



## 2 RESULTS and DISCUSSION

When applying the numerical method [4] to the spectra obtained at 4.7T, two different data sets were found for the principal components of the  $^{13}\text{C}$  shielding tensor in TCNQ cyano groups [3]; only one of the corresponding asymmetry factors ( $\eta = 0$  and 0.4) was characteristic of an axially symmetric system. Aiming to a clarification of this problem, the improvement of the experimental data for the application of the numerical method seems to be the next step; in particular, the acquisition of  $^{13}\text{C}$  spectra displaying an higher number of spinning sidebands and a better signal/noise is required. These conditions are fulfilled by running the spectra at higher static magnetic field but selecting the same MAS rate and a longer recovering delay (600s); Figure 1 shows typical  $^{13}\text{C}$  CP/MAS high resolution NMR spectra of selectively enriched TCNQ to 99%  $^{13}\text{C}$  isotope content on CN groups. Again, two data sets are obtained by a computer fit of the intensities of the lines, one of them corresponding to an axial symmetry for the cyano groups, in close agreement with that obtained at 4.7T [3]:

$\sigma_{11}$ ppm	$\sigma_{22}$ ppm	$\sigma_{33}$ ppm	$\Delta\sigma$ ppm	$\eta$
228	190	-80	-289	0.2
210	208	-80	-289	0.0

However, regarding the other set, a much lower deviation from axial symmetry is now obtained ( $\sigma_{11} - \sigma_{22}$  equal to 38ppm instead of 69ppm). Indeed, Clayden and co-workers already pointed out that similar simulated MAS spectra

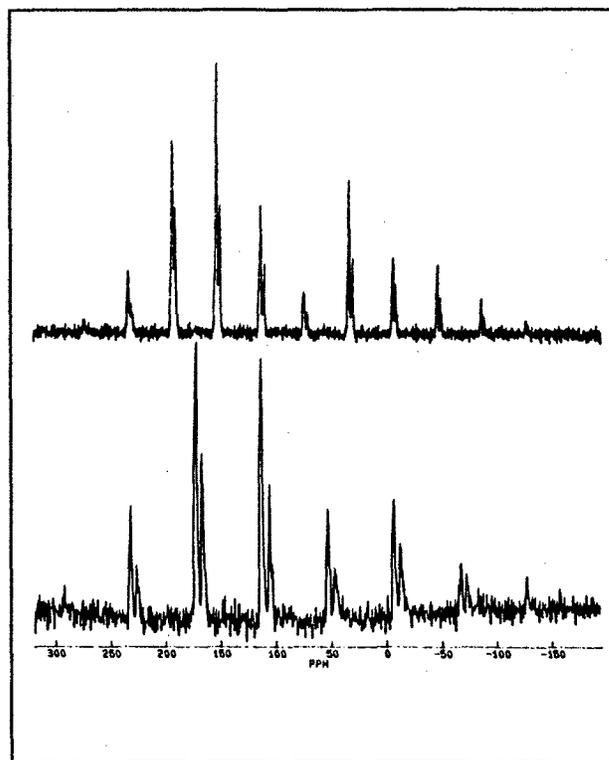


FIG.1.  $^{13}\text{C}$  CP/MAS high resolution NMR spectra of TCNQ cyano groups obtained at 75.47 (on the top) and 50.13 MHz (on the bottom) with the same spinning rate: 3.01 kHz.

are obtained when the chemical shift tensor is axial or near-axial ( $\eta < 0.1$ ) [5]; the intensity of most sidebands was found insensitive to changes in asymmetry until  $\eta > 0.2$ . On the light of these conclusions the present results are definitely acceptable.

For the acquisition of the spectra previously reported [3], too short relaxation delays were used possibly inducing a distorted lineshape for the sidebands envelope; anisotropic molecular motion would influence distinctly the relaxation times of magnetic equivalent  $^{13}\text{C}$  nuclei on TCNQ molecules perpendicular and

parallel to the static magnetic field. In fact, if 1.5s is now used instead of 600s for that duration period, at least three fits are obtained (depending on the sidebands used) with much higher residual values; comparing the data sets in this case, large uncertainties are observed for all the principal components of the shielding tensor.

The study of  $^{13}\text{C}$  TCNQ relaxation in a wide temperature range are now in progress and will certainly contribute to the understanding of these results; also, additional insight on the role of TCNQ on charge transfer complexes (like DMTM(TCNQ)<sub>2</sub> [2]) will be obtained.

To obtain the  $^{14}\text{N}$  quadrupole coupling constant from  $^{13}\text{C}$  CP/MAS spectra, run at 7.0T, the procedure previously described was used [3]; a C-N dipolar splitting close to 230 Hz should be measured now, which is in fact the case.

## References

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