Variable Temperature MAS NMR Studies of the Phase Transition in NaTCNQ

Patrick J. Barrie,[a] **Christopher J. Groombridge,**[b] **Martin C. Grossel***[c] **and Simon C. Weston**[b]

[a] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*
[b] *Department of Chemistry, Royal Holloway and Bedford New College, Egham, Surrey TW20 0EX, UK*
[c] *Department of Chemistry, University of Southampton, Highfield, Southampton SO9 5NH, UK*

^{13}C MAS NMR spectra of the sodium salt of the radical anion of 7,7,8,8-tetracyanoquinodimethane (NaTCNQ) show changes in both chemical shift position and linewidth of some resonances with temperature, and provide information about the nature of a phase transition at *ca.* 333 K.

The properties of TCNQ and its radical anion salts (*e.g.* **1**) have long been a topic of interest because of the remarkable physical properties of these charge-transfer complexes, such as electrical conductivity.[1–3] We now present high-resolution ^{13}C MAS NMR results on NaTCNQ,[4] which are obtained despite the paramagnetism of the sample and allow us to monitor the phase transition that occurs around 333 K.[5]

Fig. 1 shows the ^{13}C MAS NMR spectra at 295 and 373 K acquired using both cross-polarization and conventional single-pulse excitation (with proton dipolar coupling) techniques. The isotropic peak positions (marked by arrows) were established by varying the spinning speed and using the TOSS sideband suppression pulse sequence.

The spectra at 373 K appear less complex because of a large reduction in spinning sideband intensity compared to the spectra at 295 K indicating lower anisotropy. Both sets of specta show a combination of broad and sharp resonances, the location of the broad bands being highly temperature dependent. The sharp peaks change from a doublet and quartet pattern at 295 K (δ 145.1 and 143.5; δ 126.1, 124.2, 123.8 and 122.6, respectively) to a singlet and doublet pattern at 373 K (δ 140.8; δ 128.2 and 123.8, respectively). This is associated with a crystallographic phase transition from two to a half of a TCNQ molecule per asymmetric unit, and is considered in greater detail below. It is also interesting to note that the broad peaks are more apparent in the spectra recorded using single-pulse excitation, indicating that they cross-polarize less efficiently than the sharp resonances. Prompted by these findings we extended the temperature range of the study by use of single-pulse excitation at room temperature and above, and cross-polarization below room temperature. Sideband suppression was employed to simplify the analysis. The results are shown in Fig. 2.

At the lowest temperatures investigated (down to 233 K) all the resonances are narrow, and the spectrum is approximately independent of temperature (below *ca.* 250 K). An extensive spinning sideband pattern is evident when the spectrum is recorded without sideband suppression at these low temperatures reflecting a combination of paramagnetic coupling induced by dipolar interactions between the unpaired electron on $TCNQ^{\cdot-}$ and ^{13}C, and chemical shift anisotropy effects.

To aid spectral assignment, we also recorded spectra using the non-quaternary suppression technique[6] allowing 40 μs for dipolar dephasing. This established that the quartet at *ca.*

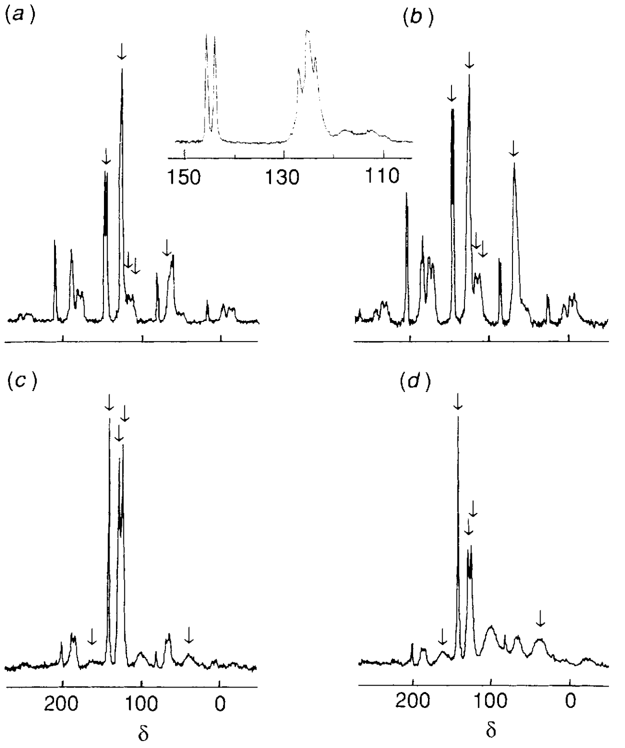


Fig. 1 ^{13}C MAS NMR spectra of NaTCNQ at 295 and 373 K both with cross-polarization (CP) and single-pulse excitation (SPE): (*a*) 295 K, CP; (*b*) 295 K, SPE; (*c*) 373 K, CP; (*d*) 373 K, SPE. Spectra were acquired on a Bruker MSL-300 spectrometer (90° pulse = 4 μs; recycle delay = 1–5 s; contact time for the CP experiments = 1–10 ms; spinning speed = 4.5 kHz; chemical shifts are quoted relative to external TMS). The sample was heated/cooled at about 5 K min^{-1} with a 10 min equilibration at each temperature. The temperature control through the thermocouple located close to the sample chamber is expected to be accurate within ±2 K.

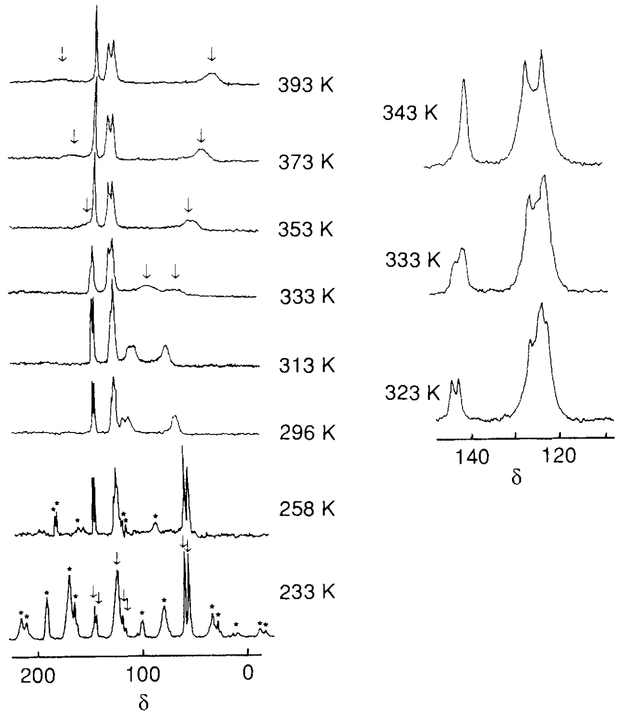
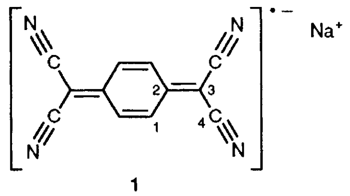


Fig. 2 Variable temperature ^{13}C MAS NMR of NaTCNQ (spinning speed = 3.5–5.0 kHz). Spectra at 258 K and above were recorded using sideband suppression (residual sidebands are marked by *). Broad isotropic peaks are arrowed. The spectrum at 233 K was recorded without sideband suppression, and has the isotropic peaks marked. INSET shows the expansion of the region of δ 100–150 around the temperature of the phase transition.



1

δ 124 in the spectrum recorded at 233 K arises from ^{13}C with directly bonded protons, *i.e.* C_1 atoms (in **1**). We note that the low temperature form of NaTCNQ[7] has two TCNQ molecules per asymmetric unit. It is difficult to assign the other peaks unambiguously from their chemical shift position alone, though we do observe that the doublet around δ 146 remains sharp and temperature independent when warming the sample, and that the doublet at δ 57/54 has very few associated sidebands (when investigated without sideband suppression) compared to the other resonances. On this basis we tentatively assign the doublet around δ 146 to C_2 sites, the doublet near δ 55 to C_3 atoms and the peaks near δ 116 (close to the CN value in the neutral moelcule[8]) to C_4 sites.

Upon warming the sample the peaks around δ 116 and 55 broaden and shift with temperature reflecting the location of the unpaired electron and the paramagnetism of the sample. This effect is at first glance similar to Knight shift behaviour; these have previously been observed for the CN groups in conducting complexes of TCNQ with quinoline, tetrathiafulvalene[8] and *N*-dimethylthiomorpholine.[9] However, NaTCNQ is a semiconductor in both its high and low temperature forms (with σ_{298} *ca.* 10^{-5} S cm^{-1})[4,5a,10] and thus has no conducting electrons. The effect observed here must therefore result from the temperature dependence of the paramagnetic contribution to chemical shift, and from possible changes in the electron location with temperature. The two peaks which are affected by this interaction probably correspond to the C_3 and C_4 sites of the molecule, as these atomic positions are expected to be in close proximity to the unpaired electron.[11,12] We ascribe the broadening of these resonances with increasing temperature to a shortening of the T_2 relaxation times for these sites caused by changes in the paramagnetic coupling with temperature, possibly reflecting a change in location of the unpaired electron. We note that it is still possible to observe a signal from these resonances at room temperature even when using recycle delays as short as 20 ms.

It is also interesting to observe the reduction in the anisotropy (as manifested in the spinning sideband patterns) of the sharp resonances with increasing temperature. Paramagnetic coupling is the sum of two contributions: the Fermi contact shift (which is probably the major cause of the changes in isotropic shift position with temperature), and the pseudo-contact interaction (which is anisotropic and thus results in spinning sidebands in the MAS experiment).[13] Both these couplings are usually inversely proportional to temperature. The reduction in spinning sideband intensity with temperature is thus in line with the expected reduction in magnitude of the pseudo-contact interaction. Chemical shift anisotropy will also contribute to spinning sideband intensity, but this is temperature independent in the absence of any molecular motional processes.

These spectra have allowed us to explore further the nature of the crystallgoraphic phase transition which has been reported to lie in the temperature range $303 < T_c < 373$ K.[5] The nature of this phase change has been investigated by a variety of methods which include: conductivity measurements (T_c = 347–373,[5a] 338[5b] and 313–323 K[5c]); infrared spectroscopy (T_c = 360 K[5d]); magnetic susceptibility measurements (T_c = 348[5e] and 345 K[5f]); and X-ray studies (T_c = 348[5g] and 332–346 K [5h]).

Fig. 2 (inset) shows expansions of the spectral regions containing the sharp resonances (assigned to C_1 and C_2) at

323, 333 and 343 K. The spectrum changes from a doublet and quartet pattern (at 323 K) to a singlet and doublet pattern (at 343 K), while it appears that both phases are present in the spectrum at 333 K. These changes were found to be reversible for both warming and cooling cycles. In the low temperature phase, NaTCNQ consists of dimerized TCNQ radical anions packed in vertical columns which alternate across the sheet in a perpendicular fashion, thereby achieving octahedral coordination of the sodium ions.[7] Since neighbouring columns are different there are two Na^+ and two $TCNQ^{\cdot -}$ moieties in the asymmetric unit. This is entirely consistent with the solid-state NMR spectra obtained below 333 K. Above this temperature the high-temperature form exists in which the two TCNQ columns are equivalent.[5h] This leads to the formation of uniform columns of TCNQ monomers with only one half of a TCNQ moiety in the asymmetric unit, though the coordination shell around the Na^+ remains unchanged. The NMR results are entirely in accord with this crystallographic change. The temperature of the transition reported here is loosely in agreement with that from the X-ray study of Konno and Saito[5h] which concluded that the two phases coexist between 332 and 346 K.

We are currently investigating similar phenomena with other cation salts of TCNQ.

The solid-state NMR spectra were obtained on the University of London Intercollegiate Research Services (ULIRS) instrument at University College London. S. C. W. acknowledges financial support from the SERC.

Received, 19th May 1992: Com. 2/02622H

References

1 H. Endres, in *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum, New York, 1980, vol. 3, ch. 5.

2 J. Kommandeur, in *Physics and Chemistry of Low-Dimensional Solids*, ed. L. Alcácer, Reidel, Boston, 1980, pp. 197–212.

3 M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355.

4 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.

5 (*a*) H. H. Afifi, F. M. Abdel-Kerim, H. F. Aly and A. A. Shabaka, *Z. Naturforsch., A Phys. Sci.*, 1978, **33**, 344; (*b*) N. Sakai, I. Shirotani and S. Minomura, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3321; (*c*) S. C. Weston, F. A. Evans, M. C. Grossel and G. S. Mallors, *Chemtronics*, 1991, **5**, 125; (*d*) R. Bozio and C. Pecile, *J. Chem. Phys.*, 1977, **67**, 3864; (*e*) J. G. Vegter, T. Hibma and J. Kommandeur, *Chem. Phys. Lett.*, 1969, **3**, 427; (*f*) J. G. Vegter and J. Kommandeur, *Mol. Cryst. Liq. Cryst.*, 1975, **30**, 11; (*g*) H. Terauchi, *Phys. Rev. B, Solid State, Ser 3*, 1978, **17**, 2446; (*h*) M. Konno and Y. Saito, *Acta Crystallogr., Sect. B*, 1975, **31**, 2007.

6 S. J. Opella and M. H. Frey, *J. Am. Chem. Soc.*, 1979, **101**, 5854.

7 M. Konno and Y. Saito, *Acta Crystallgor., Sect., B*, 1974, **30**, 1294.

8 A. M. Vainrub, I. A. Heinmaa, M. A. Alla, S. Kh. Viya and E. T. Lippmaa, *JETP Lett.*, 1985, **41**, 571.

9 F. Rachdi, M. Ribet, P. Bernier and M. Almeida, *Synth. Metals*, 1990, **35**, 47.

10 W. J. Siemons, P. E. Bierstedt, R. G. Kepler, *J. Chem. Phys.*, 1963, **39**, 3523; N. Sakai, I. Shirotani and S. Minomura, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3314.

11 H. Johansen, *Int. J. Quantum Chem.*, 1975, **9**, 459.

12 J. S. Miller, J. H. Zhang, W. M. Reiff, D. A. Dixon, L. D. Preston, A. H. Reis Jr., E. Gebert, M. Extine, J. Troup, A. J. Epstein and M. D. Ward, *J. Phys. Chem.*, 1987, **91**, 4344.

13 A. Nayeem and J. P. Yesinowski, *J. Chem. Phys.*, 1988, **89**, 4600.