



## New insights into the structure and chemistry of Titan's tholins via $^{13}\text{C}$ and $^{15}\text{N}$ solid state nuclear magnetic resonance spectroscopy

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### ABSTRACT

Tholins are complex C,N-containing organic compounds produced in the laboratory. They are considered to provide materials that are analogous to those responsible for the haze observed in Titan's atmosphere. These compounds present an astrobiological interest due to their ability to release amino acids upon hydrolysis. Their chemical structure has been investigated using a large number of techniques. However, to date no detailed nuclear magnetic resonance (NMR) study has been performed on these materials despite the high potential of this technique for investigating the environment of given nuclei. Here  $^{13}\text{C}$  and  $^{15}\text{N}$  solid state NMR spectroscopy was applied to obtain new insights into the chemical structure of tholins produced through plasma discharge in gaseous  $\text{N}_2\text{—CH}_4$  mixtures designed to simulate the atmosphere of Titan. Due to the low natural abundance of these isotopes, a  $^{13}\text{C}$  and  $^{15}\text{N}$ -enriched tholin sample was synthesized using isotopically enriched gas precursors. Various pulse sequences including  $^{13}\text{C}$  and  $^{15}\text{N}$  single pulse,  $^1\text{H—}^{13}\text{C}$  and  $^1\text{H—}^{15}\text{N}$  cross-polarisation and  $^1\text{H—}^{15}\text{N—}^{13}\text{C}$  double cross-polarisation were used. These techniques allowed complete characterisation of the chemical and structural environments of the carbon and nitrogen atoms. The NMR assignments were supplemented and confirmed by *ab initio* electronic structure calculations for model structures and molecular fragments.

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### 1. Introduction

Titan, the largest moon of Saturn, is characterized by a dense atmosphere, mainly composed of  $\text{N}_2$  (ca. 97%) and  $\text{CH}_4$  (ca. 2%). In the upper atmosphere, methane and nitrogen molecules undergo dissociation under the influence of solar UV radiation and electron impacts, followed by recombination reactions leading to a large variety of organic molecules (Waite et al., 2007). Some of these compounds form a thick, orange-coloured haze composed of solid organic aerosols that subsequently fall to the surface or remain in suspension in the atmosphere.

To gain insight into the chemical composition and structural nature of these complex organic compounds, analogous materials are produced in the laboratory, in particular using plasma dis-

charge in gaseous  $\text{N}_2\text{—CH}_4$  mixtures that are designed to simulate Titan's atmosphere (Coll et al., 1999; Imanaka et al., 2004; Szopa et al., 2006). These materials are commonly termed "Titan's tholins", derived from the Greek term for "muddy" (Sagan and Khare, 1979). Depending on the experimental conditions, their composition, structure and spectral properties can vary largely. Some tholins mimic the optical properties of Titan's aerosols in the visible range (Khare et al., 1984a). Furthermore, tholins present an interest for astrobiology as they were shown to release amino acids upon hydrolysis (Thompson and Sagan, 1989; Neish et al., 2009) and nucleobase after X-ray irradiation (Pilling et al., 2009).

Titan's tholins have been analysed using a wide variety of techniques ranging from bulk elemental analysis (McDonald et al., 1994; Coll et al., 1999; Sarker et al., 2003; Szopa et al., 2006; Quirico et al., 2008), pyrolysis (Khare et al., 1984b; Ehrenfreund et al., 1995; Coll et al., 1999; Hodyss, 2005; Szopa et al., 2006; McGuigan et al., 2006) and laser desorption mass spectrometry experiments (Somogyi et al., 2005; Ganesan et al., 2007; Imanaka and Smith,

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2010) to infrared absorption, visible, UV and near-IR Raman and luminescence spectroscopy (Sagan et al., 1993; McDonald et al., 1994; Khare et al., 2002; Imanaka et al., 2004; Bernard et al., 2006; Quirico et al., 2008; Ruiz-Bermejo et al., 2008, 2009; Carrasco et al., 2009), X-ray diffraction and high resolution transmission electron microscopy (Quirico et al., 2008). The fraction of the tholins that was soluble in normal or deuterated solvents, or in the presence of crown ethers in certain cases, has been studied using electrospray ionization mass spectrometry (Sarker et al., 2003; Somogyi et al., 2005; Hodyss, 2005; Carrasco et al., 2009; Pernot et al., 2010) and gas chromatography coupled to mass spectrometry (Hodyss, 2005).

All these studies have provided a wealth of information about potential functional groups and structural building blocks present within the tholin samples. Taken together, the results converge on a structure based on a  $C_xH_yN_z$  chemistry, that can contain various oligomeric and polymeric chain or ring units, and containing a variety of C–C, C–N, N–H, etc. single or multiple bonds. It is now necessary to build on that information to refine the chemical and structural models for the Titan model tholins. Here we investigate these complex materials using solid state nuclear magnetic resonance (NMR) techniques.

NMR is a powerful tool for structure determination of complex organic molecules and solid state species, providing detailed element-specific information about local structure and chemical environments. In the present study, we used solid state NMR techniques to investigate the carbon and nitrogen bonding environments in a  $^{13}\text{C}$ - and  $^{15}\text{N}$ -enriched sample recovered from the plasma discharge synthesis experiment. Solid state NMR was preferred to solution state due to the low solubility of the studied sample (Carrasco et al., 2009). A preliminary solid state  $^{13}\text{C}$  NMR study of Titan tholins was performed by Sagan et al. (1993) but no spectrum was published and it only reported that 25% of the carbon atoms were unsaturated. We used techniques of isotopic enrichment and cross-polarisation (CP) to enhance the signal intensity combined with magic angle spinning (MAS) to reduce the broadening of the NMR peaks. We also compare the results with selected data from a parallel study of graphitic carbon nitride materials that are being developed for photocatalysis and other optoelectronic applications (Bojdys et al., 2008; Wang et al., 2009; McMillan et al., 2009).

Quantitative NMR data related to structure can be obtained by measuring relative peak intensities obtained through direct polarisation using a single pulse (SP) sequence. However, due to the low natural abundance and NMR sensitivity of the main isotopes of interest, especially  $^{15}\text{N}$ , such SP spectra often have a low signal to noise ratio. To overcome this, tholins were synthesized from isotopically enriched mixtures using pure  $^{13}\text{CH}_4$  and 30% enriched  $^{15}\text{N}_2$ . Techniques using CP pulse sequences can be used to enhance the signal intensity (Schaefer and Stejskal, 1976). These experiments involve excitation of the most abundant and NMR sensitive spins within the sample (i.e.,  $^1\text{H}$  nuclei in the case of the  $C_xN_yH_z$  tholins) and magnetisation is transferred towards less abundant spins of interest (i.e.,  $^{13}\text{C}$  or  $^{15}\text{N}$ ). During the transfer process characterized by the contact time, the  $^{13}\text{C}$  or  $^{15}\text{N}$  magnetisation increases exponentially; however, the protons are simultaneously relaxing during this period, resulting in a decrease in the overall magnetisation. The magnetisation transfer and relaxation rates depend on the local  $^{13}\text{C}$  or  $^{15}\text{N}$  environments and are influenced by the proximity to as well as the number of the excited protons, along with any molecular motions present in the system. Here we present CP spectra obtained as a function of the contact time. The analysis of these results provides new information on the spatial distribution of C, N and H nuclei within the materials.

Linkages between carbon and nitrogen atoms were also investigated by NMR, using the double  $^1\text{H}$ – $^{15}\text{N}$ – $^{13}\text{C}$  CP technique, in

which  $^1\text{H}$  magnetisation is first transferred to  $^{15}\text{N}$  nuclei which are then allowed to evolve and their magnetisation is further transferred to  $^{13}\text{C}$  (Schaefer et al., 1979). As a result, using the double CP sequence, only the  $^{13}\text{C}$  signals of those carbons that are closely coupled to  $^{15}\text{N}$  nuclei are observable and the intensity of the signal varies according to the strength of their coupling. The key parameters here are therefore the  $^1\text{H}$ – $^{15}\text{N}$  and  $^{15}\text{N}$ – $^{13}\text{C}$  contact times. One- and two-dimensional NMR experiments can be conducted, providing additional information on the C,N,H arrangements within the sample (Fujiwara et al., 1995). Double CP spectra were recorded using various  $^1\text{H}$ – $^{15}\text{N}$  and  $^{15}\text{N}$ – $^{13}\text{C}$  contact times on tholin.

One main question to be addressed concerns the structural assignment of  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR shifts obtained from the SP and CP experiments. Usually these attributions are carried out based on knowledge of functional groups within the existing NMR large data base for organic compounds. These provide useful structural analysis tools but do not always provide reliable ways to interpret the potentially unusual C–N–H bonding or molecular fragments present within tholins produced in the laboratory. Here we complemented our experimental study by carrying out *ab initio* predictions of  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR shifts for molecular models and fragments using electronic structure methods in order to support and aid in the structural interpretation of our experimental data.

## 2. Experimental

### 2.1. Samples

The tholin sample for the solid state NMR study was produced within the PAMPRE experiment using a  $\text{N}_2$ – $\text{CH}_4$  gaseous mixture submitted to a plasma discharge (Szopa et al., 2006). The gaseous mixture contained  $2.00 \pm 0.06\%$  of pure  $^{13}\text{C}$ -labelled methane (Eurisotop, Saclay, France) in  $\text{N}_2$  isotopically enriched with 30% of  $^{15}\text{N}_2$  nitrogen (Eurisotope, Fr.). That enrichment procedure enabled us to obtain single pulse (SP)  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectra in the present study. The operating conditions were 0.9 mbar total pressure, ambient laboratory temperature, and a 30 W injected radio-frequency power. The elemental composition had H/C and N/C atomic ratios of 1.1 and 0.77, respectively (Quirico et al., 2008).

### 2.2. NMR experiments and first principles calculations

The  $^{13}\text{C}$  and  $^{15}\text{N}$ -enriched tholin material prepared by PAMPRE was examined by solid state NMR using a Bruker AVANCE III 700 spectrometer at  $B_0 = 16.4\text{ T}$  with  $\nu_0(^{13}\text{C}) = 176.07\text{ MHz}$  and  $\nu_0(^{15}\text{N}) = 70.95\text{ MHz}$ , with a 3.2 mm triple resonance Bruker MAS probe, spinning at 22 kHz. Samples were spun at the magic angle using  $\text{ZrO}_2$  rotors.  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR chemical shifts were calibrated to glycine enriched in  $^{13}\text{C}$  and  $^{15}\text{N}$  and referenced with respect to TMS and nitromethane respectively. Full experimental details (e.g., number of scans (NS), recycle time (RD), etc.) are shown in the figure captions. Decomposition of spectra was performed using the dmfit software (Massiot et al., 2002).

Electronic structure calculations were carried out to support and confirm the NMR assignments. Because many of the candidate structures appear within solid state crystalline or nanocrystalline materials we chose to use the CASTEP code (version 5.5), which uses planewave basis functions to model the electronic wavefunction in the Kohn–Sham formulation of density functional theory (DFT) (Clark et al., 2005). CASTEP enables a consistent calculation of NMR shifts for molecules and solid-state systems and provides a way to discriminate between the individual atom environments predicted to occur within the tholins at various C:N:H ratios. To model NMR shifts for certain species, individual molecules or

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