that the partition functions, and derived thermodynamic properties, calculated with the 1D-HR model and therefore based on the real potential, will deviate from those calculated in the HO approximation. First conclusions on a qualitative basis can already been drawn from a comparative study of Figure 1.

For the **oxetanes** (X = O), the correction is expected to be very small, as the real potential is very close to the HO potential based on the second derivative in the equilibrium geometry.

TABLE 1: Structural Data (Bond Lengths) of the Equilibrium Geometry of the Studied Molecules[a]

		Y=NH	Y=O	Y=PH	Y=S	no exo-substitution
X=NH	φ_{puck}	15.33	13.33	18.45	14.24	29.4
	$\langle \lvert CX \rvert \rangle$	1.475	1.474	1.473	1.473	1.469
	$\langle \lvert CC \rvert \rangle$	1.513	1.521	1.509	1.508	1.535
	$\lvert CY \rvert$	1.257	1.196	1.667	1.604	
X=O	φ_{puck}	0.00	0.00	0.00	0.00	±9.8
	$\langle \lvert CX \rvert \rangle$	1.435	1.434 (1.441)	1.434	1.433	1.433
	$\langle \lvert CC \rvert \rangle$	1.509	1.518 (1.524)	1.504	1.503	1.530
	$\lvert CY \rvert$	1.255	1.194 (1.222)	1.666	1.601	
X=PH	φ_{puck}	−30.76	−33.41	−36.64	−39.9	−30.0
	$\langle \lvert CX \rvert \rangle$	1.889	1.890	1.890	1.894	1.880
	$\langle \lvert CC \rvert \rangle$	1.507	1.511	1.497	1.492	1.533
	$\lvert CY \rvert$	1.264	1.204	1.682	1.624	
X=S	φ_{puck}	0.00	0.00	±23.99	0.00	±25.8
	$\langle \lvert CX \rvert \rangle$	1.833	1.832 (1.826)	1.838	1.834	1.834
	$\langle \lvert CC \rvert \rangle$	1.512	1.518 (1.528)	1.504	1.505	1.531
	$\lvert CY \rvert$	1.258	1.197 (1.224)	1.672	1.607	
X=CH$_2$ (no endo-substitution)	φ_{puck}	±17.7	±12.2	±25.7	±20.1	±29.7
	$\langle \lvert CX \rvert \rangle$	1.514	1.521	1.510	1.508	1.534
	$\langle \lvert CC \rvert \rangle$	1.546	1.546	1.544	1.544	1.534
	$\lvert CY \rvert$	1.260	1.199	1.671	1.609	

[a] We also provide the structural data of eight four-membered rings with a single heteroatom and cyclobutane. These additional data are taken from ref 5 and are calculated on the same level of theory as the compounds studied in the present paper. Values between brackets are experimental estimates taken from refs 8,9. Bond lengths are expressed in Å.

TABLE 2: Structural Data (Bond Angles) of the Equilibrium Geometry of the Studied Molecules[a]

		Y=NH	Y=O	Y=PH	Y=S
X=NH	φ_{puck}	15.33	13.33	18.45	14.24
	$\langle \widehat{XCC} \rangle$	88.18	87.92	89.07	89.17
	$\widehat{CXC}$	92.32	93.20	90.81	91.28
	$\widehat{CCC}$	89.32	89.46	88.08	88.63
X=O	φ_{puck}	0.00	0.00	0.00	0.00
	$\langle \widehat{XCC} \rangle$	89.89	89.37 (88.48)	91.25	90.81
	$\widehat{CXC}$	92.98	93.95 (94.82)	91.43	91.89
	$\widehat{CCC}$	87.25	87.30 (88.48)	86.08	86.49
X=PH	φ_{puck}	−30.76	−33.41	−36.64	−39.90
	$\langle \widehat{XCC} \rangle$	88.17	87.03	87.44	85.76
	$\widehat{CXC}$	75.38	75.87	74.20	74.51
	$\widehat{CCC}$	100.09	100.53	99.21	100.38
X=S	φ_{puck}	0.00	0.00	±23.99	0.00
	$\langle \widehat{XCC} \rangle$	90.62	90.40	89.98	91.54
	$\widehat{CXC}$	78.53	78.97	76.53	77.50
	$\widehat{CCC}$	100.23	100.24 (100.5)	98.43	99.41

[a] Values between brackets are experimental estimates taken from refs 8,9. Bond angles are expressed in degrees.

For the **azetidines** (X = NH), the partition function will increase in the 1D-HR model, as for negative values of the puckering angle, the energy is overestimated by the harmonic potential. For **thietanes**, the low-energy plateau is well described by the quadratic energy variation, but the "walls" of the potential are missing in the HO approach. As a result, the real potential energy is higher than the quadratic estimate, and the 1D-HR partition function may be expected to be lower than its HO counterpart. As already mentioned, thietan-3-ylidenephosphine **15** is an exception and follows more or less the pattern of azetidines. The last series of molecules, the **phosphetanes** (X = PH), is characterized by a completely inappropriate harmonic potential. For all values of the puckering angle, it overestimates the real potential and, moreover, it "misses" the second (near) minimum of the puckering potential. The 1D-HR treatment is expected to generate a substantial increase of the partition function compared to the HO predictions.

To measure the influence of the puckering mode on the quantitative level, a scaling factor κ_{HR} as the ratio of the 1D-HR partition function with the HO partition function is introduced as suggested in ref 11: $Q_{\text{HR}}(T) = Q_{\text{HO}}(T)\kappa_{\text{HR}}(T)$, or

$$\kappa_{\text{HR}}(T) = \sqrt{\frac{\beta}{2\pi}}\sqrt{\left.\frac{\partial^2 V}{\partial \varphi^2}\right|_0}\int_{-\pi}^{\pi} e^{-\beta V(\varphi)}\,\mathrm{d}\varphi \qquad (1)$$

where φ is the puckering angle and $V(\varphi)$ the puckering potential, and $\beta = 1/RT$.

From this factor, one can derive the corrections on entropy and heat capacity as:

$$\Delta S(T) = R\left(\ln \kappa_{\text{HR}} + T\left(\frac{\partial \ln \kappa_{\text{HR}}}{\partial T}\right)\right) \qquad (2)$$

$$\Delta C(T) = RT\left(2\frac{\partial \ln \kappa_{\text{HR}}}{\partial T} + T\frac{\partial^2 \ln \kappa_{\text{HR}}}{\partial T^2}\right) \qquad (3)$$

Figure 2 displays these corrections ΔS and ΔC and the scaling factors κ_{HR} for all studied compounds. As argued above, only the thietanes (X = S) and the phosphetanes (X = PH) are subject to large corrections. In Table 3, the entropy and heat capacity at 298.15 K are presented for all compounds in the HO and 1D-HR model. Oxetane-3-one **6**, oxetane-3-thione **8**, thietane-3-one **14**, and thietane-3-thione **16** have a symmetry number of two, while for the other compounds, the symmetry number is unity.

The largest negative corrections are noticed for thietane-3-thione **16**, where the low-energy plateau is widest and the quadratic HO potential has the smallest curvature. The largest positive correction (both on entropy and heat capacity) is found for phosphetan-3-ylidenephosphine **11**. For the heat capacity, the changes are smaller and seem to converge to about $-R/4$, very well in agreement with the results obtained in our previous paper on four-membered rings,[5] although this topic was not explicitly discussed. At high temperatures, the contribution to the heat capacity of a single HO vibration is R; for an

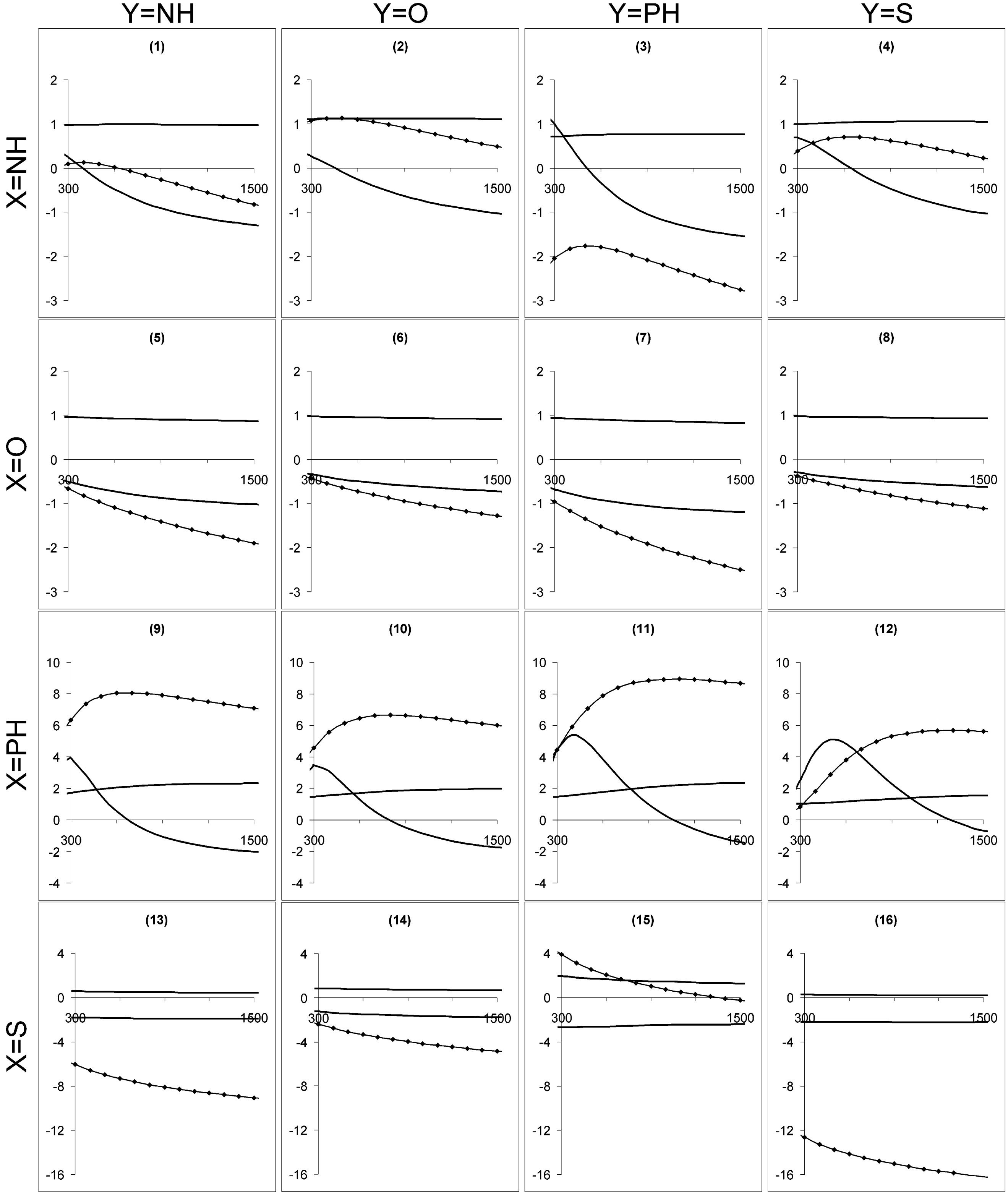


Figure 2. Plots of the entropy difference $\Delta S(T)$ in J/mol/K (diamonds line) and the heat capacity difference $\Delta C(T)$ in J/mol/K (black line) in terms of the temperature (K). Also the scaling factors $\kappa_{HR}(T)$ (dimensionless) are given as gray lines.

anharmonic vibration with finite potential energy barriers, such as internal rotations, the contribution to the heat capacity is $R/2$. Because the shape of the ring puckering potential is not quite quadratic but still with barriers going to infinity, it is not very surprising that this mode contributes about $3R/4$ to the heat capacity.

To investigate the coupling of the puckering mode with other vibrations, it is instructive to apply the recently developed extended hindered rotor (EHR) method. This methodology incorporates any rotational−vibrational coupling effect and the influence of the variable moments of inertia into the HR formalism.[11] This EHR formalism is now applied to thietane-3-thione **16** because it is one of the best candidates for substantial influence of (pseudo)rotational−vibrational coupling. In this EHR model, an additional factor appears in the integrand of eq 1 which comprises the variation of the puckering moment

TABLE 3: Entropy and Heat Capacity (at Constant Pressure), Both in J/mol/K, According to the HO and 1D-HR Model[a]

		S_{HO} (298.15 K)	C_{HO} (298.15 K)	S_{HR} (298.15 K)	C_{HR} (298.15 K)
(1)	azetidine-3-imine	291.85	77.11	291.94	77.37
(2)	azetidine-3-one	290.70	74.47	291.77	74.74
(3)	azetidin-3-ylidenephosphine	306.76	84.41	304.71	85.43
(4)	azetidine-3-thione	301.69	77.65	302.06	78.34
(5)	oxetane-3-imine	290.78	73.24	290.12	72.73
(6)	oxetane-3-one	283.31	70.50	282.87	70.16
(7)	oxetan-3-ylidenephosphine	307.02	80.74	306.06	80.06
(8)	oxetane-3-thione	294.47	73.76	294.10	73.47
(9)	phosphetane-3-imine	304.19	86.93	310.52	90.87
(10)	phosphetane-3-one	303.04	83.91	307.60	87.37
(11)	phosphetan-3-ylidenephosphine	316.75	94.06	321.18	98.50
(12)	phosphetane-3-thione	311.65	86.66	312.45	89.14
(13)	thietane-3-imine	311.51	79.94	305.45	78.16
(14)	thietane-3-one	300.90	77.17	298.51	75.92
(15)	thietan-3-ylidenephosphine	319.20	87.37	323.10	84.71
(16)	thietane-3-thione	321.53	80.70	308.92	78.51

[a] Corrections due to symmetry are included.

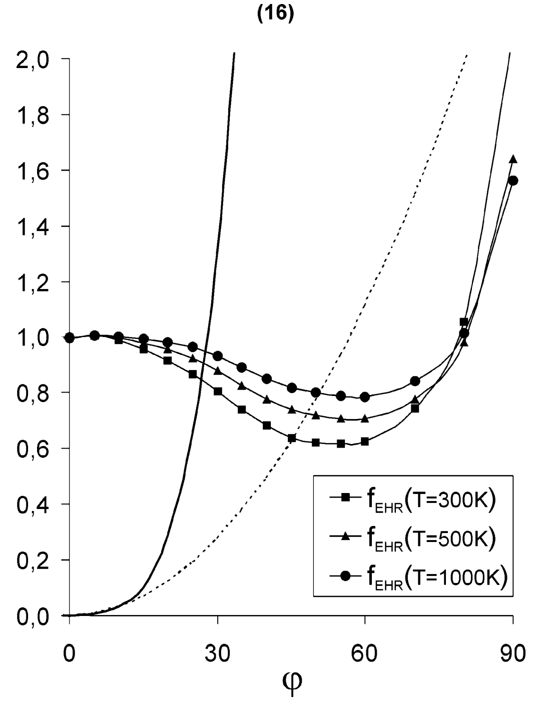


Figure 3. The EHR factor $f_{EHR}(\varphi,T)$ (eq 4) of thietane-3-thione **16** at three different temperatures. Also, the puckering potential (bold line) and its quadratic approximation (dotted line) is shown; energy values in kJ/mol.

of inertia and the variations of the vibrational temperatures in terms of the puckering angle:

$$\kappa_{EHR}(T) = \sqrt{\frac{\beta}{2\pi}} \sqrt{\left.\frac{\partial^2 V}{\partial \varphi^2}\right|_0} \int_{-\pi}^{\pi} f_{EHR}(\varphi,T)\, e^{-\beta V(\varphi)}\, d\varphi \quad (4)$$

The f_{EHR} scaling function is normalized to unity at the potential energy minimum: $f_{EHR}(\varphi = \varphi_{puck}, T) \equiv 1, \forall T$. For most potential energy variations, the exponential Boltzmann factor will be relatively small. Only for (very) low-energy values will this factor be close to unity, and the integrand will be dominated by the value of f_{EHR}. Figure 3 shows $f_{EHR}(\varphi,T)$ at some different temperatures. It is a slowly decreasing function for the angles of interest and should have only a minor influence on the scaling factor κ. The additional corrections (EHR versus HR) are less than 0.5 J/mol/K for entropy, and less than 0.2 J/mol/K for the heat capacity.

TABLE 4: (a) Structural Data of the Equilibrium Geometry of Methylenecyclobutane;[a] **(b) Entropy and Heat Capacity of Methylenecyclobutane, Both in J/mol/K, According to the HO and 1D-HR Model**[b]

(a)	mPW1B95	experimental
φ_{puck}	23.08	21.6
$\langle\|CX\|\rangle$	1.545	1.557
$\langle\|CC\|\rangle$	1.510	1.524
$\|CY\|$	1.326	1.331
$\langle\widehat{XCC}\rangle$	87.56	
$\widehat{CXC}$	88.83	
$\widehat{CCC}$	91.47	92.0

(b)	HO	HR	exp
S (298.15 K)	291.54	289.70	298.9
C (298.15 K)	85.29	82.92	87.40

[a] Experimental estimates are taken from ref 16. Bond lengths are expressed in Å and bond angles are expressed in degrees. [b] Corrections due to symmetry are included. The experimental values were taken from the NIST Database.[17]

From these data, it can be concluded that, in four-membered rings, the puckering mode is almost completely uncoupled from the other vibrations, and the 1D-HR treatment is the most appropriate model for their description.

4. Methylenecyclobutane

As the last topic, we also calculated the structure, puckering potential, and thermodynamic properties of methylenecyclobutane. Compared to the previous heterocyclic molecules, there is much more experimental and ab initio data available for this compound.[15,16] Again, the puckering potential is calculated (Figure 4a), along with the 1D-HR scaling factor κ_{HR} and resulting corrections ΔS and ΔC on entropy and heat capacity (Figure 4b). An important remark concerning the entropy of methylenecyclobutane is the difference of symmetry number of the molecule in the HO approximation (puckered structure) versus the HR description. As explained in ref 5, in the HR approach, the highest symmetry along the puckering path has to be chosen. This results in a symmetry number of two (planar structure), while it is unity for the bent HO geometry. This, combined with the HR correction, results in a slight entropy decrease. The heat capacity is not affected by this additional symmetry.

The calculated equilibrium geometry is compared with experiment in Table 4a, while the resulting values for the

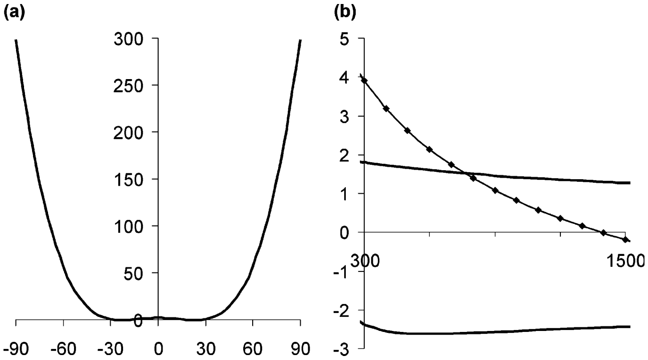


Figure 4. (a) Ring puckering potential of methylenecyclobutane. Energy values in kJ/mol, angle values in degrees. (b) Entropy difference $\Delta S(T)$ in J/mol/K (diamonds line) and the heat capacity difference $\Delta C(T)$ in J/mol/K (black line) in terms of the temperature (K). Also, the scaling factors $\kappa_{\mathrm{HR}}(T)$ (dimensionless) are given as gray lines.

thermodynamic properties are shown in Table 4b. It is clear that the agreement of ab initio values with experiment is excellent, confirming the appropriateness of the level of theory. The barrier to planarity is only 2.15 kJ/mol, while in cyclobutane, it is 6.35 kJ/mol on the same level of theory.[5] This illustrates that any exosubstitution will increase the tendency to obtain a planar geometry. Still, the ab initio puckering angle is somewhat too high, suggesting that the real barrier could be lower that 2 kJ/mol. This is also reflected in the entropy and heat capacity values of the HR approach. They are less accurate than their HO counterparts. If, however, the barrier would be smaller, the HR corrections would be similar as in the case of the oxetanes (X = O), where the entropy and heat capacity are almost unaffected at 298.15 K. Anyway, the present corrections are small and both HO and HR results are satisfactory.

5. Summary

In this paper, heterocyclic four-membered rings with a carbon−heteroatom double bond at position 3, which have potential applications in heterocyclic chemistry, but for which no experimental nor ab initio data are available, have been investigated from first principles. The general behavior of each molecule is determined by the heteroatom in the ring skeleton. The oxetane (**5**−**8**) and thietane (**13**−**16**) derivatives have a planar equilibrium structure, except for thietan-3-ylidenephosphine **15**, which exhibits a puckering angle of 24.0° and a very low barrier to planarity of 1.32 kJ/mol. The azetidine (**1**−**4**) derivatives have their ring puckered by about 15°, while the puckering angle in the phosphetanes (**9**−**12**) varies between −30.8° and −39.9°. The carbon−heteroatom double bond has only a minor influence on the geometry and potential energy variation within each class of heterocycles (oxetane, thietane, azetidine, and phosphetane derivatives).

It was also established that the 1D-HR approach is the most appropriate method for treating the puckering motion in order to calculate the molecular partition function. Especially for the thietane derivatives, the HR method generates major corrections as compared with the standard HO scheme. This is shown using the thermochemical quantities entropy and heat capacity.

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