

Vibrational study of 5-azacytosine and propanedinitrile under high pressure



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ABSTRACT

The effect of high pressure on the vibrational modes of 5-azacytosine ($C_3H_4N_4O$) and propanedinitrile ($CH_2(CN)_2$) was investigated at room temperature using a diamond anvil cell (DAC). In situ infrared and Raman spectroscopy results indicated that the ring structure of 5-azacytosine remained preserved and the band shifts induced by high pressure were fully reversible up to 13 GPa. For the open-chain structure of propanedinitrile, a polymerization reaction was observed by infrared spectroscopy almost instantly at about 15 GPa at room temperature. The same pressure-induced polymerization was observed after a week at 1 GPa, at room temperature.

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1. Introduction

Back in 1989, Liu and Cohen stepped forward the suggestion that a hypothetical β - C_3N_4 phase could exhibit a bulk modulus of the same order or slightly higher than diamond [1]. However, synthesis of β - C_3N_4 bulk samples has eluded researchers ever since. In this work, two molecular compounds containing carbon and nitrogen, one with ring structure (5-azacytosine) and the other with open-chain structure (propanedinitrile) were investigated under high pressure looking for new routes for synthesis of covalently bonded, carbonitride high hardness materials.

5-Azacytosine (6-amino-1H-1,3,5-triazin-2-one, $C_3H_4N_4O$) is a heterocyclic compound containing nitrogen and carbon atoms, similar to cytosine (one of the four DNA's bases), where the pyrimidine ring is replaced by the 1,3,5-triazin ring (Fig. 1). Podolyan and Rubin [2] performed an ab initio post-Hartree-Fock study of the infrared vibrational spectrum for two of the most stable tautomers of cytosine and 5-azacytosine. The small energy difference between the two tautomers suggests that molecular 5-azacytosine could exhibit keto-enol tautomerism [2]. On the other hand, theoretical and experimental studies using the ultraviolet absorption spectrum of 5-azacytosine indicated that it would be in the enol form in solid state [3]. Experimental data related to the Raman spectrum of 5-azacytosine was not found in the literature.

The molecular crystal propanedinitrile ($CH_2(CN)_2$) (Fig. 1d) presents four crystalline phases observed from 140 to 295 K, showing unusual re-entrant phase transitions (a sequence of two-phase transitions for which the first and third phases have the same symmetry and they are, effectively, identical) [4–10]. Furthermore, propanedinitrile is an important reagent for industrial uses, e.g., in the syntheses of pharmaceuticals, herbicides, fungicides, defoliants, dyes and polymers, because it is a weak cyanocarbon acid with an exceptional reactivity [11–12]. Previous studies of propanedinitrile at high pressures indicated polymerization induced by pressure and shear deformation [13–14].

In this work we present a comparative theoretical and experimental study about the ring structure of 5-azacytosine and the open-chain structure of propanedinitrile under high pressure, up to 15 GPa using a diamond anvil cell. A complementary Raman study of 5-azacytosine under pressure was also performed.

2. Materials and methods

The samples used in this work were 5-azacytosine (98%, Acros Organics, New Jersey, USA) and propanedinitrile (99%, Sigma-Aldrich). Samples were loaded into a Piermarini-Block diamond anvil cell (DAC) with 400 μ m culet diamond anvils (low fluorescence IIa type) and a gasket made of Waspalloy with a 250 μ m hole for infrared (IR) and Raman measurements without pressure transmitting medium (except for the IR experiments with 5-azacytosine, in which case the sample was dispersed in KBr). The pressure was measured by the ruby fluorescence method [15].

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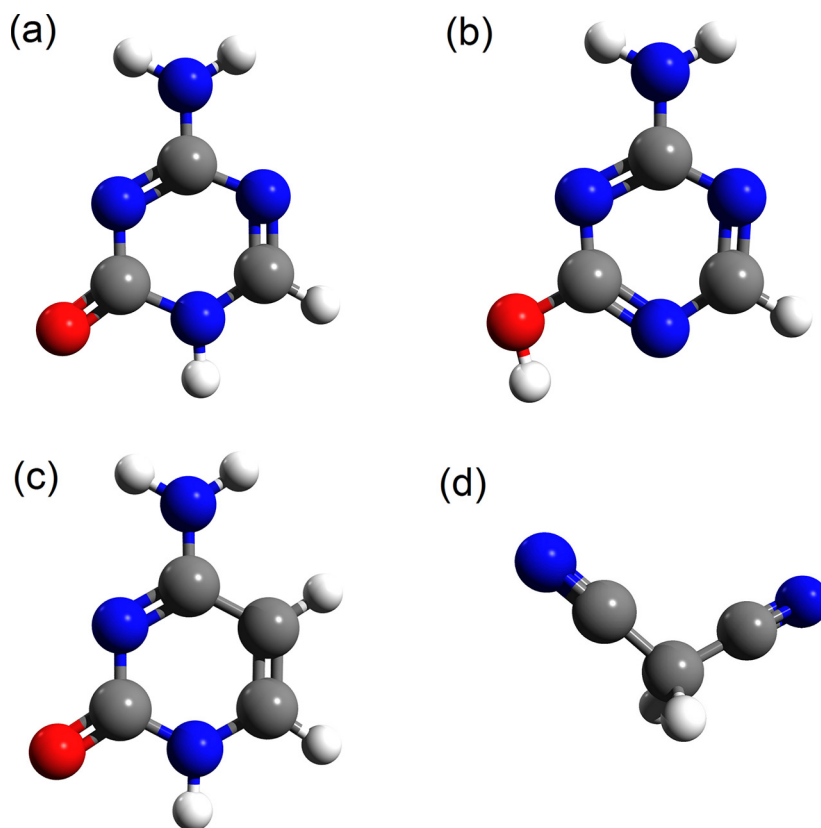


Fig. 1. (a) and (b) chemical structures of the most stable tautomers of 5-azacytosine [2], keto and enol forms, respectively, (c) cytosine, and (d) propanedinitrile. In these structures the color code is: dark gray = carbon; light gray = hydrogen; red = oxygen and blue = nitrogen atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Raman spectra at high pressures were obtained using a He–Ne laser with a nominal power of 10 mW using a Horiba Jobin-Yvon iH320 spectrometer with a CCD cooled by liquid nitrogen. Raman spectra at room conditions were obtained with a Horiba LabRAM HR Evolution spectrometer, using a He–Ne laser. Fourier transform infrared (FTIR) spectra (4 cm^{-1} resolution, 512 scans) were collected in transmittance mode using a Perkin-Elmer Spectrum 400 MIR/FIR and a Bomem MB 100 spectrometers. All measurements were performed in situ at room temperature with the sample inside the DAC for different values of pressure (up to 13 GPa for Raman measurements, and 9 GPa and 15 GPa for IR measurements of 5-azacytosine and propanedinitrile, respectively.).

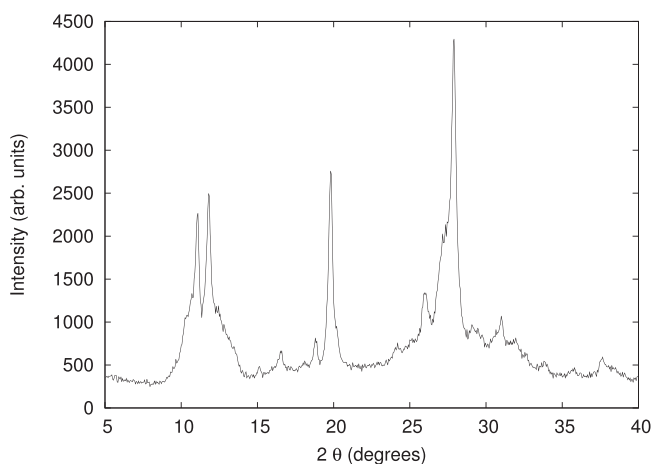


Fig. 2. X-ray powder diffraction pattern of commercial 5-azacytosine.

The X-ray diffraction pattern (XRD) of 5-azacytosine at ambient conditions was obtained in a Siemens D500 diffractometer, with Cu $K\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$), operating in Bragg–Brentano geometry and equipped with Soller slits, 1° divergence slit and 1° scattering slit in the primary beam, 0.15 mm receiving slit and a graphite monochromator in the secondary beam, with 0.05° per step, from 5° to $40^\circ 2\theta$, and an acquisition time of 1 s per step.

The band assignments were based on calculations for isolated molecules of 5-azacytosine and propanedinitrile performed at the MP2 level of theory with augmented-cc-pVDZ basis sets, using

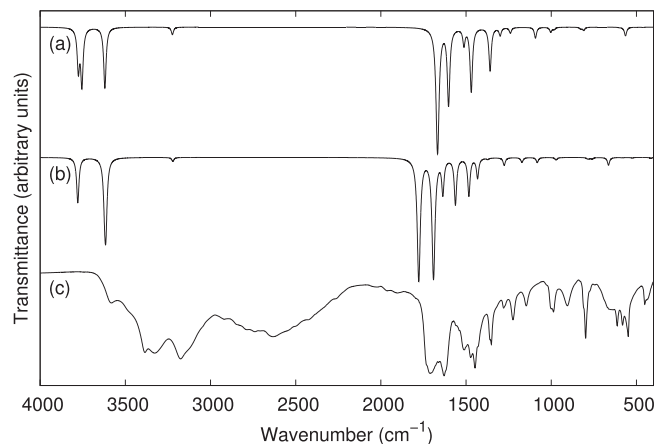


Fig. 3. Infrared spectrum for 5-azacytosine: (a) theoretical calculation for enol tautomer (unscaled); (b) theoretical calculation for keto tautomer (unscaled); (c) experimental results. Theoretical results considered a Lorentzian profile with FWHM of 15 cm^{-1} .

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