

## New insight in tholin chemical structure through $^{13}\text{C}$ and $^{15}\text{N}$ solid state nuclear magnetic resonance

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### Abstract

Tholins are complex materials synthesized in laboratory as models of the molecules occurring in the atmosphere of Titan. Using labeled gases, pure  $^{13}\text{C}$  and  $^{15}\text{N}$ -enriched tholins were synthesized and analyzed using  $^{13}\text{C}$  and  $^{15}\text{N}$  nuclear magnetic resonance. This study allowed confirming the presence of some functional groups (cyano, amino, imino) previously inferred from other techniques and to assess their relative contribution. It also indicated that some other functions (such as carbodiimide, protonated aromatic carbons) if present, only show a very low contribution and ruled out the occurrence of hydrazones.

### 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 thanks to solar UV radiation followed by recombination leading to a large variety of organic molecules including some forming a thick, orange-colored haze. These compounds also present an astrobiological interest as they are assumed to be able to release amino acids upon hydrolysis.

To get insight in the chemical composition of these complex organic compounds, analogous materials termed tholins are produced in the laboratory, through plasma discharge in gaseous  $\text{N}_2$  /  $\text{CH}_4$  mixtures simulating Titan atmosphere. Titan tholins have been analysed using a large array of techniques, converging towards a structure based on  $\text{C}_x\text{H}_y\text{N}_z$  units.

In the present study, we investigated the chemical structure of such tholins using nuclear magnetic resonance (NMR). NMR is a powerful tool to

determine the nature and environment of carbon and nitrogen in complex materials. Two nuclei were selected,  $^{13}\text{C}$  and  $^{15}\text{N}$ , so as to characterize the different types of carbon and nitrogen atoms in this material.

### 2. Material and methods

So as to enhance the signal, tholins were synthesized from pure  $^{13}\text{C}$   $\text{CH}_4$  and  $\sim 30$  %  $^{15}\text{N}$ -enriched  $\text{N}_2$  in a 98/2 ratio using the PAMPRE experiment [1]. The tholin sample was analysed through solid state NMR using a Bruker AVANCE III 700 spectrometer at  $B_0 = 16.4$  T with  $\nu_0(^{13}\text{C}) = 176.07$  MHz and  $\nu_0(^{15}\text{N}) = 70.95$  MHz, with a 3.2 mm triple resonance Bruker MAS probe, spinning at 22 kHz. Cross-polarization  $^1\text{H}$ - $^{13}\text{C}$  and  $^1\text{H}$ - $^{15}\text{N}$  (CP) and single pulse (SP) sequences were used along with  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  double CP experiments.  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR chemical shifts were referenced to glycine enriched in  $^{13}\text{C}$  and  $^{15}\text{N}$ .

### 3. Results

The  $^{13}\text{C}$  spectrum exhibits a broad signal (59 % of total C) ranging from 5 to 90 ppm due to aliphatic carbons, some of them likely involved in amine functions, along with a well-resolved peak at 121 ppm assigned to nitriles (10 %) and a dominant signal between 140 and 180 ppm, assigned to  $\text{sp}^2$  carbons with two peaks that can be clearly distinguished at 160 and 168 ppm (31 %). These  $\text{sp}^2$  carbons exhibit a lower level of protonation than the aliphatic ones.

The solid state  $^{15}\text{N}$  CP MAS spectrum shows a broad peak (accounting for 54 % of total N) between -220 and -310 ppm with maxima at -292 ppm and -274 ppm range along with two shoulders, a broad one maximizing at -256 ppm and a sharp one at -304 ppm. An additional broad signal can be seen at -198 ppm (29 %) and two peaks are well-resolved at -134 ppm

(assigned to nitrile groups, 9 %) and -356 ppm (6 %) are detected. A minor peak (2 %) can be detected at -330 ppm, a typical chemical shift for amines. Based on CP dynamics, the N responsible for peaks at -304 and -356 ppm are less protonated than the other N atoms and they exhibit a similar behaviour. It must be noted that the signal at -356 ppm falls in an unusual range of chemical shifts. Heterocyclic amines may be a priori considered to account for this chemical shift but two-dimensional experiments rule out such an assignment (see below). However, ammonium or hydrazinium ions located close to polynitrogen chains such as azides were reported to exhibit such a chemical shift [2] and should therefore be considered.

So as to specify the links between N and C in these tholins,  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  double CP experiments were performed (Figure 1). They clearly show coupling between  $\text{sp}^2$  carbons (168 and 160 ppm) and nitrogen atoms around -280 ppm, suggesting the presence of imino groups ( $\text{C}=\text{N}$ ). Such groups may also be linked to aliphatic carbons and/or to cyano groups. A coupling between the 168 ppm peak and nitrogens at -180 and -174 ppm could also be revealed. The latter is consistent with the presence of heterocycles substituted by amino groups. No correlation could be evidenced between nitrogen atoms at -356 ppm and carbons, ruling out their involvement in heterocyclic amine structures. In contrast, this suggests that such N atoms are isolated in N-rich structures and ammonium or hydrazinium compensating negatively charged polynitrogen moieties may be good candidates.

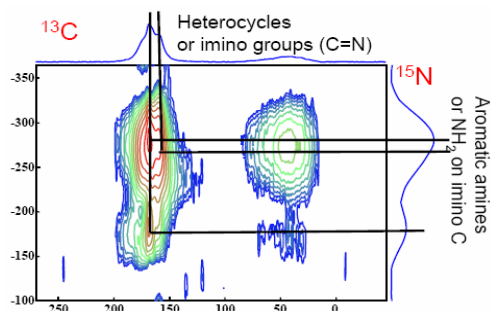


Figure 1: Two dimensional  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  double CP MAS spectra of tholin sample.

This study therefore allowed confirming the presence of some functional groups previously put forward from other techniques [3], [4]. Some structures in contrast, if present, only have a very low contribution. This is for example the case of carbodiimides, hydrazines and protonated aromatic carbons. In agreement with [4], the present study points to the lack of hydrazones.

## References

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