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Vibrational Spectra of Twist–Boat Cyclohexane

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Abstract: The infrared matrix spectra of cyclohexane condensed from both hot and room-temperature vapor have been taken. Most of the new bands found for cyclohexane agree remarkably well with those of Squillacote et al. (*J. Am. Chem. Soc.* **1975**, *97*, 3244). Additional bands are found for cyclohexane, and deuteriocyclohexane is examined for the first time. The results of normal-coordinate calculations for the twist and boat conformations agree reasonably well with the new bands, and it is concluded that the new bands are mostly likely due to the twist conformer. Reasons for the discrepancies between the frequencies of the new bands and the results of the calculations are examined.

Introduction

The various conformations of cyclohexane have been the object of intensive study ever since the original suggestion of the boat and chair forms by Sachse[2] in the 1890s. However, almost all the experimental evidence available is from studies of the stable chair form, and only indirect evidence is available with which to confront theoretical expectations for the other forms. Information on the twist–boat conformers has been limited to thermodynamic studies and theoretical calculations and studies of appropriately hindered substituted cyclohexanes. Direct information on the twist–boat itself was first obtained by Squillacote et al.,[3] who obtained the matrix-isolated infrared spectrum of the twist–boat by condensing hot cyclohexane vapor. They were able to identify vibrational bands of a new form of cyclohexane and to make a good case that this new form was indeed the twist–boat. In view of the importance of direct evidence on the twist–boat, we undertook to repeat the Squillacote et al. experiments. We have been able to obtain spectra of the new form at higher sensitivity and resolution, have obtained the spectrum of the fully deuterated molecule, and have analyzed the results by using normal-coordinate analysis.

The twist and boat forms are two conformers of cyclohexane thought to occur with an energy of about 6 kcal/mol above that of the stable chair form. The twist (D_2) and boat (C_{2v}) forms can interconvert by pseudorotation.[4,5] Calculations suggest that the twist forms are at the minima of the pseudorotation path and that the boats are the transition state about 600 calories above the twists.[4] In what follows "twist–boat" means any form along this pseudorotation path while "twist" and "boat" refer to the distinct conformers. Since the boat form is at a saddle point on the conformational energy surface, it is not expected to exist unless stabilized by the matrix.

Experimental Section

A number of different oven arrangements were tried in order to produce the matrix-isolated spectrum of the twist boat.[6] The early versions proved unsatisfactory when heated. The first was a straight-through stainless-steel tube heated by a resistance coil. The tube was packed with copper wire to increase thermal contact with the flowing gas. Decomposition of the cyclohexane occurred when the oven was heated, and the decomposition could easily be detected by the presence of infrared bands due to identifiable small molecules. We assumed that the decomposition was caused by catalytic action on the metal surfaces and next tried a quartz oven. Few products of any sort were detected with this oven, and it was found that the oven surface became covered with carbon black. The successful oven (Figure 1) also had an inner jacket of quartz, but the orifice size was increased and the orifice was put as close to the end of the tube as possible. Both these changes minimize the collisions of the hot gas with the quartz wall. This oven produced only the desired species and did so in a reproducible fashion. The orifice of this oven is probably too large for equilibrium to have been achieved in the heated section. The oven allowed the argon matrix gas either to be heated and deposited along with the cyclohexane or to be deposited without passing through the oven. The oven was attached to an Air Products, Inc. Displex closed-cycle helium refrigerator, and the matrix was formed on a CsI plate. When being exposed to the hot oven, the CsI was at a temperature of about 16 K. During deposition experiments with a cold (room-temperature) oven, the CsI was heated by a resistance heater to this same 16 K. When arranged for taking spectra, we protected the CsI plate by a heat shield and achieved a temperature of 9 K.

The chemicals used were spectroquality (99+%) cyclohexane from Matheson Coleman and Bell, C_6D_{12} (99.5% D) from Stohler Isotope Chemicals and prepurified argon (99.998%) from Matheson Gas Products. The C_6H_{12} was degassed and dried before use, and the C_6D_{12}, which came in a sealed ampule, was released under vacuum and degassed before use.

Most of the experiments were done with an argon–cyclohexane ratio of 500:1. The rate of deposition was about 1 millimol/h which provided a matrix some tenths of a millimeter thick for 15-h deposition experiments. The spectra were taken on a Nicolet 7199 Fourier transform infrared spectrometer, and all the spectra used were taken at 0.5-cm^{-1} resolution. Enough scans were taken to reduce the noise to a small value. The sensitivity was then limited by the channel spectra arising from the

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[1] To whom correspondense should be addressed.

[2] Sachse, H. *Ber.* **1890**, *23*, 1363–1370.

[3] Squillacote, M.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1975**, *97*, 3244–3246. The thermodynamic quantities quoted by these authors are not consistent with their estimated twist–boat population.

[4] Pickett, H. M.; Strauss, H. L. *J. Am. Chem. Soc.* **1970**, *92*, 7281–7290.

[5] Strauss, H. L. *J. Chem. Educ.* **1970**, *48*, 221–223.

[6] Offenbach, J. L. Ph.D. Dissertation, University of California, Berkeley, 1979.

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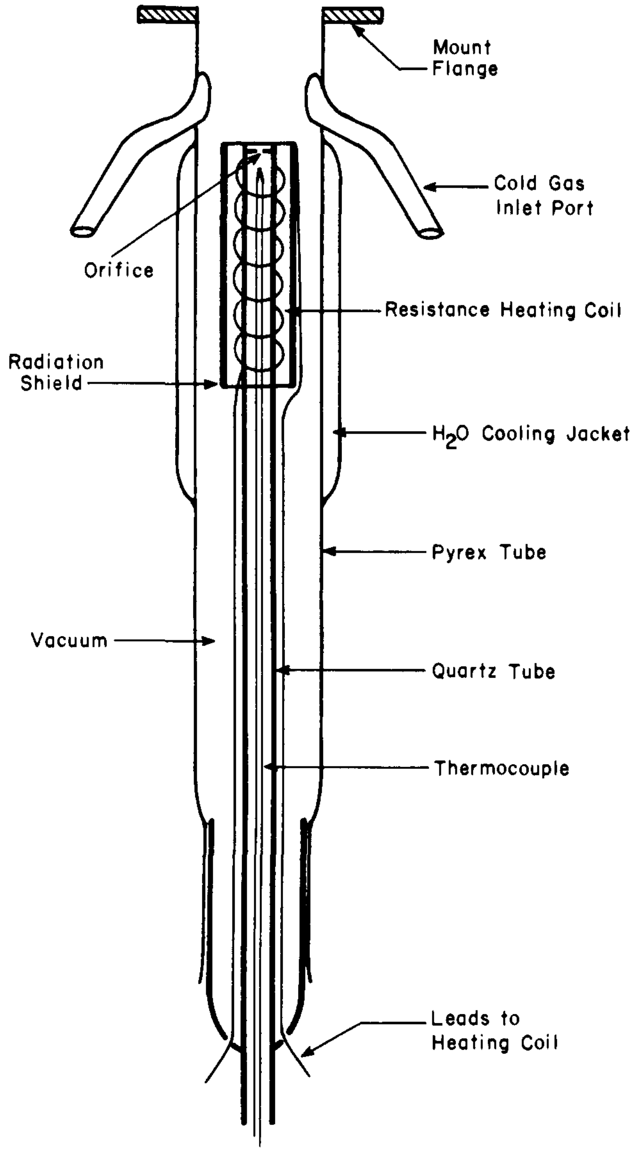

Figure 1. The resistance-heated oven. The heated portion is $1^3/_4$ in. long and has a 1.9-mm orifice. The mounting flange bolts on to the Displex cooler, and the orifice is about 2 in. from the deposition surface.

thin deposited layer and from the various cell windows.

The spectrum of cyclohexane in argon deposited from room-temperature gases was taken first and used as a reference. In early experiments, with the first versions of the oven, extensive decomposition occurred when the cyclohexane was heated and was easy to detect from the infrared spectrum of various decomposition products. In the later successful experiments, only the bands attributable to chair-form cyclohexane, to the twist-boat form, to CO_2, or to water were observed. The only water bands were found at about 1600 cm^{-1}. These bands are among the strongest water bands in the matrix and are due to both monomers and polymers of water.[7] Disconcertingly, new bands appeared in this region in the "hot" spectra. We attribute this to a change in the nature of the water polymers on deposition of the hot gas. Fortunately, all the other water bands of comparable strength are found above 3000 cm^{-1}.[7]

It is conceivable that hot cyclohexane deposited in argon produces new bands by site splitting caused by the momentarily heated and disarranged argon matrix. To rule out this possibility as well as to make sure that no decomposition occurred, we varied the deposition conditions systematically. Most of the experiments were done with the argon–cyclohexane mixture flowing through the heater. One set of experiments was done with a 10:1 mixture of argon–cyclohexane flowing through the heater and about 20 times as much argon bypassing the heater and being deposited directly. The same new bands were seen in this experiment, and the intensity ratio of the new bands to the chair bands remained the same.

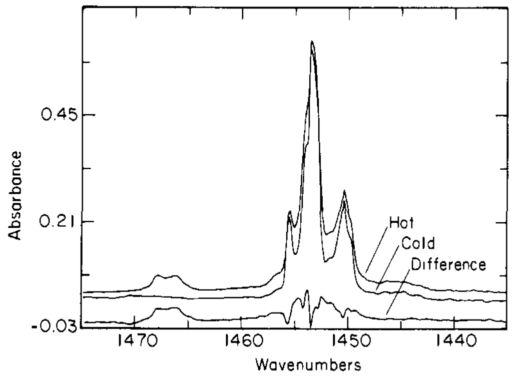

Figure 2. FTIR spectra showing the matrix spectrum of 9 K cyclohexane in argon deposited from room-temperature gases, labeled "cold", the matrix spectrum from gases heated to 1200 K, labeled "hot", and the difference. The bands of twist–boat cyclohexane appear at 1469–1466 cm^{-1} and perhaps under the chair peak at 1455–1450 cm^{-1}.

This observation eliminates from consideration most effects due to disruption of the matrix by hot gases during deposition. The split stream deposition was not used further, since it resulted in spectra (both chair and new bands) weaker by about a factor of 7, due to an unfavorable geometry (the area sampled by the infrared beam is only 4 mm^2, and we could not control the deposition geometry that accurately).

The new bands could conceivably be due to cyclohexane aggregates. This possibility was checked by running experiments with an argon:cyclohexane mixture of 250:1 instead of 500:1. The increased concentration of cyclohexane did not change the appearance of the new bands, and this makes it unlikely that aggregation effects account for the new bands.

Most of the hot experiments were run with the oven at 1200 K; tests at 1300 K showed a small decrease in the relative intensity of the new bands. This may have been due to a distortion in the oven geometry on heating to this temperature. At any rate, it is clear that we were not seeing an equilibrium amount of the new form, and succeeding experiments were run at the apparently optimum temperature of 1200 K.

Results

In the discussion that follows, we speak of the new bands as due to twist–boat cyclohexane and return to the question of whether this is actually so.

The strongest new band found is the methylene scissors band at about 1468 cm^{-1}, shown in Figure 2. The figure shows our procedure. Both the "hot" and "cold" spectra were displayed and subtracted so as to minimize the strong chair bands. New bands show up clearly in the difference spectrum. Many chair bands such as that at 1455 cm^{-1} show complex structure in the matrix. Most of this structure is completely reproducible (within the 0.5-cm^{-1} resolution and the channel spectrum background). The 1455-cm^{-1} band of the chair is due to the methylene scissors modes. There are four sets of these in the chair, of symmetries A_{1g} (R active), E_u (IR active), E_g (R active), and A_{2u} (IR active). The triplet structure represents some combination of these—perhaps the E_u band of $C_6{}^{12}H_{12}$ (split ?) and of $C_5{}^{12}C_1{}^{13}H_{12}$ and the A_{2u} band of both species. The $C_5{}^{12}C_1{}^{13}H_{12}$ should comprise about 7% of the sample.

The changes in the 1455-cm^{-1} band on condensing hot cyclohexane are real and reproducible. The changes most likely represent the appearance of new bands of the twist–boat conformer and the disappearance of specific chair bands. However, it is difficult to characterize these changes in a simple fashion in the absence of a detailed description of the "fine structure" of the bands. Also we can not be sure that the changes do not represent subtle, but reproducible, changes in the nature of the site of the chair molecule upon heating.[8,9]

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[7] Ayers, G. P.; Pullin, A. D. E. *Spectrochim. Acta, Part A*, **1976**, *32A*, 1629–1639.

[8] Computer subtraction allows the accurate determination of differences in cases in which the shifting background is not a problem. An example is the residual structure under the strong band at 1455 cm^{-1} in Figure 2. These difference features could not be due to anomalous dispersion because the samples are relatively transparent even at the peaks of the strong bands, that is, the absorption in a thickness equal to a wavelength of the infrared light is very small.

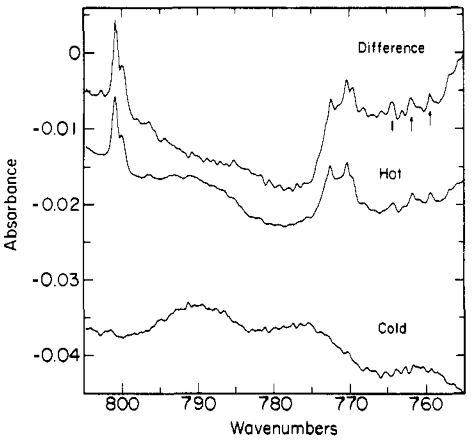

Figure 3. Spectra taken under the same conditions as those of Figure 2 with a vertical scale expanded about 10 times. New bands appear at 801 and 771 cm^{-1} (both doublets) and at 764, 762, and 759 cm^{-1} (indicated by arrows).

Table I. New Bands from Hot Cyclohexane

cyclohexane ν_{obsd}, cm^{-1}	rel peak height	Squillacote et al.[3] ν_{obsd}, cm^{-1}	Squillacote et al.[3] rel intens
1468	1.0	1471	0.98
1465		1469	1.0
1405	0.07		
1152	0.20	1153	0.26
1000			
999	0.15	1000	0.11
997			
910	0.11		
908			
888	0.13		
887			
869	0.17	869	0.38
801	0.30		
799	0.15		
772	0.28	772	0.30
770		770	0.33
764			
762	0.07	760	0.15
759			

Some of the weaker bands we have seen are shown in Figure 3. The figure shows clear split bands at 801 and 772 cm^{-1}. A curious triplet appears at 760–765 cm^{-1}. Note that Figure 3 has a vertical scale which is expanded a factor of about 10 from that of Figure 2. The features in the cold spectrum in Figure 3 are entirely due to the channel spectra that are what limit our ability to pick out new bands.[9] The three sets of bands in this figure were also seen by Squillacote et al.[3] (Table I). The table lists the other new bands, a number of which have not been reported previously.

The spectra of perdeuteriocyclohexane were more difficult to interpret. The spectra are intrinsically less intense (by a factor of 2 for pure hydrogen motions), and the perdeutered sample inevitably contained a small amount of partly light hydrogen species. The spectrum of the small amount of chair form $C_6D_{11}H$ present in our samples is of interest in its own right, and some features of this spectrum will be published separately. However, the light hydrogen species is a ubiquitous "impurity" in the spectra when trying to find weak twist–boat bands. In addition, we did fewer runs of the perdeuterated cyclohexane. In spite of these uncertainties, quite a few new bands were clearly identified. The chair scissors vibration at 1070 cm^{-1} gives rise to a new band at 1075 cm^{-1} (Figure 4) corresponding to the bands seen near 1450 cm^{-1} in the light hydrogen species. Two of the new bands (1001 and 975 cm^{-1}) are very close to bands in the cold spectrum but appear real nonetheless (Figure 5). The new bands are listed in Table II with their approximate intensities normalized to the scissors band at 1075 cm^{-1}.

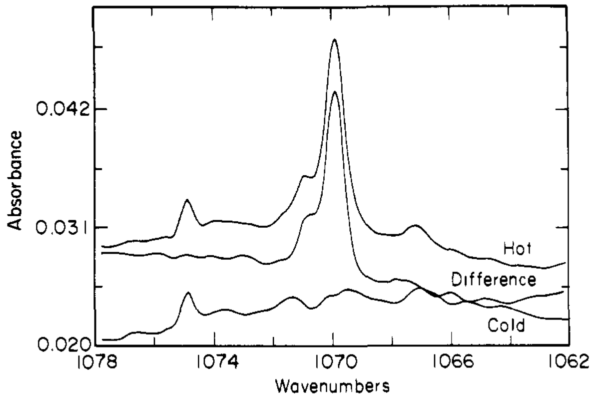

Figure 4. Spectra of perdeuteriocyclohexane taken under the same conditions as those of Figure 2. The vertical scale is expanded about 20 times that of Figure 2. A new band appears at 1075 cm^{-1}.

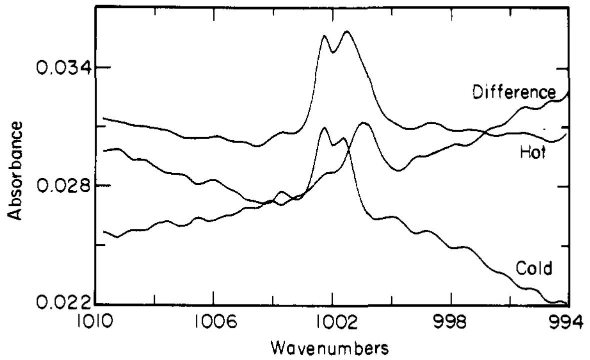

Figure 5. Spectra of perdeuteriocyclohexane at about 40 times the scale expansion of Figure 2. A doublet of chair cyclohexane appears at about 1002 cm^{-1}. A new band appears at 1001 cm^{-1}.

Table II. New Bands from Hot Perdeuteriocyclohexane

ν_{obsd}, cm^{-1}	rel peak height	ν_{obsd}, cm^{-1}	rel peak height
2138	6	1001	0.5
1195	0.5	975	0.5
1189 (br) (?)[a]		971	0.3
1151	0.5	718	1
1075	1	714	0.7
1067 (?)	0.5	713	1.3

[a] br means broad.

Calculations

The normal coordinates of chair cyclohexane have been examined many times over the past 20 years,[10,11] but until recently at least two disparate assignments seemed plausible. The two sets of assignments agree on the nature of those vibrations that give rise to the strong bands in the infrared and Raman spectra but differ on the assignment of the vibrations that give rise to only weak bands in the 900–1200-cm^{-1} region. The high symmetry of cyclohexane makes it possible to resolve the discrepancy by using the hyper Raman effect in which the A_{1u} modes, which are silent

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[9] The question has been raised of whether the channel spectra could be removed by a systematic procedure. The channel spectra in our spectra arise from a combination of reflections, a number of salt plates of different thicknesses (two windows and the deposition plate) and of the matrix itself. The resulting pattern is very complex (see the "cold" spectrum of Figure 3). More seriously, the matrices are deposited until the features to be examined are observed. No accurate measure of matrix thickness other than the channel spectrum itself is available. Consequently very weak bands such as those in Figure 3 were identified by examining spectra from repeated experiments and making sure that the features showed up at different matrix thicknesses.

[10] Hiraya, A.; Udagawa, Y.; Ito, M. *Chem. Lett.* **1979**, 433–436.

[11] Rounds, T. C.; Strauss, H. L. "Vibrational Spectra and Structure"; Durig, J. R., Ed.; Elsevier: New York, 1978; Vol. 7, pp 237–268.

Table III. Values of the Valence Force Constants[a]

K_R	4.351925		$F_{R\gamma'}$	−0.003495	
K_d	4.613507		$F_{d\gamma}$	0.10	
H_ω	1.045626		$F_{d\delta}$	0.10	
H_δ	0.551529		$F_{\gamma\omega}$	0.004215	
H_γ	0.663839		$F_{\gamma'}$	0.032283	
H_τ	−0.126935	cos 3τ[b]	F_{γ_θ}	−0.022402	
F_R	0.220248		f_γ^{θ}	0.017459 − 0.088298	cos θ
F_d	−0.019469		$f_{\gamma'}^{\theta}$	0.002300 + 0.010365	cos θ
F_{Rd}	0.10		$f_{\gamma''}^{\theta}$	0.004328 + 0.003983	cos θ
$F_{R\omega}$	0.387398		$f_{\gamma\omega}^{\theta}$	0.012066 − 0.084604	cos θ
$F_{R\gamma}$	0.261758		f_ω^{θ}	0.026790 − 0.073210	cos θ

[a] Stretch constants are in units of mdyn/Å; stretch–bend interaction constants in units of mdyn/rad. Bending constants are in units of mdyn Å/(rad)^2. The notation is defined in ref 13. The last five constants are defined in Figure 6. [b] For the twist form, the torsional angle of 31° is assigned $f^\tau = 0.0$ For very small changes in the torsional angle around 30° the small ($<10^{-3}$) f^τ leads to large effects on the lowest frequency mode. Since this constant is very small, it is set exactly to zero.

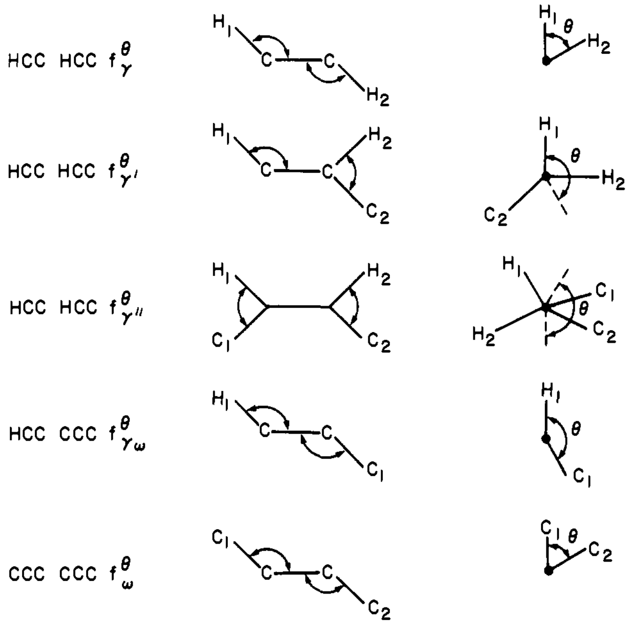

Figure 6. The bend–bend interactions for which constants are listed in Table III. Only the bend–bend interactions centered on adjacent carbon atoms are shown together with the appropriate dihedral angle, θ. The projections on the right are looking perpendicular to the central CC bond, and the dashed lines represent the projections of the HCC angle bisector onto the viewing plane. The torsional coordinate (not shown) is the sum of the three trans torsions around each CC bond in the chair form of cyclohexane, and the torsional coordinate is identical with θ in the bottom diagram.

in the other spectra, are active. The hyper Raman spectra[10] show a strong band at 1107 cm^{-1} (liquid), and, therefore, this is a band of A_{1u} symmetry. This observation is sufficient to resolve most of the discrepancies.

This band is correctly predicted at 1093 cm^{-1} by an unpublished force field of Snyder.[12] This force field, which is an improvement over the earlier one of Snyder and Schactschneider,[13] is derived from an extensive analysis of various methyl-substituted cyclohexanes. It is given in Table III and is the one we use for our analysis of the twist–boat. The force field in Table III gives similar results to the force field recently obtained by Wiberg and Shrake,[14] although the force fields differ in some important respects—the A_{1u} band is predicted by Wiberg and Shrake at 1066 cm^{-1}, for example.

For calculation of the vibrational properties of the twist–boat, force constants for the interactions of motions on adjacent methylene groups are needed. These interaction constants depend on the dihedral angle between the methylene groups but have only been defined for trans (θ = 180°) and gauche (θ = 55.5°) conformations (Figure 6) in standard force fields. We interpolated the known force constants as a function of angle to arrive at the constants listed in Table III. The torsional force constant was assumed to follow a cos 3τ dependence (Table III).

The geometry of the chair form (D_{3d}) was taken to be the one determined by electron diffraction[15] with a dihedral angle of 55.5°. The boat and twist structures were taken as the idealized structures which differ from that of the chair only by the dihedral angles of 55.5° and 0° for the boat (C_{2v}) and 31° and 64.5° for the twist (D_2). Selected results of the calculations are compared to the observations in Tables IV and V. Complete tables may be found in ref 6. Tables IV and V list only strong chair bands in the "cold chair observed" column. *All* the new bands (those in the hot spectrum but not in the cold spectrum) are listed in the "new bands observed" column. In the "calculated" columns, only the frequencies that correspond either to the strong chair bands or to the new bands are listed. The weak observed chair bands are not listed nor are the chair bands seen above 1500 cm^{-1}.

Discussion

The matrix spectra of cyclohexane and perdeuteriocyclohexane show more or less the bands expected. Tables IV and V list the strong matrix bands; the chair-form bands correspond to the infrared-allowed vibrations and are close to those in the liquid and gas cyclohexane spectra as expected. However, the bands show more structure than can easily be explained (see the 1455-cm^{-1} band in Figure 2, for example). The structure might be due to matrix perturbations which split *E* vibrations and make silent bands allowed, to C^{13} species, to combination bands, or to all of these. In the case of the perdeuteriocyclohexane, bands due to $C_6D_{11}H$ are responsible for some of the unexpected bands. We have not tried a detailed assignment of all the small features we have seen—lists of bands may be found in ref 6.

The features of the cold cyclohexane spectra, however complicated, are reproducible, and the "new" features seen on freezing the hot cyclohexane are really new. There is excellent agreement between our results for the C_6H_{12} and those of Squillacote et al.[3] (Table I). The agreement between the relative intensities is particularly striking. The reproducibility of the results under the variety of conditions described by us and by Squillacote et al. practically rules out decomposition products or other spurious effects as the source of the new spectra.

There is general agreement that the twist and boat conformations of cyclohexane lie about 5–6 kcal/mol above the chair.[3,4] The activation energy for the twist–boat conformations to go back to the chair is about 5 kcal. A substantial population of the twist–boat is expected in the heated gas,[3] and the barrier to return to the chair is high enough to expect it to be trapped. Finally, the new bands seen are reasonable for the twist–boat form as shown in Tables IV and V.

What can be said about the detailed structure of the trapped twist–boat form? The 6 twists and 6 boats can interchange by pseudorotation with the boat form providing a barrier between twist forms of perhaps 600 cal/mol.[4] The boat form is thus not a stable conformation, and the twist alone should be trapped. We have however calculated frequencies for both the twist and the boat geometries and ignored the one imaginary frequency that results for the boat.[16] The results are compared to observation in Tables IV and V.

The classification of the twist and boat bands by their correspondence to chair bands is not unique, since a given chair can form twists and boats in different orientations. The only unique classification is by the correspondence to the hypothetical D_{6h} structure.[4] This is useful in explaining intensities of the chair

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(12) Snyder, R. G., to be submitted for publication.

(13) Snyder, R. G.; Schactschneider, J. H. *Spectrochim. Acta* **1965**, *21*, 169–195.

(14) Wiberg, K. B.; Shrake, A. *Spectrochim. Acta, Part A* **1971**, *27A*, 1139–1151; **1973**, *29A*, 567–581, 583–594.

(15) Davis, M.; Hassel, O. *Acta Chem. Scand.* **1963**, *17*, 1181.

(16) The imaginary mode for the boat form is for the "unstable" mode of motion that takes the boat to the twist.

Table IV. Comparison of Cyclohexane Observed and Calculated Frequencies

mode	cold chair obsd[a]	chair calcd[b]	twist calcd[c]	boat calcd[d]	new bands obsd[e]
(3)		1464 A_{1g}(I) δ	1464 A(I) δ	1460 B_2 δ	1468
(27)	1456 1454	1457 E_u δ	1458 B_3 δ	1459 A_1 δ	1465
			1450 B_2 δ	1458 B_1 δ	
(19)		1452 E_g(I) δ	1446 B_1 δ	1454 A_1 δ	
			1440 A(I) δ	1451 A_2(I) δ	
(14)	1450	1450 A_{2u} δ	1439 B_3 δ	1445 B_1 δ	
(7)		1376 A_{1u}(I) T,W	1367 B_2 W	1389 A_2(I) W	1405
(10)		1364 A_{2g}(I) W,T	1360 B_1 W	1389 B_2 W	
(4)		1168 A_{1g}(I) P	1157 B_2 P	1153 B_2 T,W	1152
(11)		1130 A_{1u}(I) W	1138 B_2 W,T	1135 B_1 P	
(15)	1046 1020	1017 A_{2u} P	992 B_3 ω,P,W	995 B_1 ω,P	1000 999 997
(30)	904	919 E_u T,P	907 A(I) T,P	934 A_1 P	910
			892 B P,T	899 A_2(I) W,P	908
(31)	864		868 B_3 R	870 B_2 T	888
		860 E_u R			887
	860		853 B_2 R	850 B_1 P,W	869
(5)		812 A_{1g}(I) R	811 A(I) R	816 A_1 R	801 799
(23)		787 E_g(I) P	731 B_1 P	739 B_2 P	772 770
					764
			725 B_2 P	735 A_1 P	762
					759
(16)	524	516 A_{2u} ω,P	581 B_3 ω,T,P	589 B_1 ω,P	

[a] Only the strong matrix bands corresponding to allowed transitions of the chair form are listed (CH stretch bands are not listed—all other strong bands are). [b] The numbering in the first column is for the chair bands of ref 14. Only calculated bands near observed bands are listed and a complete list may be found in ref 6. The symmetry symbols are for D_{3d} symmetry. The symbol I is for an infrared inactive representation. The character of the mode is indicated by δ, scissors, T, twist, W, wag, R, rock, P, C–C stretch, and ω, CCC bend. Only the major contribution to a mode is listed. [c] Calculated bands in D_2 symmetry. [d] Calculated bands in C_{2v} symmetry. [e] *All* new bands observed are listed.

Table V. Comparison of Perdeuteriocyclohexane Observed and Calculated Frequencies[a]

mode	cold chair obsd	chair calcd	twist calcd	boat calcd	new bands obsd
numerous bands			(2 × 1070)		2138
(7)		1212 A_{1u}(I) R	1192 B_2 R	1186 B_2 R,W	1195
(27)	1164	1162 E_u R,W	1172 B_2 R,W	1167 B_2 R	1189 (br)
			1164 B_3 R,W	1162 B_1 R,W	1151
(14)	1085	1079 A_{2u} δ	1080 B_1	1109 A_2(I) W	
(10)		1076 A_{2g}(I) W	1080 B_3 δ	1090 B_1 δ	1075
(28)	1070	1068 E_u δ	1069 B_2 δ	1078 B_2 δ	
			1068 B_3 δ	1076 B_1 δ	1067 (?)
(20)		1064 E_g(I) δ	1066 A(I) δ	1071 A_1 δ	
			1061 B_1 δ	1069 A_2(I) δ	
(4)		1006 A_{1g}(I) P	992 B_2 P	994 B P,T	1001
(29)	991	977 E_u T	984 A(I) T,P	988 A_2(I) T,P	975
	987		973 B P,T	946 A_1 P,T	971
(15)	917	897 A_{2u} P	914 B_2 W,P,T	886 A_2(I) T	
				875 B_2	
(30)	721	713 E_u R,T	712 B_3 R,T	722 B_2 R,T	718
					714
			700 B_2 R,W	702 A_2(I) W,T,P	713
(31)	686	689 E_u P	693 B_1 P,T	702 A_2(I) P	
			671 A(I) T,P	695 A_1 R,W	

[a] The footnotes of Table IV apply.

bands—strong bands are those that would be allowed in the D_{6h} structure.[17] In Tables IV and V, the correspondences are just listed by frequency and are *not* rigorous by symmetry.

For C_6H_{12}, the new scissors bands are seen at high frequencies, 1468 and 1465 cm^{-1}, frequencies characteristic of a twist conformation.[3,18,19] Unfortunately, our calculations do not reproduce this shift to higher frequency, which is not surprising, since the potential function was not determined from any molecules with other than trans or gauche arrangements of methylene groups. For C_6D_{12}, the main scissors band seems to have shifted to 1075 cm^{-1} in the twist as compared to 1070 in the chair, but the situation is not as clear-cut since the scissors mix appreciably with other methylene motions.

The next new bands of C_6H_{12} are seen at 1405 and 1152 cm^{-1} and are the twist–boat bands that correspond approximately to infrared-unallowed vibrations in the chair form. Weak bands due to "unallowed" chair form bands are seen in these regions in the matrix corresponding to the weak chair form bands seen in room-temperature IR spectra, for example, at 1364 cm^{-1} in the vapor and at 1159 and 1110 cm^{-1} in the liquid.[14] The unallowed chair bands are given a small intensity by a variety of different

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(17) Pickett, H. M.; Strauss, H. L. *J. Chem. Phys.* **1970**, *53*, 376–388.

(18) Van Bekkum, H.; Hofnagel, M. A.; DeLavieter, L.; Van Veen, A.; Berkade, P. E.; Wemmers, A.; Wepster, B. M.; Palm, J. H.; Schafer, L.; Dekker, H.; Mosselman, C.; Somson, G. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1363–1371.

(19) Levin, I. W.; Harris, W. C. *Spectrochim. Acta, Part A* **1973**, *29A*, 1815–1834. Note the 1465-cm^{-1} bend in norbornane; it is assigned to the 1-bridge scissors. Our argument suggests this band may be due to a 2-bridge scissors.

mechanisms, which are perturbations by neighboring atoms or molecules in the matrix and liquid, and by Coriolis interactions in the vapor. In any case, the motions which correspond to these unallowed chair bands correspond to allowed bands in the twist or boat form and thus become relatively stronger in the twist–boat spectrum. The twist band at 1152 cm^{-1} correlates well with the calculations, while the 1405-cm^{-1} band, if it is indeed a fundamental, is considerably higher than that calculated. The next set of chair bands, at 1046 and 1020 cm^{-1} in the matrix, are seen with considerable intensity in vapor-phase cyclohexane spectra, and one or the other is assigned by most authors to the allowed A_{2u} fundamental. Our calculations fit the corresponding observed twist band at about 1000 cm^{-1} nicely. The assignment of new bands at about 909, 887, and 869 cm^{-1} seems straightforward (Table IV). The new band at about 800 cm^{-1} corresponds to the chair-form band seen in the Raman spectrum and usually assigned at 802 cm^{-1}, although calculated here as 812 cm^{-1}. However, this assignment corresponds to an infrared inactive A mode for the twist form (this motion would remain A for any twist form). This mode is allowed in the boat form or for a twist conformation which is distorted toward the boat. Such a distortion requires little energy and could be caused by the matrix. The new bands at about 770 and 760 cm^{-1} might well be the split mode (23) of the chair, but, if so, the calculation for the boat and twist is much too low. Finally, we list the last strong chair band that we see at 524 cm^{-1}. One might expect to find the corresponding twist band, but we did not.

The C_6D_{12} twist bands are similar to those of the C_6H_{12}. We have already mentioned the scissors band at 1075 cm^{-1}. The new band at 2138 cm^{-1} is a binary combination of two of the many scissors modes. The rest of the new bands with the exception of the new band at 1189 cm^{-1} have straightforward assignments. Again, there are a few strong chair vibrations for which we have not observed twist counterparts.

Conclusions

We have produced a new form of cyclohexane by heating cyclohexane vapor and trapping the resulting new species in a cold matrix. This new form gives reproducible infrared spectra as shown by our experiments and those of Squillacote et al.[3] The experiments of Squillacote et al.[3] also showed that the new species reverts to chair cyclohexane on warming the matrix. We have formed the deuterated version of the new species.

The twist conformation of cyclohexane is the stable high-energy form and is expected to be observed in this experiment. The twist form is not expected to be rigid, however, and so normal-coordinate calculations were performed on both the twist and the boat geometries. These calculations are consistent with the twist possibly distorted along the pseudorotation path by the matrix. We conclude that we have produced the twist form in both its hydrogen and perdeuterated versions. However, the normal-coordinate calculations are not accurate enough to provide a detailed structure for the new species or even to exclude some different (but unexpected!) conformation of cyclohexane.

Finally, we examine the possible causes of the discrepancies between the calculations and the observed spectra. These may be due to four different effects: (1) the distortion of the molecule by the matrix and the "matrix shift" of the bands (we have tried to take the distortion of the molecule into account by calculating two extreme geometries, the ideal twist and the ideal boat structures; no attempt has been made to consider the matrix shift); (2) inaccuracy in determining the geometry of the undistorted conformations (the detailed geometry of the twist and boat conformations are not known, but they certainly involve small changes in the ring angles[4] and hydrogen positions that we have not taken into account; such changes in detailed geometry can cause changes in the calculated frequency as has been shown for the chair form[11]); (3) the observation[20,21] that the axial and equatorial hydrogens in chair-form cyclohexane have different frequencies (these different frequencies are *not* accounted for by force fields of the type we have used and require that in a valence force field, torsion–torsion or similar interaction constants that link nonadjacent methylene groups be included; the lack of such terms introduces unknown problems when calculating the twist and boat frequencies[22]); (4) as mentioned above, the force constants, of necessity, transferred from molecules which have standard trans/gauche geometry (we have tried to interpolate these constants to the expected nonstandard geometry of the twist and boat but have little measure of the accuracy of this procedure). Much more work remains to be done to define force constants and structures to the accuracy that would be required to reproduce the frequencies of these nonstandard structures to the limits of the experiments.

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[20] Snyder, R. G., private communication.

[21] Henry, B. R.; Hung, I.-Fu.; MacPhail, R. A.; Strauss, H. L. *J. Am. Chem. Soc.* **1980**, *102*, 515–519 and further unpublished results.

[22] A force field that contains explicit H–H interaction and similar cross-ring repulsions might do better at predicting the trends on changing conformations. We did Consistent Force Field calculations by using the programs and force fields developed by Warshel.[23] However, this gave the wrong direction for the *changes* in the scissors modes in going from chair to twist as well as rather poor results for the chair frequencies themselves.

[23] Warshel, A. In "Modern Theoretical Chemistry"; Segal, G., Ed.; Plenum Press: New York, 1977; Chapter 5, pp 133–172.