Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: M. Peo , J. C. Scott & E. M. Engler (1985): Proton NMR Study of the SDW in $(TMTTF)_2$ SCN, Molecular Crystals and Liquid Crystals, 119:1, 303-306

To link to this article: http://dx.doi.org/10.1080/00268948508075175

Mol. Cryst. Liq. Cryst. 1985, Vol. 119, pp. 303-306
0026-8941/85/1194-0303/$10.00/0

Printed in the United States of America

PROTON NMR STUDY OF THE SDW IN $(TMTTF)_2SCN$

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Abstract Proton NMR measurements (T_{2*}, T_2 and T_1) have been made on $(TMTTF)_2SCN$ at temperatures between 4 and 300 K. Two maxima in the spin lattice-relaxation rate, near 60 K and 110 K, are associated with the rotational motion of the methyl groups. The metal insulator transition, at 160 K, is signaled by only a very weak anomaly in T_1. Inhomogeneous line broadening below the spin-density-wave transition, at 8.8±0.1 K, indicates a SDW amplitude of order 10%. A strong asymmetric lambda anomaly is observed in the relaxation rate at the transition. When compared to earlier results on TMTSF analogs, these data imply that the nature of the spin-density-wave ground state is surprisingly little affected by the opening of the gap at 160 K.

The organic conductor $(TMTTF)_2SCN$ is known, on the basis of susceptibility measurements,[1] to have an antiferromagnetic ground state below a transition temperature of about 10 K. On the other hand the the conductivity reveals a metal-insulator transition in the vicinity of 160 K.[1] Therefore the transition to the antiferromagnetic ground state cannot be driven by Fermi-surface nesting, in the manner usually envisioned for a spin-density-wave instability.[2,3] The question then arises as to how the ground state, and the Néel transition differ between this material and the other Bechgaard salts, such as $(TMTSF)_2PF_6$[4,5] or $(TMTTF)_2Br$,[6,7] which have metal-insulator transition driven by SDW onset. In this paper, we report the results of proton NMR experiments which were undertaken in order to address this question. In particular, linewidth measurements are used to determine the amplitude of the antiferromagnetic order parameter, and spin-lattice relaxation rate measurements give information on the critical fluctuations in the vicinity of the Néel temperature.

Since the results of this study are reported in a paper recently accepted for publication elsewhere,[8] and since space is rather limited, we confine

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ourselves here to a summary of the important results. The reader is referred to ref. 8 for further details.

All measurements were performed using a high-power pulse NMR spectrometer, Bruker model CXP-100. The linewidth was determined from the characteristic free induction decay time (T_{2*}) of either the solid-echo (above T_N) or the spin-echo (below T_N). In the low temperature phase, we found the line to be inhomogeneously broadened, such that a spin-echo could be observed with a phase memory time (T_2) considerably longer than (T_{2*}). (See fig. 1a) This is the behaviour expected for the onset of antiferromagnetic order,[9,10] where the electronic moments create inhomogeneous local fields at inequivalent proton sites. Spin-lattice relaxation rates were obtained using standard inversion recovery techniques.

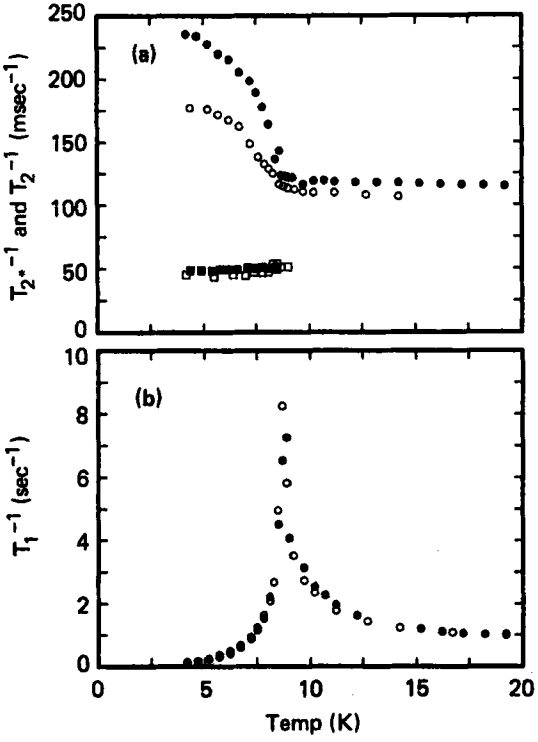

FIGURE 1. (a) Inverse linewidth (T_{2*}^{-1}, circles) and spin-echo relaxation rate (T_2^{-1}, squares) at 24.5 (open symbols) and 49 MHz (solid). Above the transition temperature (8.8 K) no spin-echo is observed. (b) Spin lattice relaxation rate (T_1^{-1}) at the same two frequencies.

Since an earlier attempt[11] to study the Néel transition of $(TMTTF)_2SCN$ had revealed no anomalous behaviour in the NMR properties, we took particular care to ensure that the temperature was stable and to determine, as accurately as possible, the sample temperature. By calibration *via* the superconducting transitions of niobium and tantalum, we are able to determine the phase transition temperature in $(TMTTF)_2SCN$ as 8.8 ± 0.1 K.

The magnitude of the inhomogeneous line-broadening below T_N (fig. 1a) corresponds to an internal local field distribution of width approximately 2-4 Gauss. Since the dipolar field of one electron occupying a wavefunction predominantly on the sulphur atoms is expected to wave a root-mean-square value of 50 Gauss at the proton sites,[12] we conclude that the antiferromagnetic sublattice magnetization in $(TMTTF)_2SCN$ is less than, but of order, 0.1 Bohr Magneton. This is comparable to the values obtained for the SDW systems $(TMTSF)_2PF_6$[10] and $(TMTTF)_2Br$.[6] Hence, surprisingly, it seems that the fact that $(TMTTF)_2SCN$ is insulating above T_N makes little difference to this ground state property.

We may understand this result if we view the metal-insulator transition (near 160 K) as Mott-Hubbard localization, brought about only indirectly by the anion-ordering which itself has no $2k_F$ component. The magnitude of the energy gap (~1000 K) compared to the conduction bandwidth (4000 K) corresponds to a localization length of roughly one-lattice spacing. A simple calculation shows that even for this moderate wavefunction overlap, the net spin density in each unit cell is reduced to 0.1 μ_B. In this (oversimplified) view the regime between 8.8 and 160 K is described as a paramagnetic insulator, with small disordered moments interacting antiferromagnetically with near neighbours along the chain. The Néel temperature is where these moments order three-dimensionally.

This picture is supported by the spin-lattice relaxation rate (T_1^{-1}) data around T_N. A pronounced lambda anomaly is observed, similar to that in three-dimensional antiferromagnets,[13] but the maximum relaxation rate, of about 10 sec^{-1}, is an order of magnitude less. On the other hand, it is considerably larger than that measured in the SDW systems, which have been found both experimentally[6,9,10] and theoretically[12,14] to show a weak logarithmic divergence due to fluctuations of the SDW gap. Since the amplitude of the magnetic moments vanish at the transition temperature, there is no direct coupling of critical magnetic fluctuations to the nuclei for the SDW case.

We extended the T_1 measurements over the entire range up to room temperature. Two additional anomalies are found at roughly 60 and 100 K. They can be attibuted to the thermally activated motion of the methyl groups, undergoing hindered rotation among three equivalent orientations. Both anomalies, including their frequency dependence are well described by the Bloembergen, Purcell, Pound relationship for a classical rotor.[15] We therefore conclude that the observation of two anomalies is related to the

presence of inequivalent methyl groups in the low symmetry crystal structure of $(TMTTF)_2SCN$.

Finally, there is only a very weak feature in the T_1 data near the metal insulator transition at 160 K, barely visible above the background. This is consistent with the view that the metal insulator transition is not accompanied by the onset of large localized moments.

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