Structural Transition in the Quasi-Two-Dimensional Organic Superconductor $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br Studied by $^{13}$C MAS NMR**

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Several superconducting charge transfer salts with various counteranions have been synthesized with the BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene, abbreviated as ET) molecule[1,2] Among these, $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br (here referred to as the $\kappa$-Br salt) has the highest critical temperature at ambient pressure ($T_c = 11.6$ K) [3]. An important question about these compounds concerns the influence of the non-centrosymmetric anion ordering on the electronic properties at low temperature. The issue has already been investigated in detail in the context of one-dimensional conductors such as (TMTSF)$_2$ClO$_4$.[4] In two-dimensional ET salts, another kind of ordering effect occurs due to the freezing of the ethylene groups of ET but the relationship between electronic properties and ordering remains so far an unsettled question. The quasi-two-dimensional (2D) crystal structure of $\kappa$-(ET)$_2$-Cu[N(CN)$_2$]Br is orthorhombic ($a = 12.9$ Å, $b = 30$ Å, $c = 8.5$ Å, space group Pnma) with alternating conducting layers composed of ET–ET face-to-face dimers and insulating layers of Cu[N(CN)$_2$]Br polymeric anion chains along the $c$-axis in $ac$-planes.[5] The two terminal ethylene groups of ET molecules adopt two different conformational positions: staggered or eclipsed. As the activation energy between these conformations is small, at room temperature the motion between the two positions is very fast, but at lower temperature, the ethylene groups freeze out in an ordered eclipsed configuration (the same effect exists in $\kappa$-Cl but only partly in $\kappa$-I, where two groups are eclipsed for one staggered).

Conventional X-ray studies of $\kappa$-X salts (X = Cl, Br, I) have not enabled any structural phase transition to be detected[5,6] whereas an X-ray “monochromatic” Laue photographic method has led to the observation of the formation of a superlattice that doubles the $c$ parameter at about 200 K in the $\kappa$-Br salt (but such an effect has not been detected in other structurally similar salts, such as $\kappa$-Cl, $\kappa$-I, $\kappa$-CN, and $\kappa$-Cu(NCS)$_2$).[7] $T_1$ ^1H NMR measurements on single crystals indicate a freezing of the ethylene motion around 200 K[8,9] and $^{13}$C NMR reveals a large and strongly inhomogeneous (Knight shift dependent) broadening of NMR lines at 180 K[10] or 150 K.[11]

In this work, we report high resolution $^{13}$C MAS (magic angle spinning) NMR experiments in $\kappa$-Br. First, we analyze the measured shift tensor to determine the electronic spin densities on central carbon sites. In the second part, we discuss the results of NMR measurements as a function of temperature, i.e., the splitting of the NMR lines below 250 K and evidence for an incommensurate transition at about 170 K.

We used a sample made of 10% of a powder compound that was 100% enriched on the central carbons of the ET molecule by the Larsen–Lenoir method[6,12] and of 90% of a non-enriched compound. The use of the MAS method[13] to average dipolar interactions enables us to obtain narrow lines. There are four dimers per unit cell but, because all the dimers are crystallographically equivalent and the dimmer contains an inversion center in accordance with orthorhombic structure, only two lines from the central carbons are expected.

In a first step, we used direct single-pulse irradiation of the $^{13}$C to examine enriched materials. As only central carbon atoms are enriched, only two peaks and their spinning sidebands due to the anisotropy of each site are expected. Figure 1 shows examples of the $^{13}$C single-pulse MAS NMR spectra that were recorded at 99.6 MHz on a Bruker MSL 400 spectrometer with spinning rates from 2.5 to 5 kHz. The NMR total shielding tensor in a metal is the sum of the chemical (orbital) and Knight (spin) shift tensors: $\mathbf{K}_{TOT}(T) = \mathbf{K}_{CHEM}(T) + \mathbf{K}_{S}(T)$. In a MAS NMR spectrum, each independent site provides a central line shifted from the bare Larmor frequency by the isotropic value of the shielding tensor $\mathbf{K}_{TOT}(T)$ plus spinning sidebands shifted by the spinning frequency.

Changing the spinning rate allows the central lines to be identified, which gives the isotropic shifts directly. The large number of sidebands for both lines is due to the strong anisotropy of the shift tensors. The principal values of the shift tensors were determined from the ratio of the

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In accordance with the fact that the experimentally determined principal axes of the Knight shift tensor do not coincide exactly with those of the ET molecule, Soto et al. assigned the higher $K_{zz}$ ($K^I$) to the outer site, based on the angular study of the line positions and the linewidth. In contrast, Mayaffre et al. attributed the higher $K_{zz}$ ($K^I$) to the inner site, with the assumption that the anisotropy of the two tensors is due in a first approximation to the electron density of the 2p orbitals of the carbon atoms. We chose this second assignment in accordance with our following measurements of spin density on the two central carbon atoms.

In a second step, we used a cross-polarization pulse sequence to examine the ethylenic and intermediate carbon nuclei. In a cross-polarization sequence, the proton magnetization is transferred to the carbon nuclei. The magnetization transfer depends on the contact time and on the distance between protons and $^{13}$C nuclei. It occurs via $^1$H–$^{13}$C dipolar couplings and is turned on by simultaneous irradiation of both channels during the contact time. For very short distances, the transfer occurs rapidly whereas at larger distances the thermodynamic equilibrium between proton and carbon spins requires a longer time to become established; a longer contact time is then needed. By using very short contact time in the cross-polarization sequence, we suppress all the carbon lines except those of the terminal carbons because of their proximity to the protons. The rapid movement of ethylenic groups causes these lines to be averaged and thus to appear as very narrow. By optimal choice of the contact time, we aimed to separate the lines due to the intermediate and central carbon nuclei. Although the intermediate carbon atoms are closer to the protons than the central ones, the partial enrichment of the sample on the central positions enhances the intensity of the lines from the central carbon nuclei. Thus, for a given contact time, comparable intensity is found for both classes of carbon nuclei and it is impossible to separate the two classes. Finally, we found the following shifts: for the terminal carbon nuclei, 31 ppm with no shift anisotropy, and for the intermediate carbon nuclei, two poorly resolved lines around 135 ppm and 125 ppm with an anisotropy of nearly 150 ppm (see Fig. 3).

**Determination of Spin Densities on the Two Central Carbon Atoms:** The spin densities on the central carbon and the neighboring sulfur nuclei were calculated using a simple model based on dipolar interactions. The Knight shift is due in a first approximation to the dipolar interaction between the 2p electrons and the nuclear spin. The anisotropy of the tensor reflects the anisotropy of the 2p orbitals and the amplitude of this anisotropy is related to the spin density at the carbon site. We found, in accordance with our hypothesis, that the inner site has a stronger anisotropy than the outer site and thus a larger spin density. To evaluate the spin densities more precisely, we introduced dipolar interactions between the orbitals of near-neighbor nuclei (carbon and sulfur nuclei) and the carbon nucleus, taking

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**Fig. 1.** $^{13}$C MAS NMR spectra of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br at a) 300 K with 5 kHz spinning rate and b) 200 K with 4.15 kHz spinning rate. "1" and "2" mark the two isotropic shifts of the central carbon atoms. The splitting of the line 1 shown in (b) appears below 250 K. This splitting is actually better seen in the conducting CHEM and the different distance of each central carbon to the inversion center of a dimer (Fig. 2). We call the site closer to the center inner and the other one, outer.

**Fig. 2.** Site labeling in the BEDT dimer.
The spin densities at the sulfur nucleus and at the neighboring carbon atoms are proportional to each other. We then calculate the spin densities for the two central carbon sites and the sulfur atoms. We obtain the following spin densities for carbons: \( f_C^{\text{inner}} = 0.0500 \) and \( f_C^{\text{outer}} = 0.0375 \). These are in accordance with the measurements on the \( \kappa \)-Cu(NCS)\(_2\) salt made by Vainrub\(^{[18]} \) (\( f_C = 0.0426, 0.0433, 0.0521, \) and 0.0688; the structure of this salt gives four different central carbon sites). For the sulfur atoms we obtain \( f_S^{\text{inner}} = 0.39 \) while a semi-empirical calculation\(^{[19]} \) gives a spin density almost twice that on the central carbon atoms. It is rather unlikely that the sulfur atom, which is more electronegative than the carbon atom, has a lower spin density. However, the effect of the sulfur atoms enters only as a small correction in the total Knight shift, so that our data are not very sensitive to it. Moreover, the constant \( A_C^{\text{dip}} \) used for the dipolar interaction between the 3p\(_z\) orbital of sulfur and the carbon nucleus is probably overestimated: the carbon–sulfur dipolar field was calculated by approximating the average of 1/3 over the 3p\(_z\) orbital of sulfur atom by 1/r\(_{CS}\). This approximation does not take into account the difference of electron spatial distribution between 2p\(_z\) and 3p\(_z\) orbitals.

Temperature Dependence of the Isotropic Knight Shifts: If it is assumed that the chemical shift is temperature independent, the variation of the total shift is due to the variation of the Knight shift. Figure 4 shows this dependence with temperature. According to Equations 2–4, this weak decrease is due to susceptibility and this decrease is exactly the same as that recorded by Vainrub\(^{[18]} \) in \( \kappa \)-(ET)\(_2\)-Cu(NCS)\(_2\). Below 260 K a splitting of the line with the greatest Knight shift (inner site) is clearly observed. It is the first time that such a splitting has been observed in this type of compound. This splitting increases as the temperature decreases (0.1 ppm at 253 K, 16 ppm at 233 K, and 18 ppm at 213 K down to 183 K). Above 193 K no splitting appears (nearly 1.5 ppm). However, considering the linewidth (0.5 ppm), this effect may exist at higher temperature without being observed. We think that the split-
tings of the two lines appear at the same temperature and are actually due to the same phenomenon. The amplitude of the splitting is related to the Knight shift of the site. It is not possible to evaluate the anisotropic shift tensor because of the weakness of the splitting, but the two new lines resulting from the splitting seem to have different anisotropies.

At 173 K, a spectacular change in the spectra arises suddenly. The outer site line becomes dramatically broader (~20 ppm) while the inner site line disappears. This effect, already noticed by Mayaffre et al.\(^{[10]}\) is explained by a broadening proportional to the Knight shift. This broadening is so important for the inner site (because of its strong Knight shift) that on the scale of our measurements the line is averaged and no side band can be observed. We verified by cross-polarization sequences that the shift of ethylenic carbon nuclei is independent of the temperature (in agreement with the absence of a Knight shift). At 183 K, a broadening by a factor of about three of the narrow line arising from the terminal carbon atoms allows us to measure the freezing temperature of the ethylenic groups. Measurements carried out on a single crystal (Fig. 5) showed such a dramatic broadening of the lines below 180 K\(^{[8,9]}\) or 150 K.\(^{[10]}\) This broadening strongly depends on the Knight shift. For the orientation of magnetic field used for Figure 5 (field in the plane of the molecules), the line c, for which the Knight shift is zero, is not broadened. The broadening seems to be proportional to the Knight shift.

![Fig. 5. \(^{13}\)C NMR spectra at different temperatures of a single crystal of \((\text{ET})_2\text{Cu}(\text{NCS})_2\text{Br}\) with the magnetic field parallel to the molecular plane.](image)

We attribute this evolution of the spectra with temperature to an incommensurate distortion of the electron density. In the organic superconductor \((\text{ET})_2\text{Cu}(\text{NCS})_2\), such a transition has been observed by a neutron diffusion study.\(^{[20]}\) The freezing of the ethylene groups in eclipsed or staggered conformations explains the existence of an incommensurate modulation around 180 K. Other evidence of this phenomenon has been provided by Vainrub et al.\(^{[21,22]}\) by means of MAS NMR measurements and theoretical analysis in terms of weak Anderson localization. The spectra showed a relatively weak temperature dependence from room temperature to 210 K, a dramatic broadening of the lines of central carbons of ET molecules appearing below 200 K. The \(\kappa\)-Br salt displays the same behavior as \((\text{ET})_2\text{I}_3\). A large broadening of the NMR line is observed around the freezing temperature of the ethylene groups and this broadening could be explained by an incommensurate transition of the electronic density. However, the X-ray “monochromatic” Laue photographic studies suggest a commensurate transition due to a displacement of anions chains along the \(c\)-axis, which is not in accordance with our measurements because such a commensurate transition would only split the line. However, Nogami et al.\(^{[7]}\) have deduced a commensurate transition from measurements of the \(ac\)-plane component of the modulation vector (the \(b^*\) component could not be resolved because of the great value of the corresponding unit cell parameter). Therefore we may expect that the interplane \((b^*)\) component of modulation vector is non-fractional and so creates incommensurability.

An important question concerns the relationships between this transition and the freezing of ethylene groups. Our measurements seem to show that the temperature of \(\text{CH}_2\) freezing and the temperature of this transition are very close (as for \(\beta_{\text{ET}}(\text{ET})_2\text{I}_3\)). The displacement seen in diffuse X-ray scattering experiments should have been detected in a NMR study, which is a more sensitive technique. As nothing else in this temperature range occurs, we think that the appearance of a superstructure and the broadening of lines are due to the same physical phenomenon. Most likely, the freezing of ethylene groups is involved in the transition, but since this can only produce a commensurate modulation, it cannot be entirely responsible for the observed phenomenon. The structural modifications caused by the freezing of the ethylene groups can nevertheless help the stabilization of an electronic incommensurate transition. The incommensurate distortion of the lattice sets in only when the configuration of the ET molecules is fixed.

As for the splitting observed below room temperature, this may perhaps be related to a loss of symmetry (distortion) of the orthorhombic structure. Indeed, another compound of the \(\kappa\)-ET family, \(\kappa\)-(ET)_2Cu(NCS)_2, has a slightly monoclinic structure and shows many physical properties similar to those of \((\text{ET})_2\text{Cu}(\text{NCS})_2\text{Br}\). The fact that the line is doubled means that only one symmetry element is destroyed. The loss of the inversion center of each dimer probably requires more energy than the loss of the equivalency between all the dimers in the unit cell. Therefore, the inversion center of each dimer should be preserved in a first approximation.
In conclusion, this work reports the first high resolution $^{13}$C NMR study of the organic superconductor $\kappa$-(ET)$_2$-Cu[N(CS$_2$)$_2$]Br via MAS and cross-polarization techniques with $^{13}$C-enriched ET molecules. The Knight shift tensor of the central carbon atoms has been derived. A lowering of the symmetry below 273 K has been deduced from the splitting of the $^{13}$C MAS NMR lines of the central carbons. A distortion of the organic lattice occurs below about 200 K when the motion of the ethylene groups is frozen. The incommensurate character of the distortion is implied by the inhomogeneous broadening of the NMR lines. This feature rules out the commensurate nature claimed from earlier diffuse X-ray scattering experiments.

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Fabrication of Magnetic Spider Silk and Other Silk-Fiber Composites Using Inorganic Nanoparticles**

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Spider dragline silk is a semicrystalline biopolymer with a unique combination of high tensile strength, high elasticity, and high modulus. The 0.2 to 10 $\mu$m diameter silk fibers have a higher breaking energy than other natural or synthetic fibrous polymers, far exceeding that of high tensile steel and Kevlar on a weight-for-weight basis.[3] Thus, silk fibers could have important applications in impact-proof textiles or other structural fabrics where strong, flexible materials are desirable. Moreover, the inherent biocompatibility of silk could be exploited in the preparation of new strong biomaterials for use in artificial tendons or non-allergenic sutures.[2] A further possibility might be to modify the properties of silk fibers by integration with those of other materials to give functionalized hybrid composites with enhanced or entirely new applications. For example, cross-linking of dragline silk fibers with organic polymeric precursors produces an apparent improvement in the tensile strength.[3]

Although silk is a highly hydrophobic, insoluble biopolymer, it has recently been shown that dragline spider silk can undergo a reversible transformation to a supercontracted state when placed in water or polar organic solvents.[4] These observations suggest a possible general route to the functionalization of silk fibers by aqueous-based interactions with the modified supercontracted state. In this paper we describe a specific approach in which hybrid silk materials are prepared by binding inorganic nanoparticles to the surface and near-surface regions of silk fibers immersed into colloidal sols.

Our main focus has been on the fabrication of magnetic spider silk fibers. Bundles of ca. 200 individual silk fibers were prepared by cutting 3 cm lengths of dragline spider silk from a continuous spool produced by *Nephila edulis*. We used dragline silk originating from the Major Ampullate glands, and the threads were drawn mechanically from immobilized but fully awake spiders at a speed of 2 cm/s onto either 1 cm diameter glass tubes or photographic slide frames. These bundles were suspended by tweezers and

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