

THE IR, RAMAN AND NMR SPECTRA AND CONFORMATIONS OF CYCLOHEXYL-ALLENE

A. GATIAL*, A. HORN, P. KLAEBØE, C. J. NIELSEN and B. PEDERSEN
Department of Chemistry, University of Oslo, 0315 Oslo 3 (Norway)

H. HOPF and C. MLYNEK.
Institute of Organic Chemistry, Technical University of Braunschweig,
D-3300 Braunschweig (FRG).

ABSTRACT

Three conformers of cyclohexylallene, designated I, II and III, were observed in the IR and Raman spectra. Metastable crystals formed by annealing an amorphous solid from 80 K to 140 K, and crystals formed under a pressure of 30 kbar at ambient temperature, contained conformer II. The stable crystals obtained after heating the metastable crystals to 195 K contained conformer I. The conformer III was observed as a minor component in a nitrogen matrix heated to 900 K before deposition.

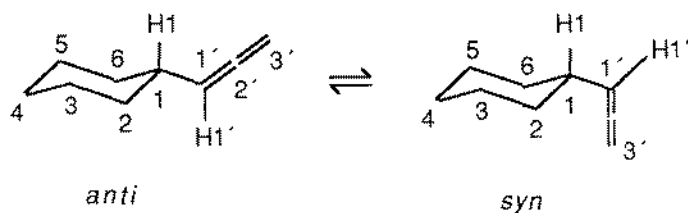
Negligible intensity variations between the bands of conformer I and II were observed with nozzle temperatures 300-900 K in the argon and nitrogen matrices, indicating a $\Delta H^0(I-II)$ below 0.4 kJ mol^{-1} while $\Delta H^0(III-II)$ was equal to 6.5 kJ mol^{-1} and a barrier higher than ca. 11 kJ mol^{-1} was observed between the latter. Variable temperature measurements in Raman indicate $\Delta H^0(I-II) \approx 0.9 \text{ kJ mol}^{-1}$ in the liquid.

The ^{13}C NMR spectra show that in deuteromethanol solution the equatorial conformer dominates ($\approx 2\%$ *a* at 193 K, $\Delta G^0(a-e) \approx 6.4 \text{ kJ mol}^{-1}$). Analysing the temperature dependence of the vicinal H-H coupling across the cyclohexane - allene carbon bond on the basis of a *gauche* \leftrightarrow *anti* equilibrium it is found 40% *anti* and 60% *gauche* in methanol solution at ambient temperature. We conclude that the abundant conformers II and I being respectively the *anti* and the *gauche* conformer, while III is the *anti* axial conformer.

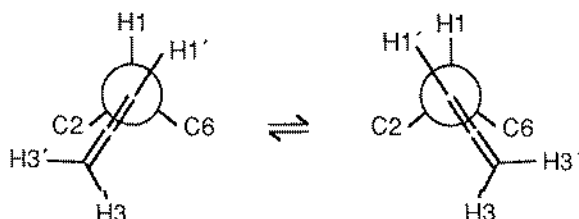
INTRODUCTION

To our knowledge, the conformations of cyclohexylallene (CHA) has not previously been studied by spectroscopic or other structural methods (for a recent review of the conformational equilibria of substituted cyclohexanes see ref. 1). There are *a priori* possibilities for equatorial and axial allene in addition to C_5 or C_1 molecular symmetry due to restricted rotation around the C-C bond joining the cyclohexyl and allyl groups, thus, giving rise to several possible conformations. The most likely equatorial conformers are:

* On leave from Department of Physical Chemistry, Slovak Technical University, 81237 Bratislava, Czechoslovakia.



Close to the *syn* conformation there are two *gauche* conformations:



In the related vinylcyclohexane the Gibbs free energies $\Delta G^0(a-e)$ (refs. 2,3) and the $\Delta G^0(\textit{gauche-anti})$ (ref. 4) have been determined in solution by NMR. These results show that the two equatorial conformers *anti* and *gauche* have nearly the same abundance at ambient temperature whereas the corresponding axial conformers have a Gibbs free energy ca. 6.2 kJ mol⁻¹ higher at 180 K (ref. 3). Our preliminary NMR data, to be discussed below, reveal similar conformer stabilities for CHA.

The low temperature IR and Raman spectra of CHA show that two crystalline solids have been obtained by different annealing technique, and each crystal contains a different conformer of CHA. Thus, this is one of the rare cases in which complete IR and Raman spectra of two different conformers have been recorded, rather than the common experience of one conformer isolated in the crystal and a mixture of conformers being present in the vapour and liquid states. In spite of the complexity of this molecule (23 atoms and four theoretical conformations) a complete analysis of the spectra has been attempted and will be published later.

EXPERIMENTAL

CHA was synthesized by reacting the cyclohexyl magnesiumbromide with methyl propargylether in the presence of CuBr according to a literature procedure (ref. 5), and purified by preparative gas chromatography. The IR spectra were recorded with Bruker FTIR spectrometers IFS-88 (4000-400 cm⁻¹) and IFS-114c (600-50 cm⁻¹) as well as on a Perkin-Elmer model 225 dispersive spectrometer. Matrix isolation spectra in the ratio 1:500 were obtained in argon and nitrogen matrices at ca. 14 K with a Displex model

CSW-202 (Air Products). The inlet system was equipped with an electrically heated nozzle of quartz, and the vapour-matrix gas mixtures were heated to 313, 450, 650 and 900 K before being quenched on the cold window. After recording the spectra, the matrices were annealed to 38 and 34 K in the argon and nitrogen matrices, respectively, and the IR spectra recorded again. A diamond anvil cell combined with a 4x beam condenser was employed for the high pressure IR spectra.

Raman spectra were recorded with a Dilor RTI 30 spectrometer, interfaced to the Aspect 2000 computer, and excited by a Spectra Physics model 2000 argon ion laser. The spectra were recorded at various temperatures of the sample in an ampoule, surrounded by a Dewar and cooled with gaseous nitrogen, and as a solid deposit on a copper finger cooled with liquid nitrogen.

^1H and ^{13}C NMR spectra were recorded of the sample dissolved in deuteromethanol held at various temperatures between ambient and 180 K with a Varian XL 300 spectrometer. TMS was used as an internal reference.

RESULTS

Low temperature IR and Raman spectra

Deposited on a cold window at 80 K the IR spectrum of the amorphous phase was quite similar to that of the liquid. After annealing to 160 K crystal 2 was formed and many bands of the amorphous phase vanished. When the sample was annealed to ca. 200 K, close to the melting point, another crystal 1 was formed with a spectrum quite different from the former (see the solid, dashed and dotted curves of Figs. 1 and 2). Obviously, two different conformers (II and I) were present in crystals 2 and 1.

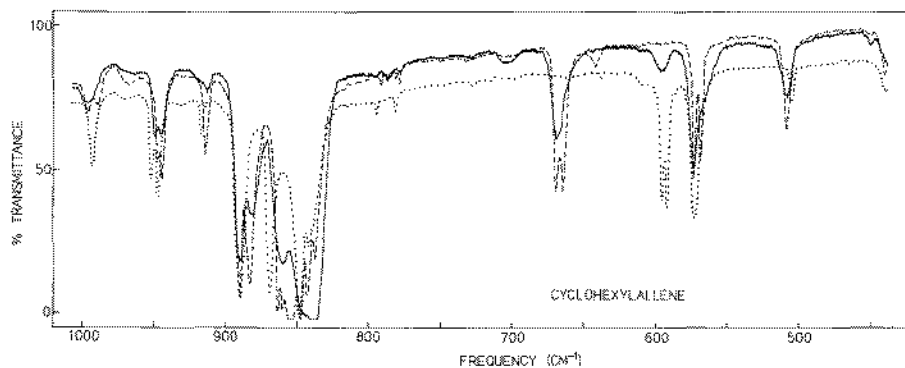


Fig. 1. IR spectra of cyclohexylallene (CHA) as an amorphous solid (solid line), as a crystal, annealed to 160 K (crystal 2, dashed line) and as a crystal, annealed to 200 K (crystal 1, dotted line), temperature 85 K.

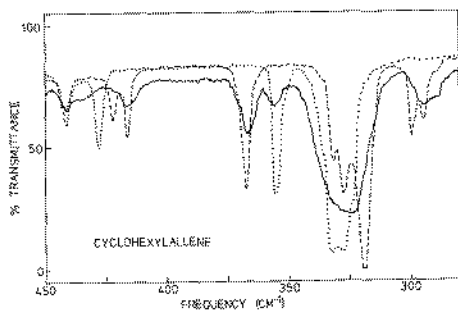
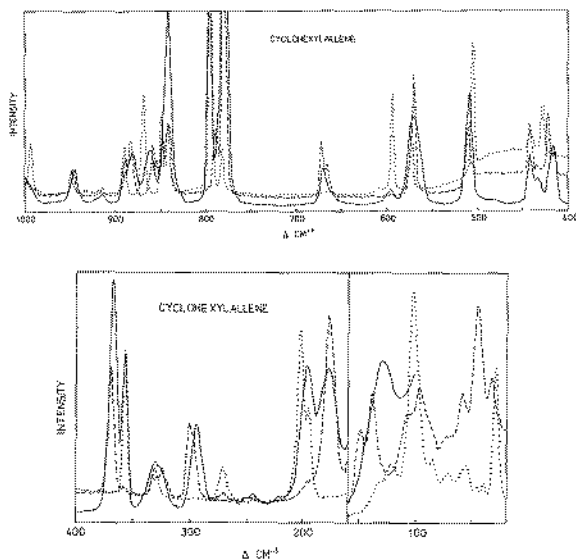


Fig. 2. IR spectra of CHA as an amorphous solid (solid line), as a crystal, annealed to 160 K (crystal 2, dashed line) and as a crystal, annealed to 200 K (crystal 1, dotted line), recording temperature 85 K.

After crystal 1 was formed, we were not able to obtain crystal 2 by cooling, suggesting that the latter phase is metastable. Corresponding results were obtained in a Raman cryostat cooled with liquid nitrogen. The crystals 1 and 2 were also formed in a Miller-Harney (ref. 6) cell, cooled by gaseous nitrogen (Figs. 3 and 4). Series of Raman spectra were recorded of CHA as a liquid in the temperature range from 296 to a slightly supercooled liquid at 190 K. The integrated band intensities were carefully measured, and the enthalpy differences between the conformers were determined with van't Hoff plots, giving $\Delta H^0(I-II) \approx 0.9 \text{ kJ mol}^{-1}$.



Figs. 3 and 4. Raman spectra of CHA as an amorphous solid at 131 K (solid line), as crystal 2 annealed to 163 K, recorded at 153 K (dashed line) and as crystal 1 annealed to 198 K, recorded at 169 K (dotted line).

High pressure IR spectra

When CHA was compressed in a diamond anvil cell, a polycrystalline solid was formed at approximately 30 kbar. The IR spectra revealed that this high pressure phase contained molecules of conformer II. It was not possible by increasing or reducing the pressure to form a crystal containing conformer I at ambient temperature.

Matrix isolation IR and Raman spectra

Among the large number of IR spectra of the matrix isolated species recorded, a CHA spectrum, matrix isolated in nitrogen is shown in Fig. 5. The spectrum was obtained with a nozzle temperature of 900 K. Bands belonging to both conformers I and II are observed in the spectrum. In addition, new IR bands situated at 1368, 1160, 1125, 830, 708 and 519 cm^{-1} were observed which were absent in the spectra recorded at room temperature. In addition, the matrix bands at 1316 and 1022 cm^{-1} were strongly enhanced with increasing nozzle temperature. All these bands are attributed to a high energy conformer III, practically absent at ambient temperature. Eventually, the bands of conformer III overlap those of conformers I or II as appeared to be the case for the 1316 and 1022 cm^{-1} bands.

When the matrices were annealed to 33 K (nitrogen) or 35 K (argon) various spectral changes occurred, as apparent from the solid (unannealed) and the dashed (annealed) curves. Thus, the bands attributed to conformer I from the crystal spectra were diminished, those of conformer II were enhanced in intensities after annealing. Obviously, the conformational equilibrium is shifted towards the thermodynamically slightly more stable conformer II, suggesting a barrier of approximately 7-8 kJ mol^{-1} . Furthermore, although the enthalpy difference between these conformers is very low (see below), conformer II obviously is the more stable both in the vapour and liquid states. The bands of conformer III, however, did not change significantly upon annealing, even when the sample was annealed for 16 h, indicating a barrier larger than 11-12 kJ mol^{-1} between conformer III and those of I and/ or II.

The enthalpy differences between the conformers were estimated from the matrix

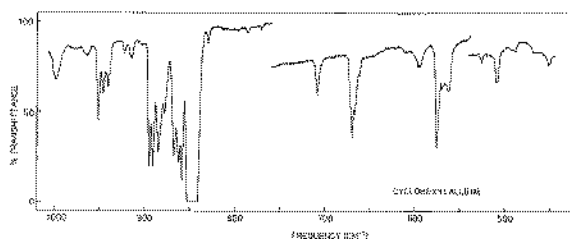


Fig. 5. IR spectrum of CHA in a nitrogen matrix at 14 K, nozzle temperature 900 K (1:500).

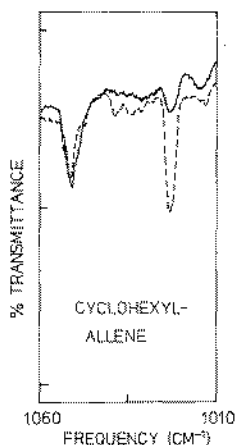


Fig. 6. IR spectra of CHA in nitrogen matrices at 14 K, nozzle temp.: 313 K (solid) and 900 K (dashed).

band intensities (before annealing) as a function of temperature. A negligible temperature variation between the intensities of conformer I and II bands were observed, and from three band pairs an enthalpy difference $\Delta H^0(I-II)$ below 0.4 kJ mol^{-1} was estimated. A quite different situation occurred when the intensities of the "pure" conformer III bands at 708 , 526 or 451 cm^{-1} were ratioed against the conformer II bands at 661 or 367 cm^{-1} . The rapidly increased intensity of the conformer III bands with temperature, suggested a large enthalpy difference and values for $\Delta H^0(III-II)$ equal to ca. 6.5 kJ/mol were obtained.

As an example, the matrix spectra in nitrogen, recorded at 313 K (solid line) and at 900 K (dashed line) are shown in the $1060-1010 \text{ cm}^{-1}$ range in Fig. 6. The bands at 1051 and 1030 cm^{-1} are due to conformers I and II, the band at 1015 cm^{-1} belongs to II while the band at 1024 cm^{-1} belongs to II and III. As is apparent, the latter band is strongly enhanced at higher temperatures because of the increased concentration of conformer III.

In Fig.7 an IR spectrum of CHA in the vapour phase is presented. Because of the large band widths in the vapour, the majority of the lines are caused by overlapping I and II conformer bands. Exceptions are those at 590 (I), 670 (II), 1009 (I), 1217 (I) and 1235 cm^{-1} (II). The relative intensities of the lines are in good agreement with the approximately equal abundance between conformers I and II.

¹³C NMR spectra

The room temperature ^1H decoupled ^{13}C NMR spectrum was assigned from DEPT-spectra and by comparing with the corresponding spectrum of vinylcyclohexane (ref. 3): δ 37.9 (C-1), 34.2 (C-2,6), 27.1 (C-3,5), 27.3 (C-4), 96.6 (C-1'), 208.9 (C-2')

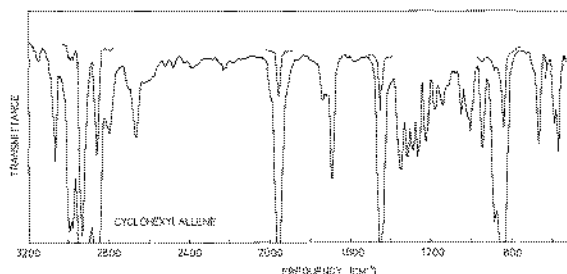


Fig. 7. IR spectrum of CHA as a vapour, path ca. 5 m , pressure ca. 2 torr , res. 1 cm^{-1} .

75.5 C-3'). As no sizeable reduction in chemical shift (4-7 ppm) of the γ -carbons compared to pure cyclohexane (δ 27.1) expected for an axial substituent is observed, the dominant conformer in solution is probably the *e*-conformer (as it has been found for vinylcyclohexane).

At 193 K peaks from both the *e* and the *a* conformer was found in the spectrum: *e*-CHA: δ 38.1 (C-1), 34.1 (C-2,6), 27.3 (C-3,5), 27.1 (C-4), 96.7 (C-1'), 208.3 (C-2') and 75.9 C-3'). For *a*-CHA only two small peaks were observed: δ 31.0 (C-2,6), 22.0 (C-3,5). The intensity ratio between corresponding peaks shows that about 2% of the *a*-conformer is present. That corresponds to $\Delta G^{\circ}(a-e) \approx 6.4$ kJ mol⁻¹. Buchanan (ref. 3) found $\Delta G^{\circ}(a-e) \approx 6.2$ kJ mol⁻¹ for vinylcyclohexane at 173 K.

¹H NMR spectra

The allene part and the multiplett from H1 could be analyzed as first order spectra. At ambient temperatures we found: δ 5.100 (d 6.0; t 6.7 Hz) H1'; 4.643 (d 3.2; d 6.7) H3', H3''; 1.959 (d 6.0; t 3.2; t 11.0 Hz) H1.

We have followed Buchanan (ref. 2) and analyzed the temperature dependence of the vicinal J(H1-H1') on the basis of a *gauche* \leftrightarrow *anti* equilibrium. Then

$$J(H1-H1')_{\text{obs}} = yJ_g + (1-y)J_t \text{ with } J_t = 11.0 \text{ Hz and } J_g = 2.5 \text{ Hz}$$

y is the amount of *gauche* conformer. In the preliminary data the uncertainty is high. We find $\Delta H^{\circ}(anti-gauche) \approx 0.2$ kJ mol⁻¹ and $\Delta S^{\circ}(anti-gauche) = -5.3$ J mol⁻¹K⁻¹. That corresponds at ambient temperature to 40% *anti* and 60% *gauche* conformer. As the statistical weight of the *gauche* conformer is two (as shown by the value of $\Delta S^{\circ}(anti-gauche)$ found), *anti* is the conformer with minimum energy.

DISCUSSION

The spectral data can be interpreted in terms of four conformers in CHA. It seems quite definite that the two abundant conformers I and II both are equatorial. They have an enthalpy difference of less than 0.4 kJ mol⁻¹ in the vapour and ca. 0.9 kJ mol⁻¹ in the pure liquid. The barrier of 7-8 kJ mol⁻¹ lie in the expected range for rotation around the C-CH(=C) equatorial bond. More uncertain is the assignment of conformers II and I to the *anti* (symmetry C_s) and *gauche* (C₁). For the sake of brevity, a very extensive experimental table, derived for the spectral data of CHA cannot be given here.

The Raman polarization data for the bands belonging to either conformer I or II (and not overlapping I and II which is the majority) reveal 3 polarized and 2 depolarized bands for I and 4 polarized and 7 depolarized for II. Since only the *anti* conformer should have depolarized Raman bands, the data suggest that the *anti* conformer should be the II and *gauche* should accordingly be conformer I. Also, the normal coordinate analysis gives a better agreement between the observed and calculated frequencies when I and II are attributed to *gauche* and *anti*, respectively. Finally, this interpretation is in

agreement with the results for vinylcyclohexane (ref. 4) and with the present NMR results (see above).

The conformer III for which approximately 7 separate bands and 3 bands coinciding with other fundamentals were observed (see above), is undoubtedly due to one or two of the axial conformers, *anti* (C_s) and *gauche* (C_1). The large enthalpy difference ΔH° of approx. 6.5 kJ mol^{-1} between conformers III and II and the higher barrier (conformer III did not vanish when annealed to 36 K) agrees with axial conformers and makes the situation very similar to that of vinylcyclohexane (refs. 2, 3).

Although conformer II had the lowest enthalpy in solution, our data suggest that crystal 2 containing this conformer was metastable, since we have so far not been able to form crystal 2 from 1 by temperature variations. At high pressure, however, a crystal containing conformer II (which does not need to be crystal 2) was the only one observed.

In a forthcoming paper the complete assignment of conformer I and II bands will be presented, based upon the experimental data and on the results of a force constant calculation in which an extensive force field derived for 1,4-dihalogcyclohexanes (ref. 7) was applied. This force field has later been applied to a number of other substituted cyclohexanes with satisfactory results. Furthermore, more complete ^1H NMR data obtained with higher resolution will be reported.

Acknowledgement

The authors are grateful to Aud M. Bouzga for careful recording of the NMR spectra and to G. Isaksen for purifying the compound by preparative GC. AG acknowledges a post doctorate fellowship from NTNF.

REFERENCES

1. P. Klæboe, A. Gatial and C. J. Nielsen, Recent Developments in Molecular Spectroscopy (Eds. B. Jordanov, N. Kirov and P. Simova), World Scientific Publ., Singapore (1989) p. 75.
2. E. L. Eliel and M. Manoharan, J. Org. Chem. 46 (1981) 1959.
3. G. W. Buchanan, Can. J. Chem. 60 (1982) 2908.
4. G. R. de Maré and S. Lapaille, Org. Magn. Resonance 13 (1980) 75.
5. L. Brandsma and H. D. Verkruijsse, Synthesis of Acetylenes, Allenes and Cumulenes, Elsevier, Amsterdam (1981), p. 158.
6. F. A. Miller and B. M. Harney, Appl. Spectrosc. 24 (1970) 291.
7. T. Woldbaek, C. J. Nielsen and P. Klæboe, J Mol. Struct. 66 (1980) 31.