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PHYSICAL PROPERTIES OF TCNQ SALTS WITH ALIPHATIC DERIVATIVES OF BENZODIAZINE

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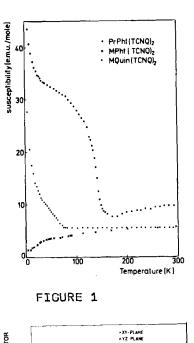
Abstract Magnetic and ESR studies for a new family of Q-1-D TCNQ salts with aliphatic derivatives of benzodiazine donors were performed and discussed.

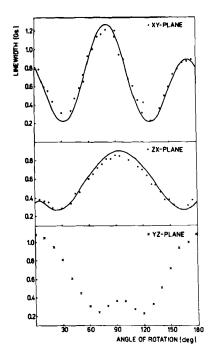
EXPERIMENTAL

We chose for investigation a new family of organic Q-1-D TCNQ salts with aliphatic derivatives of benzo-diazine donors: N-methyl-phtalazinium (MPht), N-propyl-phtalazinium (PrPht), and N-methyl-quinoxalinium (MQuin).

The temperature dependence of magnetic susceptibility χ was determined by Faraday method. The diamagnetic contribution has been determined by Pascal rule. The thermal variations of the paramagnetic parts of susceptibilities (χ_{ρ}) are shown in Fig.1.

The first derivative spectra of the X-band ESR absorption were measured at room temperature as a function of the crystal orientation, for three perpendicular axis. The linewidth values of single and narrow ESR lines are strongly angular dependent and change in the range from 20 to 130 µT; the spectrum anisotropy was below 190 µT. The g-factor anisotropy for three perpendicular axis for PrPht (TCNQ) is shown in Fig.2,





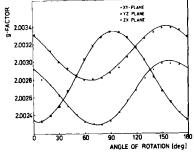


FIGURE 3

FIGURE 2

- FIGURE 1 The static paramagnetic susceptibility versus T.
- FIGURE 2 g-factor anisotropy for PrPht (TCNQ)2.
- FIGURE 3 ESR-linewidth anisotropy for PrPht (TCNQ). Solid curves are the best fit to Eq.2 with $\mathcal{L}=0.32$, $\beta=0.58$.

whereas the angular dependence of the ΔH is shown in Fig.3 (ΔH is a linewidth).

DISCUSSION

The χ_{p} of the salts are strongly dependent on the sample composition (Fig.1). The susceptibility of MPht(TCNQ), decreases with temperature down to 4 K. In spite of weak T-dependence one can notice the change in the character of this dependence near 72 K; this is appreciable by susceptibility derivative analysis (dy/dT=ffT)). Above 72 K the salts is a "metal-like" semiconductor with the large, strongly T-dependent mobility. 1 It ellows us to consider the high temperature susceptibility as a sum of Pauli susceptibility and T-dependent component described either by thermaly activated function of B/T $\exp(-\Delta/T)$, where Δ is an activation energy, near 370 K, and B is an adjustable constant equals 0.2, or by Lee, Rice and Anderson² model with $T_0=360~\mathrm{K}$ and $\gamma_o = 2.3 \times 10^{-4}$ e.m.u./mole. Below 72 K the salt is the semiconductor with both conductivity and susceptibility thermal activated. We obtained an agreement with the experiment, describing the low temperature susceptibility by

$$\chi_{\text{para}} = \chi_{\text{para}}^{\text{TCNQ}} + \chi_{\text{para}}^{\text{MPht}}$$
(1)

with χ TCNQ = A/T exp(- Δ /T) where Δ = 55.5 K and MPht is very weakly T-dependent function of Bonner--Fischer type.

The magnetic susceptibility of MQuin $(TCNQ)_2$ at high temperature (T>80 K) can be considered as a Pauli type susceptibility, below this temperature the Curie like component dominate. The principal g values and their direction cosines are given in Table 1.

The fact that the g-factor of the salts approximates the g-tensor of a single TCNQ molecule shows that the contribution of the donor molecules is negligible as well as that the g-factor in these salts is unaffected by the interchain delocalization.

The principal g values and the direction cosines.

Sample	g-factor	direction cosines		
MPht TCNQ2	g _x =2.00258	.4473	.3162	.8366
	gv=2.00 3 37	.147	.8967	4176
	g _z =2.00236	.8822	3098	354
PrPht TCNQ2	$g_{x}^{-}=2.00236$.5722	.82	.129
_	g _v =2.00337	.4812	323	8149
	g _z =2.00331	.6641	4725	5794
MQuin TCNQ2	$g_{x}^{-}=2.00312$. 1406	.6495	.7472
_	g _v =2.00374	. 963 6	.0834	. 2539
	g _z =2.00259	.2272	7558	614

The experimental angular variations of ΔH in PrPht (TCNQ), can by fairly well described by an expression given by Takagi and Kawabe.4

$$\Delta H = \mathcal{L}(3\cos^2\theta - 1)^2 + \beta\sin^4\theta$$
 (2) where θ is an angle between the direction of applied magnetic field and the normal to the magnetic layers or the X-axis , \mathcal{L} and β are T-dependent parameters (Fig.3). A large exchange interaction or high magnetic dilution effect can be responsible for this small ΔH .

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