

Calculation of Pseudorotational Moments of Inertia of Cyclopentane Derivatives Using Molecular Mechanics Method

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Pseudorotation (PR) of cyclic molecules is discussed. It is shown that PR can be considered as a special type of internal rotation with pseudorotational moment of inertia (PMI) as an important characteristic. The dependence of the PMI of a molecule upon the phase angle of PR and the nuclear trajectories is discussed. A method is proposed for the calculation of PMI from geometrical parameters of molecules. The moment of inertia of internal rotation for 1,2-dichloroethane in gauche conformation is calculated in order to test the proposed method. The obtained value is in good agreement with the values given by the Pitzer method. Pseudorotational moments of inertia of cyclopentane and its derivatives are calculated. Calculated values are compared with those adjusted to fit experimental entropy. The dependence of the PMI of cyclopentane derivatives upon their molecular mass is discussed.

Introduction

Pseudorotation (PR) is a special type of inversion of five-membered rings in molecules.¹ It is a coordinated periodic change of dihedral angles between bonds, which form the ring (see Figure 1). Like torsional vibrations, PR is connected with restricted changes of dihedral angles, otherwise the ring would be broken. But there are some signs that make us classify this type of intramolecular motion not as vibration but as hindered internal rotation. PR is connected not with a parabolic potential barrier but with a periodic one. Therefore, after sufficient excitation, PR, like the rotation of a top in a molecule, acquires directed nature (Figure 1), when the kinetic energy of PR exceeds its potential energy. As a result, the contribution of PR to heat capacity at high temperatures tends not to the value of R , but to $R/2$.¹

The contributions of PR into thermodynamic functions are usually calculated as contributions of hindered internal rotation using a potential function and an effective moment of inertia.^{1,7–12} The moment of inertia is adjusted so that the calculated entropy of the gas is put into agreement with the experimental value. There is an estimate of the value of the pseudorotational moment of inertia of cyclopentane from spectral data.² In this work a method is proposed for the calculation of pseudorotational moments of inertia from geometrical parameters of molecules on the basis of a physical interpretation of this quantity.

Method

1. Mechanical Approach. A moment of inertia, I , is a measure of the inertness of a body toward rotation that is expressed by three equivalent equations:

$$E = I\omega^2/2 \quad (1)$$

$$d\omega/dt = M/I \quad (2)$$

$$L = I\omega \quad (3)$$

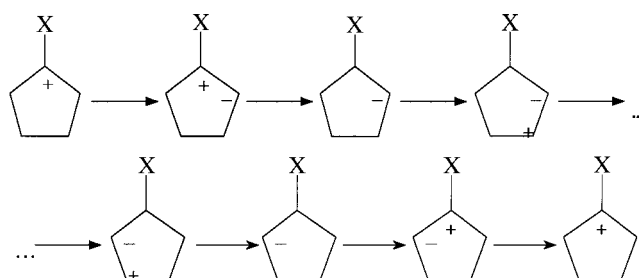


Figure 1. Scheme of pseudorotation of a cyclopentane derivative molecule. The C atoms, which are not marked, are in the plane. The atoms marked with + are above it, the atoms marked with – are under it. Position of the plane itself is not stationary during PR.

where E is the kinetic energy of rotation, ω is the angular velocity, M is the angular force, which accelerates rotation, t is the time, and L is the angular momentum. During the rotation of a rigid body around a fixed axis, each of its points moves along the circumference with a constant velocity. During PR of a molecule each of its nuclei, in general, moves nonuniformly along a complicated closed trajectory. Due to the cyclic nature of PR it can be characterized by a coordinate–phase angle, φ , which determines unequivocally the position of every atom in any moment:

$$\vec{r}_i = \vec{r}_i(\varphi) \quad (4)$$

where \vec{r}_i are periodic functions of φ . If there is no other motion of a molecule except pseudorotation, then the kinetic energy of pseudorotation can be expressed as a sum of the kinetic energies of the atoms (v_i is a velocity of i th atom):

$$E = \frac{1}{2} \sum m_i v_i^2 = \frac{1}{2} \sum m_i (d\vec{r}_i/dt)^2 \quad (5)$$

If we equate the right-hand sides of expressions 1 and 5, we obtain

$$\frac{I\omega^2}{2} = \frac{1}{2} \sum m_i (d\vec{r}_i/dt)^2 \quad (6)$$

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$$I = \frac{\sum m_i (\dot{d}\vec{r}_i/dt)^2}{\omega^2} = \frac{\sum m_i (d\vec{r}_i/dt)^2}{(d\varphi/dt)^2} = \sum m_i (d\vec{r}_i/d\varphi)^2 \quad (7)$$

The moment of inertia, I , defined in this way, is a measure of the inertness of a mechanical system toward cyclic movement of its constituent particles along certain trajectories, in particular, of a molecule toward PR. In a general case, I is a function of the phase angle φ .

Similar results can be obtained from eqs 2 and 3. In this case we should introduce a new quantity, which has no physical meaning, R_i , the effective radius for each of the atoms:

$$R_i = |d\vec{r}_i/d\varphi| \quad (8)$$

If the nuclear trajectories are not determined analytically, an instant value of I can be found from the approximate formula:

$$\langle I \rangle = \sum m_i ((\Delta x_i)^2 + (\Delta y_i)^2 + (\Delta z_i)^2) / \Delta\varphi^2 \quad (9)$$

The error caused by this approximation is small if while making calculations one follows the rules given in the next section. It should be noted that the value of $\langle I \rangle$, obtained from eq 9, is not an arithmetical average value of I in the interval $\Delta\varphi$.

2. Calculation of the Nuclear Trajectories. The nuclei coordinates at different stages of conformational changes of molecules can be calculated with the molecular mechanics method using the dihedral driver procedure.³ They correspond to a fixed value of one of the dihedral angles and optimized values of other geometrical parameters. For the investigation of PR, one of the dihedral angles of the ring β should be fixed. Calculation by the formula 9 demands the nuclei coordinates at two different values of the selected angle, β_1 and β_2 .

The dihedral angle β itself cannot be a phase angle of pseudorotation, because a complete turn around the corresponding bond does not occur. It is convenient to define the phase angle, for example, in the following way:

$$\beta = \beta_{\max} \cos(\varphi) \quad \varphi = \arccos(\beta/\beta_{\max}) \quad (10)$$

Molecular mechanics gives static coordinates of nuclei and does not guarantee that obtained trajectories will correspond to the result of the effect of force fields on a system of moving nuclei. Centrifugal phenomena, which arise during excitation of PR, are not taken into consideration. The choice of different angles of the ring as a fixed angle β for the investigation of PR leads to somewhat different pathways, which, however, will coincide in points of energy minimums and in saddle points of the potential energy surface of the molecule's conformational changes. As will be shown below, differences in pathways are small and do not bring substantial uncertainty into the calculation of the moment of inertia. For the correct application of eq 9, contributions of translational motion and general rotational of the molecule during the transition from one configuration into another one should be excluded. In practice it can be done as follows:

(1) The nuclei coordinates of the molecule in two configurations, $X_i^{(1)}$ and $X_i^{(2)}$, corresponding to two different values of the selected dihedral angle of the ring, β , are calculated using the dihedral driver procedure. The phase angle and its increment are determined.

(2) The center of mass of the molecule in both configurations is superposed with the origin of the coordinate system. Hence,

$$\sum m_i \vec{r}_i^{(1)} = \sum m_i \vec{r}_i^{(2)} \quad (11)$$

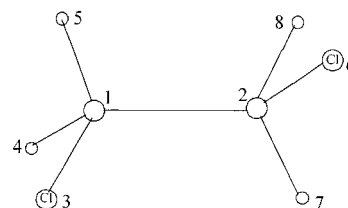


Figure 2. Numeration of atoms in the 1,2-dichloroethane molecule.

(3) The molecule in configuration 2 is rotated to fulfill the condition of absence of general rotation between the configurations 1 and 2, which results from Newton's laws:

$$\sum m_i \vec{r}_i^{(1)} \times \Delta \vec{r}_i = 0 \quad (12)$$

or

$$\sum m_i \vec{r}_i^{(1)} \times \vec{r}_i^{(2)} = 0 \quad (13)$$

The authors are not aware of the ways of analytical transformation of coordinates to satisfy the conditions 12 and 13. Therefore, the rotation is realized by an iteration procedure using a specially created computer program.

A value of $\Delta\varphi$ should not be too small, so that the limited accuracy of optimization in the molecular mechanics method would not cause additional error. At the same time, it should not be too big, so that the curvature of the trajectory would be taken into account to a sufficient extent. We consider the values of $\Delta\varphi$ of about 5° acceptable.

3. Testing of the Method. Calculation of the Moment of Inertia for Conventional Internal Rotation. The moment of inertia for internal rotation of the 1,2-dichloroethane molecule in gauche conformation (see Figure 2) was calculated by the proposed method. The nuclear coordinates for the values of the dihedral angle Cl-C-C-Cl = 60° and 65° , which satisfy conditions 11 and 12, are presented in Table 1. The angle Cl-C-C-Cl was chosen as the phase angle for internal rotation. The value of the moment of inertia $I = 28.857 \times 10^{-47}$ kg·m² was obtained. The Pitzer's method⁴ gives values $I = 28.293 \times 10^{-47}$ kg·m² at $\varphi = 60^\circ$ and $I = 29.403 \times 10^{-47}$ kg·m² at $\varphi = 65^\circ$.

4. Choice of the Phase Angle and the Average Moment of Inertia. The choice of the phase angle determines the type of dependence of the pseudorotational moment of inertia upon the phase angle. Such a phase angle can be chosen so that the moment of inertia will be constant. Let us call it the natural phase angle. The value of $\Delta\varphi$ in eq 9 can be taken equal to 2π , embracing the whole pseudorotational path:

$$I_0 = \sum m_i \left(\int d\vec{r}_i \right)^2 / 4\pi^2 = \sum m_i l_i^2 / 4\pi^2 \quad (14)$$

Since any phase angle changes from 0 to 2π and the path length of each nucleus l_i does not depend on the choice of the phase angle, the value of the moment of inertia I_0 , obtained from eq 14, does not depend on the choice of the phase angle and is equal to the moment of inertia, calculated on the basis of the natural phase angle. In practical calculations, values of l_i can be obtained by numerical integration.

It can be shown that

$$I_0 = 1/2\pi \int_0^{2\pi} I(\varphi)^{1/2} d\varphi \quad (15)$$

It can be necessary to determine the value of natural phase angle θ during PR in order to express the potential energy during PR as a function of the phase angle, consistent with the constant

TABLE 1: Calculation of the Moment of Inertia for Internal Rotation of 1,2-Dichloroethane^a

no.	atom	$\varphi = 60^\circ$			$\varphi = 65^\circ$			$(\Delta r_i)^2$
		x	y	z	x	y	z	
1	C	0.6792	-1.0026	0.3554	0.6691	-0.9761	0.3740	0.00115
2	C	-0.6792	-1.0026	-0.3554	-0.6691	-0.9761	-0.3740	0.00115
3	Cl	1.6776	0.4223	-0.0581	1.7085	0.4112	-0.0651	0.00113
4	H	1.2754	-1.8947	0.0536	1.2542	-1.8911	0.1233	0.00532
5	H	0.5646	-1.0110	1.4641	0.5241	-0.9394	1.4786	0.00698
6	Cl	-1.6776	0.4223	0.0581	-1.7085	0.4112	0.0651	0.00113
7	H	-0.5646	-1.0109	-1.4641	-0.5240	-0.9393	-1.4786	0.00699
8	H	-1.2754	-1.8947	-0.0536	-1.2542	-1.8911	-0.1233	0.00532

^a Coordinates are in Å; isotope-averaged atomic masses are used in calculations.

value of the reduced moment of inertia. Suppose that some phase angle φ is chosen and the dependence $I = I(\varphi)$ and the value of I_0 are determined. Such a phase angle $\theta = \theta(\varphi)$ should be found that $I(\varphi) = I_0 = \text{const}$.

$$\sum m_i (d\vec{r}_i/d\theta)^2 = \sum m_i \left[\frac{(d\vec{r}_i/d\varphi)^2}{(d\theta/d\varphi)^2} \right] = I(\varphi)/(d\theta/d\varphi)^2 = I_0 \quad (16)$$

$$d\theta/d\varphi = (I(\varphi)/I_0)^{1/2} \quad (17)$$

Approximation and integration of eq 17 can give values of the natural phase angle, θ , which corresponds to intermediate configurations of the molecule on the pseudorotational path and to corresponding values of the potential energy. Then a dependence $V = V(\theta)$ can be found.

5. Calculation of the Contributions of Pseudorotation into Thermodynamic Functions. Classical and Quantum-Mechanical Approach. Assumption about the separation of PR from the general rotation should not cause a large error in the calculation of thermodynamic functions, because the moment of inertia of general rotation undergoes small changes during the pseudorotation cycle. The contributions of PR into thermodynamic functions can be calculated in the classical approximation by traditional formulas, taking into account the limitation of the region where classical approach is admissible:^{5,6}

$$Q = (2\pi kT)^{1/2}/(\sigma h) \int_0^{2\pi} (I(\varphi))^{1/2} e^{-V(\varphi)/kT} d\varphi \quad (18)$$

The moment of inertia $I(\varphi)$ and the potential energy $V(\varphi)$ should be consistent, i.e., they should be the functions of the same phase angle φ .

Supposing that PR is separated from other kinds of intramolecular motion, the pseudorotational energy levels can be calculated by solving the Schrödinger equation for hindered rotation around a fixed axis:

$$-\frac{1}{8\pi^2 I} \frac{\partial^2 \psi}{\partial \varphi^2} + V(\varphi)\psi = E\psi \quad (19)$$

If the natural phase angle θ is chosen as the phase angle φ , then the moment of inertia I will be constant and the energy levels can be obtained by the variational method using the wave functions of free rotation of a rotor with the moment of inertia I around a fixed axis as a basis or in other ways.⁶

Application

6. Application of the Method. Pseudorotational Moments of Inertia of Cyclopentane and Its Derivatives. Cyclopentane is the simplest molecule containing a five-membered ring. Owing to the absence of substituents, the complete cycle of its

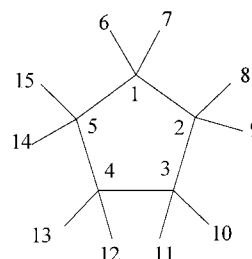


Figure 3. Numeration of atoms in the cyclopentane molecule.

PR consists of 20 equal transitions between the “twist” and “envelope” forms. Therefore, the average value of the moment of inertia can be calculated for one of such transitions, for which $\Delta\varphi = 2\pi/20 = 18^\circ$. Designation of the atoms is given in Figure 3, and geometrical data for the calculation are in Table 2. The value of $I_0 = 9.27 \times 10^{-47} \text{ kg}\cdot\text{m}^2$ was obtained. The value of $I_0 = 10.59 \times 10^{-47} \text{ kg}\cdot\text{m}^2$ was selected to put the calculated entropy of gas into agreement with the experimental value.¹ According to spectral data,² $I_0 = 11.0 \times 10^{-47} \text{ kg}\cdot\text{m}^2$.

Pseudorotational moments of inertia (PMI) for some cyclopentane derivatives were also calculated. The nuclear coordinates at different stages of PR were calculated by the MM2 method using the dihedral driver procedure. The changes of dihedral angles were set for the transition between the envelope and twist conformations. The envelope conformation is characterized with the equality $\angle C(2)-C(3)-C(4)-C(5) = 0^\circ$ (substituted atom is C(1) in Figure 3). For the twist conformation the following equalities are kept: $\angle C(1)-C(2)-C(3)-C(4) = \angle C(3)-C(4)-C(5)-C(1)$, $\angle C(4)-C(5)-C(1)-C(2) = \angle C(5)-C(1)-C(2)-C(3)$.

The initial structure was created using nonrestricted geometry optimization. Dihedral angles were altered from the values that correspond to the minimum of potential energy (the envelope conformation for cyclopentanol, methylcyclopentane, bromocyclopentane, chlorocyclopentane, and fluorocyclopentane, and the twist conformation for cyclopentanone) to the values that correspond to the energy maximum on the pseudorotational path. It is most convenient to carry out the conversion between conformations by varying successively changing angles $\angle C(1)-C(2)-C(3)-C(4)$ and $\angle C(3)-C(4)-C(5)-C(1)$ or $\angle C(4)-C(5)-C(1)-C(2)$ and $\angle C(5)-C(1)-C(2)-C(3)$. In this case angles corresponding to the envelope and twist conformations can be established precisely (up to $\pm 0.5^\circ$).

For the cyclopentanone molecule the conformation was changed from the twist form to the envelope form, i.e., the phase angle was varied within 90° .

Cyclopentanol, methylcyclopentane, bromocyclopentane, chlorocyclopentane, and fluorocyclopentane molecules are characterized by two potential energy minimums of unequal depth, which correspond to equatorial and axial envelope conformations. They are separated by an energy maximum, which

TABLE 2: Calculation of the Pseudorotational Moment of Inertia of Cyclopentane^a

no.	atom	twist			envelope			$(\Delta r_i)^2$
		x	y	z	x	y	z	
1	C	-0.7289	1.0188	-0.2547	-0.7401	1.0059	-0.2677	0.00046
2	C	-1.2208	-0.3783	0.1478	-1.2077	-0.3759	0.2064	0.00361
3	C	0.0066	-1.2957	-0.0012	-0.0056	-1.2904	-0.0793	0.00627
4	C	1.2251	-0.3657	-0.1455	1.2347	-0.3762	-0.0737	0.00536
5	C	0.7180	1.0269	0.2537	0.7153	1.0414	0.2149	0.00172
6	H	-0.7385	1.1196	-1.3666	-0.7731	1.0572	-1.3825	0.00535
7	H	-1.3463	1.8394	0.1824	-1.3558	1.8386	0.1484	0.00125
8	H	-2.0897	-0.7146	-0.4666	-2.1417	-0.7131	-0.3030	0.02946
9	H	-1.5446	-0.3550	1.2162	-1.4025	-0.3412	1.3053	0.02834
10	H	0.1096	-1.9573	0.8920	0.0704	-2.1099	0.6745	0.07211
11	H	-0.0904	-1.9527	-0.8986	-0.1236	-1.7633	-1.0838	0.07127
12	H	1.5535	-0.3401	-1.2125	1.7270	-0.3992	-1.0756	0.05233
13	H	2.0945	-0.6927	0.4731	1.9906	-0.6945	0.6831	0.05489
14	H	0.7262	1.1303	1.3652	0.7335	1.2332	1.3147	0.01318
15	H	1.3266	1.8532	-0.1850	1.3168	1.8358	-0.2876	0.01094

^a Coordinates are in Å; isotope-averaged atomic masses are used in calculations. Symmetry is not enforced.

TABLE 3: Pseudorotational Moments of Inertia of Cyclopentane Derivatives and Resulting Ideal Gas Entropies

compd	formula	M , kg·kmol ⁻¹	I , 10 ⁻⁴⁷ kg·m ²	S° (g, 298.15 K), J·K ⁻¹ ·mol ⁻¹	method	ref
cyclopentane	C ₅ H ₁₀	70.134	10.59	292.9	thermodyn	1
			11.0	—	spectral	2
cyclopentanone	C ₅ H ₈ O	84.119	9.27	292.3	mechanical	this work
			12.28	316.7	thermodyn	7
methylcyclopentane	C ₅ H ₉ CH ₃	84.161	8.16	315.0	mechanical	this work
			18.0	339.9	thermodyn	8
cyclopentanol	C ₅ H ₉ OH	86.134	12.68	338.4	mechanical	this work
			16.6	348.0	thermodyn	9
fluorocyclopentane	C ₅ H ₉ F	88.125	12.62	346.9	mechanical	this work
			18.0	328.1	thermodyn.	10
chlorocyclopentane	C ₅ H ₉ Cl	104.579	13.93	327.0	mechanical	this work
			19.32	339.5	thermodyn	11
1,1-chloromethylcyclopentane	C ₅ H ₈ CH ₂ Cl	118.606	16.00	338.7	mechanical	this work
			15.24	359.9	thermodyn	12
bromocyclopentane	C ₅ H ₉ Br	149.030	16.61	360.3	mechanical	this work
			18.10	—	mechanical	this work

corresponds to a twist conformation. A cycle of PR consists of two symmetrical parts, so the phase angle in calculation was varied within 180°.

Conformations were changed for these molecules both from an axial to an equatorial one and in the opposite direction. At the first stage the conformation was changed from the envelope to the twist form. Then the obtained twist conformation was taken as the initial one, and dihedral angles were changed toward the other envelope conformation.

Calculated values of PMI of the above-mentioned molecules together with the literature values are given in Table 3. Ideal gas entropies calculated on the basis of the literature and our PMI are compared, as well. It is difficult to estimate a priori an error of calculation of PMI by the proposed method, because main sources of error are the incomplete separation of rotational, vibrational, and PR motion and the uncertainty of calculated nuclear trajectories during PR. A comparison of the calculated and experimental values is the best way to do it.

The accordance between the PMI calculated in this work and those estimated from thermodynamic data can be regarded as good because the latter are effective values which compensate errors of experimental determination of the gas entropy and inaccuracies of molecular parameters used for statistical calculations. A typical uncertainty of the experimental value of the entropy in the gas state, 1 J·K⁻¹ mol⁻¹, results in an uncertainty of the adjusted PMI of about 25%. And, vice versa, use of the calculated I values allows one to calculate the ideal gas entropy with an error not larger than 1–2 J·K⁻¹ mol⁻¹.

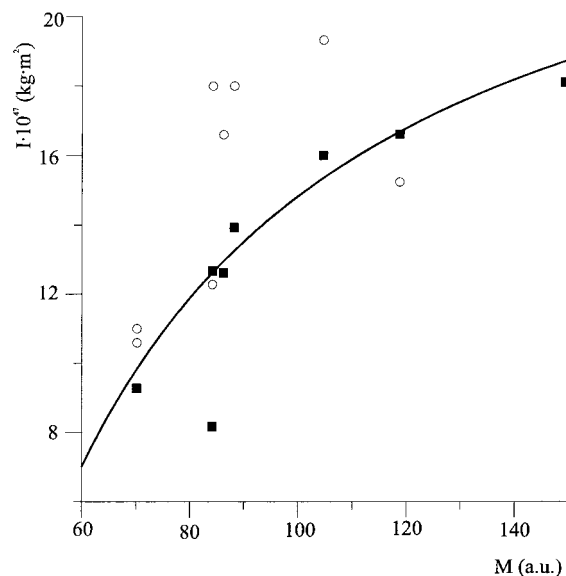


Figure 4. Dependence of pseudorotational moments of inertia of cyclopentane derivatives upon molecular mass. ■: Calculated by the present method; ○: Experimental (thermodynamic or spectral). The curve is fitted by equation: $I=26.6-1176/M$.

There is also a prominent correlation between the molecular mass and the PMI of cyclopentane derivatives with substituents at one C atom (see Figure 4), consistent with the proposed mechanical model, supposing that amplitudes of displacements

of nuclei in equally rigid molecules are approximately the same and, according to eq 14, the moment of inertia is proportional to the reduced molecular mass of a molecule consisting of the cyclopentane ring and a substituent:

$$I[10^{-47} \text{ kg m}^2] = 26.6 - 1176/M \quad (20)$$

Cyclopentanone deviates from eq 20: its molecule is more rigid due to the sp² atom C, and the calculated *I* value is smaller.

Conclusion

The proposed method allows one to calculate contributions of PR to thermodynamic functions with precision close to experimental methods.

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