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The Barrier to Interconversion of Cyclohexene

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Abstract: The interconversion process between twisted conformations of cyclohexene via a bent intermediate form is reexamined utilizing previously published far-infrared data along with molecular mechanics (MM3) calculations. This process is treated as a periodic one-dimensional hindered pseudorotation, and it is demonstrated that the anharmonicity in the vibrational data is compatible with a barrier to interconversion in the 8.4–12.1-kcal/mol range. This range is higher than the MM3 value of 7.22 kcal/mol or published values from *ab initio* calculations.

The lowest energy conformation of cyclohexene is a half-chair (twisted) form with C_2 symmetry and a twist angle, as reported from microwave work,[1] of 30 ± 2°. The cyclohexene ring can interconvert from one twisted form to another via the boat (bent) conformation with C_s symmetry (Scheme 1). Recently we have analyzed the far-infrared spectra of cyclohexene and five of its deuterated isotopomers[2] and used the data to define a two-dimensional vibrational potential energy surface in terms of the bending and twisting coordinates. This surface has a barrier to planarity (energy difference between the planar C_{2v} form and the twist form) of 13.4 ± 1.4 kcal/mol and a barrier to interconversion of *approximately* 10.3 kcal/mol.[2] Since the spectroscopic data only extend about 3 kcal/mol above the potential energy minima, the barrier heights represent values derived from smooth extrapolations of the potential energy surface. On the other hand, the surface is based on more than eighty experimental twisting, bending, and combination frequencies and thus is very well defined up to about 3 kcal/mol above the energy minima.

Anet and co-workers[3] have also examined the conformational changes of cyclohexene using molecular mechanics (MM3) and *ab initio* calculations and vapor-phase NMR measurements. Their MM3 results predict a barrier to interconversion of 6.6 kcal/mol and a shallow minimum of 0.08 kcal/mol below the barrier for the bent conformation. The *ab initio* calculations, carried out at moderate levels, predict barriers to interconversion of 5.5–6.6 kcal/mol. The NMR studies were limited by a lack of vapor pressure below −73 °C, but the authors estimated that the broadening due to the slowing of ring inversion must be less than 1 Hz. This value was then used to calculate 7.95 kcal/mol as the upper limit for the interconversion barrier of cyclohexene.

In the present paper we examine and put into perspective the seeming contradiction between our vibrational study[2] and the theoretical and NMR studies of Anet and co-workers.[3] At the outset, we want to point out that the NMR maximum (7.95 kcal/mol) for the interconversion process and our vibrational value (10.3 kcal/mol) are not very different since we have noted[2] that our value could be somewhat lower (perhaps down to the 8–9-kcal/mol range). We will demonstrate, however, that the calculated MM3 and *ab initio* barriers are too low to be compatible with our spectroscopic results.

Figure 1 shows a coordinate system for the bending (B) and twisting (T) coordinates, as previously defined,[2] of cyclohexene. When both coordinates are zero, the molecule has the high energy planar (P) form. The lowest energy twist forms are labeled T while each bent form of intermediate energy is labeled B. Because the barriers are large, essentially all of the molecules at room temperature are at T, a twisting minimum, and vibrate with bending (υ_B) and twisting (υ_T) frequencies of 165 and 276 cm^{-1}, respectively. It is the anharmonicities and frequency shifts in various excited states (see Table IV of ref 2) of υ_B and υ_T which were used to determine the two-dimensional vibrational potential energy surface. The dotted line in Figure 1 represents the interconversion pathway, and this can be defined in terms of a phase angle ϕ if the bending and twisting coordinates are transformed into polar coordinates. This is analogous to a hindered pseudorotation of a five-membered ring,[4–6] so this process might be termed a pseudo-pseudorotation. At either energy minimum T, the coordinate ϕ defines a pure bending motion, but this gradually takes on more and more twisting as the bending conformation is approached. At the bending conformations B, ϕ represents pure twisting motion. The other polar coordinate r represents a radial motion which is pure twisting at T ($\phi = 90°$ or 270°) and pure bending at B ($\phi = 0°$ or 180°). When $\phi \neq n \times 90°$ for n = integer, both r and ϕ represent vibrational motion involving both ring-bending and ring-twisting. Anet has utilized a twisting coordinate ω_{3456} to calculate MM3 and *ab initio* energies for different conformations. The pseudorotational angle ϕ, which increases as ω_{3456} increases, used here is a better representation of the vibrational motion and we have used it instead of ω_{3456}.

We have repeated the MM3 calculations and obtained slightly different results from Anet. Our barrier is 7.22 kcal/mol (instead of 6.6) and the energy dip at $\phi = 0°$ and 180° (boat or bent conformation) was calculated to be 0.60 kcal/mol instead of 0.08 kcal/mol. Figure 2 shows the MM3 potential energy we have calculated as a function of ϕ. This curve makes it possible within the one-dimensional approximation to calculate the bending vibrational frequencies and, most importantly, the associated anharmonicity. To do this we have utilized a potential function of the form[4,7,8]

$$V = {}^1/_2 \sum V_n(1 + \cos(n\phi)) \qquad (1)$$

where the potential energy constants V_n for n = 2, 4, and 6 have been utilized. A reasonably good fit with the calculated MM3

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(8) This function produces equivalent solutions with $-V_n(1 - \cos(n\phi))$ terms except that eq 1 has the energy minimum of $V = 0$ without the need to add a constant term.

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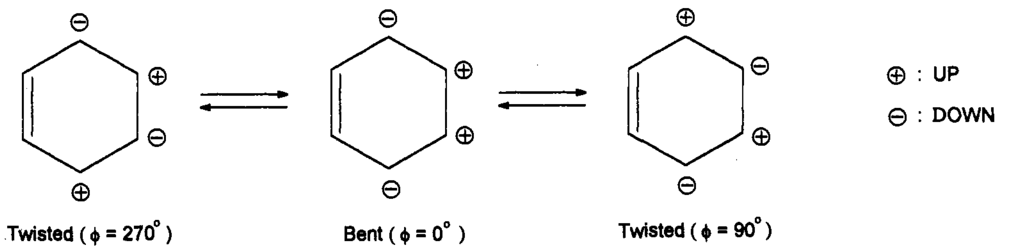
Scheme 1



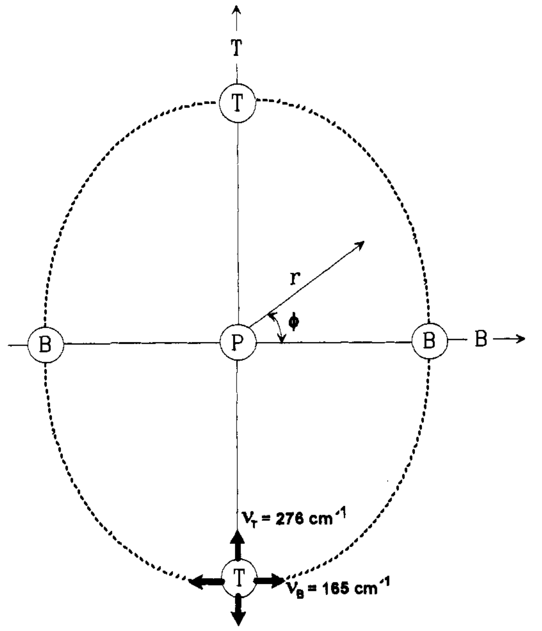


Figure 1. Cartesian (B = bending, T = twisting) and polar (r = radial, ϕ = pseudorotational) coordinates for the out-of-plane motions of cyclohexene.

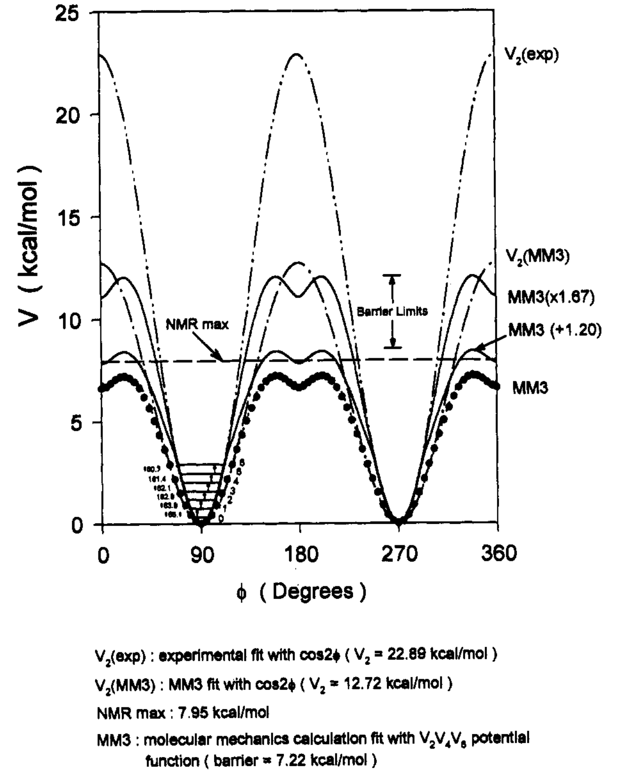


Figure 2. Pseudorotational potential energy curves and observed transitions for cyclohexene.

Table 1. Observed and Calculated Vibrational Frequencies (cm^{-1}) for Various Potential Energy Functions with Different Barriers

		calcd			
transition	exp	V_2(exp)[a]	V_2(MM3)[b]	$V_2V_4V_6$[c]	MM3 ×1.67)[d]
0–1	165.1	165.1	165.1	165.1	165.1
1–2	163.9	164.2	163.5	163.3	164.1
2–3	163.0	163.4	161.9	161.2	163.0
3–4	162.2	162.5	160.2	158.9	161.8
4–5	161.4	161.6	158.6	156.3	160.5
5–6	160.7	160.7	156.8	153.6	159.2
(0–1)–(5–6)	4.4	4.4	8.3	11.5	5.9
barrier (cm^{-1})	3600[e]	8008	4451	2518	4185
barrier (kcal/mol)	10.3	22.9	12.7	7.2	12.1

[a] $V(\mathrm{cm}^{-1}) = 8008(1 + \cos 2\phi)/2$; $B = 0.86$ cm^{-1}. [b] $V(\mathrm{cm}^{-1}) = 4451(1 + \cos 2\phi)/2$; $B = 1.56$ cm^{-1}. [c] $V(\mathrm{cm}^{-1}) = 2531(1 + \cos 2\phi)/2 - 756(1 + \cos 4\phi)/2 - 130(1 + \cos 6\phi)/2$; $B = 1.59$ cm^{-1}. [d] $V(\mathrm{cm}^{-1}) = 4201(1 + \cos 2\phi)/2 - 1255(1 + \cos 4\phi)/2 - 216(1 + \cos 6\phi)/2$; $B = 0.95$ cm^{-1}. [e] Two-dimensional value (ref 1).

values at different ϕ's was obtained with V_2 = 2531 cm^{-1} (7.2 kcal/mol), V_4 = −756 cm^{-1} (2.2 kcal/mol), and V_6 = −130 cm^{-1} (0.4 kcal/mol) and a barrier of 7.2 kcal/mol. This potential function ($V_2V_4V_6$), together with the selection of the pseudorotational constant[4,7] B = 1.59 cm^{-1} to scale the frequencies, can then be used to calculate the bending frequencies. These are compared in Table 1 to those observed. What is evident is that the observed anharmonicity is much less than that predicted by this MM3 model. The frequency difference, for example, observed between the 0–1 and 5–6 transitions is 4.4 cm^{-1} while the MM3 model predicts 11.5 cm^{-1}. This means that up to the v = 6 quantum state (about 1060 cm^{-1} or 3.03 kcal/mol above the energy minimum) the actual potential function is considerably steeper than predicted by MM3. It also very strongly suggests that the potential energy barrier is quite a lot higher than the 7.22-kcal/mol value from the MM3 calculation. In order to gain more insight into the bending (pseudorotational) potential function, we have fit the observed bending frequencies with a function using only a V_2 term with a value of 22.9 kcal/mol (8008 cm^{-1}) while V_4 = V_6 = 0. This calculation [V_2(exp)] greatly overestimates the barrier height by ignoring the effect of a dip or flattening of the curve corresponding to the bent form, but it does a good job of representing the potential energy for the lowest 3 kcal/mol. Thus, the frequencies calculated for this function (Table 1 and Figure 2) almost perfectly match the observed values. For comparison purposes we have used the same form of the potential energy function to fit the lower region of the MM3 curve. The results for this [V_2(MM3)] are also shown in Table 1 and Figure 1, and the difference between the 0–1 and 5–6 transitions can be seen to be 8.3 cm^{-1}. Again the MM3 curve, this time considering only the lower region of the potential function, greatly overestimates the anharmomnicity (i.e. the curve is not steep enough).

Figure 2 also shows the quantum states and observed bending transitions. The NMR maximum value for the interconversion barrier of Anet is also shown. The steepest potential function, V_2(exp), should be a reasonably accurate representation of the steepness of the potential curve, *but* only up to about 3 or 4 kcal/mol. The molecular mechanics and *ab initio* calculations[3] both predict a flat-topped potential function in the vicinity of the bending conformation (ϕ = 0° and 180°). Whether a dip is actually present is difficult to ascertain. The primary question appears to be at what level the potential curve flattens. An estimate of this level can be made as follows. We assume the V_2(exp) curve, which fits the data up to 3.0 kcal/mol, to be accurate up to that level (at ϕ = 68.7°, 111.3°, 248.7°, and 291.3°). At the same values of ϕ, MM3 calculates the potential energy to be only 1.80 kcal/mol or 0.60 of the "experimental" curve. If we then scale the MM3 curve up by this correction factor of 1.0/0.60 = 1.67, it then matches the "experimental" curve for the lowest 3.0 kcal/mol and results in a barrier to interconversion of 12.1 kcal/mol. This value assumes that the MM3 calculation underestimates the potential energy consistently as a function of ϕ as a fraction of the true value. Table 1 and Figure 2 present the $V_2V_4V_6$ potential function based on the MM3 calculation and scaled by 1.67 along with the calculated frequencies. This is labeled MM3(scaled). The anharmonicity can be seen to be nearly correct, although a slightly high barrier would improve this. If the underestimation is assumed to be a constant 1.2 kcal/mol instead of a constant fraction (see Figure 2), then the barrier would be about 8.4 kcal/mol. This range of barriers, 8.4–12.1 kcal/mol, thus estimated is not at all inconsistent with our two-dimensional vibrational model which yielded a value of 10.3 kcal/mol.[2] The lower limit is slightly higher than Anet's NMR maximum, but experimental limitations (low vapor pressure) made it difficult to obtain a more accurate NMR value.

The calculated MM3 barrier of 7.22 kcal/mol is quite different from the older MM2 value of 4.77 kcal/mol.[2] The difference is due to the different force constant parametrizations between the two programs. Anet's value of 6.6 kcal/mol suggests there may be somewhat different constants even in different versions of MM3. It would not be surprising to us for even the improved MM3 program to give a 20% error in the cyclohexene barrier to interconversion. An uncertainty of this magnitude would put it well within our estimated range of values.

In summary, the vibrational data for the bending show a small degree of anharmonicity which is compatible only with a potential function which is steeper than calculated by MM3. On the other hand, the steeper potential function is compatible with NMR results only if the function has a relatively flat top reducing the barrier to interconversion. The vibrational data set a lower limit for the interconversion barrier slightly higher than the NMR maximum value. Unfortunately, vibrational data have not been taken to high enough energies to get a more accurate value. Similarly, NMR results have not been able to zero in on the exact value.

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