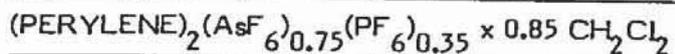


NMR STUDY OF THE QUASI-ONE DIMENSIONAL ORGANIC METAL



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ABSTRACT

Measurements of the temperature and frequency dependences of the proton spin lattice relaxation rate and of the proton and carbon Knight shifts in the title compound are presented. The results are interpreted in terms of a quasi-one dimensional microscopic conduction electron mobility and of the local unpaired spin densities at the carbon sites of the perylene donor molecules. An estimate is given for the mean residence time τ_{\perp} of a conduction electron on a stack of perylene molecules, $\tau_{\perp} \approx 3.5 \cdot 10^{-10}$ s.

INTRODUCTION

From measurements of the dc-conductivity [1] and of the thermo power [2] it is known that the title compound (subsequently referred to as "the perylene salt") is a quasi one-dimensional conductor. From the increase of its conductivity with decreasing temperature T (down to $T \approx 180$ K, where a phase transition takes place) it is concluded that it is an organic metal. This conclusion is supported by the thermo power data. These and other measurements [3,4] probe crystals of the perylene salt on the macroscopic level. NMR offers the possibility to probe them on the microscopic level. With this in mind we performed NMR experiments of two types. First, we measured the spin-lattice relaxation rate $1/T_1$ of the protons in the perylene salt as a function of both the temperature T and the Larmor frequency ν_L . These measurements were supplemented by a study of the spin-lattice relaxation rate in the rotating frame, $1/T_{1\rho}$. The general result of this part of the study is (i) a confirmation of the one-dimensional nature of the conductivity of the perylene salt on the microscopic level and (ii) an estimate of the mean residence time τ_{\perp} of a conduction electron on a given stack of perylene molecules, see below. The second type of experiments concerned the Knight shifts of both the protons and carbons in the donor molecules perylene. The spin densities derived from these data point to the formation of an "easy" path for the migration of the conduction electrons along the stacks of perylene molecules in crystals of the perylene salt.

EXPERIMENTAL

The temperature dependence of $1/T_1$ was measured in a field $B_0 = 6.3$ Tesla ($\nu_L = 270$ MHz) by pulsed NMR methods. Powder samples were used. The results are presented in Fig. 1. The dependence of $1/T_1$ on ν_L was measured at six frequencies ranging from 20 MHz to 270 MHz, see Fig. 2. The spin-lattice relaxation rate in the rotating frame, $1/T_{1\rho}$, was measured at $\nu_L = 270$ MHz for $\nu_1 = \gamma B_1/2\pi$ in the range $15 \text{ kHz} < \nu_1 < 150 \text{ kHz}$. Knight shifts of protons were measured using a combination of line-narrowing multiple pulse sequences [5] and rapid magic angle sample spinning (MASS) [6]. These techniques are required to suppress the dipole-dipole interactions of the protons which otherwise would mask totally the (small) Knight shifts. The Knight shifts of the C-13 nuclei were measured using proton-carbon cross polarization, proton decoupling and MASS. To overcome problems with the limited penetration depth of the rf in the conducting material, sparking in the presence of high rf fields which are required for decoupling, and eddy currents in the rapidly spinning samples we used finely powdered samples diluted in KBr (dilution ratio 1:7).

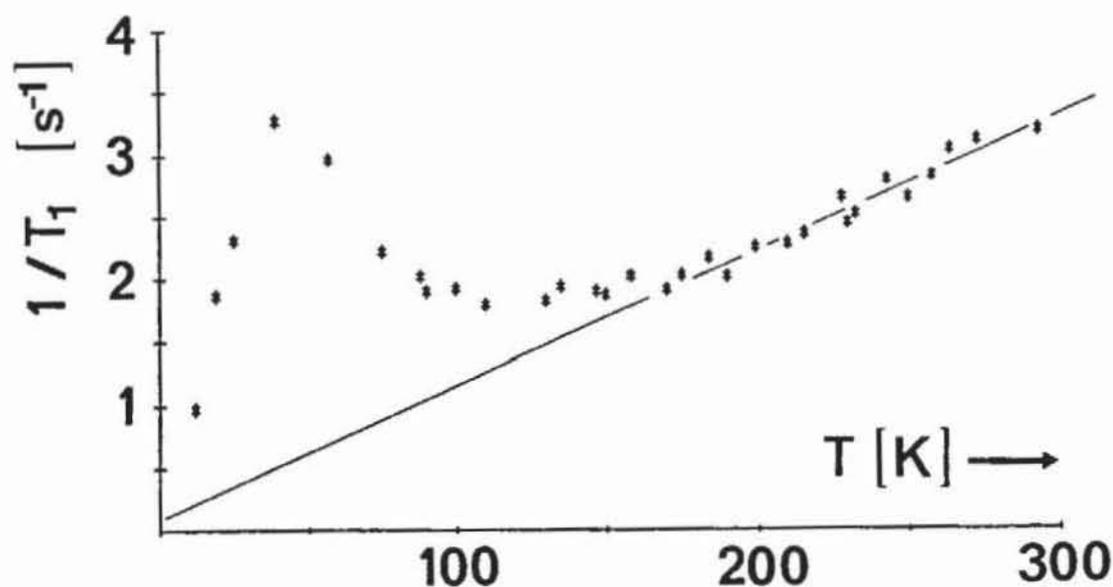


Fig. 1. Temperature dependence of the proton spin-lattice relaxation rate $1/T_1$ of the perylene salt. The Larmor frequency is 270 MHz.

RESULTS AND DISCUSSION

a) relaxation

For $T > 180$ K the relaxation rate $1/T_1$ is proportional to T (see Fig. 1). This is the expected behaviour of a nuclear spin system relaxed through its coupling to the spins of a degenerate Fermi electron gas. The data in Fig. 1 therefore support the view that the perylene salt is an organic metal for $T > 180$ K. At $T \approx 180$ K a phase transition takes place and the material becomes a semi-conductor. Other relaxation mechanisms than the

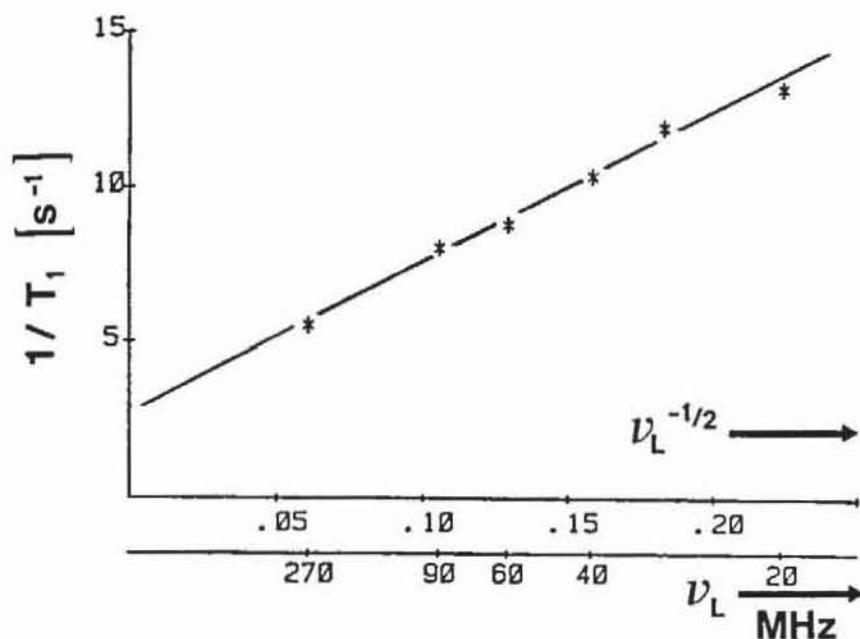


Fig. 2. Dependence of the proton spin-lattice relaxation rate $1/T_1$ of the perylene salt on the Larmor frequency ν_L . The temperature is $T = 296$ K.

coupling to the conduction electrons become dominant for the protons. The peak of $1/T_1$ vs. T at $T \approx 50$ K is associated, in particular, with their coupling to the F-19 spins of reorienting PF_6 groups. With respect to the temperature dependence of $1/T_1$ the perylene salt behaves analogously to the fluorantene salts studied by Mehring *et al.* [7]. In Fig. 2 we have plotted the dependence of $1/T_1$ on the Larmor frequency ν_L . Two scales are shown, the lower one gives ν_L directly, the upper one is linear in $\nu_L^{-1/2}$. As can be seen $1/T_1$ is linear on this scale. It is well known that a linear dependence of $1/T_1$ vs. $\nu_L^{-1/2}$ signalizes a one-dimensional motion of the spins which relax the nuclei, provided their correlation time τ_c is short enough. This means that the one-dimensional motion of the conduction electrons in the perylene salt inferred from the macroscopic measurements mentioned above is also confirmed on the microscopic level. The correlation time involved which we now call τ_u because it relates to the motion of the electrons along the stacks, can be estimated from the Fermi energy $\mathcal{E}_F: \tau_u = a\sqrt{m_e/2\mathcal{E}_F}$ (a = distance of the perylene molecules along the stacks, $a = 4.29$ Å; m_e = eff. electron mass). \mathcal{E}_F is known from measurements of the thermopower and the optical reflexion coefficient, $\mathcal{E}_F = 0.65$ eV [2,3] from which $\tau_u \approx 10^{-15}$ s follows. This is certainly short enough for determining the dimensionality of the motion via the $1/T_1(\nu_L)$ dependence. The $\nu_L^{-1/2}$ proportionality of $1/T_1$ is expected to break down when the Larmor frequency becomes so low that the effective probing time T_{eff} of the spin system in the relaxation experiment becomes longer than the mean residence time τ_L of an electron on a given stack. For $T_{eff} > \tau_L$ the material appears as three dimensional to the relaxation experiment. The theory of nuclear spin relaxation by conduction electrons tells that the effective probing time T_{eff} is equal to the electronic Larmor period $T_{Le} = 1/\nu_{Le}$ in the applied field B_0 [8]. Unfortunately we could not access fields B_0 low enough to make $T_{Le} > \tau_L$. However, we

have measured $1/T_{1\rho}$ at low enough rotating fields B_1 . Theory suggests that $1/T_1(\nu_L) = 2/T_{1\rho}(\nu_L)$ for $\nu_L = \nu_1$ [9]. In the range $15 \text{ kHz} < \nu_1 < 150 \text{ kHz}$ $1/T_{1\rho}$ was found to be essentially constant and equal to about 40 s^{-1} . The extrapolation of both the $1/T_1$ and $1/T_{1\rho}$ data sets leads to an intersection at $\nu_L \approx 0.35 \text{ MHz}$ corresponding to $\nu_{Le} \approx 230 \text{ MHz}$. The relation $2\pi \cdot \nu_{Le} \cdot \tau_L = 1/2$ where ν_{Le} is to be taken at the intersection then finally gives $\tau_L \approx 3.5 \cdot 10^{-10} \text{ s}$.

b) Knight shifts

Fig. 3a shows a proton NMR spectrum of the perylene salt recorded while the sample was irradiated with the BR-24 multiple pulse sequence [10] and, at the same time, spun about the magic angle at a rate of 2.5 kHz. Fig. 3b shows a similarly recorded spectrum from pure perylene. We take the position of the line from pure perylene as the reference for the Knight shifts in the perylene salt. Four resonances (1) ... (4) are discernible in the spectrum of the salt. Peak (4) is from adamantane, a small amount of which was added to the sample for spectrometer adjustment reasons and for providing an internal reference.

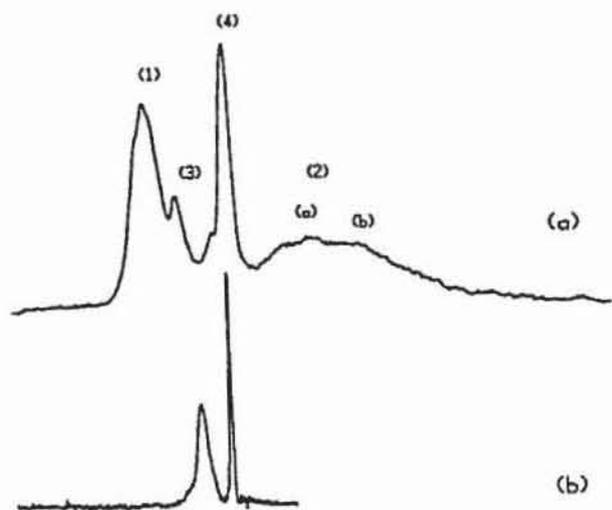


Fig. 3. High resolution proton spectrum of the perylene salt (a) and of pure perylene (b). The separation of peaks (1) and (4) is 13 ppm. A MREV-8 sequence was used for spectrum (a), whereas spectrum (b) was recorded using a BR-24 multiple pulse sequence.

Peak (3) is from inclusions of CH_2Cl_2 which was used as a solute during the crystallization of the perylene salt. This interpretation of peak (3) was checked by recording an analogous spectrum from a sample in which the perylene molecules were nominally fully deuterated. In this spectrum peak (3) has a much stronger relative intensity. Peak (1) at +4.8 ppm relative to the line of pure perylene and the broad, almost coalescing peaks (2a) and (2b) at about -18 and -24 ppm are from the perylene salt. These three peaks correspond to the three chemically inequivalent proton sites H(1), H(2) and H(3) in perylene, see Fig. 4. To assign the lines we calculated the unpaired electron spin densities ρ_j at the carbon sites 1 ... 6 for a free perylene ion with, however, a net charge of $+0.55 |e|$ following the MO procedure of McLachlan [11]. The factor 0.55 results from the fractional charge transfer in the salt. We then used McConnell's empirical relation $A_{Hj} = Q \cdot \rho_j$ with $Q \approx -28 \text{ Gauss}$ to

calculate the hyperfine coupling constants A_{Hj} from which the Knight shifts can be calculated using the equation $K_j = 1/\hbar \cdot \gamma_N / \gamma_e \cdot A_{Hj} \cdot \chi_p / N$. N is the number of electrons per unit volume; χ_p , the paramagnetic susceptibility, is known from measurements [4]. The following results are obtained: H(1): -21.8 ppm; H(2): +3.1 ppm; H(3): -16.2 ppm. On this basis we propose that lines (1), (2a) and (2b) in spectrum 3a are to be assigned to protons H(2), H(3) and H(1), respectively. We comment further below on the implications of these results with regard to the unpaired spin densities on the carbon sites.

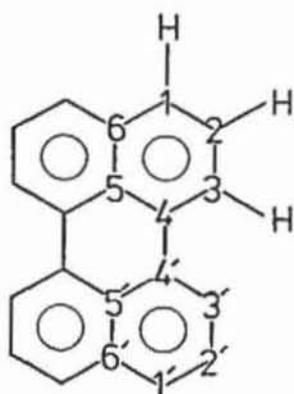


Fig. 4. The perylene molecule

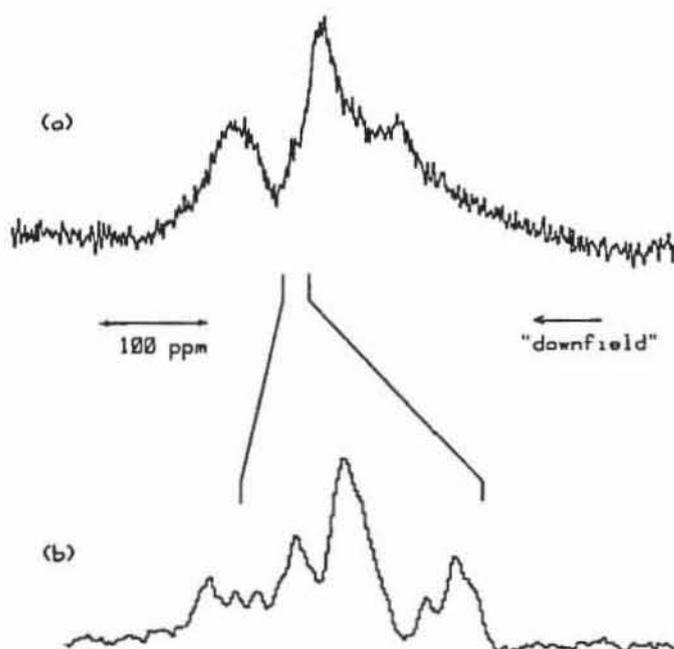


Fig. 5. High resolution C-13 spectrum of the perylene salt (a) and of pure perylene (b).

Figs. 5a and 5b show C-13 spectra of the perylene salt and of pure perylene recorded with cross polarization for signal enhancement, proton decoupling and MASS. Note that the range of the chemical shifts in pure perylene is small compared with the Knight shifts in the metallic salt. The center of gravity of the resonances in pure perylene is used as the reference for the Knight shifts. In the salt we observe three broad peaks at +80 ppm, -13 ppm and -70 ppm. We again calculated theoretical Knight shifts, starting from the ρ_j of the free perylene ion mentioned above and using McConnell-type relations between the ρ_j and the carbon hyperfine coupling constants A_{Cj} which must take into account, however, exchange interactions between electrons on neighbouring atoms [12]. The Knight shifts K_j obtained in this way for the carbons 1 ... 6, cf. Fig. 4, are +69.5, -50, +42, -8, -12 and -57 ppm, respectively. It is pleasing to see that these Knight shifts come in 3 groups (+69.5, +42); (-8, -12); (-50, -57) which may be associated with the three observed broad lines. Using this partial assignment, readjusting the ρ_j and computer simulating spectra taking into account also the proton Knight shift data as well as interrelations of the charge

densities we eventually derived the carbon Knight shifts listed in column 2 of Table 1. These, in turn, imply the readjusted spin densities ρ_j listed in column 3. The ρ_j listed in column 4 are derived from the proton data, those in column 5 come directly from the MO calculation of the free ion. The essential message contained in these numbers is that the incorporation of the perylene ion into the stacks of the perylene salt results in an accumulation of unpaired spin density in position 3, and in an accompanying decrease in positions 5 and 6. A closer look at the structure of the perylene salt reveals that the arrangement of the stacks is such that carbon atoms 3 and 3' of neighbouring perylene molecules are right on top of each other. The accumulation of spin density in these positions strengthens the intermolecular interactions at these positions and suggests the formation of an "easy" path for the diffusive migration of the conduction electrons along the stacks.

Table 1. Unpaired spin densities in the perylene salt

Nucleus	K_j /ppm/	ρ_j (exp.C)	ρ_j (exp.H)	ρ_j (MO-theory)
1	+86	+0.09	+0.087	+0.079
2	-64	-0.011	-0.017	-0.011
3	+74	+0.095	+0.066	+0.086
4	-11	+0.007		+0.0224
5	-15	-0.037		-0.0055
6	-73	-0.045		-0.0174

REFERENCES

- 1 D. Schweitzer *et al.*, J. Physique C3, 44 (1983) 1433.
- 2 K. Bender, diploma thesis, Heidelberg, 1983.
- 3 P. Koch *et al.*, Mol. Cryst. Liq. Cryst., 86 (1982) 87.
- 4 I. Moritz *et al.*, Solid State Comm., 48 (1983) 281.
- 5 U. Haeberlen, High Resolution NMR in Solids, Academic Press, New York 1976.
- 6 B. Schnabel, Proceedings 19th Colloque Ampere, Heidelberg, 1976.
- 7 M. Mehring *et al.*, Phys. Rev. Lett., 53 (1984) 2441.
- 8 T. Moriya, J. Phys. Soc. Jap., 18 (1963) 516.
- 9 J. Winter, Magnetic Resonance in Metals, Oxford, 1971.
- 10 D. Burum and W.K. Rhim, J. Chem. Phys., 71 (1979) 944.
- 11 A.D. McLachlan, Mol. Physics, 3 (1960) 233.
- 12 K. Wüthrich, NMR in Biological Research, North-Holland, Amsterdam, 1976.