

## THE IR AND RAMAN SPECTRA AND CONFORMATIONS OF CYCLOHEXYL AZIDE

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### ABSTRACT

Cyclohexyl azide was synthesized and the vibrational spectra recorded in several phases including: liquid at various temperatures, amorphous and crystalline at 90 K and high pressure crystal at ca. 60 kbar. Additional IR spectra were recorded in argon and nitrogen matrices with nozzle temperatures of 300, 500 and 700 K.

The conformations of cyclohexyl azide are characterized by the equatorial(e) and axial(a) azide group with e being more stable by  $1.8 \pm 0.3$  (vapour) and  $2.0 \pm 0.3$  kJ mol<sup>-1</sup> (liquid). Additional restricted rotation around the C-N bond gives rise to two azide orientations of C<sub>s</sub> and C<sub>1</sub> symmetry at least in the a conformation with a barrier of less than 8 kJ mol<sup>-1</sup>. The compound crystallized in the e (C<sub>s</sub>) conformer both at low temperature and at high pressure unlike the isoelectronic cyclohexyl isocyanate. The spectra are interpreted with the aid of force constant calculations.

### INTRODUCTION

We have for a long time been interested in the conformational equilibria of substituted cyclohexanes and recently the isocyanato (CYNCO) (ref. 1) and ethynyl cyclohexanes (ref. 2) were studied. In addition a series of organic azides were synthesized and studied by spectroscopy, electron diffraction (ref. 3) and by ab initio calculations (ref. 4) in our laboratory. With restricted rotation around the C-N bond, both CYAZ and CYNCO can have different end group conformers (C<sub>s</sub> and C<sub>1</sub>) both for the equatorial (e) and axial (a) cyclohexane substituents. Our provisional spectroscopic results for cyclohexyl azide (CYAZ) which is isoelectronic with CYNCO (ref.1) will be presented in this paper.

### EXPERIMENTAL

CYAZ was synthesized from the corresponding bromide and sodium azide in DMF in the presence of 12-Crown-4 as a phase transfer catalyst. The IR spectra were recorded on a Perkin-Elmer model 225

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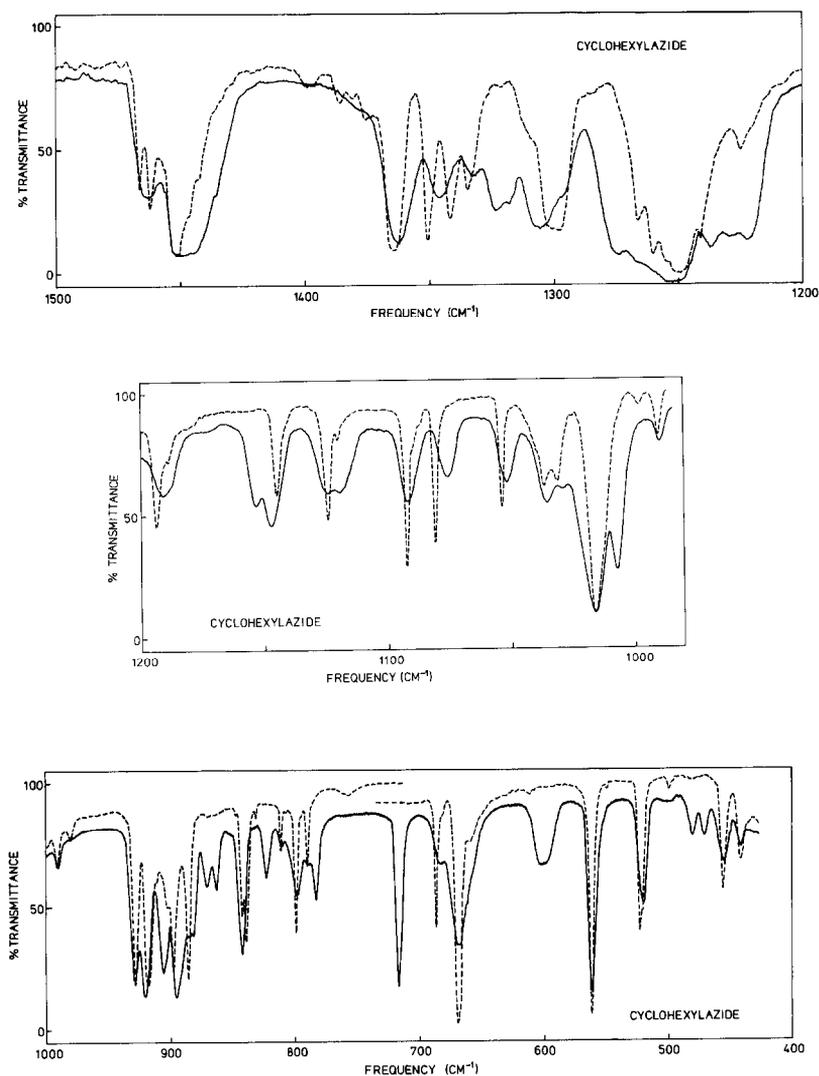


Fig. 1 a,b,c. IR curves of CYAZ at 90 K, full line amorphous, dotted line annealed, crystalline sample.

and on a Bruker 114C FTIR spectrometer, while the Raman spectra were obtained with a Dilor RT30 spectrometer excited by a Spectra Physics model 2000 argon ion laser. Matrix isolated IR spectra in argon and nitrogen matrices were obtained with an Air Products cryostat equipped with a heated nozzle of quartz. A diamond

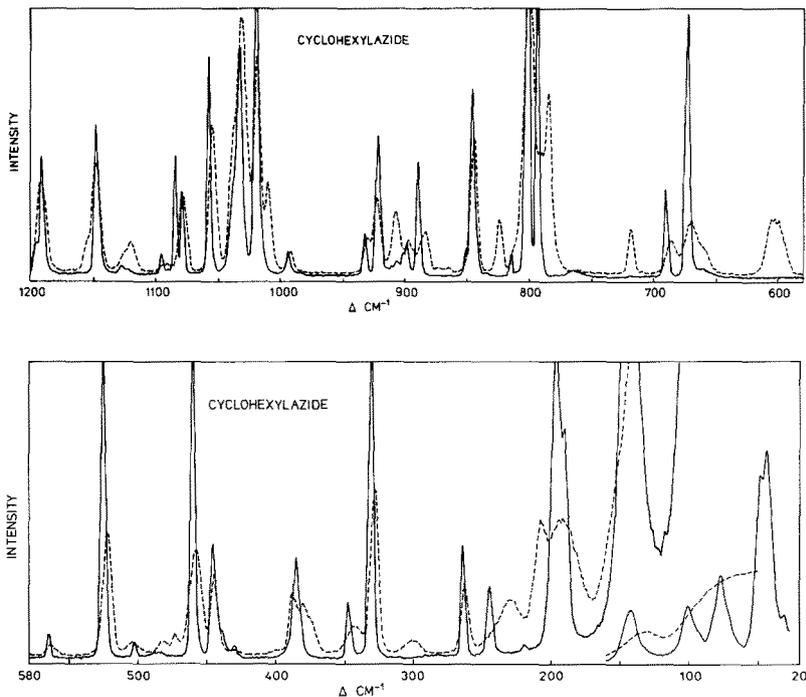


Fig. 2 a,b. Raman curves of CYAZ at 90 K, dotted line amorphous, full line annealed, crystalline sample.

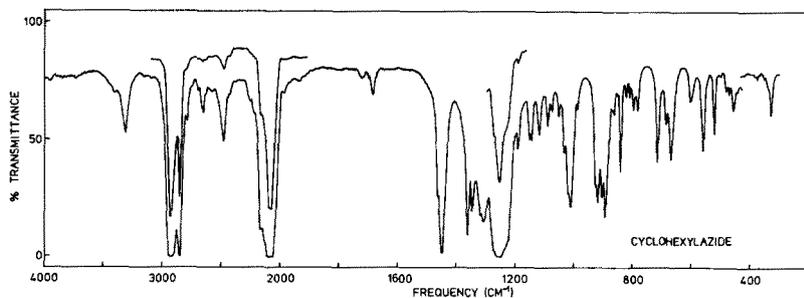


Fig. 3. IR spectrum of liquid CYAZ.

anvil cell combined with a 4x beam condenser was employed for the high pressure spectra.

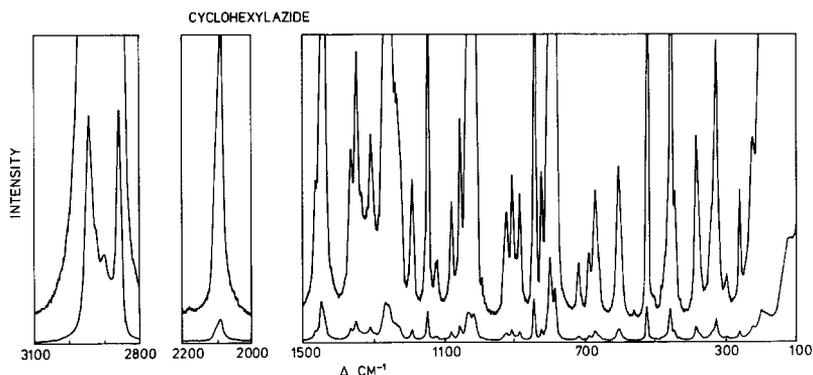


Fig. 4. Raman Spectrum of liquid CYAZ.

## RESULTS

### Low temperature spectra

The IR spectra of CYAZ as amorphous and annealed crystalline solids at 90 K are given in Figs. 1 a,b,c while the corresponding Raman curves are given in Figs. 2 a,b. The liquid IR and Raman spectra are shown in Figs. 3 and 4, respectively. It is clearly seen that the following number of IR and Raman bands present in the amorphous solid (and in the liquid) vanish in the crystal spectra (Raman values): 1324 vw, 1318 vw, 1224 vw, 1150 w, 1119 vw, 1002 w, 906 w, 887 m, 863 vw, 822 w, 783 m, 715 w, 659 w,sh, 603 m, 599 m, 481 vw, 470 vw, 383 w, 295 w and 200 w  $\text{cm}^{-1}$ . These bands are assigned to one or more conformers present in the amorphous solid and disappearing in the crystal (Figs. 1 and 2). From  $^{13}\text{C}$  NMR data  $\Delta G^{\circ} = G^{\circ}(\text{a}) - G^{\circ}(\text{e})$  was determined as 2.602  $\text{kJ mol}^{-1}$  at 180 K in  $\text{CFCl}_3$  solution (ref. 5) for CYAZ compared with 2.117  $\text{kJ mol}^{-1}$  for CYNCO at 193 K (ref. 6). Thus, the e conformer was the more stable and CYAZ undoubtedly crystallizes equatorial like all other monosubstituted cyclohexanes studied except cyano and isocyano cyclohexane (ref. 7). In particular, there is a striking similarity between the crystal spectra of CYAZ and CYNCO (ref. 1) revealing both molecules to crystallize in the e conformer.

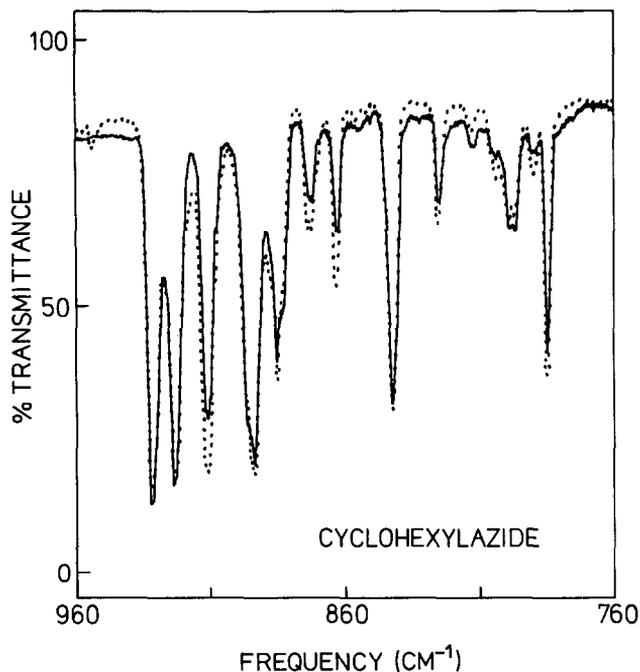


Fig. 5. CYAZ in  $N_2$  matrix deposited at 14 K, nozzle temperatures 300 K, solid line; 700 K, dotted line.

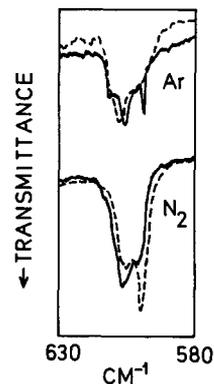


Fig. 6. CYAZ in matrices, nozzle temp. 300 K, before annealing, solid line; after annealing, dashed line

### High pressure spectra

When compressed in the diamond anvil cell, CYAZ crystallized at a rather high pressure (ca. 60 kbar). The high pressure IR spectrum is not included for the sake of brevity, but is quite similar to those of the low temperature crystal (Fig. 1). Unlike CYNCO which crystallized in the a-conformer under pressure (ref. 1) CYAZ maintained the e conformer also in the high pressure crystal.

### Enthalpy difference between the conformers

The enthalpy difference  $\Delta H^{\circ} = H^{\circ}(a) - H^{\circ}(e)$  was determined in two ways:

- (1) CYAZ was mixed with argon and nitrogen in the ratio 1:500 and deposited on the CsI window (14 K) through a heated quartz nozzle at 300, 500 and 700 K (Fig. 4). Assuming that the conformer ratio of the vapour was trapped in the matrix, the relative peak heights were employed to determine  $\Delta H^\circ$ . From the band pairs 440 e, 470 a; 445 e, 478 a; 824 a, 842 e; 863 a, 884 e; 870 a, 896 e, a vapour value of  $\Delta H^\circ = 1.8 \pm 0.3 \text{ kJ mol}^{-1}$  was obtained. The a bands were considered "pure" since they vanished completely in the crystal spectra, the e bands were assumed to be "pure" on the basis of force constant calculations.
- (2) Raman spectra of liquid CYAZ were recorded at various temperatures between 295 and 210 K when the sample was cooled by gaseous nitrogen inside a Dewar (ref. 8). The band pairs 522 e, 603 a; 822 a, 843 e; 906 a, 920 e were employed in the calculations and a value of  $\Delta H^\circ = 2.0 \pm 0.3 \text{ kJ mol}^{-1}$  was obtained for the liquid. Thus, the enthalpy differences between the e and a conformers of CYAZ in the vapour and the liquid were the same within the experimental uncertainty.

#### Matrix effects

When the samples of CYAZ deposited in argon and nitrogen matrices at ca. 14 K were annealed to ca. 34 K some puzzling features were observed. As illustrated in Fig. 5 the peaks at 605 and 599  $\text{cm}^{-1}$  both interpreted as axial bands diminished and increased in intensities, respectively, after annealing in argon and visa versa in nitrogen. A number of other axial bands appeared as doublets in the matrices and changed oppositely in argon and nitrogen after annealing. The normal coordinate calculations on CYAZ and experience from other cyclohexanes reveal that the e and a conformer bands are frequently separated by considerable shifts making them appear as distinct bands in the liquid spectra. The conformers due to restricted rotation around the C-N bonds, however, fall within a few wave numbers and can at best be detected in the matrix spectra.

Thus, the matrix effects are tentatively explained as the presence of two staggered azide conformers of symmetry  $C_s$  and  $C_1$ . Small enthalpy differences  $\Delta H^\circ$  (less than  $0.6 \text{ kJ mol}^{-1}$ ) and conformational barriers of 9 and  $6 \text{ kJ mol}^{-1}$  in nitrogen and argon matrices, respectively, were determined for ethyl azide (ref. 9).

As a secondary azide the C-N rotational barriers of CYAZ are probably not quite like those of ethyl azide. However, we believe that the axial conformers of  $C_s$  and  $C_1$  symmetry might be stabilized to a different extent in nitrogen and in argon matrices, as recently observed for a halogenated cyclobutane (ref. 10). Alternatively, the dihedral angle of the axial  $C_1$  conformer might relax differently in the two matrices, giving rise to slightly different bands after annealing.

It was observed that the axial bands at 1232, 1225, 1022, 1008 and  $782\text{ cm}^{-1}$  (but not the remaining axial bands) were more intense in the nitrogen than in the argon matrices both before and after annealing. The same was true for the equatorial bands at 923 and  $884\text{ cm}^{-1}$ . Since these observations cannot reflect differences in the  $e/a$  conformational ratios, they must be caused by specific infrared band enhancements of certain modes in the matrices.

Only small annealing effects were observed for the  $e$  bands of CYAZ in the argon and nitrogen matrices. A negligible enthalpy difference between the  $C_s$  and  $C_1$  azide orientations in the abundant  $e$  conformer is suggested.

#### Normal coordinate calculations

A force field for CYAZ was derived by transferring force constants from a series of substituted cyclohexanes (refs. 1,2) and azides (refs. 3,9) partly based upon scaled ab initio force constants (ref. 4). The fundamentals were calculated for all the four possible conformers  $\underline{e}$  ( $C_1$ ,  $C_s$ ) and  $\underline{a}$  ( $C_1$ ,  $C_s$ ), and a good agreement between the observed  $\underline{e}$  and  $\underline{a}$  modes was obtained. The azide orientation has a minor effect on the calculated frequencies, resulting in closely situated  $C_1$  and  $C_s$  bands both within the  $\underline{e}$  and  $\underline{a}$  conformers. Exceptions are the N = N stretch around  $1290\text{ cm}^{-1}$  and the N = N  $\equiv$  N in plane bend which are both quite conformational sensitive (ref. 3,5,9).

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