The infrared and Raman spectra, conformations and *ab initio* calculations of 4-Azidobut-1-yne.

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The IR spectra of 4-azidobut-1-yne were recorded in the vapour and liquid states and as amorphous and crystalline solids at liquid nitrogen temperature. The Raman spectra of the liquid in the temperature range 232-295 K and as a crystal at 148 K were obtained. Additionally, IR spectra in argon and nitrogen matrices were recorded, applying the hot nozzle technique.

The compound can exist in five conformers labelled *GG*, *GG'*, *GA*, *AG* and *AA*, referring to the conformations around the C-C and the C-N bonds, respectively. Fully optimized *ab initio* geometries for all five conformers have been calculated at the SCF level. The conformers can be divided into the low energy conformers *GG*, *AA* and *AG* (0, 0.1, 0.3 kJ mol^{-1}) and the high energy conformers *GA* and *GG'* (both 2.4 kJ mol^{-1}).

Some of the strongest bands missing in the crystal increased their intensities in the matrix spectra upon annealing, suggesting that the most stable conformer is not present in the crystal. The scaled *ab initio* frequencies indicated that the conformer present in the crystal phase is *AG*. In the liquid and matrices the most stable conformer is *GG* followed by *AG* and *AA*. All the five conformers were observed in the liquid at room temperature and trapped in the argon matrix.

1. INTRODUCTION

Due to restricted rotation around the C-C bond (*gauche* or *anti*) and the C-N bond (*gauche* or *anti*) 4-azidobut-1-yne (HC≡C-CH$_2$-CH$_2$-N$_3$ later to be called BUTAZ can exist in five distinct conformations as shown in Fig. 1. These conformers are labelled *GG*, *GG'*, *GA*, *AG* and *AA* where the first and second letters mark the conformations around the C-C and the C-N bonds, respectively [1,2].

Several organic azides with a -CH$_2$N$_3$ moiety as for example azidoacetonitrile (N≡C-CH$_2$N$_3$) [3], 3-azidopropyne (propargylazide HC≡C-CH$_2$N$_3$) [4], azido-2-butyne (CH$_3$C≡C-CH$_2$N$_3$) [5], azidoethane (CH$_3$-CH$_2$N$_3$) [6] and 3-azidopropene (CH$_2$CH=CH$_2$N$_3$) [1,2] have been studied experimentally by electron diffraction, by vibrational spectroscopy and by *ab initio* methods employing a DZ basis set.

The experimental results of the first three acetylenic azides [3-5] reveal that the compounds exist in one conformation only having *gauche* orientation around the C-N bond with dihedral angles of 52°, 37° and 37° from the *syn* orientation. From the orientation of the azido group towards the π-electron system of the multiple acetylenic bond, a stabilization has been confirm-

ed. The same is true for 3-azidopropene [1,2] in which two conformers (*GG*, *SG*), having similar orientation of the azido group towards the vinyl are the most stable among the five possible conformers. In BUTAZ the distance to the multiple bond is longer and a smaller stabilization effect can be expected.
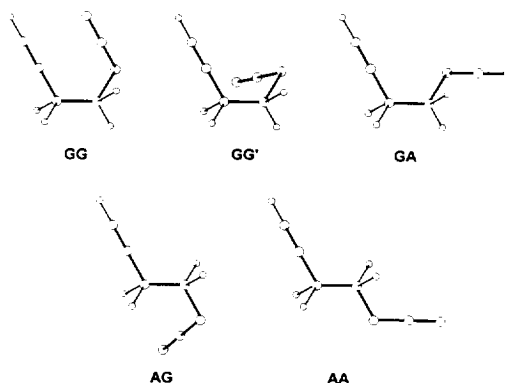

Fig. 1. The five conformations of 4-azidobut-1-yne (BUTAZ).

2. EXPERIMENTAL

The sample was synthesized as described previously [7]. The IR and Raman spectrometers, the cryostats and the methods employed have been described in earlier work [2-5].

3. RESULTS AND DISCUSSION

We reproduce in Fig. 2 as examples from a number of recorded spectra the IR spectra in Ar (top) and N_2 matrix (bottom) at the nozzle temperature 313 K together with the spectra after annealing. A comparison between the Raman spectra of the liquid at 295 K and the crystal at 148 K is shown in Fig. 3.

3.1. Liquid and amorphous solid spectra

We expect 23 vibrational modes below 1500 cm^{-1} for BUTAZ. From a simple counting of the IR and Raman bands of the liquid and amorphous solid, additional bands can be seen, meaning that the sample probably exists in at least two conformers. From measurements of the Raman spectra at different temperatures, very small relative intensity changes were obtained, suggesting small energy differences between the main BUTAZ conformers.

3.2. Crystal spectra

In contrast to 3-azidopropene [1,2] BUTAZ crystallized readily. Comparison with the amorphous IR and the liquid Raman spectra revealed that several of the strongest bands vanished (Fig. 3). From these results it can be established that BUTAZ like 3-azidopropene does not crystallize in the most stable conformer (marked as I) but in a conformer II.

3.3. Matrix spectra

The less stable conformers can also be distinguished by matrix isolation IR spectroscopy, using the hot nozzle technique. However, the matrix spectra recorded with the nozzle

temperatures 313 and 600 K are very similar both in the N_2 and Ar matrices. Some weak bands at 313 K are even weaker at 600 K, suggesting that the barriers are low (around 5-6 kJ mol^{-1}) and that an interconversion has occurred. The spectra of the N_2 matrix contain fewer bands than the Ar matrix and some weak bands are missing (Fig. 2) indicating a smaller barrier in N_2 than in Ar. The BUTAZ conformers can be divided into two groups according to the position around the C-C bond: *gauche* conformers (*GG, GG', GA*) and *anti* conformers (*AG, AA*). Interconversion between the conformers is more rapid for rotation around the C-N bond than the C-C bond (with higher barriers) After applying 'mild' and 'strong' annealing of the Ar and N_2 matrices four groups of bands could be distinguished:

(1) bands which increase in relative intensity on both annealing processes [the most stable conformer in the matrices (conformer I)]

(2) bands which after mild annealing do not change or increase their relative intensities very slightly. After strong annealing they decrease their relative intensities and are identical with the bands present in the crystal [second most stable (conformer II)]

(3) bands which after mild annealing decrease their intensities and after strong annealing practicaly disappear [the third most stable (conformer III)]

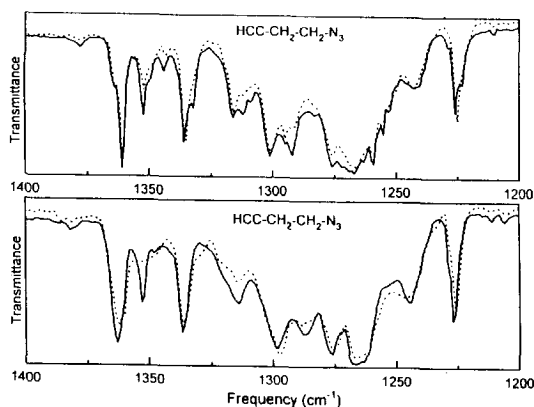(4) bands which practically disappear after mild annealing [the least stable (conformers IV and V)].

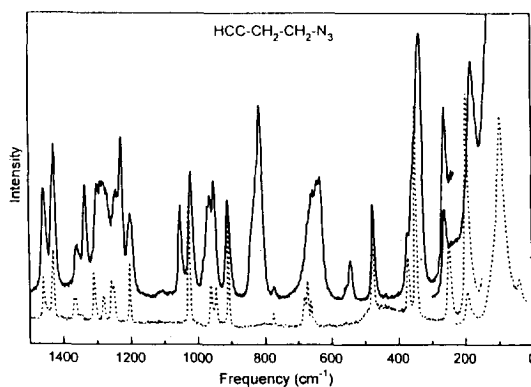Fig. 2. IR spectra of BUTAZ in Ar (top) and.N_2 matrices at 13 K before and after annealing (dotted line).

Fig. 3. Raman spectra of BUTAZ as a liquid at 295 K (solid line) and a crystal at 148 K (dotted line).

3.4. *Ab initio* calculations and normal coordinate analysis

Since we have no information about the structure of BUTAZ from direct methods, an *ab initio* study was carried out. Fully optimized geometries of all five conformers of BUTAZ were calculated on the Hartree-Fock SCF level using the HONDO-like *ab initio* program and standard Huzinaga TZP basis set [8,9]. To improve the accuracy of the *ab initio* energies, electron correlation (MP2) were calculated without reoptimizing the geometry. The SCF optimized geometries were checked on non-negative vibrational modes by vibrational analysis, and zero point vibrational energies VIB0 were calculated. The following *ab initio* energies for all five BUTAZ conformers together with MP2 corrections and zero point vibrational energies (VIB0) relative to *AA* were obtained: *GG* (0.68); *GG'* (2.95); *GA* (2.56); *AG* (0.80) and *AA* (0.00 kJ mol^{-1}).

The BUTAZ conformers can be divided into two groups according to the energies: low (*GG, AG, AA*) and high energy conformers (*GG', GA*). The calculated energies do not allow us to decide which conformer is the most stable because the differences 0.3 kJ mol^{-1} (0.8 kJ mol^{-1} after including the zero point vibrational energy) is within the uncertainties.

The scaled *ab initio* force field represents a good approximation and the calculated frequencies are a good diagnostic tool for conformational analysis. Optimization of the *ab initio* calculated frequencies of all the five BUTAZ conformers were carried out with six scaling factors, transferred from 3-azidopropene. A very good agreement with the observed and calculated wavenumbers for *AG* was obtained, revealing this conformer to be present in the crystal phase (conformer II). The *GG* conformer frequencies were correlated with those of group I and the *AA* conformer frequencies with those of group III.

4. CONCLUSIONS

From the vibrational spectra and the normal coordinate results it can be concluded that in BUTAZ the most stable conformer is *GG, AG* is the second most stable and is present in the crystal phase while the third most stable conformer is *AA*. These three conformers differ slightly in their energies since very small temperature variations of the Raman liquid spectra were observed. Unfortunately, we were not able to estimate the experimental energy differencies neither from the Raman liquid spectra due to high overlaping of the bands from different conformers nor from the matrix spectra where partial interconversion of the conformers occured. The bands from the group IV can be assigned to the least stable *GG'* and *GA* conformers.

Compared with the conformationally similar 3-azidopropene, it is seen that shifting the π-electron system of the multiple bond one atom further away from the azido group decreases the stabilization effect. Thus, the energy difference between the low and the high energy conformers in BUTAZ is approximately half of that in 3-azidopropene [1,2]. Conformers with orientation of the azido group around the C-N bond having this group far from the multiple bond belong to the least stable in 3-azidopropene (*GA, SA*) but for BUTAZ one of them belongs to the most stable conformers (*AA*).

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