Far-infrared and Raman study of monohydrogenated cyclopentene-3-h and -4-h ring puckering and ring twisting in the gas phase

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stabilization of either tautomer is gained with these intermolecular contacts.

Therefore, the combination of ^{13}C CPMAS results for **3**, their comparison with those for several 1,3-diaryl-1,3-diketones in the solid state, and AM1 calculations provides a mutually supportive picture. Two-site hydrogen exchange between tautomers of almost equal energy is strongly implied both in solution and in the solid phase.

Conclusion

Proton transfer within the enolic ring in 1-phenylbutane-1,3-dione in the solid state has been explored by means of ^{13}C CPMAS spectroscopy. Comparison with chemical shift information obtained in solution for this compound and for related 1,3-diaryl-1,3-diketones in both phases leads to the conclusion that the equilibrium composition in the former compound is similar in solution and in crystals, with a small preference for the methyl keto tautomer. AM1 calculations support the above conclusion; i.e., they correctly predict that the enolic form of 1-phenyl-butane-1,3-dione is more stable than the diketo form. Furthermore, optimization of the structure of the enol tautomer gives two separate minima in which the labile proton is bonded to each oxygen, with bond lengths corresponding to alternation of double and single bonds, as found in ordered systems. A weak intermolecular interaction modeled as a hydrogen–bonded isolated dimer does not lead to significant stabilization of either tautomer.

Far-Infrared and Raman Study of Monohydrogenated Cyclopentene-*3-h* and *-4-h* Ring Puckering and Ring Twisting in the Gas Phase

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Monohydrogenated cyclopentenes C_5D_7-*3-h* and C_5D_7-*4-h* have been synthesized and their vapor-phase infrared and Raman spectra have been recorded. For each molecule approximately 10 infrared bands in the 60–130-cm^{-1} region and a similar number of Raman bands in the 70–180-cm^{-1} region are assigned to ring-puckering transitions. Some side bands due to ring-puckering transitions issuing from the ring-twisting excited state are present in the infrared spectra. A series of ring-twisting infrared Q branches is also observed for each molecule in the 310–360-cm^{-1} region. The analysis of the spectra shows that a unidimensional asymmetrical ring-puckering potential energy function $V(x) = V_2x^2 + V_3x^3 + V_4x^4$ must be used to reproduce the data correctly. The potential energy barrier, dihedral angle, and the energy difference between the two potential wells are determined. They are in good agreement with the results of the previous study of monodeuterated cyclopentenes. This confirms that the isotopic monosubstitution in the allylic positions induces an asymmetry not only in the kinetic energy function but also in the potential energy function. Two distinct cyclopentene conformers with different energies are thus produced, the more stable being that with a CH bond in the axial position. The simultaneous excitation of both ring-puckering and ring-twisting modes is shown to result in a higher potential energy, indicating that the two motions are anticooperative.

Introduction

The conformational changes in molecules presenting low barriers and the effects of these changes on their chemical properties are of special interest to chemists and biochemists. The understanding of such phenomena needs consideration of simple models before one tackles the interesting problems of large naturally occurring compounds.

The large-amplitude, low-frequency puckering motion occurring in the four- and five-membered rings is important in this respect and cyclopentene may be considered as a prototype molecule for such a study.[1–4] Many spectroscopic studies of this compound and of several of its isotopic derivatives have already been performed in the gas phase.[5–22] Most of the infrared and/or Raman spectra have been analyzed in terms of one-dimensional quartic–quadratic ring-puckering potential energy function of the form $V(x) = V_4x^4 + V_2x^2$, *x* being the puckering coordinate.[5–13,15–17] This treatment, based on the usual assumption that a low-fre-

quency, large-amplitude motion can be adiabatically separated from the remaining higher frequency, small-amplitude motions,

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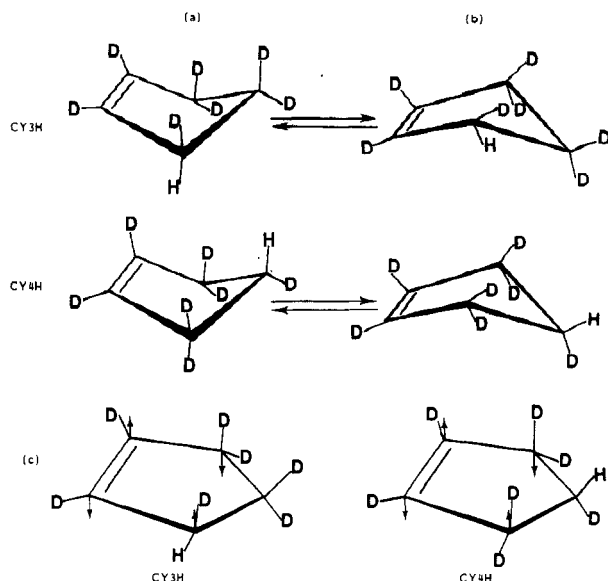[‡] Laboratoire de Chimie Organique du Silicium et de l'Etain.

Figure 1. (a, b) Conformational exchange between the two conformers of cyclopentenes Cy3H and Cy4H. (c) The ring-twisting motion representation for the two monohydrogenated derivatives.

Figure 2. Raman ring-puckering spectra of gaseous cyclopentene Cy3H and Cy4H at 298 K (asterisk denotes Cy3H lines in the Cy4H spectrum).

has proved to be very satisfactory. The use of a reduced mass varying with the puckering coordinate was shown to improve greatly the calculation, but not to affect the calculated inversion barrier.[9-17] All these studies have shown that cyclopentene has a nonplanar equilibrium ring structure with a dihedral angle of about 26° and presents two equivalent potential wells separated by a barrier varying between 233 and 215 cm⁻¹ from cyclopentene-h_8 to cyclopentene-d_8. This agrees well with the electron diffraction[19] and microwave studies.[20-22]

To account for the variations in the potential energy functions and barrier heights of four isotopic derivatives (-d_0, 1-d_1, -$1,2,3,3$-d_4, and -d_8), various models allowing the mixing of methylene rocking with the ring-puckering in the kinetic expansion were used but were not efficient.[9,11,12] On the contrary, a two-dimensional treatment involving the ring-puckering and the ring-twisting modes seemed to improve the correlation between isotopic forms.[14]

For the cyclopentenes exocyclically monosubstituted in the allylic positions, the planar ring is no more a plane of symmetry and odd-powered terms are no longer precluded by symmetry in the potential energy function. Functions of the type $V(x) = V_4 x^4 + V_3 x^3 + V_2 x^2$ have proved to reproduce successfully the observed spectra, with the major conclusion that the potential presents now inequivalent minima.[23-26] The infrared and Raman spectra of gaseous monodeuterated cyclopentene-3-d (Cy3D) and -4-d (Cy4D) have been analyzed by using such a function.[15-17] A puckering barrier height of 232.7 and 233.9 cm⁻¹ was determined for Cy3D and Cy4D, respectively, the conformer with a CD bond in equatorial position being found to be the most stable one (ΔE = 4.1 and 2.8 cm⁻¹ for Cy3D and Cy4D, respectively), in good agreement with ab initio and spectroscopic correlations between the CH bond lengths and strengths.[27-29]
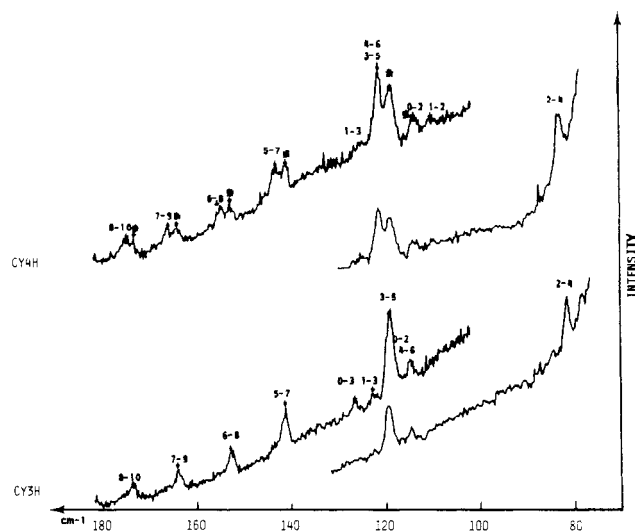
For a better understanding of the ring-puckering motion and to examine thoroughly the effect of isotopic monosubstitution on the potential energy function, barrier height, and conformer stability, we have prepared the monohydrogenated cyclopentenes-d_7-3-h_1 (Cy3H) and -d_7-4-h_1 (Cy4H) and recorded their infrared and Raman spectra. The two puckered conformers are represented in Figure 1 for the two molecules.

In this paper, only the low-frequency data are analyzed. Both one-dimensional symmetrical and asymmetrical models are investigated for the determination of the ring-puckering potentials in the ground and in the first excited ring-twisting vibrational state. A forthcoming paper will be devoted to the study of the stretching CH spectral region.

Experimental Section

1. Synthesis. Cyclopentene-d_7-3-h_1 (Cy3H) and cyclopentene-d_7-4-h_1 (Cy4H) were prepared from perdeuterated cyclopentadiene[30] by radical addition of tributyltin deuteride[31,32] followed by an electrophilic scission of the C–Sn bond with an allylic transposition of the double bond.[33,34] (For a more detailed description of this synthesis, see ref 35.)

The isotopic purity of the final compounds were checked by ¹H, ²H, and ¹³C NMR, infrared, and mass spectroscopy. It was higher than 96%. However, cyclopentene Cy4H could only be obtained mixed with cyclopentene Cy3H in almost equal proportion.

2. Instrumental Measurements. The far-infrared spectra were recorded on a Brucker 113V FTIR spectrometer working under vacuum with a resolution of 0.5 cm⁻¹. The gaseous samples were contained in a Wilks multiple reflection long-path cell equipped with high-density polyethylene windows. A path length of 11 m was used. A pressure of 90 Torr was introduced into the cell maintained at about 298 K. Up to 400 spectra were added together and the water vapor parasite lines were removed by subtraction of a run performed under the same conditions but with a partial pressure of air instead of cyclopentene in the cell.

The Raman spectra were recorded on a Z24 Dilor triple monochromator equipped with a Hamamatsu R943-02 Peltier effect refrigerated photomultiplier. A Spectra Physics 171 argon

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TABLE I: Ring-Puckering Transitions (Observed and Calculated with Two Potential Models) in the Raman and Infrared Spectra of Gaseous Cyclopentene Cy3H^a Compared with Those of Perdeuterated Cyclopentene (Ref 11)

transitions	C_5D_8^{b} ν_{obs}, cm^{-1}	I_{obs}	C_5D_7-3-h ν_{obs}, cm^{-1}	I_{obs}	asym potential^c ν_{cal}, cm^{-1}	I_{cal}	sym potential^d ν_{cal}, cm^{-1}	I_{cal}
				Raman				
$\Delta n = 2$								
0–2	107.7	0.7	117.6^e	0.9^e	117.3	0.68	115.5	0.74
1–3	118.0	(1.0)	122.3	0.33	121.8	0.7	123.2	0.8
2–4	77.1	0.6	80.3	0.93	80.0	0.93	79.8	0.93
3–5	115.3	1.4	118.6^e	(1.0)^e	118.6	(1.0)	118.8	(1.0)
4–6	112.0	0.6	113.6	0.55	113.7	0.74	113.8	0.73
5–7	134.8	0.8	140.2	0.82	138.8	0.75	138.8	0.74
6–8	145.6	0.6	152.0	0.65	150.7	0.61	150.7	0.6
7–9	156.5	0.6	163.4	0.44	162.7	0.48	162.7	0.5
8–10	166.5	0.5	172.5	0.35	173.0	0.37	173.0	0.36
$\Delta n = 1$								
1–2			113.6		113.5	0.32	115.2	0.22
$\Delta n = 3$								
0–3			125.8	0.36	125.6	0.37	123.6	0.25
				Infrared				
$\Delta n = 1$								
0–1			(4.0)^f		3.83	5 × 10^{-5}	0.37	5 × 10^{-5}
1–2	108.2	0.4	113.5	0.34	113.5	0.34	115.2	0.62
2–3			(8.2)^g		8.3	0.04	8.0	0.04
3–4	68.0	0.4	70.5	0.45	71.7	0.89	71.7	0.92
4–5	47.3	0.4	(47.1)^h		47.0	0.59	47.0	0.53
5–6	64.8	(1.0)	67.5	(1.0)	66.8	(1.0)	66.8	(1.0)
6–7	69.6	0.8	72.9	0.8	72.0	0.94	72.0	0.94
7–8	75.6	0.7	79.2	0.76	78.7	0.85	78.7	0.85
8–9	80.7	0.6	84.5	0.71	84.1	0.7	84.1	0.7
9–10	85.3	0.5	89.2	0.56	89.0	0.56	89.0	0.56
10–11	89.3	0.5	93.2	0.56	93.4	0.42	93.4	0.42
11–12	92.8	0.4	97.4	0.38	97.5	0.3	97.4	0.3
$\Delta n = 2$								
0–2			117.9	0.44	117.3	0.6	115.5	0.3
1–3					121.8	0.6	123.2	0.33
$\Delta n = 3$								
0–3	117.7	0.5	125.4	0.29	125.6	0.4	123.6	0.68
2–5	123.0	0.4			126.0	0.65	126.8	0.66

^{a} The reduced mass is $g(x) = 5.7251 \times 10^{-3} - 3.0529 \times 10^{-4}x - 8.8111 \ 10^{-3}x^2 + 3.2459 \times 10^{-3}x^3 - 1.8688 \times 10^{-1}x^4 - 9.4082 \times 10^{-3}x^5 + 6.5928 \times 10^{-1}x^6$. ^{b} From ref 11. $^c V(x) = -26452x^2 + 953x^3 + 754020x^4$. $^d V(x) = -26402x^2 + 752987x^4$. ^{e} Calculated from computer deconvolutions. ^{f} Mean frequency inferred from observed 0–3 and 1–3 Raman bands or 0–2 and 1–2 infrared and Raman bands. ^{g} Mean frequency inferred from observed 1–3 and 1–2 Raman bands or 0–3 and 0–2 infrared and Raman bands. ^{h} Mean frequency inferred from observed 5–3 and 6–4 Raman bands or 4–3 and 6–5 infrared bands.

ion laser 514.5-nm beam at 3 W, filtered by a Photo Physics laser monochromator, was used as the exciting radiation. The spectral resolution was 1.3 cm^{-1}. The gaseous compounds were transferred under vacuum into a cylinder Pyrex cell equipped with two windows tilted with a Brewster angle for multiple reflections. In this cell, the gas-phase pressure in equilibrium with the liquid was 300 Torr at 298 K.

Results and Discussion

1. *Ring-Puckering Spectra*. (a) *Results*. Figures 2 and 3 show the Raman and far-infrared spectra of gaseous Cy3H and Cy4H in the ring-puckering region. In the Raman spectrum of Cy4H, the lines indicated with an asterisk correspond to the Cy3H impurity, whereas the far-infrared spectrum of Cy4H is the result of the subtraction of the infrared spectrum of pure Cy3H from the infrared spectrum of the Cy4H/Cy3H mixture.

Tables I and II list the recorded band maxima and assignments along with the calculated frequencies which will be discussed later. The ring-puckering transitions of the perdeuterated cyclopentene-d_8, as observed and assigned in ref 11, are also reported for comparison. In view of the small spectral differences observed between the monohydrogenated and the perdeuterated molecules, the assignments of the infrared and Raman lines for the former follow directly those already established for the latter.[11] As for this perdeuterated compound[11] or for the monodeuterated ones,[15,16] the most intense Raman band corresponds to the 3–5 transition instead of the 3–1 transition as in the other cyclopentene derivatives.[7,8,12,13]
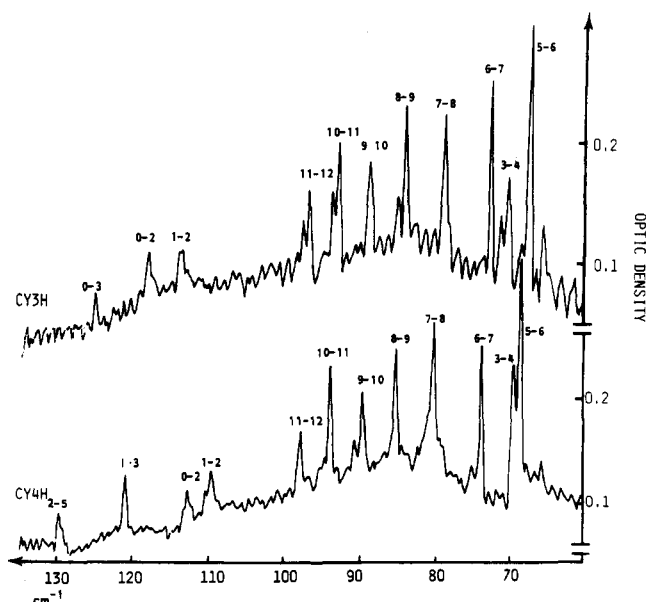

Figure 3. Far-infrared ring-puckering spectra of gaseous cyclopentene Cy3H and Cy4H at 298 K.

As observed in the previous similar studies,[5–8,11,12,16] the far-infrared frequencies correspond to single quantum transitions and the Raman bands to changes of two in the ring-puckering quantum

TABLE II: Ring-Puckering Transitions (Observed and Calculated with Two Potential Models) in the Raman and Infrared Spectra of Gaseous Cyclopentene Cy4H^a Compared with Those of Perdeuterated Cyclopentene (Ref 11)

transitions	C$_5$D$_8$^{b}		C$_5$D$_7$-4-h					
	ν_{obs}, cm^{-1}	I_{obs}	ν_{obs}, cm^{-1}	I_{obs}	asym potential^c		sym potential^d	
					ν_{cal}, cm^{-1}	I_{cal}	ν_{cal}, cm^{-1}	I_{cal}
			Raman					
Δn = 2								
0–2	107.7	0.7	113.0	0.4	113.7	0.64	112.0	0.75
1–3	118.0	(1.0)	122.0 (sh)		122.0	0.69	121.7	0.83
2–4	77.1	0.6	80.1	0.9	79.8	0.94	79.2	0.94
3–5	115.3	1.4	120.7^e	(1.0)^e	120.4	(1.0)	119.7	(1.0)
4–6	112.0	0.6	120.1^e	0.9^e	119.2	0.75	118.8	0.74
5–7	134.8	0.8	142.5	0.65	142.5	0.74	141.7	0.73
6–8	145.6	0.6	154.2	0.43	154.8	0.59	154.0	0.59
7–9	156.5	0.6	165.2	0.43	166.8	0.47	166.0	0.46
8–10	166.5	0.5	174.0	0.4	177.2	0.35	176.2	0.35
Δn = 1								
1–2			109.8	0.2	111.7	0.32	111.5	0.2
Δn = 3								
0–3			124.4	0.2	124.0	0.38	122.2	0.24
			Infrared					
Δn = 1								
0–1			(2.7)^f		2	10^{-4}	0.48	10^{-4}
1–2	108.2	0.4	110	0.30	111.7	0.4	111.5	0.62
2–3			(11.2)^g		10.3	0.06	10.3	0.06
3–4	68.0	0.4	69.6	0.63	69.5	0.91	68.9	0.92
4–5	47.3	0.4	(50.5)^h		50.9	0.66	50.8	0.66
5–6	64.8	(1.0)	68.7	(1.0)	68.3	(1.0)	68.0	(1.0)
6–7	69.6	0.8	74.1	0.7	74.1	0.93	73.7	0.94
7–8	75.6	0.7	80.5	0.8	80.7	0.83	80.2	0.83
8–9	80.7	0.6	85.5	0.74	86.1	0.68	85.6	0.68
9–10	85.3	0.5	90.0	0.53	91.0	0.53	91.0	0.53
10–11	89.3	0.5	94.2	0.63	95.5	0.39	95.0	0.4
11–12	92.8	0.4	98.3	0.4	99.7	0.28	99.0	0.3
Δn = 2								
0–2			112.8	0.22	113.6	0.5	112.0	0.26
1–3			121.0	0.3	122.0	0.52	121.7	0.28
Δn = 3								
0–3	117.7	0.5			124.0	0.44	122.2	0.68
2–5	123.0	0.4	130.0	0.2	130.7	0.58	130.0	0.58

^{a}The reduced mass is $g(x)$ = 5.8359 × 10^{-3} + 2.9769 × 10^{-4}x − 4.1121 × 10^{-3}x^2 + 4.9844 × 10^{-3}x^3 − 2.1642 × 10^{-1}x^4 − 1.2376 × 10^{-2}x^5 + 6.6827 × 10^{-1}x^6. ^{b}From ref 11. ^{c}$V(x)$ = −25520x^2 + 370x^3 + 737124x^4. ^{d}$V(x)$ = −25127x^2 + 723172x^4. ^{e}Calculated from computer deconvolutions. ^{f}Mean frequency inferred from observed 0–3 and 1–3 Raman bands or 0–2 and 1–2 infrared and Raman bands. ^{g}Mean frequency inferred from observed 1–3 and 1–2 infrared and Raman bands or 0–3 and 0–2 Raman bands. ^{h}Mean frequency inferred from observed 4–2, 5–3, and 6–4 Raman bands or 4–3, 5–2, and 6–5 infrared bands.

number (except for several jumps originating from levels below the barrier (Tables 1 and II)). The addition of the observed infrared frequencies allows us to predict and to assign the observed Raman frequencies in the 100–130-cm^{-1} region, where it is not straightforward on the basis of the perdeuterated compound, in particular for Cy3H. The complementary nature of the two types of spectra and the excellent correlation between the data make the interpretation clear for each molecule.

The infrared spectrum of Cy3H (Figure 3) shows some side bands resulting from transitions in the first excited vibrational state of the twisting mode, as already observed in previous infrared studies of cyclopentene derivatives.[6,11-13] They are more difficult to observe in the Cy4H spectrum which is the result of subtraction of spectra.

(*b*) *Calculation.* In the present case of monohydrogenated molecules (as for the monodeuterated ones[15-17]), we must check whether the observed frequencies an intensities are better reproduced by using an asymmetrical potential of the form $V(x)$ = V_4x^4 + V_3x^3 + V_2x^2 as required by symmetry considerations or whether only a symmetrical potential is sufficient to analyze these data.

The calculated transition frequencies depend also to a lesser extent on the model assumed for the puckering motion, which determines the reduced mass expansion used in the kinetic energy part of the matrix calculation. We have selected a reduced mass function depending on the puckering coordinate calculated by a computer program which assumes the basic bissector model described by Malloy.[9] Numerous studies have shown that a reduced

mass expansion, calculated by using more sophisticated models involving the rocking of α and β methylene groups, improves the calculation only slightly and requires two additional parameters, themselves determined.[9,11,12] Since isotopic substitution results in an asymmetrical kinetic energy expansion, both odd and even terms are necessary for the expression of the reduced mass expansion.[15-17,36] Seven terms (through g_6x^6) are used. They are reported for each molecule in Tables I and II.

Intensities I_{mn} for m–n puckering infrared transition are calculated from

$$I_{mn} \propto \nu_{mn} \left[\exp\left(-\frac{E_m}{k_BT}\right) - \exp\left(-\frac{E_n}{k_BT}\right) \right] \left(\frac{\partial \mu}{\partial x}\right)_0^2 \langle m|x|n \rangle^2 \quad (1)$$

where ν_{mn} is the transition frequency and the exponential term represents the usual Boltzman factors. The spectra are dominated by $n \rightarrow m = n + 1$ transitions. It has been effectively shown that the first-order term in the development of the dipole moment $\bar{\mu}$ is predominant.[1-5]

The Raman transition intensities are calculated from

$$I_{mn} \propto (\bar{\nu}_0 - \bar{\nu})^4 \exp\left(-\frac{E_n}{k_BT}\right) \left(\frac{45\bar{\alpha}_{mn}^2 + 7\gamma_{mn}^2}{45}\right) \quad (2)$$
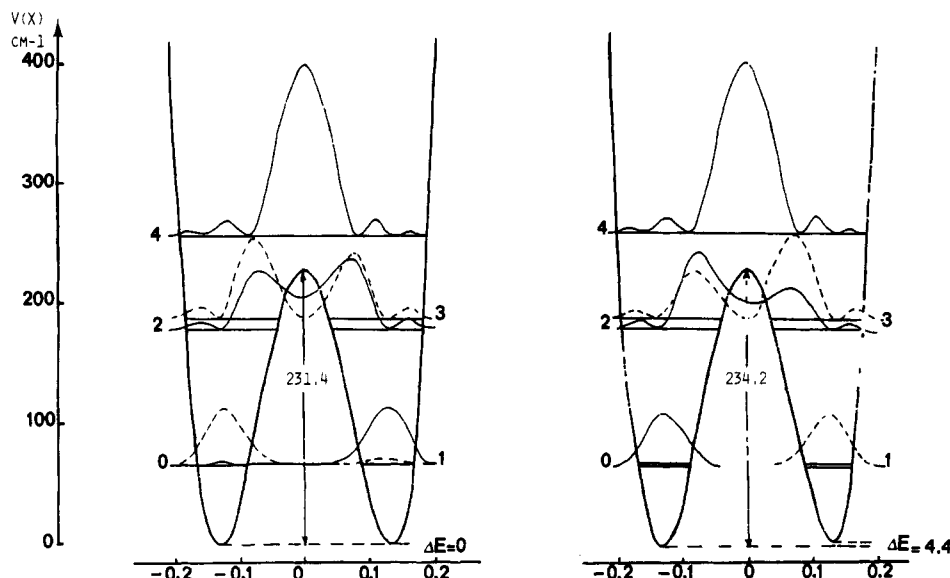
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Figure 4. Comparison between the energy levels and the probability of the corresponding wave functions in a symmetrical (a, left) and an asymmetrical (b, right) ring-puckering potential for Cy3H (the values of the potential parameters are those of the Table I).

with $\bar{\nu}_0$ and $\bar{\nu}$ the wavenumbers of the incident radiation and of the vibrational mode and $\bar{\alpha}$ and γ^2 the invariants of the molecular polarizability tensor. Every element α_{uv} ($uv = X, Y, Z$) of the polarizability tensor is developed in a Taylor series in the ring-puckering coordinate x:

$$\alpha_{uv} = \alpha_{uv}{}^0 + \left(\frac{\partial \alpha_{uv}}{\partial x}\right)_0 x + \frac{1}{2}\left(\frac{\partial^2 \alpha_{uv}}{\partial x^2}\right)_0 x^2 + \dots \quad (3)$$

The polarizability of the transition between the levels m–n is given by the expression

$$[\alpha_{uv}]_{mn} = \left(\frac{\partial \alpha_{uv}}{\partial x}\right)_0 \langle m|x|n\rangle + \frac{1}{2}\left(\frac{\partial^2 \alpha_{uv}}{\partial x^2}\right)_0 \langle m|x^2|n\rangle + \dots \quad (4)$$

A calculation of the polarizability tensor of the cyclopentene-h_8 has shown that the second-order term in (4) is unusually large, explaining the predominance of the overtone transitions $n \to m = n + 2$ in the Raman spectra.[37] As this situation exists in the perdeuterated[11] and in the monohydrogenated [this work] derivatives, it can be supposed that the polarizability tensor expansion is very similar:

$$I_{mn} \propto (\bar{\nu}_0 - \bar{\nu})^4 \exp\left(-\frac{E_n}{k_B T}\right)[\langle m|x^2|n\rangle]^2 \quad (5)$$

For both Cy3H and Cy4H molecules, we have fitted the coefficients of the potential $V(x) = V_2 x^2 + V_3 x^3 + V_4 x^4$ to reproduce the observed frequencies and intensities with either $V_3 = 0$ (symmetrical potential) or $V_3 \neq 0$ (asymmetrical potential).

(c) Discussion. As expected, only the transitions below the barrier are sensitive to the V_3 parameter. Indeed, as seen in Tables I and II, there is little difference between the calculation realized with either $V_3 = 0$ or $V_3 \neq 0$ for most of the transitions. But the frequencies of the 0–2, 1–2, and 0–3 transitions are better reproduced when $V_3 \neq 0$ (Tables I and II). The 0–1 splitting cannot be measured directly, but it is accurately deduced from the frequency differences of the infrared and Raman bands corresponding to the 0–3, 1–3, or the 0–2 and 1–2 transitions (Tables I and II). Its value is much larger than that involved in the kinetic energy term alone and is thus a striking argument in favor of an asymmetrical potential (Figure 4).

In the cases of both symmetrical and asymmetrical potentials, there is rather poor agreement between the absolute experimental

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TABLE III: Ring-Puckering Levels, Potential Barrier Heights, Energy Differences, and Dihedral Angles in the Ground and First Excited Vibrational Ring-Twisting State Calculated with Asymmetrical Potential $V(x) = V_4 x^4 + V_3 x^3 + V_2 x^2$

| | C_5D_7-3-h, cm^{-1} | | C_5D_7-4-h, cm^{-1} | |
puckering quantum no. n	ground state $\|0,n\rangle$	1st excited twisting vibrational state $\|1,n\rangle$	ground state $\|0,n\rangle$	1st excited twisting vibrational state $\|1,n\rangle$
0	0.00	0.00	0.00	0.00
1	3.85	11.50	2.00	2.66
2	117.30	111.75	113.75	104.10
3	125.60	128.85	124.05	122.10
4	197.30	194.95	193.55	187.70
5	244.25	252.55	244.40	247.60
6	311.05	324.15	312.75	320.20
7	383.05	402.10	386.90	399.20
8	461.70	486.35	467.55	484.50
9	545.80	576.10	553.70	575.30
potential barrier, cm^{-1}	234.20	207.20	221.75	190.35
ΔE, cm^{-1}	4.40	12.75	1.75	2.40
$\theta,^a$ deg	25.90	24.90	25.40	24.50
V_2, cm^{-1}	−26452.4	−25854.6	−25521.0	−24435.0
V_3, cm^{-1}	952.0	3281.0	370.0	624.6
V_4, cm^{-1}	754024.3	832589.3	737124.0	789216.6

^{a}The dihedral angles were calculated by averaging the extremes of the potential.

and calculated intensities. This problem has already been observed in all the other previous studies, even when a two-dimensional potential was used.[5-17] It might be due in part to the neglect of the higher order terms in the electrical anharmonicity development. Nevertheless, the trend in the relative intensities of the observed bands is better reproduced when $V_3 \neq 0$, in particular for the 0–3 and 1–3 Raman transitions and for the 1–2, 0–2, and 0–3 infrared transitions (Tables I and II). For example, in the case of Cy3H, a symmetrical potential would infer a very strong band at 115.5 cm^{-1}. None is observed in the infrared and Raman spectra (Figures 2 and 3).

The asymmetrical potential solution is thus preferred. The calculated puckering energy levels of Cy3H and Cy4H in the asymmetrical potential, the barrier height H defined as the energy difference between the top and the deeper minimum, the energy difference ΔE between the two minima, and the dihedral angle θ are listed in Table III. Of course, the precision of these results (a few percent and about 10% for H and E, respectively) depends

on several factors, including the validity of the one-dimensional potential and the accuracy of the frequency measurements.

The value of the dihedral angle θ, calculated by averaging the extremes of the potential, is around 25.5°, in good agreement with the previous determinations[12,14,16] (the minima of the potential functions occur approximately 1.5° higher). This value is between that determined by microwave 22°[20-22] and by electron diffraction 29°.[19]

The value of ΔE, determined with about 10% error, can be considered as significant. In the previous study of Cy3D and Cy4D,[16] this energy difference was assumed to result essentially from the difference of the vibrational energy of the two conformers. For a given conformation, the vibrational energy can be written

$$E = \sum_i hc\bar{\nu}_i(v_i + \tfrac{1}{2})$$

where $\bar{\nu}_i$ is the frequency of the ith vibrational mode and v_i its quantum number. As the frequency differences between the two conformations cannot be exactly known for all the internal modes, it was assumed that the major contribution to the vibrational partition function difference comes from the stretching CH and CD modes of the CHD group, as already observed for toluene and nitromethane[39]

$$\Delta E = \frac{1}{2}hc\Delta\bar{\nu}_{CH}\left(1 - \frac{1}{2^{1/2}}\right) \qquad (6)$$

with

$$\Delta\bar{\nu}_{CH} = \bar{\nu}_{CH}^{eq} - \bar{\nu}_{CH}^{ax} \quad \text{and} \quad \bar{\nu}_{CD} = \frac{1}{2^{1/2}}\bar{\nu}_{CH} \qquad (7)$$

From this hypothesis, it can be deduced that the same ΔE value must be found for the monohydrogenated and the monodeuterated derivatives. This value is indeed very similar for Cy3H (4.4 cm⁻¹) and Cy3D (4.1 cm⁻¹) and for Cy4H (1.75 cm⁻¹) and Cy4D (2.8 cm⁻¹). By averaging the ΔE values of Cy3H and Cy3D and those of Cy4H and Cy4D,[16] we can deduce the following from (6): for the 3-substituted isomers $\Delta\bar{\nu}_{CH}$ = 29 cm⁻¹; for the 4-substituted isomers $\Delta\bar{\nu}_{CH}$ = 15 cm⁻¹. The ab initio calculation gives a difference of 2×10^{-3} and 1×10^{-3} Å between the CH axial and CH equatorial bond length for the 3- and 4-position, respectively.[27] Thus, the above values correspond to a stretching frequency difference of about 15 cm⁻¹ for a CH bond length variation of 10^{-3} Å. In spite of the crude approximation involved by the relation (6), this variation is in good agreement with the correlation established by MacKean[28] and by Aljibury et al.[29] between CH bond lengths and strengths. As the CH bond is longer when in the axial position ($r^{ax} > r^{eq}$ and then $\bar{\nu}_{CH}^{ax} < \bar{\nu}_{CH}^{eq}$),[27] the conformer with an axial CH bond (Cy3H(a) or Cy4H(a)) is more stable than that with an equatorial CH bond (Cy3H(b)) and Cy4H(b)).

The value of the barrier height H is 234.2 cm⁻¹ for Cy3H, very close to the value found for Cy3D and Cy4D[16] and for the perhydrogenated cyclopentene.[5-9] It is only 221.8 cm⁻¹ for Cy4H, close to the value found for the perdeuterated and -1,2,3;3-d_4 derivatives.[11,12] The barrier heights determined with a symmetrical potential are almost the same (231.5 and 218.3 cm⁻¹ for Cy3H and Cy4H, respectively).

As the mixing of the methylene rocking modes in the kinetic expansion leaves the barrier value virtually unchanged,[11,12] the variations of the barrier height, when calculated with a one-dimensional treatment, were assumed to result essentially from the coupling of the ring-puckering motion with the ring-twisting mode (325–390 cm⁻¹).[13] Indeed, Bauman et al. have shown that the same two-dimensional potential energy function involving the two interacting ring-twisting and ring-puckering modes with a barrier height of 232 cm⁻¹ reproduces the experimental data of four isotopic derivatives (-1-d_1, -1,2,3,3-d_4, -d_8, and -d_0).[14] This potential does represent a picture closer to reality. But it is not
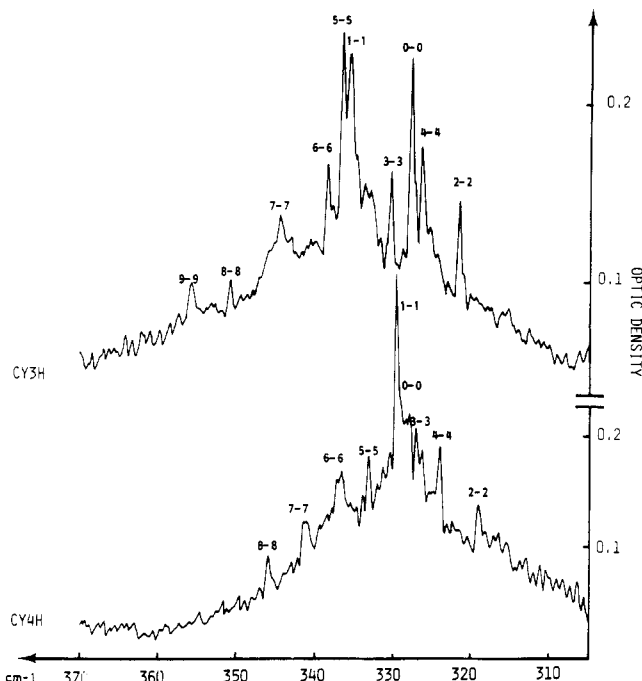

Figure 5. Infrared ring-twisting spectrum of gaseous Cy3H and Cy4H at 298 K.

perfect, in particular for the polydeuterated derivatives (from -d_4 to -d_8). For these molecules, the frequency decrease of the methylene rocking modes (down to 460 cm⁻¹ [13]) could involve a supplementary coupling requiring a three-dimensional treatment, as done for the 1,3-disilacyclobutane.[38] On the other hand, we wondered whether this coupling is the same for the various isotopic derivatives. Indeed, the spectra of cyclopentene-d_0 and -d_8 of C_s symmetry conform closely to the C_{2v} selection rules expected for a planar molecule.[12] The coupling between ring-twisting (A₂) and ring-puckering (B₂) is then not symmetry favored. On the contrary, the spectra of the partially deuterated derivatives of C_1 symmetry behave close to C_s selection rules and coupling between ring-twisting (A″) and ring-puckering (A″) is symmetry allowed.

However, in the case of the molecules studied here with an asymmetrical potential, a two-dimensional treatment is a very complex problem as odd coupling terms are involved and symmetry factorization is no more possible.[40] In regard to the intrinsic errors in the determination of the barrier height value (±1 or ±2%) and to the neglected effects mentioned above, the small difference (<6%) of the barrier values as calculated by a one-dimensional treatment is acceptable.

2. Ring-Twisting Spectra. (a) *Results.* Due to the reduction of symmetry, as observed in the other partially deuterated cyclopentenes,[12,14-16] the infrared spectra of Cy3H and Cy4H exhibit ring-twisting Q branches, as shown in Figure 5 (the Cy4H spectrum is obtained after subtraction of the pure Cy3H spectrum from the mixed Cy4H/Cy3H spectrum).

The fundamental ring-twisting frequency is 327.7 and 329.1 cm⁻¹ for Cy3H and Cy4H, respectively. The other lines of the spectra reveal the coupling of this mode with the ring-puckering. They are tabulated in Table IV along with the assignments.

(b) *Calculation.* The analysis of the observed bands has been performed by fitting the parameters V_2, V_3, and V_4 of the ring-puckering potential in the first excited ring-twisting vibrational level in the one-dimensional formalism. The intensities are only indicative as they are calculated as a simple Franck–Condon factor since the exact dependence of the dipole moment variation of the ring-twisting mode with the ring-puckering coordinate is more difficult to determine than in the CH/CD stretching vibration case.[15-17,41]

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TABLE IV: Ring-Twisting Transitions in the Infrared Spectra of Gaseous Cyclopentenes Cy3H and Cy4H

transitions[a]	C_5D_7-3-h_1[b]				C_5D_7-4-h_1[c]			
	ν_{obs}, cm^{-1}	I_{obs}	ν_{cal}, cm^{-1}	I_{cal}	ν_{obs}, cm^{-1}	I_{obs}	ν_{cal}, cm^{-1}	I_{cal}
(1,0)–(0,0)	327.7	1.0	327.7	1.0	329.1⎫	1.0	329.1⎫	1.0
(1,1)–(0,1)	335.5	0.9	335.4	0.97	329.8⎭		329.8⎭	
(1,2)–(0,2)	321.6	0.35	322.2	0.53	319.1	0.2	319.4	0.28
(1,3)–(0,3)	330.3	0.5	331.0	0.5	327.1	0.4	327.2	0.27
(1,4)–(0,4)	326.2	0.58	325.3	0.35	323.9	0.35	323.2	0.19
(1,5)–(0,5)	336.6	0.94	336.0	0.28	332.0	0.27	332.2	0.15
(1,6)–(0,6)	338.4	0.5	340.8	0.2	336.5	0.27	336.5	0.11
(1,7)–(0,7)	344.3	0.3	346.7	0.14	341.3	0.14	341.4	0.08
(1,8)–(0,8)	351.0	0.11	352.3	0.1	346.0	0.15	346.1	0.05
(1,9)–(0,9)	355.7	0.11	357.9	0.06			350.7	0.03

[a] The levels are labeled (n',n) where n' is the ring-twisting quantum number and n the ring-puckering quantum number. [b] The fitted ring-puckering potential in the first excited vibrational ring-twisting state is $V'(x) = -25855x^2 + 3281x^3 + 832589x^4$. [c] The fitted ring-puckering potential in the first excited vibrational ring-twisting state is $V'(x) = -24435x^2 + 624x^3 + 789216x^4$.

(c) Discussion. The agreement between the observed and calculated frequencies is satisfactory (Table IV). The calculated parameters V_2, V_3, and V_4 of the ring-puckering potential in the first excited ring-twisting vibrational level are tabulated in Table III with the corresponding energy levels, barrier height, and dihedral angle values. The calculated ring-puckering transition frequencies in this first excited ring-twisting vibrational state reproduce well the side bands observed in the ring-puckering infrared spectra (Figures 2 and 3).

As discussed above, the one-dimensional treatment for the inversion motion is only an approximation. Then, the potential function parameters are only "effective" and their values reflect the effect of all the interactions with the other internal modes.[42] Thus, the analysis of their variations from the ground state to the first excited vibrational state of ring-twisting could offer some information about the interaction of the two motions.[42] In this excited state we observe a small decrease of the quadratic term (around 3%) and a greater increase of the quartic term (around 9%) and of the cubic term (70 and 240% for Cy4H and Cy3H,

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respectively), which induce a decrease of about 12% of the barrier height (Table III). The potential energy is thus increased when both motions are simultaneously excited showing, in good agreement with the previous studies,[14] that the two motions somewhat hinder each other. The asymmetry of the two ring-puckering potential wells is seen to increase more strongly for Cy3H (×3) than for Cy4H (×1.5). As illustrated in Figure 1c, the atoms in position 3 are effectively more affected by the ring-twisting motion than those in position 4.

Conclusions

In this study, the one-dimensional ring-puckering potential functions of two monohydrogenated cyclopentene derivatives C_5D_7-3-h and C_5D_7-4-h have been determined in the ground and in the first excited ring-twisting vibrational state from the analysis of the infrared and Raman spectra.

The present work confirms the results previously obtained with the corresponding monodeuterated derivatives C_5H_7-3-d and C_5H_7-4-d;[15,17] in addition to the asymmetry in the vibrational kinetic expansion,[15,16,36] the isotopic monosubstitution in the allylic position does produce a more or less pronounced asymmetry in the ring-puckering potential function of cyclopentene. It leads thus to two distinct conformers with slightly different energies. This energy difference is found to be around 4 cm^{-1} for the 3-substituted derivatives and around 2 cm^{-1} for the 4-substituted ones. It is related to the variations of the CH and CD bond lengths (and hence stretching vibrations) of the CHD group in the two conformers, that with a CH bond in the axial position being the most stable one. The slight differences found for the barrier height for the two monohydrogenated derivatives have been discussed in the light of the validity of a one-dimensional treatment.

The analysis of the ring-puckering potential function in the first excited ring-twisting vibrational state gives some information about the interaction between the two ring motions. This interaction is shown to be anticooperative.