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^{13}C CP-MAS NMR of Azacycle-Thiourea Inclusion Compounds

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^{13}C CP-MAS NMR spectra of thiourea host-guest inclusion compounds containing amines, 1-azabicyclo[2.2.2]octane, 1,4-diazabicyclo[2.2.2]octane, 3-azabicyclo[3.2.2]nonane and 1, 3, 5, 7 tetrazadamantane at 25°C are reported. Chemical shifts of the confined guest molecule with respect to those diluted in $CDCl_3$ and CCl_4 reveal a weaker interaction of the amine with the medium. The magnitude of the average of the ^{13}C---^{14}N residual dipolar interactions produced by the amplitude motions of the amine guest molecules in the channel depends on the strength of the host-guest hydrogen bonding.

Keywords: ^{13}C CP-MAS NMR, thiourea, inclusion compounds

INTRODUCTION

Thiourea like urea forms crystalline host-guest inclusion compounds in which a variety of guest molecules of appropriate size and shape are inserted in van der Waals cavities arising from an extensive hydrogen bond nesting of thiourea molecules [1–3]. Most of these compounds may be described as constituted by matrices with hexagonal, linear channels in which the guest species are located, Figure 1.

The products of the classical inclusion of hydrocarbons in a thiourea network [4] as well as those of the other species containing functional groups such as amines [5] are examples of these kinds of compounds.

If the guest species cannot be comfortably accommodated in the cavities defined by the

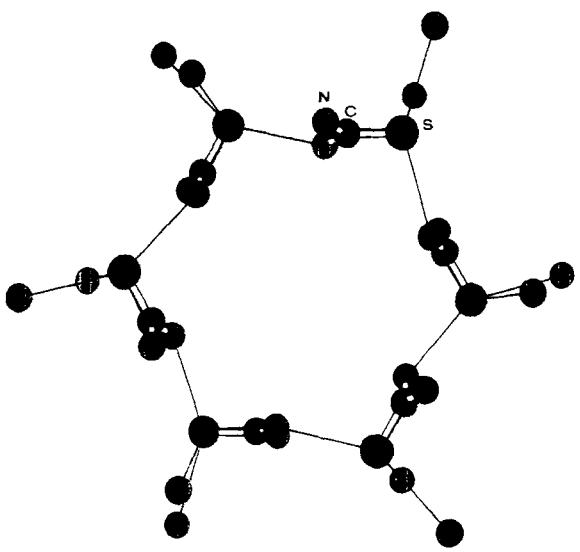


FIGURE 1 Typical thiourea host structure. Cross section viewed along the channel axis.

host, the system may lead to separated phases, to specific Lewis acid-base adducts [6–7], or to a different kind of inclusion compound e.g., to lamellar structures [8].

Although X-ray diffraction analysis is the most important and indispensable tool for determining the nature and structural properties of inclusion compounds, it provides little information about the dynamic properties of the confined species. Such knowledge is interesting for learning about both the nature of host-guest interactions and the projection of these compounds as biological models or as new materials and can be better obtained by NMR techniques. Since the behavior of organic molecules placed in environments such as those occurring within clathrate cavities is expected to differ from that of the same molecule in other phases [9], the comparison of the NMR properties of the guest species in different states may be useful for understanding the inclusion phenomena.

Some systems with relatively inert guest species e.g., cyclohexane/thiourea and halogenated cyclohexane/thiourea are very well characterized by both X-ray and NMR techniques. However, information on other systems with chemically more active guest species like amines is rather limited [5]. In order to contribute to both, knowledge of the structural aspects of thiourea/amine systems and the development of methods for investigating the dynamics of chemical species in restricted spaces, an NMR study of the azabicyclic compounds 1-azabicyclo[2.2.2]octane (quinuclidine, Q), 1,4-diazabicyclo[2.2.2]octane (DABO), 3-azabicyclo[3.2.2] nonane (ABN), and 1, 3, 5, 7-tetrazadamantane (hexamethylenetetramaine, HMTA) in solution and inserted in thiourea matrices has been performed.

EXPERIMENTAL SECTION

Commercially available reagents were used as received. The products were obtained from solutions of both amine and thiourea in methanol by slow solvent evaporation at room temperature. Hexagonal needles for the compounds with Q and ABN, and plates for DABO and HMTA were separated after about 48 h, washed with cold methanol, and dried under vacuum. Thiourea to amine ratios reported in Figure 2 were determined by both elemental microanalysis (Perkin Elmer 240C microanalyzer) and ^{1}H-NMR spectroscopy in dimethyl-d_6 sulfoxide solution. Products were further characterized by optical microscopy inspection, X-ray diffraction analysis of microcrystalline samples, and multinuclear NMR spectroscopy.

Solution, high resolution ^{1}H and ^{13}C NMR data were obtained with a Bruker AMX-300 spectrometer. The ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectra were recorded on a Bruker MSL-100 at a frequency of 100.63 MHz. The polycrystalline powder samples were spun at a frequency of 4 kHz. The numbers of scans varied between 200 and 1200 with 5.5 μs, 90° pulses; 1 ms cross-polarization contact time; 41 ms acquisition time during proton decoupling; and 5 s recycle delay. The chemical shifts are given relative to TMS, Powder X-ray diffractograms were recorded in the range $2° > 2\theta > 50°$ on a Siemens D-5000 diffractometer using Cu-K_α radiation (40 KV, 30 mA) and a graphite monochromator (λ = 1.5418 Å). Diffractograms of the samples, ground to a fine powder in order to reduce the likelihood of the crystallites exhibiting

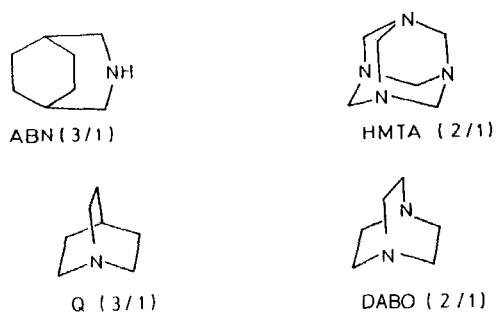


FIGURE 2 Schematic molecular structures of guest species and thiourea/amine ratios in the respective inclusion compounds.

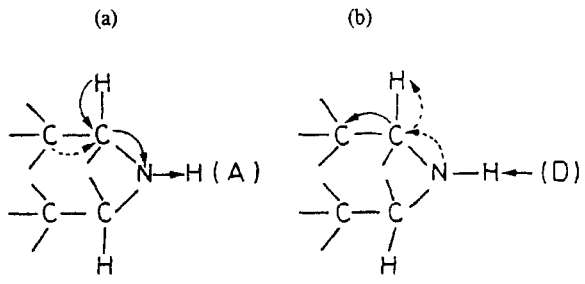
a preferred orientation, always show simple phases corresponding to the expected previously described host structures [5, 8].

RESULTS AND DISCUSSION

Analytical as well as further characterization of the products clearly show that the heterocyclic amines are actually included in the thiourea matrix.

The ^{13}C CP-MAS NMR spectra of the solids at room temperature show a pattern which is similar to those of the corresponding amine as a pure liquid or dissolved in chloroform or carbon tetrachloride. In Table I the chemical shifts of amines inserted in the thiourea matrix are compared with those of the amine in the above-mentioned solvents. The influence on the NMR spectra of the amines of an environment as chloroform, able to interact by hydrogen bonding with the solutes, is indeed reflected in the chemical shift changes observed during transition from the concentrate to dilute amine solutions in this solvent.

The influence of hydrogen bonding on the ^{13}C chemical shifts may in general be understood by the sigma electron push-pull effects [10] as described in the following scheme, which shows



SCHEME

the charge displacements, in our case from Q(a) and toward ABN(b), produced by the acceptor or donor solvents via hydrogen bonding association. Interestingly, the ^{13}C-chemical shifts of the amines inserted in the thiourea correspond to free amines or at least to amines undergoing interactions with a medium weaker than those dissolved in either $CDCl_3$ or an inert solvent as CCl_4. Therefore, thiourea channels in these cases appear to be perfect van der Waals cavities. According to the isovalent hybridization concept [10], the interaction of the basic quinuclidine nitrogen atom with the acidic solvent should induce an increment of s-character of the C_α hybrid orbitals directed toward its neighbors, but the N-atom produces a high field shift of its ^{13}C—NMR signal. The relatively low chemical shift of the C_α in the quinuclidine inserted in the thiourea matrix points to poor host-guest inter-

TABLE I ^{13}C-NMR Chemical Shifts of Azacycle Compounds. Comparison of the Chemical Shifts in the Thiourea Inclusion Compounds with those in $CDCl_3$(1% p/v[a] and satured[b]) and CCl_4 Solutions

Compound	Medium State	^{13}C-Chemical Shifts		
		C_α	C_β	C_γ
Q	TU	48.27	27.80	21.74
	$CDCl_3$[a]	47.83	26.76	20.76
	$CDCl_3$[b]	47.79	26.76	20.88
	CCl_4	47.92	27.37	21.33
ABN	TU	52.20	30.97	25.63
	$CDCl_3$[a]	55.83	32.84	25.38
	$CDCl_3$[b]	55.77	32.79	25.34
	CCl_4	54.57	31.57	24.41
DABO	TU	47.42		
	$CDCl_3$[a]	47.37		
	$CDCl_3$[b]	47.39		
	CCl_4	47.92		

actions. By similar arguments, the interaction of the ABN N—H proton with a donor environment should induce a reduction of the charge density seen by the $^{13}C_{\alpha}$ nucleus leading to low field shifted NMR resonances. According to that, ABN-host interactions are lower than those observed in dilute solutions. The chemical shift values for DABO inserted in thiourea are similar to those in $CDCl_3$ and somewhat lower than in CCl_4, indicative that the host-guest interactions in this case are larger than the cases discussed above. The behavior of 2(TU)(HMTA), which appears to be different, is discussed below.

Furthermore, the MAS ^{13}C—NMR spectra of the compounds show a relatively broad resonance (line width ≈140–200 Hz) at about 180–182 ppm corresponding to the carbon of the thiourea molecule; similar chemical shift values have been reported previously [11] for hydrocarbon/thiourea systems. ^{13}C—NMR measurements of pure crystalline thiourea and of thiourea in $CDCl_3$ solution show single resonance lines at 180.8 and 184, 5 ppm, respectively.

For ^{13}C nuclei directly bonded to nitrogen (^{14}N, $I=1$), MAS frequently gave powder patterns consisting of approximately 1:2 (or 2:1) doublets because the ^{13}C—^{14}N residual dipolar interaction is not averaged to zero by MAS-NMR [13]. The axis of quantization of the ^{14}N nucleus is tilted from the direction of the static magnetic field as a consequence of the interaction between the ^{14}N nuclear quadrupole moment and the electric field gradient at the ^{14}N nucleus [11, 12]. As shown in Figure 3, which reproduces the ^{13}C CP-MAS NMR spectrum of the 3(thiourea)-quinuclidine inclusion compound, high amplitude motions of the amine guest molecules in the channel average the residual dipolar interactions between ^{13}C and ^{14}N to less than 10 Hz, showing the spectrum as

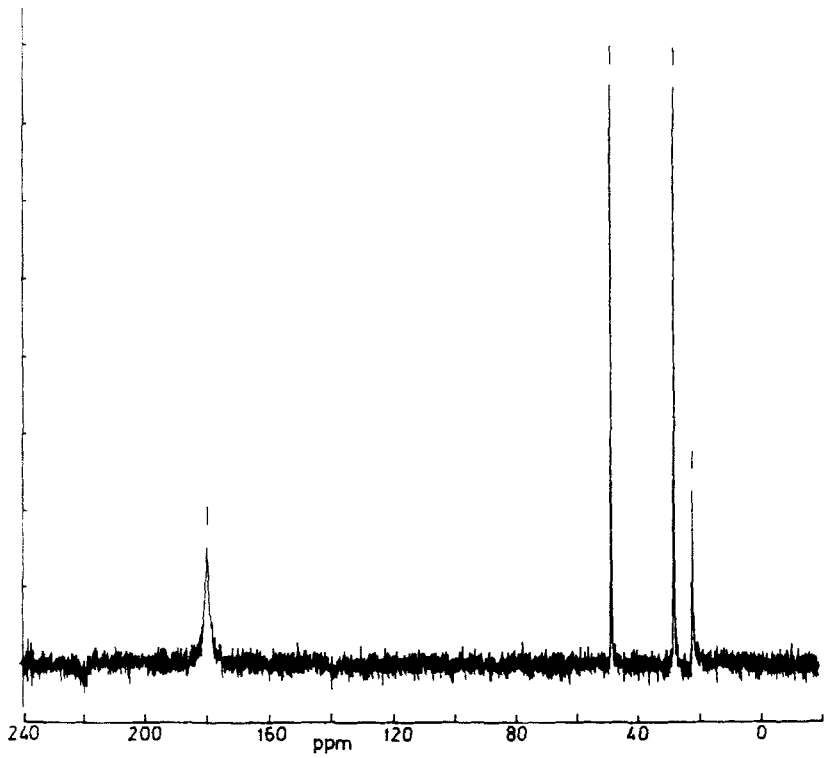


FIGURE 3 ^{13}C CP-MAS NMR spectrum of the 3(TU) (Q) at room temperature. Resonance line at about 179.80 ppm is assigned to the carbon of the thiourea molecule.

only a single sharp line for C_α and the typical asymmetric doublet is not observed. However, for the more symmetrical DABO guest, higher $^{13}C—^{14}N$ residual dipolar interactions are observed, probably due to the additional nitrogen atom, but splitting is not observed (Fig. 4). Similar behavior has been observed for DABO not included at 355 K, but at lower temperature, the doublets arise [14].

As Table II shows, 3-azabicyclo[3.2.2]nonane appears to be the guest with the largest interaction in respect to the others. Typical thiourea chlatrates and an incipient doublet give rise (Fig. 4), this can be due to the larger size of the amine or the weaker host-guest interaction.

For the compound 2(TU)(HMTA), $^{13}C—^{14}N$ residual dipolar interactions are apparently maximal, so quantitative measurements were unsuccessful. In this last compound, in contrast to the typical thiourea inclusion compound, there is extra hydrogen bonding between the host and guest molecules. The hexamethylenetetramine molecules are indeed intercalated in a layered network formed by bidimensional nesting of thiourea molecules, thus each hexamethylenetetramine is tethered to two different thiourea molecules through H—bonds (N_{host}—N_{guest}=3.073 Å) [8], Figure 5. Thus, the amine-thiourea hydrogen bonding is the dominant cause of the restricted motion that gives rise to the larger residual dipolar splitting in the MAS NMR spectrum.

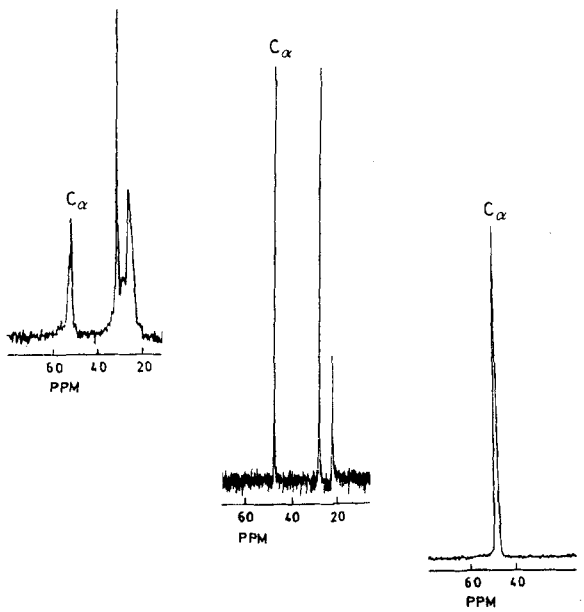


FIGURE 4 ^{13}C CP-MAS NMR spectra of the amine guest confinated in the thiourea host recorded at 298 K at 100.63 MHz. [a]ABN, [b]Q, [c]DABO.

TABLE II ^{13}C-MAS NMR Spectra. Width of the C_α Resonance Line of Azacycle Compounds inserted in Thiourea

Inclusion Compound	C_αLine Width (Hz)
3(TU)(Q)	10
3(TU)(ABN)	171
2(TU)(DABO)	80

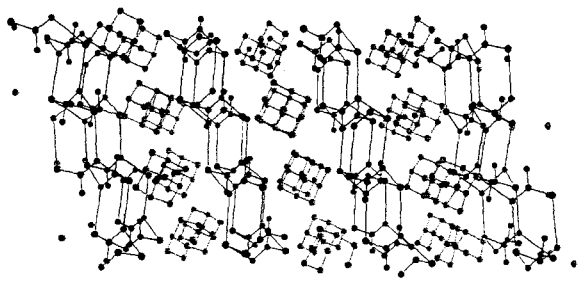


FIGURE 5 The supramolecular structure of 2(TU)(HMTA), view in the directional plane of the layered arrangement of thiourea molecules in which the hexamethylenetetramine molecules are intercalated.

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