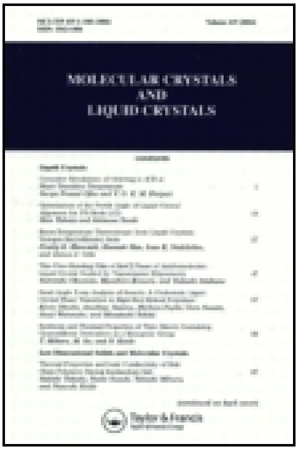

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Physical Properties of TCNQ Salts with Aliphatic Derivatives of Benzodiazine

Andrzej Graja [a] , Lucyma Firleo [a] & Andrzej Radchel [b]

[a] Institute of Molecular Physics, Polish Academy of Sciences, 60179, Poznan, Poland
[b] Institute of Chemistry, A. Mickiewicz University, 60780, Poznan, Poland
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PHYSICAL PROPERTIES OF TCNQ SALTS WITH ALIPHATIC DERIVATIVES OF BENZODIAZINE

ANDRZEJ GRAJA, LUCYNA FIRLEJ
Institute of Molecular Physics, Polish Academy of Sciences, 60179 Poznań, Poland

ANDRZEJ RAJCHEL
Institute of Chemistry, A.Mickiewicz University, 60780 Poznań, Poland

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 benzodiazine 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_p) 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)$_2$ is shown in Fig.2,

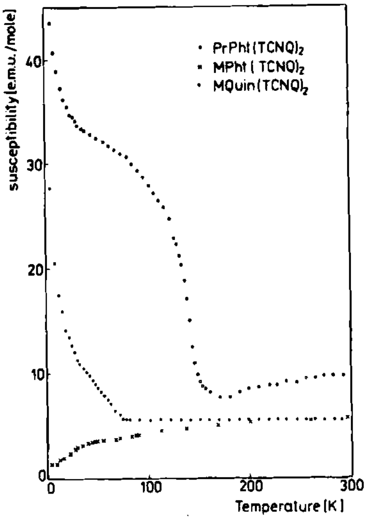

FIGURE 1

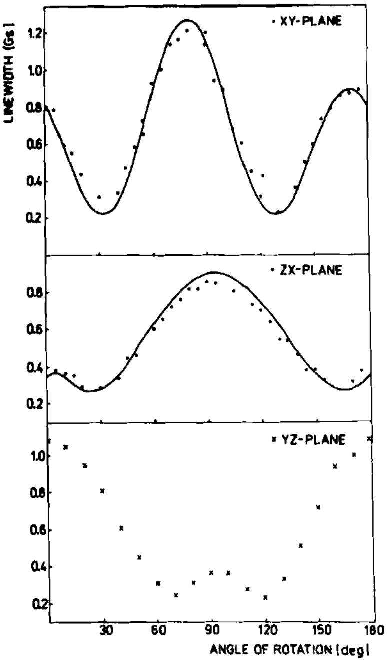

FIGURE 3

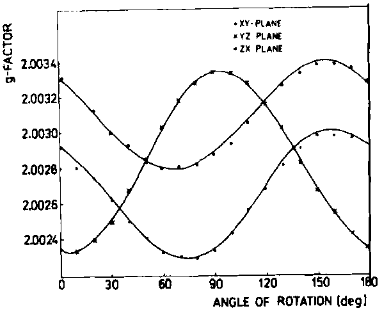

FIGURE 2

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)$_2$. Solid curves are the best fit to Eq.2 with $\alpha = 0.32$, $\beta = 0.58$.

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$(TCNQ)_2$ 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 ($d\chi/dT=f(T)$). Above 72 K the salts is a „metal-like" semiconductor with the large, strongly T-dependent mobility.[1] It allows 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 Anderson[2] model with T_0=360 K and χ_0 =2.3x10^{-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

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

with $\chi_{para}^{TCNQ} = A/T \exp(-\Delta/T)$ where Δ = 55.5 K and χ_{para}^{MPht} is very weakly T-dependent function of Bonner-Fischer type.[3]

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.

TABLE I The principal g values and the direction cosines.

Sample	g-factor	direction cosines		
MPht TCNQ$_2$	g_x=2.00258	.4473	.3162	.8366
	g_y=2.00337	.147	.8967	-.4176
	g_z=2.00236	.8822	-.3098	-.354
PrPht TCNQ$_2$	g_x=2.00236	.5722	.82	.129
	g_y=2.00337	.4812	-.323	-.8149
	g_z=2.00331	.6641	-.4725	-.5794
MQuin TCNQ$_2$	g_x=2.00312	.1406	.6495	.7472
	g_y=2.00374	.9636	.0834	.2539
	g_z=2.00259	.2272	-.7558	-.614

The experimental angular variations of ΔH in PrPht$(\mathrm{TCNQ})_2$ can by fairly well described by an expression given by Takagi and Kawabe.[4]

$$\Delta H = \mathcal{L}(3\cos^2\theta - 1)^2 + \beta \sin^4\theta \qquad (2)$$

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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