New insights in tholin chemical structure using solid state ^{13}C and ^{15}N NMR spectroscopy S. Derenne[1], E. Quirico[2], C. Szopa[3], G. Cernogora[3], B. Schmidt[2], V. Less[4] and P. F. McMillan[4]. [1]LCBOP, UMR CNRS BioEMCo, Paris, France (sylvie-derenne@enscp.fr), [2] LPG UMR5109 Université Joseph Fourier/CNRS Grenoble, France, [3]SA Verrières le Buisson France, [4]Dept Materials University College of London GB.

Introduction: The chemical compositions and structures of Titan's aerosols are still unknown, so that the use of analogs formed in laboratory experiments is still necessary for atmospheric modeling and analysis of data from the space-based missions. Various different types of experiment have been carried out worldwide during the past 30 years to produce and evaluate such analogs, termed *tholins*. The experiments can be classified into two groups, depending upon whether light sources or an electric discharge are used to produce the materials [1]. Note tholins may also be used as useful analogs of cometary refractory organics.

Even after >30 years of dedicated chemical and physical investigations, their chemical composition and structure are still far from being elucidated and correlated with the synthesis route. The tholins consist of complex disordered macromolecular solids based on the light elements, that are generally poorly soluble in known solvents, and they are very difficult to characterize. They have been investigated using various analytical techniques (e.g. [2]), including infrared spectroscopy (e.g. [2]), Raman spectroscopy, pyrolysis, double laser desorption, elemental analysis, etc. A review of these analyses can be found in [3,4]. None of these analyses provided a clear picture of the chemical structure of tholins. Compiling data from different publications can be a tricky enterprise, as the analysis generally concerns distinct samples, formed under different experimental conditions.

We present the first characterization of tholins through solid state ^{13}C and ^{15}N Nuclear Magnetic Resonance (NMR) spectroscopy. These techniques were shown to be powerful in the study of refractory organic materials such as the insoluble organic fraction from meteorites [5, 6]. So as to enhance the signal, pure ^{13}C and ~ 30 % ^{15}N tholins were synthetized with the PAMPRE experiment at Service d'Aéronomie (Verrières le Buisson France) [1]. Two groups of samples SA98 and SA90 were obtained from N_2:CH_4 mixtures with respectively, 2 and 10 % of CH_4. Tholins were studied along with a HCN "polymer" synthesized by R. Minard and a graphitic carbon nitrides termed g-CN, synthesized at University College of London (V. Less and P. F. McMillan), following the procedure defined by [7].

Results:

SA90. The solid state ^{13}C CP/MAS NMR spectrum of SA90 is dominated by a broad peak ranging from 0 to 60 ppm and maximizing at 37 ppm and also shows two minor peaks around 120 and 166 ppm. These assignments were confirmed by using a single pulse sequence which resulted in a drastic decrease of the intensity of the high-field signal, thus indicating that it is mainly composed of protonated aliphatic carbons. Some of these carbons may be linked to nitrogen as in amines Moreover, in the SP spectrum, this signal exhibits a shoulder at 14 ppm which may be assigned to carbon from methyl groups. A narrow peak is observed at 117 ppm, indicating the presence of nitrile functions C≡N, along with a broad signal between 150 and 180 ppm, centred at 167 ppm and showing a slight shoulder around 160 ppm. It must be noted that carbons adjacent to nitrogen in six-membered nitrogen heterocycles usually occur in the 150-160 ppm range but these chemical shifts increase when the heterocycle is substituted. Chemical shifts are lower in six-membered nitrogen heterocycles. Carbons in triazines and tetrazines are detected above 160 ppm. Interestingly, no signal is observed between 125 and 150 ppm, pointing to a virtual lack of non-substituted unsaturated carbons. This is in agreement with the lack of protonated aromatic carbons suggested by infra-red spectroscopy [8].

The solid state ^{15}N NMR spectrum first confirmed the presence of nitrile functions with a clear signal around -125 ppm. It also shows a broad signal between – 240 and -320 ppm with a shoulder extending down to -370 ppm. This shoulder lies in the typical range for amines, thus confirming infra-red conclusions [8]. The broad peak which ranges between -240 and -320 seems to be composite as it exhibits several sub peaks although a noise origin cannot be excluded. This range is usually considered as typical for nitrogen in five-membered heterocycles such as pyrroles or indoles. However, this is not consistent with the ^{13}C chemical shifts except if carbons are substituted. Based on their ^{13}C chemical shifts, triazine moieties appeared as good candidates for structural moieties in tholins. We therefore recorded the ^{15}N NMR spectrum of pure triazine and obtained a chemical shift of – 103 ppm. This value must be compared to that of – 63 ppm in pyridine and – 85 ppm in pyrimidine, considered that the latter values are shifted to – 150 and -173 ppm respectively
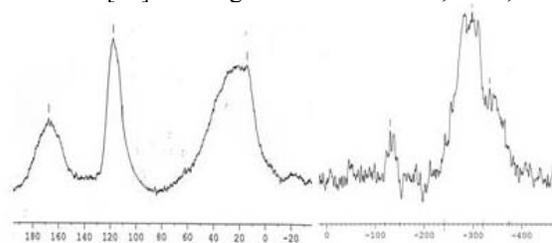
in case of substitution of adjacent carbons by amino groups. Moreover, these amino groups show ^{15}N chemical shifts of – 300 ppm. It must also be noted that a further shift occurs when a positive charge is borne by the heterocycle (down to – 180 ppm for pyridinium) but there is no evidence for the occurrence of such a charge in tholins. The involvement of triazinic rings bearing amino substituents is further supported by the chemical shifts of melamine, 167 ppm for ^{13}C according to Zhang and – 207 ppm for [15]N (value obtained on a model compound) and by data obtained on carbon nitride. Two structures based on triazinic rings were proposed by Zhang for the carbon nitride g-CN. The authors reported signals in ^{13}C NMR at 159 and 166 ppm. We performed ^{15}N NMR spectroscopy on a sample of carbon nitride provided by the authors and obtained a major signal at – 247 ppm in the range of the broad tholin peak. Another compound which is often considered as an homologue of tholins is the "HCN polymer". We therefore recorded ^{13}C and ^{15}N NMR spectra of such a polymer. The ^{13}C spectrum is dominated by a peak around 165 ppm, consistent with an extended trazinic structure as proposed by [9], and a broad signal is observed in the aliphatic region. Additional fine structures can be observed. As for the ^{15}N NMR spectrum, it appears highly similar to that of the tholins with a predominant broad signal between -260 and -350 ppm along with a less intense one around -120 ppm. It must be noted that the signal around -280 ppm in tholins may also be assigned to carbodiimides (-N=C=N-) functions as indicated by the spectrum of a reference compound (cyclohexylcarbodiimide). Hydrazones (N-N=C) and hydrazines (N-N) should also be considered and model compounds will be examined for their chemical shifts. The presence of isonitriles might have been considered on the basis on ^{13}C NMR as they are detected in the 155-160 ppm range but it can be ruled out from ^{15}N NMR as no signal could be detected at -200 ppm.

SA98 The solid state ^{13}C NMR spectrum of SA98 exhibits the same signals as that of SA90 but major differences can be observed in the relative abundances. Indeed, while the 0-60 ppm peak was predominant over the 140-180 ppm in SA90 with an intensity ratio of ca. 3 (determined on single pulse spectra), the latter is only of 0.5 in SA98, thus pointing to a much higher aromaticity in SA 98. Moreover in SA98 spectrum, the low-field signal is split into two peaks at 158 and 167 ppm. When the ^{15}N NMR spectrum is considered, it is dominated, as in the case of SA 90, by a broad peak between -240 and -320 ppm with a shoulder down to -370 ppm. This shoulder assigned to amino groups is much less intense in SA98, in agreement with a lower contribution of hydrogen in the initial gas mixture.

Moreover, two sub-maxima at -270 and -290 ppm can be clearly distinguished in SA 98. In addition to this broad signal, as in SA 90, a peak is observed at -126 ppm, assigned to nitriles.

Conclusion : NMR analyses evidence major chemical structures in tholins as aliphatic functions, amines, triazine rings, nitriles, and possibly carbodiimides. Hydrazines and hydrazones are also suspected. NMR also shows that this polymeric carbon nitride is significantly different than other amorphous carbon nitrides [10], as much less chemical functions are present. The lack of non-substituted rings, especially benzene, is intriguing as earlier works report their presence [11]. Furthermore, the absence of benzene questions tholin's relevancy of Titan's aerosols, as benzene has been identified as a major compound of Titan's upper atmosphere. In contrast, as far as we are aware, no triazine was reported in Titan's atmosphere. Another puzzling result is the lack of isonitrile functions, identified by IR spectroscopy by [2,8]pointing to the efficiency of NMR to help in IR assignments. Comparison between SA90 and SA98 evidences the decrease in aliphatic and amine functions, and the increase in triazine compounds, and likely carbodiimides, consistently with [8]. These observations are fully consistent with IR/Raman spectroscopy [8].

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^{13}C and ^{15}N NMR spectra of SA98