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Vibrational Frequencies and Conformational Stability of 1,4-Cyclohexanedione in the Gas Phase As Studied by Infrared and Raman Spectroscopy and ab Initio Calculations

Toru Egawa,[†] Arnold del Rosario, Kevin Morris, and Jaan Laane*

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

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The gas-phase infrared and Raman spectra of 1,4-cyclohexanedione have been measured at 225 and 300 °C, respectively. Geometry optimizations and vibrational ab initio calculations were carried out at the MP2/6-31G** level. It was found that the observed spectra are reproduced by assuming the coexistence of twist and chair conformers. Some vibrational bands in the infrared spectra showed splitting and temperature dependent intensities, indicating that the twist conformer has a lower enthalpy than that of the chair conformer.

Introduction

The conformation of 1,4-cyclohexanedione (CHDO, see Figure 1) has been investigated over several decades using a variety of experimental methods. X-ray diffraction studies carried out by two separate research groups revealed that this molecule assumes the twisted-boat conformation with C_2 symmetry in the solid phase.[1−4] This finding has also been confirmed by means of infrared spectroscopy by Alvik et al.,[5] who examined spectra of both the liquid phase and of solutions. On the basis of the number of CH_2-deformation bands, these workers concluded that the molecule assumes the twist conformation with D_2 symmetry in these phases. Allinger and coworkers[6] also recorded the infrared and Raman spectra of liquid CHDO. They found many coincidences between the infrared and Raman spectra, which excluded the possibility of the C_{2h} chair conformer with a center of symmetry. Combining this finding with results from STO-3G and 3-21G ab initio calculations, they also concluded the predominance of the twist conformer undergoing a pseudorotational vibration that leads to the twisted-boat form. However, they also suggested the existence of a minor (presumably, the chair) conformer.

The first report on the conformation of CHDO in the gas phase was the dipole moment study by Rogers and Canon.[7] They reported dipole moment values of 1.39 and 1.44 D at 468 and 490 K, respectively. Allinger and Freiberg[8] explained this finding as a result of a pseudorotation-like vibration between a nonpolar twist conformer and a polar twisted-boat form, which is the same physical picture proposed later for the liquid phase.[6] On the other hand, Klemperer's group[9] measured the dipole moment of CHDO using molecular beam electric resonance (MBER) and reported that this molecule is nonpolar. On the basis of this finding, they assumed the gas phase conformer to be the chair. However, Allinger et al.[10] claimed that the zero dipole moment could also be interpreted by their twist and twisted-boat pseudorotation model. Cowan et al.[11] and Dougherty et al.[12] measured the ultraviolet photoelectron spectra (UPS) of several dicarbonyls containing CHDO. From the very small splitting of the two ionization energies (∼0.2 eV) arising from the two weakly interacting carbonyl groups, they assumed that CHDO in the gas phase assumes the twist conformation.

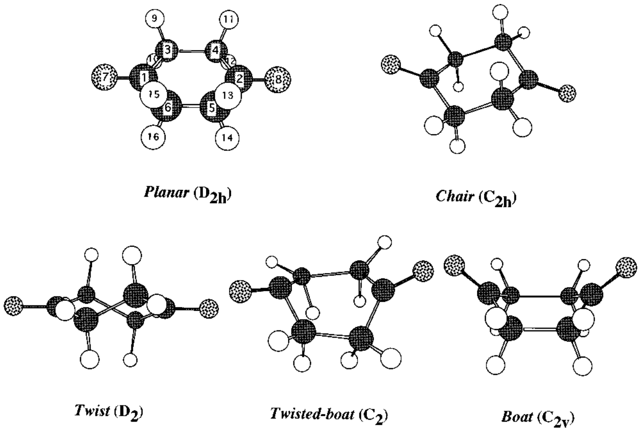

Figure 1. Conformations and atomic numbering of 1,4-cyclohexanedione.

A review of these previous studies demonstrates that the lack of vibrational spectra of CHDO in the vapor phase has made it difficult to understand the conformation of CHDO in the gas phase (twist, chair, or both). The low vapor pressure and the instability of the sample at high temperature[6] have made the measurement of the gas phase spectra very difficult.

In the present study, the infrared and Raman spectra of CHDO have been measured using special high-temperature cells. In addition, the results of the MP2/6-31G** ab initio calculations were used to assist the analysis of the experimental data. As we have recently initiated work on the fluorescence spectra of CHDO in its $S_1(n,\pi^*)$ state in order to analyze its carbonyl wagging motions, an understanding of the ground state for this molecule is also critical.

Experimental Section

The sample of 1,4-cyclohexanedione (CHDO) was purchased from Aldrich and purified by recrystallization using cyclohexane solvent.

Mid-infrared spectra were measured from 400 to 4000 cm^{-1} using a Digilab FTS-60 Fourier transform spectrometer with a resolution of 0.5 cm^{-1}. A high-temperature 15 cm infrared cell made of stainless steel was used with KBr windows. The cell, wrapped with insulation and Nichrome wire, was heated to 225 °C. The sample pressure was estimated to be 60 Torr. The sample temperature was measured by a thermocouple at the outer wall of the cell, so the accuracy of the measurements was approximately ±10 °C.

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* Corresponding author.

[†] Present address: Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

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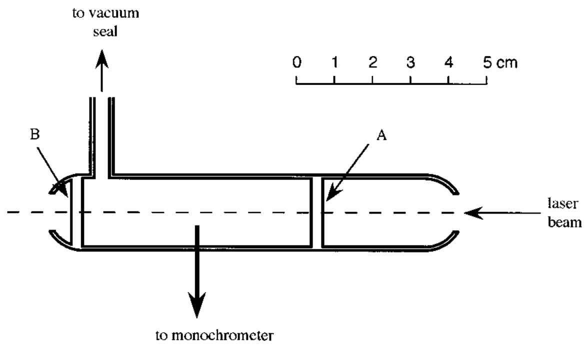

Figure 2. High-temperature gas phase Raman cell.

The Raman spectrum in the gas phase was measured in the 75−1800 cm^{-1} region using a Coherent Radiation Inova 100 argon ion laser operated at 7 W at 514.5 nm and a Jovin Yvon U-1000 double monochromator. An Instruments SA CCD detector was used. When the sample of CHDO was heated, it began to decompose slowly before a temperature high enough to provide enough vapor pressure for the measurement of the Raman scattering could be reached. Therefore, the glass high-temperature Raman cell described in ref 13 was used with a slight modification (see Figure 2). The window A is located nearer to the cell center in comparison with the original design in order to minimize cooling and hence the deposition of the unvaporized sample on this window. Window B is located near the end position in order to make this surface slightly cooler than the rest of the cell. The unvaporized sample and the decomposed products are collected effectively only on this window during the measurements so that they do not disturb the incoming laser beam or the measurement of the Raman scattering. A sample temperature of 300 °C was used. Because of the weak signal and the slow decomposition of the sample, the measurement of the depolarization ratios was not carried out.

The infrared and Raman spectra recorded are shown in Figures 3a and 4a, respectively, and the observed vibrational wavenumbers are listed in Table 1.

Theoretical Calculations

Geometry optimizations of 1,4-cyclohexanedione were carried out for the planar, twist, chair and boat forms at the MP2 level (frozen core)[14] by using the 6-31G** basis set.[15] The computer program GAUSSIAN 92[16] was used. The resultant structural parameters and the energies are listed in Table 2. This table shows that the chair and twist forms are significantly more stable than the other two forms with the chair calculated to be only 0.10 kcal mol^{-1} lower in energy than the twist. This result is qualitatively consistent with the result of the 3-21G ab initio calculations reported by Allinger et al.[6] The C_1-C_3 ($C_{sp^2}-C_{sp^3}$) and C_3-C_4 ($C_{sp^3}-C_{sp^3}$) distances for the twist and chair conformers listed in Table 2 are close to the mean values of the corresponding bonds in the solid phase (1.515 and 1.536 Å, respectively) reported by Mossel and Romers.[2] On the other hand, the $C_1{=}O_7$ distances are slightly longer than the corresponding mean value in the solid phase (1.211 Å). The optimization was also attempted for the twisted-boat form but it converged to the twist conformer.

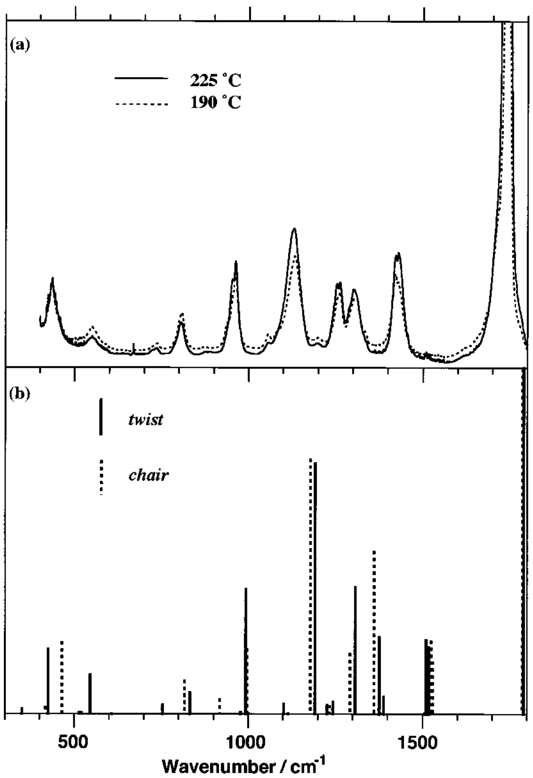

Figure 3. Experimental (a) and theoretical (b) infrared spectra of 1,4-cyclohexanedione.

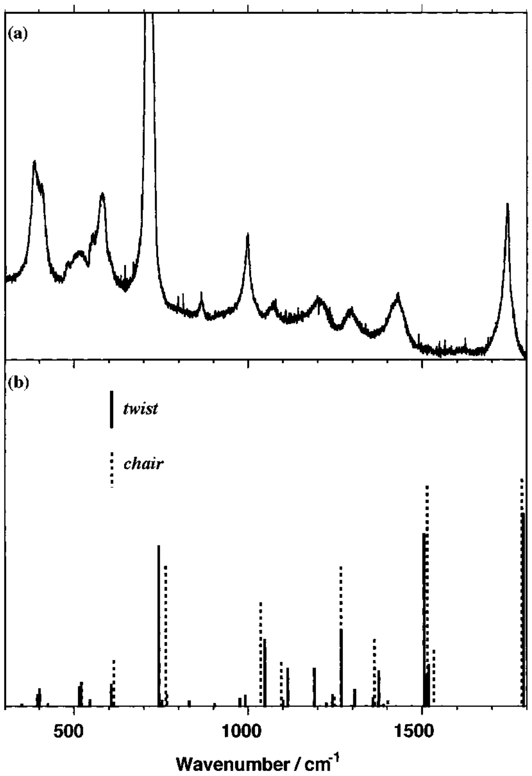

Figure 4. Experimental (a) and theoretical (b) Raman spectra of 1,4-cyclohexanedione.

The vibrational frequencies and infrared absorption intensities for the twist and chair forms were also calculated using the same basis set as that used in the structural optimization. A similar calculation was attempted for the boat, but this form was found to correspond to a saddle point of the potential surface. Harmonic force constants in the Cartesian coordinate, F_x, of the twist and chair conformers were also obtained and they were converted into the force constants, F_{ij}, in symmetry coordinates in order to evaluate the potential energy distribution. Although the actual symmetries of the twist and chair conformers are D_2 and C_{2h}, respectively, the vibrational modes are numbered according to the D_{2h} symmetry of the planar form, to treat these two conformers consistently. The axes for the planar form were

TABLE 1: Observed and Calculated Vibrational Wavenumbers of 1,4-Cyclohexanedione in the Gas Phase (in cm^{-1})

IR[a]	Raman	twist (D_2)	calcd[b]	chair (C_{2h})	calcd[b]
2973.7		ν_8 CH_2 asym str	3206.0	ν_{22} CH_2 asym str	3210.8
		ν_{11} CH_2 asym str	3204.0	ν_{38} CH_2 asym str	3216.0
2918.5		ν_{16} CH_2 sym str	3124.5	ν_{26} CH_2 sym str	3128.5
2846.6		ν_{26} CH_2 sym str	3121.1		
	1745.6	ν_2 C=O sym str	1791.3	ν_2 C=O sym str	1787.4
1741.7		ν_{27} C=O asym str	1789.2	ν_{27} C=O asym str	1786.4
	1433.6	ν_{28} CH_2 deform	1506.0	ν_{17} CH_2 deform	1515.7
1430.6*				ν_{28} CH_2 deform	1528.6
				ν_{33} CH_2 deform	1524.3
1422.5		ν_{17} CH_2 deform	1518.9		
		ν_{33} CH_2 deform	1511.1		
1337.1		ν_{18} C−C asym str	1389.4		
1306.7		ν_{12} CH_2 twist	1376.4		
1301.4*				ν_{23} CH_2 twist	1361.9
	1302.5			ν_4 CH_2 wag	1364.1
1262.1		ν_{34} CH_2 wag	1307.6		
1253.2*				ν_{34} CH_2 wag	1292.6
	1205.2			ν_{12} CH_2 twist	1268.6
1203.0		ν_{39} CH_2 twist	1243.3		
1198.0				ν_{39} CH_2 twist	1233.6
1130.2		ν_{35} C−C asym str	1191.5		
1125.2*				ν_{35} C−C asym str	1178.9
	1074.2	ν_9 CH_2 twist	1114.2	ν_9 CH_2 twist	1096.4
1056.5		ν_{13} CH_2 rock	1101.6		
	1000.8	ν_5 C−C sym. str	1048.7	ν_5 C−C sym. str	1037.2
961.8		ν_{36} C−C asym str	992.7		
953.8*				ν_{36} C−C asym str	996.7
888.2				ν_{24} CH_2 rock	917.2
876.5[c]					
	867.9	ν_{24} CH_2 rock	903.7		
806.0		ν_{40} CH_2 rock	832.0	ν_{30} C−C asym str	816.7
735.8		ν_{30} C−C asym str	753.4		
	714.8	ν_6 C−C sym str	743.8	ν_6 C−C sym str	764.0
	582.8	ν_{41} C=O out of pl	607.0	ν_{14} C=O out of pl	614.5
550.0	554.9	ν_{31} ring breathing	545.5		
	516.6	ν_{14} C=O out of pl	520.6		
		ν_{20} C=O in pl	515.2	ν_{20} C=O in pl	522.4
434.7		ν_{37} C=O in pl	425.1	ν_{37} C=O in pl	464.5
	386.0	ν_7 ring breathing	400.4	ν_7 ring breathing	395.1
				ν_{21} ring breathing	394.9

[a] Split pairs are marked by brackets. The high-temperature peaks are marked with asterisks. [b] Obtained from the MP2/6-31G** calculations. [c] Unassigned peak.

TABLE 2: Structural Parameters and Energies of 1,4-Cyclohexanedione Obtained from MP2 (Frozen Core)/6-31G ab Initio Calculations[a]**

		planar (D_{2h})	twist (D_2)	chair (C_{2h})	boat (C_{2v})
bond lengths (Å)	$C_1{-}C_3$	1.5199	1.5202	1.5172	1.5176
	$C_3{-}C_4$	1.5346	1.5297	1.5393	1.5484
	$C_1{=}O_7$	1.2274	1.2254	1.2267	1.2266
	$C_3{-}H_9$	1.0913	1.0950	1.0887	1.0880
	$C_3{-}H_{10}$	1.0913	1.0892	1.0942	1.0934
bond angles (deg)	$C_6C_1C_3$	122.16	115.56	114.90	116.03
	$C_1C_3C_4$	118.92	112.03	110.95	113.26
	$O_7C_1C_3$	118.92	122.22	122.55	121.97
	$H_9C_3H_{10}$	105.02	106.78	108.22	107.21
	$C_1C_3H_9$	105.22	107.37	108.77	107.42
	$C_1C_3H_{10}$	105.22	108.33	108.15	106.71
	$C_4C_3H_9$	110.71	109.76	111.64	111.51
	$C_4C_3H_{10}$	110.71	112.33	109.02	110.42
dihedral angles (deg)	$C_1C_3C_4C_2$	0.00	−56.84	51.01	0.00
	$O_7C_1C_3C_4$	180.00	−152.18	126.22	135.91
nonplanarity parameters (deg)			−30.97[b]	48.37[c]	41.79[c]
energies	E/E_h[d]	−382.75920	−382.77609	−382.77625	−382.76572
	$E_{relative}$/kcal mol^{-1} [e]	10.70	0.10	0.00	6.61

[a] See Figure 1 for the atom numbering. For the twist , H_9 is the axial hydrogen and for the chair and boat, H_9 is the equatorial hydrogen. [b] Angle between the $C_3{\equiv}C_6$ and $C_4{\equiv}C_5$ diagonals. [c] Dihedral angle between the $C_6{-}C_1{-}C_3$ and $C_6{\equiv}C_3{-}C_4{\equiv}C_5$ planes. [d] E_h (hartree) is the atomic unit of energy. [e] Energy relative to the chair conformer.

chosen[17] so that the *x*-axis is perpendicular to the molecular plane and the *z*-axis passes through the two C=O bonds. Hence, the *y*-axis bisects the two $C_{sp^3}{-}C_{sp^3}$ bonds. For consistency, the axes for the twist conformer were chosen so that the *z*-axis passes through the C=O bonds and the *y*-axis bisects the two $C_{sp^3}{-}C_{sp^3}$ bonds. As a result, the B_2 and B_3 species for the twist conformer are exchanged as compared with those adopted by Allinger et al.[6] The relationship among the symmetry species for the planar, twist, and chair conformers is as follows:

planar (D_{2h})	twist (D_2)	chair (C_{2h})
A_g (7)	A	A_g
B_{1g} (3)	B_1	B_g
B_{2g} (5)	B_2	A_g
B_{3g} (6)	B_3	B_g
A_u (4)	A	A_u
B_{1u} (6)	B_1	B_u
B_{2u} (6)	B_2	A_u
B_{3u} (5)	B_3	B_u

where the numbers of the vibrational modes are listed in parentheses.

The frequency of the boat deformation (ν_{42}) predicted for the twist conformer is only 37.5 cm^{-1}, which comes from the fact that this vibrational mode corresponds to the pseudorotational motion which deforms the geometry into the boat form via the twisted-boat form. This was recognized by Allinger et al.[6,8] On the other hand, the corresponding frequency of the chair conformer (66.9 cm^{-1}) is significantly higher, suggesting that there is a high barrier between this conformer and the boat form caused by the C−H eclipsing. In Figures 3b and 4b, the predicted infrared and Raman intensities are shown by vertical bars. Because the calculation of Raman intensities was not available in the MP2 level calculations, the Raman intensities were obtained by RHF/6-31G** calculations although the frequencies themselves were taken from the results of the MP2/6-31G** calculations. These intensities are shown in Figure 4b.

Results and Discussion

The infrared spectrum obtained at 225 °C was confirmed to be the gas phase spectrum of CHDO rather than condensed liquid because of the following:

(1) The vibrational frequencies recorded were different from those reported for the liquid phase.[18] For example, the antisymmetric C═O stretching band frequency in the liquid phase is 1718 cm^{-1}, while that obtained in the present spectra is 1741.7 cm^{-1}.

(2) In the course of cooling the cell, some spectra were also measured. Slightly below the reported melting point of the sample (78 °C), the vibrational frequencies observed agreed with those of the liquid sample. At a lower temperature, new peaks appeared in the infrared spectrum whose frequencies coincided with those of the solid sample.[18] These liquid and solid peaks appear to arise from the sample condensed on the KBr windows.

The infrared spectrum measured at 190 °C contains some liquid peaks as well as the vapor peaks. However, the 225 °C spectrum does not contain the peaks of the condensed phases. The Raman spectrum obtained in the present study is similar to the liquid Raman spectrum of ref 6. However, some peak frequencies are significantly different from those for the corresponding liquid peaks. For example, the symmetric C═O stretching band frequency in the liquid phase is reported to be 1711 cm^{-1}, while that obtained in the present spectrum is 1746 cm^{-1}.

As shown in Figure 3a, some vibrational bands of the infrared spectrum (at about 960, 1260, and 1430 cm^{-1}) show splitting, and their relative intensities are temperature dependent. In addition to these, bands at 1130 and 1300 cm^{-1} also show poorly resolved splitting. These splittings are not observed in the liquid phase spectra.[5,18] On the basis of the results of the geometry optimization, it is likely that these splittings come from the two conformers (most possibly, the twist and chair) coexisting in the gas phase. Of these two conformers, only the chair conformer has a center of symmetry, and hence the mutual exclusion rule should hold. Thus, it should be possible to tell which conformer corresponds to the high-temperature peaks by comparing the infrared and Raman spectra. However, as shown in Figures 3a and 4a, the comparison does not give a clear conclusion. For example, the split pairs appearing at 960, 1130, and 1260 cm^{-1} in the infrared spectrum disappear in the Raman spectrum, although one component of the each pair is expected to be Raman active. This phenomenon can be explained as follows. These vibrational frequencies of the twist and chair conformers result from the B_{2u} modes of the planar D_{2h} structure, which is Raman inactive and infrared active. Therefore, even in the nonplanar twist conformation, these modes can only give very weak Raman intensity. On the other hand, several CH_2 bending modes (rocking, twisting, and scissoring) have similar frequencies at about 1300 and 1430 cm^{-1}. Thus, even if one mode appearing in the infrared spectrum disappears in the Raman spectrum because of the mutual exclusion rule, another mode with a similar frequency may appear in the Raman spectrum (accidental coincidence). This situation is quite similar to the case reported for 9,10-dihydroanthracene.[19]

To obtain information about the conformational stability, the observed spectra were compared with the theoretical predictions from MP2/6-31G** calculations. As clearly shown in parts a and b of Figure 3, the observed infrared spectrum is quite well reproduced by the ab initio calculations although the calculated frequencies are not scaled. The assignments of the observed bands are quite straightforward. Agreement between the observed and theoretical Raman spectra is also satisfactory. The assignments of the observed vibrational bands are listed in Table 1. It should be noted that almost all the calculated frequencies are consistently overestimated by only 3−5%. For the two split bands appearing at 1430 cm^{-1}, the higher frequency peak (1430.6 cm^{-1}) has higher intensity at the higher temperature. That is, this peak corresponds to the higher enthalpy conformer. From Figure 3b this pair can be assigned to the CH_2 deformation modes (ν_{33} and ν_{17} of the twist conformer and ν_{33} and ν_{28} of the chair conformer). Among these four bands, those of the twist conformer have lower frequencies than those of the chair conformer. Hence, it can be concluded that the chair conformer has higher enthalpy than the twist conformer. This feature is consistent also with other split pairs. That is, the higher enthalpy components of the split pairs are assigned to the chair conformer. The only exception is the pair at 960 cm^{-1}, where the higher enthalpy component seems to be assigned to the twist conformer. However, considering that the theoretical frequencies for this pair are very close to each other, this assignment could easily be exchanged, thus confirming the model that the chair is the higher enthalpy form.

As mentioned above, it was found that 1,4-cyclohexanedione exists as a mixture of the twist and chair conformers in the vapor phase, with the former being more stable. This may seem to be inconsistent with the results of the geometry optimization by MP2/6-31G** ab initio calculations, which revealed that the chair conformer has 0.10 kcal mol^{-1} lower energy than the twist conformer (see Table 2). However, the sum of the theoretical zero-point energies of the vibration for the chair conformer is calculated to be 0.36 kcal mol^{-1} larger than that of the chair conformer (84.19 vs 84.55 kcal mol^{-1}, respectively). By adding these values to the optimized energies to obtain the enthalpy difference, ΔH_0, it is clear that the chair conformer has a theoretical enthalpy 0.26 kcal mol^{-1} higher than that of the twist. In addition, the free energy difference, ΔG, and the relative abundace, C_{twist} and C_{chair}, were estimated by using the vibrational and rotational partition functions calculated from the theoretical vibrational frequencies and rotational constants (4.509, 1.512, and 1.208 GHz for the twist conformer and 4.128, 1.611, and 1.266 GHz for the chair conformer). It was found that the chair conformer has slightly lower free energy at the temperature range of the present measurement of the infrared spectra (190−225 °C) and, hence, it becomes more abundant than the twist. On the other hand, the gradient, $\mathrm{d}\ln(C_{\text{chair}}/C_{\text{twist}})/\mathrm{d}(1/T)$ is still negative, which means the chair conformer has more population at 225 °C than at 190 °C. This prediction is qualitatively consistent with the conclusions discussed above.

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Supporting Information Available: The definitions of the symmetry coordinates (Table IS), the unscaled force constants, F_{ij}, of the twist (Table IIS) and chair (Table IIIS) conformers, and the vibrational frequencies (Table IVS) obtained from the frozen core MP2/6-31G** ab initio calculations (10 pages). Ordering information is given on any current masthead page.

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