

# 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

### 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. 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, termed Titan's tholins, are produced in the laboratory, in particular using plasma discharge in gaseous  $\text{N}_2 - \text{CH}_4$  mixtures with similar proportions as in Titan's atmosphere. Titan's tholins have been analysed using a wide variety of techniques which 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  $\text{C}_x\text{H}_y\text{N}_z$  chemistry that can contain 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's tholins. Here 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.

## 2. Results

### 2.1 Characterization of carbon chemical environments using $^{13}\text{C}$ NMR

The solid state  $^{13}\text{C}$  MAS single pulse (SP) spectrum of the tholin shows a dominant peak at 140-180 ppm that contains at least two contributions corresponding to  $\text{sp}^2$ -bonded carbon atoms. This region which accounts for 60 % of the total C can contain substantial contributions from heterocyclic aromatic species containing triazine ( $\text{C}_3\text{N}_3$ ) rings and/or heptazine ( $\text{C}_6\text{N}_7$ ) units, as well as C involved in imino groups ( $\text{C}=\text{N}$ ) although a contribution from isocyanato groups ( $-\text{N}\equiv\text{C}$ ) or carbodiimide moieties ( $-\text{N}=\text{C}=\text{N}-$ ) cannot be excluded. There is also a broad signal extending between 5-100 ppm due to aliphatic C (29 %), and a well-resolved peak at 121 ppm (11 %) that is characteristic of nitrile species ( $-\text{C}\equiv\text{N}$ ). Variable contact time ( $t_{\text{CP}}$ )  $^1\text{H}$ - $^{13}\text{C}$  cross-polarisation (CP) experiments indicated that the aliphatic C are mainly protonated contrary to the  $\text{sp}^2$ -bonded ones. Some of the aliphatic carbons are linked to N incorporated within amine functional groups and others are clearly involved in methyl species. A minor contribution of non-protonated aromatic carbons could also be present.

## 2.2 Characterization of nitrogen chemical environments using $^{15}\text{N}$ NMR

The single pulse solid state  $^{15}\text{N}$  MAS experiments confirm the presence of nitrile (-134 ppm) groups in the tholin sample, accounting for 11 % of total N. A main broad peak (56 %) occurs between -230-340 ppm with maxima at -272 ppm and -304 ppm, along with two shoulders at -330 and -256 ppm. An additional broad signal (29 %) occurs throughout the -160 to -230 ppm range with maxima near -185 ppm and -170 ppm. The occurrence of amino-substituted six-membered heterocycles is supported by resonances both in the range of the amino substituents and of the imino functions from the rings, although other types of substituents (such as some bearing cyano groups) might also be present. The occurrence of isocyano groups is consistent with the  $^{13}\text{C}$  NMR data, along with a low contribution of carbodiimide entities to the NMR spectra. There is also a sharp peak at -356 ppm (6 %) that we assign to the presence of  $\text{NH}_4^+$  species or heterocyclic amines.

## 2.3 N-C interactions studied via $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$ double CP-MAS NMR

To specify further the linkages occurring between N and C centres in the tholin sample,  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  double CP experiments were performed. Based on our previous experience obtained with the  $^{15}\text{N}$  CP MAS spectra above, we selected  $^1\text{H}$ - $^{15}\text{N}$  contact times at 0.5 and 5 ms. A variable  $^{15}\text{N}$ - $^{13}\text{C}$  contact time experiment was then performed to highlight the N-C coupling characteristics and to select the most appropriate values for the 2D NMR experiments.

The 2D spectrum recorded with  $t_{\text{CP1}} = 5$  ms and  $t_{\text{CP2}} = 5$  ms and a recycle time of 5 s (Fig. 1) clearly shows the coupling between the C atoms resonating at 168 ppm with the N atoms at -280 ppm and to a lesser extent with N at -174 ppm, suggesting the presence of amino groups attached to C atoms contained within heterocyclic structures. In contrast, C centres at 160 ppm are only correlated with the N contributions from the main  $^{15}\text{N}$  peak at -282 ppm. When the aliphatic carbons are considered, two types are distinguished at 31 and 44 ppm, and both are coupled with the broad N signal around -278 ppm. The present double CP experiments also suggest the coupling of nitrogen resonating at -280 ppm with a cyano group. As mentioned above, a correlation is observed between  $^{15}\text{N}$  at -280 ppm and  $^{13}\text{C}$  at 168

ppm. Based on their chemical shifts, these N and C species may belong to an imino group suggesting the occurrence of a  $\text{C}=\text{N}-\text{C}\equiv\text{N}$  moiety.

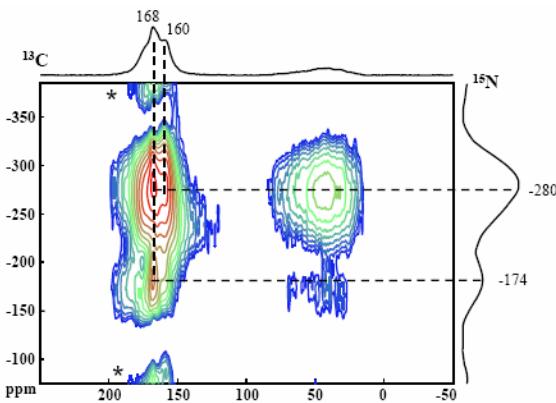


Figure 1: 2D  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  CP MAS NMR spectrum of tholin sample

## 3. Conclusion

The present  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR study indicate that the model tholin structure is mainly based on unsaturated C-N bonded units, contained within  $\text{sp}^2$  bonded species such as imines or aromatic triazine or heptazine units, or nitrile ( $-\text{C}\equiv\text{N}$ ) groups. Amino groups ( $-\text{NH}_2$ ) are also present, most likely linked to  $\text{sp}^2$ -bonded C as are some methyl ( $-\text{CH}_3$ ) groups. Along with previous mass spectrometry and FTIR, UV-visible and FT-Raman investigations, this places additional and new constraints on the likely structures and compositions of the Titan's tholin.

