^{13}C HIGH RESOLUTION NMR STUDY OF METHYL-DIETHYL SULFONIUM TCNQ 1 : 2 COMPLEX

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Solid state high resolution ^{13}C NMR studies of a 1 : 2 charge transfer complex of TCNQ with diethyl-methyl sulfonium S + Et$_2$Me(TCNQ)$_2$ are presented. The metallic shifts of TCNQ resonances are interpreted as due to the Pauli paramagnetism of conducting electrons and quantitatively connected with inhomogeneous spin density distribution over (TCNQ$_2$)$^-$ dimer. A singularity of NMR parameters at $T = 330$ K is observed and described as a structural phase transition occurring in the S + Et$_2$Me cation sublattice.

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1. Introduction

The 1 : 2 charge transfer complex of TCNQ with methyl-diethyl sulfonium, S + Et$_2$Me(TCNQ)$_2$, is a quasi one-dimensional organic semiconductor whose conductivity ($\sigma_{RT} \approx 10^{-2}$ Ω^{-1} cm^{-1}) is dominated by n-type impurities with electronic levels localized inside the gap [1]. The preliminary ^{13}C high resolution NMR experiments have detected a singularity of temperature dependence of positions and relaxation times for some of ^{13}C resonances of the complex at $T = 330$ K [2], even if no anomaly in electronic properties investigated by the other techniques has been reported [1, 3]. In this paper we describe the observed anomaly of NMR parameters in the terms of structural phase transition occurring in cation sublattice. The attribution of ^{13}C resonances in the NMR spectrum of the complex is revised in the light of recent calculations of spin density distribution over TCNQ^{2-} dimer. The observed spread of TCNQ lines in the complex with respect to the neutral molecule is discussed in terms of paramagnetic Knight shift.

2. Experimental

The TCNQ complex with diethyl-methyl sulfonium cation was obtained from S+Et$_2$Me iodide by a standard Melby method and its composition was confirmed by elemental analysis and UV spectroscopy.

^{13}C NMR spectra of powdered crystalline samples were recorded on a Bruker CXP 200 spectrometer working at 50.3 MHz. High resolution in the solid state was achieved using MAS (magic angle spinning) and CP (cross polarization) techniques; an accumulation of $\approx$ 2000 scans was necessary to obtain a good sensitivity. All shifts were reported to tetramethylsilane (TMS) via adamantane as a secondary reference.

3. Results and discussion

The NMR resonance position is a local probe of magnetic field caused by electrons surrounding a given nucleus. In conducting medium (as S + Et$_2$Me(TCNQ)$_2$ is) the shift of the resonance with respect to the Larmor frequency of spectrometer is due to the both electrons localized on molecular orbitals (chemical shift) and the delocalized "conduction" electrons (Knight shift). In order to accede directly to the metallic properties of the system these components should be separated one from the other. Generally, the Knight shift values are obtained by referring the resonances in conducting compound to these in corresponding neutral material. We applied this method to the complex studied, although a neutral molecule is only a crude approximation of chemical shift reference, as the chemical shift tensor is usually charge-transfer dependent.

Figure 1a shows the ^{13}C high resolution NMR spectrum of neutral TCNQ. Due to the occurrence of a center of symmetry in molecule the number of inequivalent resonances of its 12 carbons sites is reduced to 6. The doublet at 132.7 and 133.9 ppm corresponds to the four hydrogen-bonded carbons in quinone ring; the single peak at 152.1 ppm is assigned to the two other carbons in the ring and the line at 91.4 ppm is due to their first neighbors. Finally, the group of lines centered at 110 ppm (103.6, 107.7 and 115.7 ppm) is attributed to the four cyano groups (the origin of splitting of this resonance is discussed in [4]).

The spectrum of S + Et$_2$Me(TCNQ)$_2$ spreads over a wide range of shifts (from 300 to −50 ppm) (Fig. 1b). In addition to the TCNQ lines, there are 5 resonances due to the carbon sites of S + Et$_2$Me counterion, assembled into three groups. The doublet at 4.3 and 7.0 ppm corresponds to methyl carbons in ethyl. The lines at 45.6 and 63 ppm are assigned to the −CH$_2$− groups and the single line at 25.7 ppm to the sulphur-bonded methyl carbon. The remaining resonances located at 293.8, 131.7, −38.9 and −43.5 ppm correspond to the TCNQ carbons. The further analysis of the spectrum using standard techniques of delayed acquisition and variable contact time experiment is not possible as the resonances are broadened [2] and the signal-to-noise ratio is low; therefore the detailed resonance assignment comes indirectly from the analysis of spin density distribution over TCNQ species.

The dispersion of the TCNQ anion spectrum with respect to the neutral molecule is a consequence of an appearance in conducting medium of a Knight shift, which in organic conductors is mainly due to the Pauli susceptibility (χ_P) of itinerant electrons. For a given j nucleus the corresponding Knight shift K_j is given by the formula

$$K_j = 2\pi\chi_P A_j / h\gamma_e\gamma_n, \tag{1}$$

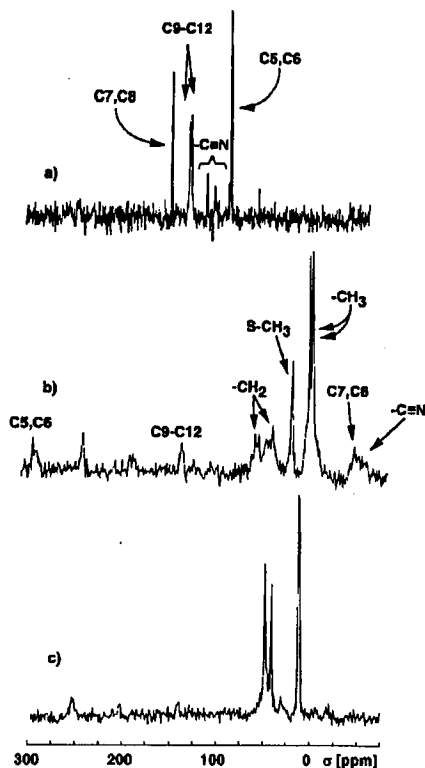where γ_e, γ_n are the gyromagnetic ratios of respectively the electron and [13]C

Fig. 1. ^{13}C high resolution NMR spectrum of: (a) neutral TCNQ, (b) S + Et$_2$Me(TCNQ)$_2$ at room temperature, (c) S + Et$_2$Me(TCNQ)$_2$ at $T = 350$ K.

nucleus and A_j is the isotropic part of hyperfine interaction tensor [5]:

$$A_j = 2\pi\left(a_j \rho_j + \sum_{k \neq j} a_k \rho_k\right) \tag{2}$$

with $a_j = 100$ MHz for secondary carbons, $a_j = 85$ MHz for tertiary carbons and $a_k = -39$ MHz; ρ_j are the spin densities of various carbon sites of molecule.

We calculated the spin density distribution in (TCNQ$_2$)$^-$ using extended Hückel theory approximation (for details see [6]) assuming that the A and B molecules in TCNQ dimer are both charged with 1/2 electron. The resulting ρ_j values are collected in Table; the carbon sites numbering is given in Fig. 2. The spin density distribution is almost identical over both molecules of dimer; in addition the spin densities have similar values within 4 groups of carbons: the hydrogen-bonded carbons C9–C12, the two other carbons from quinone ring C7 and C8, the cyan groups –C≡N (C1–C4) and their nearest neighbours C5 and C6. Thus, even if there is 24 carbons in TCNQ dimer, only 4 resonances of unresolved structure are observed. The electron spin density is particularly high on the C1–C8 sites as high electronegative cyan groups attract the unpaired electron towards the ends of molecule; according to Eq. (1) the resonances corresponding to these sites should be the most shifted with respect to the neutral TCNQ. As
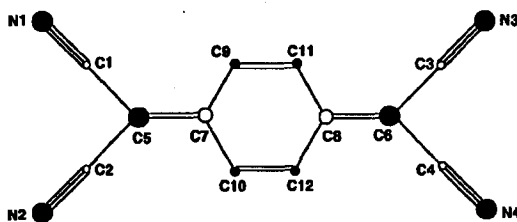
Fig. 2. Carbon sites numbering and graphical representation of spin density distribution in TCNQ molecule. The diameter of circles is proportional to the spin density; the open circles denote negative spin densities.

TABLE

Spin density distribution over TCNQ dimer in S+Et$_2$Me(TCNQ)$_2$ complex.

Atom	Molecule A	Molecule B
C1	−0.033	−0.034
C2	−0.033	−0.034
C3	−0.033	−0.034
C4	−0.033	−0.035
C5	0.188	0.195
C6	0.188	0.193
C7	−0.083	−0.088
C8	−0.082	−0.088
C9	0.017	0.014
C10	0.017	0.010
C11	0.016	0.014
C12	0.015	0.011
N1	0.095	0.095
N2	0.095	0.095
N3	0.095	0.095
N4	0.095	0.095

the Knight shift of a nucleus scales by its A_j value, the C5 and C6 resonances are expected to be shifted to the low magnetic fields and those of C7 and C8 sites — to the high fields. Thus the line at 293.8 ppm is attributed to C5 and C6, and this at −43.5 ppm to C7 and C8 carbons. On the contrary, the resonances of hydrogen-bonded carbons, almost unaffected by the electron transfer on molecule, should remain unshifted. Consequently we assign the line located at 131.7 ppm to these carbons. The remaining resonance at −38.9 ppm corresponds to the carbons of cyan groups. This definitive assignment of ^{13}C resonances in high resolution NMR spectrum of S + Et$_2$Me(TCNQ)$_2$ complex is presented in Fig. 1b; we stress that the attribution of TCNQ resonances given in [2] is wrong.

There are two additional pieces of information which arise from the spin density calculations. First, the crystallographic studies of the systems showed that due to the "ring over bond" arrangement of TCNQ in the stacks there is a high molecular overlap between C5–C7, C6–C8, C9–C11 and C10–C12 carbons of adjacent molecules. As the two first sequences present a high (positive or negative) spin density on both carbon sites within the sequence, they constitute the way for conducting electrons in the stacks. Secondly, we have plotted the experimental Knight shifts of TCNQ resonances as a function of A_j constants resulting from calculated spin density distributions. The $K_j(A_j)$ dependence is linear with the slope directly proportional to the Pauli susceptibility of the system. The estimated χ_P value, $\chi_P \approx 15 \times 10^{-4}$ emu/mole is comparable with the susceptibility values found for the other conducting TCNQ complexes.

According to the temperature variation of resonance position (temperature range $300 < T < 350$, as an example Fig. 1c shows the spectrum of complex at $T = 350$ K), the ^{13}C resonances of $S+Et_2Me(TCNQ)_2$ can be divided into two groups. The resonances of $S+Et_2Me$ cation located at 7.0, 25.0 and 45.6 ppm and those of quinone ring sites at -43.5 and 131.7 ppm are practically temperature independent. On the other hand, the positions of the remaining resonances of the cation, at 4.3 and 63.0 ppm and these of carbons from the ends of TCNQ molecule (at -38.9 and 293.8 ppm) are strongly temperature dependent. A careful analysis revealed a singularity in the temperature dependence of resonance position centered at $T = 330$ K and accompanied by a large hysteresis around this temperature, of ≈ 10 K. In the case of $-C\equiv N$ and $-CH_2-$ sites, a jump of resonance position of ≈ 20 ppm was also observed (Fig. 3). We interpret this behaviour as a sign of a structural phase transition occurring in the cation sublattice and consisting in a reorientation of one of the ethyl groups of $S+Et_2Me$. (Both cation orientations are present in the structure in the transition temperature range; see Fig. 3) Such reorientation should influence the spin density distribution on the TCNQ anions, at least on the sites from the ends of molecule structurally close to the ethyl group. This is the reason for the abrupt change of the shift of $-C\equiv N$ resonance at phase transition. The singularity in the Knight shift of the C5 and C6 carbons is much less marked as these sites are further of cations [2] and the spin density on the sites surrounding them is small. As the cyan groups are not involved in conduction process it explains the lack of any signature of the phase transition in the electrical transport parameters.

A quantitative analysis of temperature dependence of T_1 relaxation times of $S+Et_2Me(TCNQ)_2$ carbons is difficult because of small intensity and recover of resonances of sites involved in phase transition; in addition the temperature of high resolution NMR experiment was limited above the transition to $T \approx 350$ K. The relaxation rate $1/T_1$ which is thermally activated below the phase transition and of about 1 s^{-1} decreases by the factor of two and change the character at $T = 330$ K; above the transition $1/T_1$ decreases when temperature increases. This behaviour, although observed for all cation resonances, is particularly marked for the ethyl carbons which exhibit also a singularity of Knight shift at the transition. As the system is conducting, the observed T_1 and Knight shift values should obey Korringa law; actually it seems to be the case, but the precise verification of this relation is charged with a large experimental error.
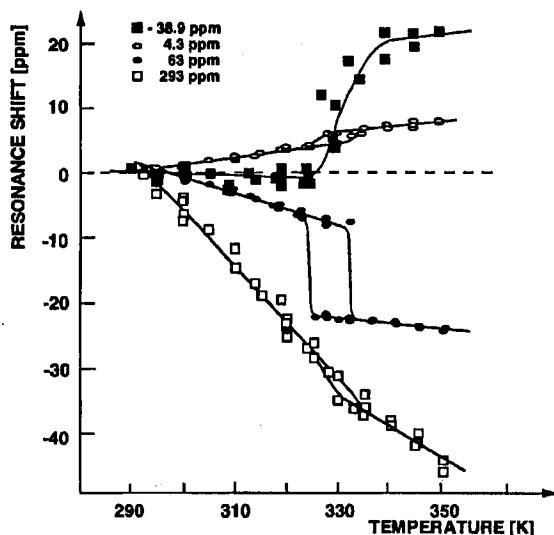
Fig. 3. Temperature dependence of resonance position for the resonances of S+Et$_2$Me cation carbons located at 4.3 and 63.0 ppm and for the carbons from the ends of TCNQ molecule, at -38.9 and 293.8 ppm; the shifts are reported to the respective room temperature positions of resonances.

4. Conclusions

^{13}C high resolution NMR study confirms a conducting character of S+Et$_2$Me(TCNQ)$_2$. The spread of complex spectrum over ≈ 350 ppm is due to the shifts of TCNQ carbon resonances with respect to these of neutral molecule. The shifts are of metallic (Knight) type and reflect an inhomogeneous spin density distribution over the anion. The anomaly in temperature variation of Knight shifts and T_1 relaxation times occurring at $T = 330$ K is due to the reorientation of one of ethyl groups of cation in crystal structure. This structural phase transition is not observed in electrical transport measurements as it affects TCNQ carbon sites not involved in the charge conduction.

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