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Applicability of the Hindered Rotor Scheme to the Puckering Mode in Four-Membered Rings

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The hindered rotor scheme, originally developed for internal rotors in flexible chains (Van Speybroeck, V.; Van Neck, D.; Waroquier, M.; Wauters, S.; Saeys, M.; Marin, G. B. *J. Phys. Chem. A* **2000**, *104*, 10939), is extended to puckering motions in four-membered rings. The applicability of the approach is tested in a variety of heterocyclic compounds for which the partition function, entropy, and heat capacity are calculated. The entropy may be substantially altered by a correct description of the puckering mode. The equilibrium puckering angle ranges between 0° and 30° depending on the heterosubstitution X (CH_2, O, S, NH, PH, C=O, C=S, C=NH, C=PH) in the four-membered ring.

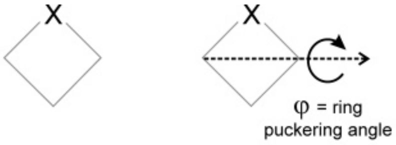
1. Introduction

Strained cyclic molecules are of fundamental nature in heterocyclic chemistry, as many biological processes are directed by compounds bearing a heterocyclic moiety. These small cyclic compounds have, aside from the standard vibrational modes, skeletal motions which involve the entire backbone of the molecule. These are the so-called ring vibrations. The potential energy associated with these ring vibrations is not purely harmonic in nature, but can exhibit various minima leading to a number of stable ring conformers. They show large similarities with internal rotations in flexible chains, apart from the fact that they are constrained. It is now generally accepted in the literature that the harmonic oscillator approximation (HO) fails for the description of the thermodynamic quantities of such flexible molecules, exhibiting a number of torsional modes about single bonds. The one-dimensional hindered rotor (1D-HR) scheme (e.g., refs 1−5) is a conceptually simple but accurate model to overcome this problem. This approach is nowadays used by many authors for treating internal rotations. The number of theoretical works on the description of low vibrational modes in cyclic molecules and their influence on the partition function is far more limited. A study of Katzer and Sax on the thermochemical properties of structurally related silicon hydrides[6] revealed that the impact of ring puckering can become very important in four- and five-membered rings.

The aim of this article is to extend the hindered rotor scheme to ring vibrations, which are characterized by a strongly anharmonic potential. The partition function of this specific mode is manually constructed by calculating the energy levels in the puckering potential. The approach is tested on four-membered rings of the structure given in Scheme 1.

All these molecules with X different from CH_2 have potential applications in heterocyclic chemistry, while the cyclobutanone derivatives have been shown to have a large application in various domains.[7]

SCHEME 1



1 X= **CH_2**: cyclobutane
2 **O**: oxetane
3 **S**: thietane
4 **NH**: azetidine
5 **PH**: phosphetane
6 **C=O**: cyclobutanone
7 **C=S**: cyclobutanethione
8 **C=NH**: cyclobutylideneamine
9 **C=PH**: cyclobutylidenephosphine

Experimental studies, employing various techniques, on the spectra of numerous cyclic molecules (refs 8−24, and references therein) provide extensive information on the ring puckering of four-membered rings. Apparently, for many of these compounds, the equilibrium structure does not correspond to the most symmetrical geometry, being the planar conformation, but is mainly determined by the balance of two opposing forces.[25] Minimizing Bayer or angle strain results in a planar form, whereas the torsional or Pitzer strain is lower in a puckered geometry.

On the basis of minor assumptions, the potential energy barrier between the equilibrium and planar structures can be determined from the experimental spectrum. The geometries on the other hand require more detailed information and are somewhat harder to assess. This is best illustrated by the study of cyclobutane, where the coupling of the ring puckering and the CH_2 rocking motion is crucial for determining the equilibrium geometry.[9]

In addition to these experimental studies, many computational ab initio studies have been performed[16−22] with the principal aim of reproducing the puckering barrier and equilibrium angle. The latter quantities seem hard to reproduce and require high post-Hartree−Fock levels of theory,[17] while present density functional theory (DFT) and second-order Møller-Plesset (MP2) studies in general failed to come close to the experimentally

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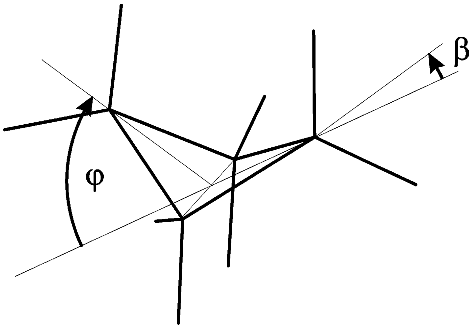

Figure 1. Schematic representation of cyclobutane, defining the puckering pseudorotation. Also, the CH_2 rocking angle β is defined.

determined values. As the theoretical predictions are susceptible to good predictions of the geometrical features and puckering potential, a validation of the electronic level of theory used will be given.

2. Theoretical Models

The molecular partition function associated with the internal degrees of freedom is systematically evaluated following the standard procedure within the harmonic oscillator approximation (HO). The latter assumes only small variations around the equilibrium configuration, which may be described by a quadratic potential energy surface. Nowadays, it is well-known that the HO approximation fails in an accurate reproduction of the partition function of molecules that have internal modes in the low vibrational spectrum that do not correspond with pure vibrations. Among them, internal rotations about single bonds are certainly the most known and have been widely studied. The one-dimensional hindered rotor scheme (1D-HR) has been put forward as a computationally attractive and accurate scheme for treating internal rotations beyond the HO approximation.[5] In this approach, the global rotation and the internal rotations are decoupled, and each internal rotation is described in one dimension, ignoring the coupling between adjacent torsional modes. The reduced moment of inertia is kept fixed at the value of some reference geometry, often taken as the most stable configuration.

In this paper, a similar methodology is followed for large-amplitude vibrations that correspond to ring inversions. In this case, the rotation axes connect two nonbonded atoms, as schematically shown in Figure 1 for cyclobutane.

The frequency calculation gives all normal modes of the molecule and enables one to select those vibrational modes that correspond with pseudorotations. For the four-membered rings under study, only one ring-puckering vibration is present, but for larger cyclic systems, this number increases.

The shape of the potential function associated with the ring puckering depends on the structural features inhibiting the ring vibration. This function is calculated along the lines of refs 4 and 5 by pointwise geometry optimizations at fixed out-of-plane angles, thereby relaxing all other degrees of freedom.

To evaluate the new molecular partition function, one has to replace the harmonic oscillator contribution to the partition function as obtained from the standard quantum chemical packages by a manually constructed partition function, based on the second-order derivative of the potential energy along the puckering angle and combined with its reduced moment of inertia. The need of this procedure was established in earlier work of the authors.[26,27]

The ring-puckering partition function Q_{1D} can be obtained quantum mechanically or classically, depending on the temperature range of interest. For low temperatures (below 400 K), a quantum mechanical treatment is needed, and one has to solve the one-dimensional Schrödinger equation

$$\left[-\frac{\hbar^2}{2I^{\mathrm{red}}}\frac{\partial^2}{\partial\phi^2}+V(\phi)\right]\psi_k(\phi)=\epsilon_k\psi_k(\phi) \tag{1}$$

The quantity I^{red} represents the generalized reduced moment of inertia,[5,28] and $V(\phi)$ is the potential associated with the pseudorotation. The Schrödinger equation is solved by the numerical procedure outlined in ref 3, yielding all rotational energy eigenvalues ϵ_k required for the evaluation of the partition function of the ring vibration defined by

$$Q_{1D}^{\mathrm{HR}}=\frac{1}{\sigma}\sum_k g_k\exp\left(-\frac{\epsilon_k}{kT}\right) \tag{2}$$

with σ the symmetry number of the pseudorotational top, and g_k the degeneracy of the energy level k.

For temperatures above 500 K, the quantum mechanical and classical partition function are expected to converge. The classical partition function is obtained as an integral

$$Q_{1D}^{\mathrm{HR}}=K(T)\int_{-\pi}^{\pi}\mathrm{d}\varphi\,\sqrt{I^{\mathrm{red}}}\,\exp[-\beta V^{1D}(\varphi)] \tag{3}$$

with $K(T)=\sqrt{2\pi k_{\mathrm{B}}T/h^2}$. These results can be enhanced by the use of the Pitzer−Gwinn correction factor,[29] extending the validity of the classical approach to lower temperatures.

Once the molecular partition function is known, the entropy and heat capacity can be readily evaluated

$$S=R\left[\ln Q_{\mathrm{tot}}+T\left(\frac{\partial\ln Q_{\mathrm{tot}}}{\partial T}\right)\right] \tag{4}$$

$$C=RT\left(2\frac{\partial\ln Q_{\mathrm{tot}}}{\partial T}+T\frac{\partial^2\ln Q_{\mathrm{tot}}}{\partial T^2}\right) \tag{5}$$

3. Results and Discussion

Level of Theory Study on Cyclobutane 1, Azetidine 4, and Thietane 3. An appropriate level of theory for the subsequent study must be selected. This is done on the basis of a brief level of theory study on cyclobutane, azetidine, and thietane for which experimental data are available.[8,9,12−14] All ab initio calculations were performed using the *Gaussian 03* software package[30] with the 6-31+G(d,p) basis set, which is a valuable compromise between computational cost and accuracy.[31] A variety of DFT-based methods are tested, which can be divided as follows: pure DFT functionals (BP86, BLYP), hybrid DFT (HDFT) functionals (B3LYP, PBE1PBE, mPW1PW91, mPW1k), and hybrid meta-DFT (HMDFT) functionals (B1B95, BB1k, mPW1B95, mPWB1k). An overview of diverse DFT functionals is given in ref 32 and references therein.

Cyclobutane is by far the most thoroughly investigated molecule, and this species is used as a starting point for our level of theory study. A summary of the experimental history on this molecule is given in ref 17, while our results are compared with the experimental values of Egawa et al.[9] Table 1 contains the barrier height V_0 and several structural parameters of the equilibrium geometry, i.e., the puckering angle $\varphi_{\min}$ at the energetically favored geometry and the rocking angle β, defined as the angle between the $H\hat{C}H$ bisector and the bisector of the corresponding $C\hat{C}C$ angle (Figure 1). Also, the coupling

TABLE 1: Summary of the Levels of Theory Analyses on Cyclobutane,[a] Azetidine,[b] and Thietane[c,d]

	cyclobutane **1**				azetidine **4**	thietane **3**	
	V_0 (kJ/mol)	φ_{min}	β	δ	φ_{min}	V_0 (kJ/mol)	φ_{min}
			DFT				
BP86	4.29	27.1	4.3	0.16	28.4	2.06	23.8
BLYP	3.20	25.2	4.0	0.16	27.1	1.57	22.1
			HDFT				
B3LYP	3.69	25.7	4.1	0.16	26.6	1.53	22.0
PBE1PBE	5.11	27.9	4.5	0.16	28.2	2.12	23.9
mPW1PW91	4.73	27.4	4.4	0.16	27.8	1.88	23.1
mPW1k	5.11	27.8	4.5	0.16	27.4	1.84	23.0
			HMDFT				
B1B95	5.84	29.3	4.7	0.16	29.3	2.71	25.4
BB1K	6.33	29.7	4.8	0.16	29.1	2.71	25.3
mPW1B95	6.35	29.7	4.8	0.16	29.4	2.85	25.8
mPWB1k	6.55	30.0	4.8	0.16	29.2	2.84	25.6
			post-HF				
MP2/6-311+G(d.p)[19b]	32.36						
CCSD(T)/cc-pVQZ[17]	6.53	29.6	5.7	0.19			
			CBS-limits				
B3LYP[17]	3.59	26					
MP2[17]	8.09	32					
experimental	6.10 ± 0.02	27.9 ± 1.6	6.2 ± 1.2	0.22 ± 0.05	29.7 ± 1.4	3.28 ± 0.02	26 ± 2

[a] Showing the barrier height V_0 and the geometrical parameters of the potential minimum structure: the puckering angle φ_{min}, and the CH_2 rocking angle β, along with the derived coupling parameter $\delta = \beta/\varphi$. Experimental values are obtained from ref 9. [b] Showing the puckering angle φ_{min}. Experimental values are obtained from ref 14c. [c] Showing the barrier height V_0 and equilibrium puckering angle φ_{min}. Experimental values are obtained from ref 12. [d] Bond lengths are in angstroms, while (dihedral) angles are in degrees.

parameter $\delta = \beta/\varphi$ is reported, as frequently referred to in other literature works. The two most significant quantities are the barrier height V_0 between the equilibrium D_{2h} structure and the planar D_{4v} conformation and the puckering angle φ_{min}. The experimental value of V_0 is 6.10 kJ/mol. DFT methods using pure functionals (BP86 and BLYP) fail in accurately reproducing this energy barrier, whereas the hybrid meta-DFT functionals perform well.

Further comparison with the experimental puckering angle φ_{min} (27.9° ± 1.6°) reveals that HMDFT methods slightly overestimate the puckering angle, whereas HDFT methods give the most accurate value for this angle. Comparison of the calculated bond lengths (not shown) with experimental values reveals that the functionals optimized for kinetics (mPW1k, BB1k, mPWB1k) are unable to produce acceptable values for the bond lengths. The coupling parameter δ is about 0.16 for all calculations, while experiment suggests 0.22.

Also, azetidine is well-investigated by the experiment[14] and is characterized by a single well potential. The best-performing functionals for azetidine are again the B1B95 and mPW1B95 functionals. The results for thietane show that only hybrid meta-DFT functionals give acceptable accuracy for the barrier height and puckering angle (cf. Table 1).

During the further course of this article, the mPW1B95 functional is used for thermodynamic analysis of all four-membered heterocyclic and carbonyl compounds.

In addition to the DFT level of theory study, we present some post-Hartree−Fock and CBS-limit results on cyclobutane and oxetane, as reported in refs 19b and 17. It can be concluded that MP2 does not perform well for these systems, whereas the very time-consuming CCSD(T) level is excellent. However, the computationally efficient mPW1B95 method gives comparable accuracy to the CCSD(T) method.

Ring Puckering Potentials. The shape of the potential (Figure 2) associated with the ring inversion is determined by the puckering angle at equilibrium and the barrier to inversion. These quantities together with important bond lengths and bond angles are given in Table 2 for the studied molecules. Two types of potentials occur: a symmetrical double minimum or an asymmetrical shape. Azetidine (**4**) and phosphetane (**5**) exhibit asymmetrical single and double well potentials, respectively. Azetidine has only one minimum with the N−H bond in the equatorial position (positive values of φ), whereas for phosphetane, the conformer with the P−H bond in the axial position (negative values of φ) is lowest in energy.[22] The lone pair of phosphorus is much more spread out than that of nitrogen and orients itself in an equatorial position, away from the ring structure.

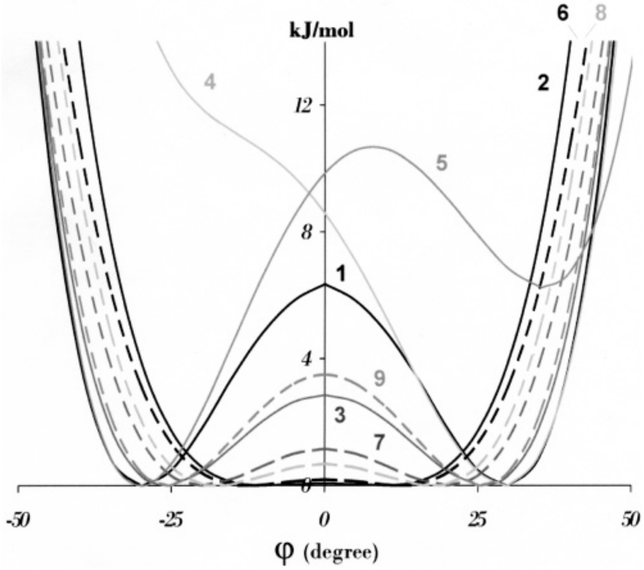

Figure 2. Puckering potential (kJ/mol). Potential energy profiles of cyclobutane **1**, oxetane **2**, thietane **3**, azetidine **4**, phosphetane **5**, cyclobutanone **6**, cyclobutanethione **7**, cyclobutylideneamine **8**, and cyclobutylidenephosphine **9**.

Azetidine is a nice example of the interplay between theory and experiment. Originally, an asymmetric double well potential

TABLE 2: Main Parameters of the Equilibrium Geometry of the Selected Molecules and Barrier Height V_0 in kJ/mol Calculated at the mPW1B95/6-31+G(d,p) Level of Theory[a]

	V_0 (kJ/mol)	φ_{min}	$\lvert$C−C$\rvert$	$\lvert$C−X$\rvert$ (X = C, O, S, N)	$\lvert$C = X$\rvert$ (X = O, S, N)	∠CCC
cyclobutane **1**	6.35	29.7	1.534	1.534		91.9
oxetane **2**	0.06	9.8	1.530	1.433		84.2
thietane **3**	2.85	25.8	1.531	1.834		95.7
azetidine **4**		29.4	1.469	1.535		85.4
phosphetane **5**		−30.0	1.533	1.880		96.1
cyclobutanone **6**	0.18	12.2	1.546	1.521	1.199	90.6
cyclobutanethione **7**	1.16	20.1	1.544	1.508	1.609	88.8
cyclobutylideneamine **8**	0.68	17.7	1.546 1.546	1.509 1.519	1.260	89.7
cyclobutylidenephosphine **9**	3.49	25.7	1.543 1.544	1.511 1.509	1.671	88.3

[a] The second lines for cyclobutylideneamine and cyclobutylidenephosphine refer to the bonds on the side of the NH or PH orientation. Bond lengths are in angstroms, while (dihedral) angles are in degrees.

function was proposed with stable equatorial and axial conformers.[14a] On the basis of suggestions of theory, the experiments were re-evaluated. It was concluded that the axial conformer is unstable and that the potential has only one single minimum which corresponds to a puckered conformation with the N−H bond in the pseudoequatorial orientation. The origin of the asymmetry must be traced back to the pyramidal nitrogen atom. All other molecules under study here, i.e., cyclobutane, oxetane, thietane, cyclobutanone, thiocyclobutanone, cyclobutylideneamine, and cyclobutylidenephosphine, have a symmetrical double well potential function. The barrier height and the puckering angle can be rationalized to a large extent using the concept of competing angle and torsional strain. Cyclobutane has the highest barrier to ring inversion, as it has four pairs of eclipsing hydrogen atoms in the planar ring conformation. The heteroelement in the four-membered ring has a major influence on the puckering angle and barrier height, as can be illustrated by comparing thietane and oxetane. The former compound is characterized by large carbon−sulfur bonds and a larger bond angle between the carbons (95.7°) in order to minimize the angle strain, but as a consequence, a larger puckering (25.8°) is observed. Cyclobutanone represents an example of an extremely fine balance between angle and torsional strain. Because of the sp^2 hybridization of the carbon atom at the carbonyl group, angle strain will increase more rapidly with ring puckering than in the other molecules. This is counterbalanced by torsional strain of three eclipsing methylene groups, resulting in a nearly vanishing barrier to ring inversion.

Frequency Spectrum. The vibrational analysis shows that all four-membered rings possess one low-lying frequency, i.e., below 250 cm^{-1}, that corresponds to the ring puckering vibration. The frequency of the latter mode is at least four times smaller than that of the next normal mode in the vibrational spectrum. This motivates the treatment as a one-dimensional problem. Once, however, substituted cyclobutanes containing a number of heavy elements in the side chain are considered, a one-dimensional approach could be insufficient. This item may be interesting for future research.

Molecular Partition Functions. In Figure 3, the ratio of the molecular partition functions calculated in the HR and HO approximation are shown. Depending on the X (cf. Scheme 1) in the four-membered ring, the partition function is reduced or enhanced by approximately a factor of 2. We will now rationalize these results on the basis of a detailed study of the quantum mechanical energy levels in the puckering potential of cyclobutane, oxetane, and azetidine, which are shown in Figure 4. Additionally, the values for the partition function of the puckering mode are given in the HO and HR approximation.

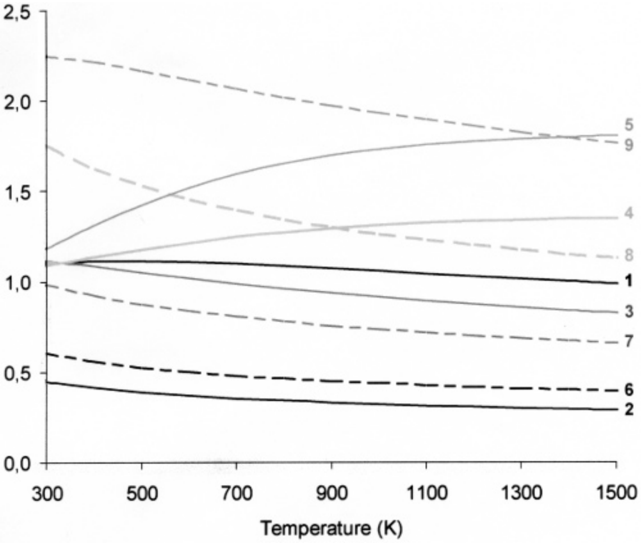

Figure 3. The ratio of the HR partition functions with the HO partition functions for all four-membered ring compounds studied: cyclobutane **1**, oxetane **2**, thietane **3**, azetidine **4**, phosphetane **5**, cyclobutanone **6**, cyclobutanethione **7**, cyclobutylideneamine **8**, and cyclobutylidenephosphine **9**.

The partition function is largely affected by the density of states in the low-energy spectrum. In this case, the classical evaluation of the partition function is also justified. When the puckering is treated as a vibrational mode in the HO approximation, the energy levels are equidistant, and the interlevel energy spacing is determined by the force constant of the harmonic oscillator potential at the equilibrium puckering angle. In the case of cyclobutane, the low-energy levels are (nearly) doubly degenerate because of the two energy wells which are separated by an energy barrier of 6.25 kJ/mol. An important aspect which must be taken into account for calculating the partition function is the symmetry number of the puckering mode. For cyclobutane, this number amounts to two, because of the symmetrical shape of the potential function and because of indistinguishable stable conformers at +30° and −30° of the puckering angle; both conditions are needed to allow the use of a symmetry number. The global effect is only a slight increase of the partition function, because of the compensating effect of the double degeneracy and the symmetry number. For oxetane, the partition function decreases by approximately 2 in the HR approximation. The energy levels are only slightly altered, but the major effects originate from the symmetry number of 2. For azetidine, the puckering potential is not symmetric, and only a slight increase of the partition function is noticed.

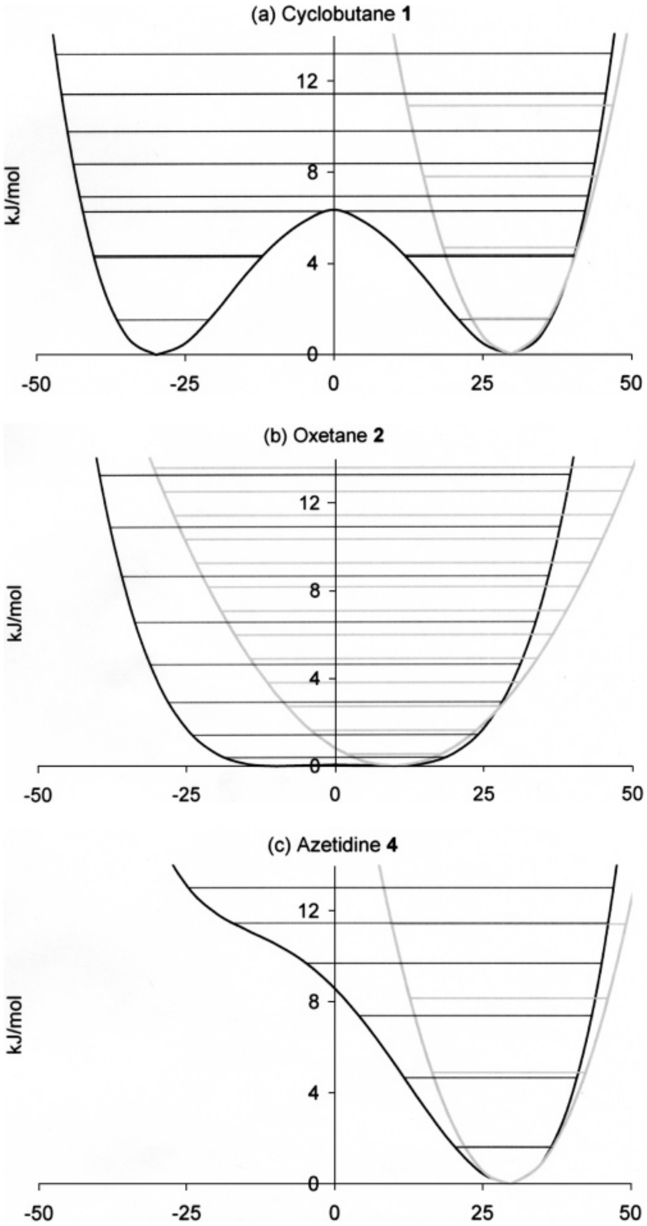

Figure 4. Energy levels in the HO (grey) and 1D-HR (black) approach for (a) cyclobutane **1**, (b) oxetane **2**, and (c) azetidine **4**.

To understand the results of cyclobutylideneamine (**8**) and cyclobutylidenephosphine (**9**) (Figure 3), one important remark needs to be made about the symmetry number of the puckering mode. Also, for these molecules, the ring inversion is characterized by a double symmetrical well potential, but the conformers at positive and negative values of the puckering angle are now geometrically different. The N−H (P−H) bond of the imine (phosphine) moiety is either oriented to the front or the back of the molecule, as schematically shown in Figure 5. In this case, no symmetry number may be applied. This explains the large influence of the HR model on the partition function for these molecules, as in the HO approach, only half of the conformers are taken into account.

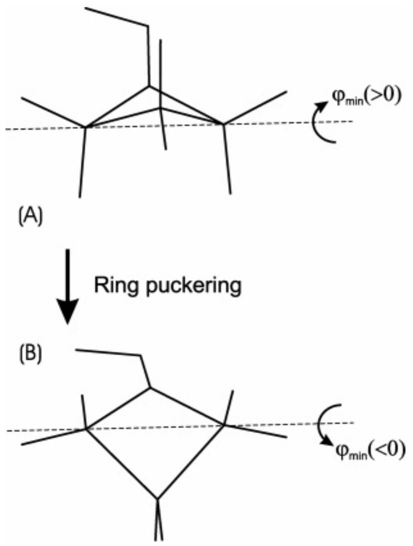

Figure 5. Two possible distinct conformers (A, B) of compounds **8** or **9**, accessible through ring puckering. Starting from A, conformer B cannot be reached using global rotation only.

TABLE 3: Experimental and Calculated Values of Entropy *S* and Heat Capacity *C* at Temperatures Defined between Brackets[a]

mPW1B95	*S* (298.15 K)	*C* (298.15 K)	*C* (600 K)
		cyclobutane **1**	
exp. (ref 33)	265.39	73.35	140.00
HO	262.43	68.46	140.86
1D-HR	263.70	68.34	138.89
		oxetane **2**	
exp. (ref 33)	265.26	61.99	119.60
exp. (ref 34)		61.50	121.31
HO	278.63	61.36	119.87
1D-HR	269.61	59.07	117.61
		thietane **3**	
exp. (ref 33)		69.24	127.23
HO	283.94	68.05	125.76
1D-HR	284.30	65.94	123.08
		azetidine **4**	
exp.			
HO	271.46	64.55	130.20
1D-HR	273.10	66.76	131.39
		phosphetane **5**	
exp.			
HO	285.32	75.37	140.50
1D-HR	289.28	80.62	141.32
		cyclobutanone **6**	
exp. (ref 34)		74.31	139.91
HO	298.43	78.42	142.11
1D-HR	291.94	76.17	140.00
		cyclobutanethione **7**	
exp.			
HO	305.84	81.16	144.99
1D-HR	304.04	78.60	142.53
		cyclobutylideneamine **8**	
exp.			
HO	296.78	80.84	151.73
1D-HR	299.32	78.26	149.31
		cyclobutylidenephosphine **9**	
exp.			
HO	308.14	87.54	158.09
1D-HR	314.70	85.87	155.62

[a] All units in J/mol/K.

Thermodynamic Quantities. Some results for the entropy and the heat capacity are listed in Table 3 in the HO and HR approximation, together with the experimental values when available. The heat capacity is nearly unaffected by the method for constructing the partition function. The origin must be traced back to the large separation between the lowest and next-lowest frequency mode in the vibrational spectrum. It is generally known that for the heat capacity not only low frequencies are important but also a range of intermediate modes. The latter

TABLE 4: Experimental and Calculated Values of Entropy *S* at 298.15 K for Different Levels of Theory with the 6-31+G(d,p) Basis Set[a]

S (298.15 K)	mPW1B95	B3LYP	PBE1PBE	B1B95
		cyclobutane **1**		
exp. (ref 33)	265.39	265.39	265.39	265.39
HO	262.43	263.66	262.99	262.93
1D-HR	263.70	264.59	264.14	264.14
		oxetane **2**		
exp. (ref 33)	265.26	265.26	265.26	265.26
HO	278.63	283.18	284.91	280.19
1D-HR	269.61	261.21	269.79	270.13

[a] All units in J/mol/K.

are not present for the studied molecules, resulting in a good performance of the HO approximation for the heat capacity. The heat capacity of phosphetane (**5**) (at 298.15 K) is affected somewhat more, because of the presence of the second conformer, which is not described in the HO approach.

The entropy is affected more, e.g., in the case of oxetane, a correction of 9 J/mol/K is observed, bringing the prediction closer to the experiment.

The ab initio results of Table 3 are calculated using the selected mPW1B95/6-31+G(d,p) level of theory. The selection of this level was based on its capability to reproduce the correct geometry and potential barrier height. It is now instructive to examine the influence of other ab initio levels in reproducing the entropy. For this purpose, the entropies of cyclobutane and oxetane, for which experimental estimates are available, are calculated with the B3LYP, PBE1PBE, and B1B95 functionals (all combined with the 6-31+g(d,p) basis set). Results are given in Table 4. The correction due to 1D-HR can be very large and may strongly vary depending on the level of theory. In oxetane, the 1D-HR corrections with respect to HO fluctuate from 9 to 22 J/mol/K. The final 1D-HR predictions of the entropies, however, are all close to each other and are in reasonable agreement with experiment.

4. Conclusion

In this article, we have adapted the hindered rotor approach for flexible chains to four-membered rings. The latter molecules exhibit one low-vibrational mode which corresponds to the puckering vibration. The puckering potentials may vary largely in terms of the heteroelement that is introduced in the ring. Most molecules are characterized by a double well symmetrical potential except azetidine and phosphetane. Depending on the system of interest, the partition function may be doubled or halved. The symmetry of the ring inversion and the shape of the potential determine the final result. The entropy undergoes the largest influence of treating the puckering mode in the HR model, whereas the heat capacity is nearly unaffected.

We found that the thermodynamic properties are only affected to a minor extent by the level of theory, provided the 1D-HR model is used.

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References and Notes

(1) Truhlar, D. G. *J. Comput. Chem.* **1991**, *12*, 266.

(2) (a) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. *Macromolecules* **1995**, *28*, 8771. (b) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 18997.

(3) Van Speybroeck, V.; Van Neck, D.; Waroquier, M.; Wauters, S.; Saeys, M.; Marin, G. B. *J. Phys. Chem. A* **2000**, *104*, 10939.

(4) Vansteenkiste, P.; Van Speybroeck, V.; Marin, G. B.; Waroquier, M. *J. Phys. Chem. A* **2003**, *107*, 3139.

(5) Van Speybroeck, V.; Vansteenkiste, P.; Van Neck, D.; Waroquier, M. *Chem. Phys. Lett.* **2005**, *402*, 479.

(6) Katzer, G.; Sax, A. F. *J. Phys. Chem. A* **2002**, *106*, 7204−7215.

(7) (a) Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797−827. (b) de Meijere, A. *Houben-Weyl Methods in Organic Chemistry: Carbocyclic Three- and Four-Membered Ring Compounds*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1997; Vols. E17e and E17f.

(8) (a) Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1703−1707. (b) Meiboom, S.; Snyder, L. C. *J. Chem. Phys.* **1970**, *52*, 3857−3863. (c) Cremer, D. *J. Am. Chem. Soc.* **1976**, *99*, 1307−1309.

(9) Egawa, T.; Fukuyama, T.; Yamamoto, S.; Takabayashi, F.; Kambara, H.; Ueda, T.; Kuchitsu, K. *J. Chem. Phys.* **1987**, *86*, 6018−6026.

(10) (a) Rathjens, G. W., Jr.; Gwinn, W. D. *J. Am. Chem. Soc.* **1953**, *75*, 5629−5633. (b) Rathjens, G. W., Jr.; Freeman, N. K.; Gwinn, W. D.; Pitzer, K. S. *J. Am. Chem. Soc.* **1953**, *75*, 5634−5642.

(11) (a) Danti, A.; Lafferty, W. J.; Lord, R. C. *J. Chem. Phys.* **1960**, *33*, 294−295. (b) Chan, S. I.; Zinn, J.; Gwinn, W. D. *J. Chem. Phys.* **1960**, *33*, 295−296. (c) Chan, S. I.; Zinn, J.; Fernandez, J.; Gwinn, W. D. *J. Chem. Phys.* **1960**, *33*, 1643−1655. (d) Chan, S. I.; Zinn, J.; Gwinn, W. D. *J. Chem. Phys.* **1961**, *34*, 1319−1329. (e) Chan, S. I.; Borgers, T. R.; Russel, J. W.; Strauss H. L.; Gwinn, W. D. *J. Chem. Phys.* **1966**, *44*, 1103−1111. (f) Ueda, T.; Shimanouchi, T. *J. Chem. Phys.* **1967**, *47*, 5018−5030. (g) Jokisaari, J.; Kauppinen, J. *J. Chem. Phys.* **1973**, *59*, 2260−2263.

(12) (a) Harris, D. O.; Harrington, H. W.; Luntz, A. C.; Gwinn, W. D. *J. Chem. Phys.* **1966**, *44*, 3467−3480. (b) Karakida, K.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1691.

(13) (a) Durig, J. R.; Lord, R. C. *J. Chem. Phys.* **1966**, *45*, 61−66. (b) Borgers, T. R.; Strauss H. L. *J. Chem. Phys.* **1966**, *45*, 947−955.

(14) (a) Carriera, L. A.; Lord, R. C. *J. Chem. Phys.* **1969**, *51*, 2735−2744. (b) Bocian, D. F.; Schick, G. A.; Birge, R. R. *J. Chem. Phys.* **1981**, *75*, 2626−2634. (c) Günther, H.; Schrem, G.; Oberhammer, H. *J. Mol. Spectrosc.* **1984**, *104*, 152.

(15) Scharpen, L. H.; Laurie, V. W. *J. Chem. Phys.* **1968**, *49*, 221−228.

(16) (a) Wright, J. S.; Salem, L. *J. Am. Chem. Soc.* **1971**, *94*, 322−329. (b) Barfield, M. *J. Am. Chem. Soc.* **1993**, *115*, 6916−6928. (c) Sorescu, D. C.; Thompson, D. L.; Raff, L. M. *J. Chem. Phys.* **1994**, *101*, 3729−3741. (d) Fisher, G.; Purchase, R. L.; Smith, D. M. *J. Mol. Struct.* **1997**, *405*, 159−167. (e) Henseler, D.; Hohlneicher, G. *J. Phys. Chem. A* **1998**, *102*, 10828−10833.

(17) Glendening, E. D.; Halpern, A. M. *J. Phys. Chem. A* **2005**, *109*, 635−642.

(18) Sellers, H.; Almlöf, J.; Saebø, S. *J. Phys. Chem.* **1987**, *91*, 4216−4218.

(19) (a) Dutler, R.; Rauk, A.; Shaw, R. A. *J. Phys. Chem.* **1990**, *94*, 118−124. (b) López, J. C.; Blanco, S.; Lesarri, A.; Alonso, J. L. *J. Chem. Phys.* **2001**, *114*, 2237−2250.

(20) Gutsev, G. L.; Adamowicz, L. *J. Phys. Chem.* **1995**, *99*, 13412−13421.

(21) Mastryukov, V. S.; Boggs, J. E. *THEOCHEM* **1995**, *338*, 235−248.

(22) Bachrach, S. M. *J. Phys. Chem.* **1989**, *99*, 7780−7784.

(23) Palafox, M. A.; Núñez, J. L.; Gil, M. *J. Phys. Chem.* **1995**, *99*, 1124−1133.

(24) Palafox, M. A.; Iza, N.; Gil, M.; Núñez, J. L. *Int. J. Quantum Chem.* **2002**, *89*, 25−47.

(25) (a) Laane, J. *J. Phys. Chem.* **1991**, *95*, 9246. (b) Legon, A. C. *Chem. Rev.* **1980**, *80*, 231. (c) Cremer, D. *J. Am. Chem. Soc.* **1977**, *99*, 1307.

(26) Van Cauter, K.; Van Speybroeck, V.; Vansteenkiste, P.; Reyniers, M. F.; Waroquier, M. *ChemPhysChem.* **2006**, *7*, 131−140.

(27) Vansteenkiste, P.; Van Neck, D.; Van Speybroeck, V.; Waroquier M. *J. Chem. Phys.* Accepted for publication.

(28) East, A. L. L.; Radom, L. *J. Chem. Phys.* **1997**, *106*, 6655.

(29) Pitzer, K. S.; Gwin, W. D. *J. Chem. Phys.* **1942**, *10*, 428.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.;

Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Wallingford, CT, 2004.

(31) (a) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 1384−1388. (b) Carbonniere, P.; Lucca, T.; Pouchan, C.; Rega, N.; Barone, V. *J. Comput. Chem.* **2004**, *26*, 384−288.

(32) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 5656−5667.

(33) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill Handbooks; McGraw-Hill: New York, 1999.

(34) *NIST chemistry webbook*; http://webbook.nist.gov/chemistry/.