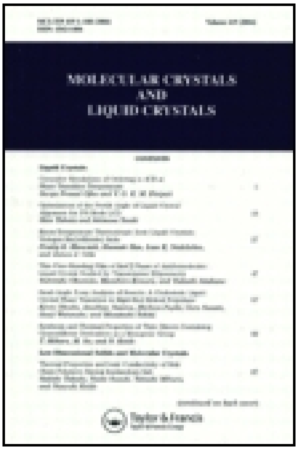

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Proton Magnetic Resonance Study of $(NMP)_x(Phenazine)_{1-x}TCNQ$

L. J. Azevedo [a], J. S. Miller [b] & A. J. Epstein [c]

[a] Sandla National Laboratories, Albuquerque, NM, 87185

[b] Dupont Central Research Station, Wilmington, DE, 19898

[c] Xerox Webster Research Center, Webster, NY, 14580

Version of record first published: 17 Oct 2011.

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 67-70
0026-8941/85/1204-0067/$10.00/0

Printed in the United States of America

PROTON MAGNETIC RESONANCE STUDY OF $(NMP)_x(PHENAZINE)_{1-x}TCNQ$

L.J. AZEVEDO
Sandia National Laboratories, Albuquerque, NM 87185

J.S. MILLER
Dupont Central Research Station
Wilmington, DE 19898

A.J. EPSTEIN
Xerox Webster Research Center
Webster, NY 14580

Abstract A nuclear magnetic resonance study of protons in the system $(NMP)_x(Phen)_{1-x}(TCNQ)$ has been undertaken for x= 0.49, 0.56, and 0.59 over the magnetic field range 1-110 kOe. We find that the spin lattice relaxation rate of protons which are hyperfine coupled to the electron spins is similiar to that observed for the organic conductor $Qn(TCNQ)_2$. In the lower temperature, high field region when the Zeeman splitting of a free electron is comparable to or greater than the temperature, the relaxation rate exhibits an exponential decrease. Diffusion rates for the conductivity as determined from the proton relaxation rate behavior do not agree with the conductivity results on the same samples suggesting that the nuclear spin relaxation in these materials is not dominated by conduction electrons.

INTRODUCTION

In the conducting organic system $(NMP)_x(Phen)_{1-x}(TCNQ)$, variation of the band filling parameter, x, results in substantial changes in conductivity[1] and susceptibility.[1,2] The role of the phenazine is to provide a neutral donor. In order to more fully understand the electronic properties of this system we have employed NMR as a local probe of the electronic motion. The details of the field and temperature dependence of the nuclear spin lattice relaxation rate can provide a microscopic picture of the electronic motion in the case where the electron and nuclear coupling is strong.

EXPERIMENTAL DETAILS

The proton relaxation rates were measured used a pulsed NMR spectrometer capable of operating over the range 1-1000 MHz. In all cases presented here the recovery of the magnetization was exponential over one decade, however, at some intermediate fields and temperatures non-exponential rates were observed.

RESULTS

In Fig. 1 we show the proton spin lattice relaxation rates for the x=0.49 sample at several fields vs temperature. The qualitative behavior is similiar for all x studied. In the low temperature regime the relaxation rates are strongly temperature and field dependent. These results are also similiar[3] to those of $Qn(TCNQ)_2$. The magnetic field dependence at a temperature of 70K for all 3 samples is shown in Fig. 2 on a logarithmic scale. First note that in the high field regime that the relaxation rate closely follows the expression $T_1^{-1} = AH^{-1/2}$ where T_1^{-1} is the nuclear spin lattice relaxation rate, A is a constant and H is the applied magnetic field. In the low field regime the relaxation rate of the x=0.49 sample approaches a constant value below fields of 5 kOe.

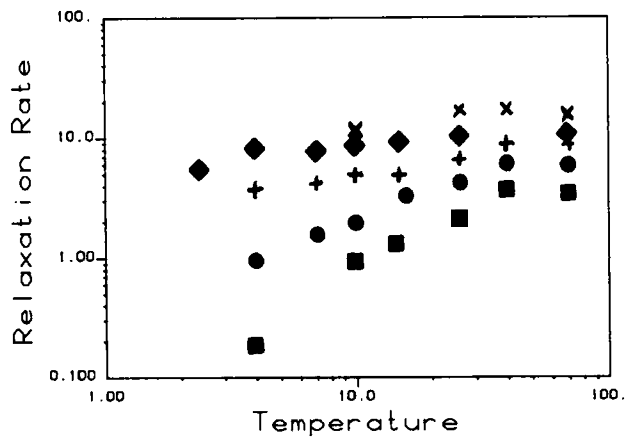

Fig. 1. Proton relaxation rate in sec^{-1} vs temperature for 110 kOe(squares), 55 kOe(circles), 27 kOe(crosses), 13 kOe(diamonds), and 5 kOe(X) for x=0.49.

DISCUSSION

It is well known that an inverse square root dependence relaxation rate can be interpreted in two ways. One obtains this dependence if the nuclear relaxation is to a spin diffusing rapidly in one dimension. Another way to obtain this field behavior is nuclear spin relaxation to a fixed paramagnetic impurity. Which behavior is dominant must be determined by a careful analysis of the results and determination(if one dimensional diffusion is the correct picture) of diffusion constants.

We have analysed these results under the assumption that nuclear spin relaxation is to a one dimensional diffusion process. In the situation where the electronic Larmor frequency is less that the longitudinal diffusion rate, $D_{\parallel}$, and greater than the perpendicular diffusion rate, $D_{\perp}$, then the relaxation rate is given by[4] $T_1^{-1} = \Omega^{+}/(2D_{\parallel}\omega_e)^{1/2}$ where the electron-proton hyperfine coupling constant and the electronic Larmor frequency.

Since a cutoff (i.e. the relaxation rate approaches a co instant at low field) is observed for the x=0.49 sample we can use the above analysis to determine both the transverse and longitudinal diffusion constants. The result is $D_{\perp} = 8 \times 10^{10}\ sec^{-1}$ and $D_{\parallel} = 10^{12}\ sec^{-1}$. Unfortunately, since all the samples display similiar relaxation rates in the high field, high temperature regime, this implies that they must have similar diffusion rates for conduction if the relaxation mechanism is due to one dimensionally diffusing charge carriers. Since the conductivity data for these values of band filling differ substantially in this temperature range the nuclear relaxation must be due to another mechanism, and not 1D diffusion of the conduction electrons as earlier proposed[5] for $Qn(TCNQ)_2$.

CONCLUSIONS

We have shown that the proton spin lattice relaxation rn $(NMP)_x(Phenazine)_{1-x}TCNQ$ is not due to the one dimensional diffusion of charge carriers. Similiarities with proton relaxation data in $Qn(TCNQ)_2$ suggest that disorder may play an important role in these materials.

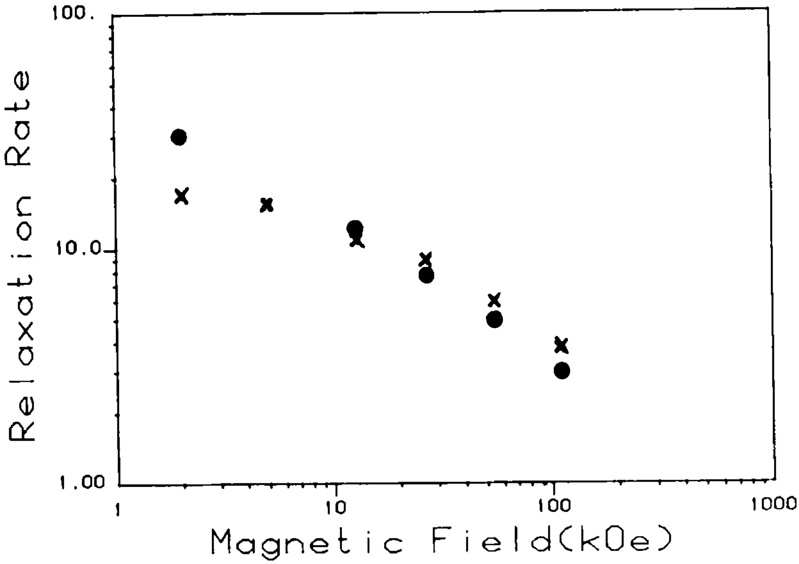

Fig. 2. Relaxation rate at 70 K for the x=0.59 (circles) and x=0.49 (X) samples vs. magnetic field. The data for x=0.56 are nearly identical to those of x=0.49.

ACKNOWLEDGEMENTS

We wish to acknowledge the expert technical assistance of D. T. Stuart. This work was supported by the U.S. Dept. of Energy under Contract Number DE-AC04-76-DP00789 and Office of Basic Energy Sciences, Materials Science Division.

REFERENCES

1. A.J. Epstein, J.W. Kaufer, H. Rommellmann, I.A. Howard, E.M. Conwell, J.S. Miller, J.P. Pouget and R. Comes, Physical Review Letters, 49, 1037(82).
2. A.J. Epstein and J.S. Miller in The physics and Chemistry of Low Dimensional Solids, ed. by L. Alcacer(D. Reidel, Holland, 1980)p. 339.
3. L.J. Azevedo, W.G. Clark, E.O. McLean and P.F. Seligmann, Solid State Comm, 16, 1267(75).
4. F. Devreux and M. Nechschein, in Quasi-One-Dimensional Conductors I, Proceedings of the International Conference, Dubrovnik, 1978, edited by S. Barisic et. al., Lecture Notes in Physics Vol. 95 (Springer, NY, 1979), p. 145.
5. F. Devreux, M. Nechtschein, and G. Gruner, Phys. Rev. Lett. 45,53(1980).