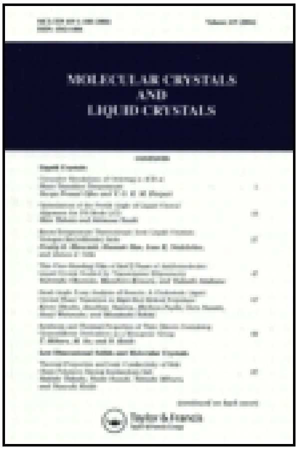

Molecular Crystals and Liquid Crystals

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

Pressure Dependence of Triplet Excitons In $(NPQn)_{.5}$ $(NBQn)_{.5}$ $(TCNQ)_2$

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To cite this article: L. Forro , G. Sekretarczyk & M. Krupski (1985): Pressure Dependence of Triplet Excitons In $(NPQn)_{.5}$ $(NBQn)_{.5}$ $(TCNQ)_2$, Molecular Crystals and Liquid Crystals, 120:1, 115-119

To link to this article: http://dx.doi.org/10.1080/00268948508075771

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 115-119
0026-8941/85/1204-0115/$10.00/0

PRESSURE DEPENDENCE OF TRIPLET EXCITONS IN $(NPQn)_{.5}(NBQn)_{.5}(TCNQ)_2$

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Abstract - N-Propyl-Qn $(TCNQ)_2$ alloyed with N-Butyl-Qn$(TCNQ)_2$ shows the characteristic two line ESR spectra due to thermally excited triplet excitones. We have performed the pressure dependence (up to 5 kbars) of zero-field splitting parameters, singlet-triplet activation energy and exchange parameters. The drastic decrease of the susceptibility and linewidth has been attributed to the increased singlet-triplet activation energy 80K/kbars. The activation energy for the exciton propagation decreases on pressure with the rate of 36 K/kbars.

INTRODUCTION

The parent compound NPQn$(TCNQ)_2$ is a linear chain system where the conducting TCNQ chain is tetramerized and within the tetramer it is slightly dimerized[1]. With full charge transfer from the NPQn donors, every dimer has one electron. At low T they are coupled into singlets but the triplet state is easily accesible. Indeed, a well resolved two line spectra is observed in 35-80 K temperature range, characteristic for the ESR of thermally activated triplet excitons[2]. Because of the high triplet exciton density and their fast moving along the chain, they scatter on each other quickly loosing their identity so the two line spectra collapse into a single resonance around 100 K, from the slow exchange limit the system passes to the fast exchange limit. At 220 K a sharp insulator to metal phase transition takes place, which is probably due to triplet exciton-lattice interaction[3].

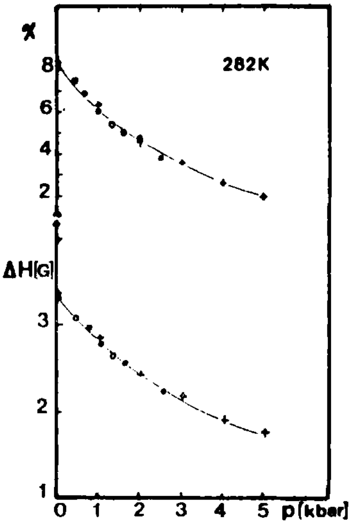
In a previous paper the effect of alloying N-Propyl-Qn((CNQ)$_2$ with N-Ethyl-Qn$(TCNQ)_2$ was presented[2]. $(NPQn)_{.5}(NEQn)_{.5}(TCNQ)_2$ was compared with NPQn$(TCNQ)_2$: the singlet-triplet separation energy is not affected, the zero-field parameters D, E are slightly decreased, but the activation energy for the spin exchange is greatly reduced, that is the triplet excitons could move more easily along the chain. So it was concluded, that the introduction of shorter N-Ethyl-Qn donors acts as a uniaxial pressure on the TCNQ chain.

In this paper we present the next steps in the study of triplet excitons in NPQn$(TCNQ)_2$-family: introduction longer N-Buthyl-Qn donor molecules in the NPQn sublattice, and applying hydrostatic pressure. For this study we have chosen $(NPQn)_{.5}(NBQn)_{.5}(TCNQ)_2$, characterized first at normal pressure than applied hydrostatic pressure up to 5 kbars.

RESULTS & DISCUSSION

Single crystal ESR spectra were measured in 200-360 K and 0-5 kbar pressure range, using an X-band spectrometer. A detailed description of the experimental setup is given in reference 4. In contrast to the parent compound where an important central peak is observed, in $(NPQn)_{.5}(NBQn)_{.5}(TCNQ)_2$ there is a hardly detectable central line. This is due to a somewhat different sample preparation[5].

The two line spectra are present from ~ 200 K up to 360 K where they collapse into a single line. We have measured the angular dependence of the dipolar splittings at room temperature and normal pressure. We have obtained $D=67.5\pm2G$ and $E=11\pm1G$ which are considerably larger than $D=45\pm2$ and $E=7\pm1G$ of NPQn$(TCNQ)_2$. This suggests stronger alternation of the TCNQ molecules in the alloy and a smaller spatial extension of the electrons bounded in triplet state. Because of the experimental conditions we couldn't obtain the zero-field splitting parameters under pressure. At certain positions we have measured the pressure dependence of the dipolar splittings. The biggest decrease is ~10% at 5 kbars.



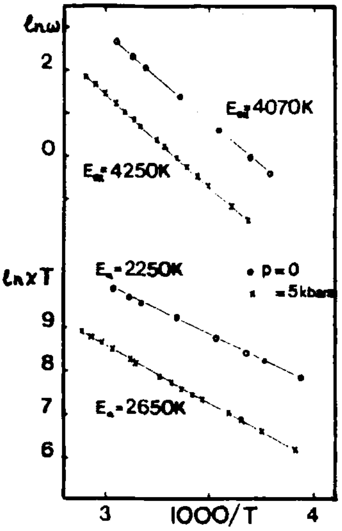


Fig.1.Pressure dependence of the susceptibility (in arbitrary units) and linewidth at room temperature for several samples.

Fig.2.Exchange frequency vs 1/T and triplet spin exciton intensity times temperature vs 1/T at normal and 5 kbars hydrostatic pressure.

Figure 1 shows the pressure dependence of the susceptibility and linewidth at room temperature for several samples. The susceptibility decreases by factor ~4 and the linewidth by factor ~2 at 5 kbars. The reason of this decrease can be seen on figure 2 where $\ln \chi T$ and $\ln\omega \sim \ln(\Delta H - \Delta H_0)$ versus inverse temperature are plotted (ΔH is the measured, ΔH_0 is the residual linewidth). This plot shows that the system obeys well the singlet-triplet statistics $\chi \sim \exp(-Ea/kT)/T$, where the singlet-triplet activation energy Ea=2250K (in NPQn(TCNQ) it is only 200K); Furthermore figure 2 shows that Ea increases on pressure, that is why χ decreases. We can calculate the pressure dependence of Ea from χ-p at room temperature. The open circles on fig.3 show these data. The full circles correspond to $\ln\chi T$ - 1/T plots at 2, 2.5, 4 and 5 kbars. Ea increases linearly on pressure with rate of 80 K/kbar. This is

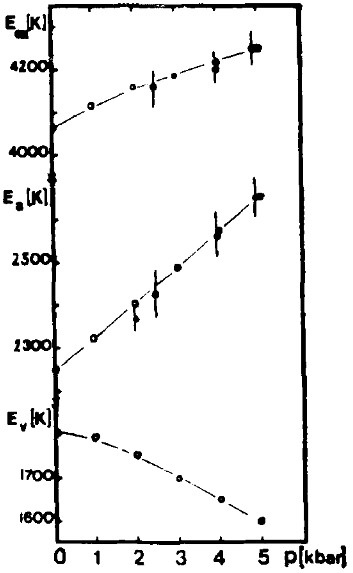


Figure 3. Pressure dependence of activation energies for spin exchange Eex, singlet-triplet separation Ea and exciton propagation E_v. Open circles (o) correspond to χ-p and ΔH-p data of fig.1, while full circles (●) are deduced from lnω -1/T and lnχT-1/T plots of fig.2.

resonable if decreasing the distance between the spins in the singlet ground state, the interaction between them becomes stronger and more and more energy is needed to break the pairs in order to excite them into triplet state. So with pressure the triplet exciton density is decreasing. The linewidth, that is the spin exchange frequency between the triplet excitons is formulated[6] by $\omega \sim \exp E_{ex}/kT \exp-(E_a+E_v)/kT$. The first term shows that the efficacity of exciton-exciton collisons and spin exchange depends on the exciton density, while the second term shows their dependence on the propagation velocity of the triplet excitons. lnω-1/T plot of fig.2 shows the increase of E_{ex} on pressure which is already expected from the pressure dependence of E_a. From the fit of ΔH-p of fig.1 and lnω-1/T plots we obtain the variation of E_{ex} with pressure plotted on figure 3. Its increase is weaker than that of E_a, it makes 36K/kbar. Simple evaluation of E_v (fig.3) shows opposite behaviour to E_a - it is decreasing with pressure. It is expected that contracting the lattice, reducing the distance between the tetrads, the propagation of excitons along the chain becomes easier.

In conclusion, alloying the NPropyl-Qn donor sublattice with longer N-Buthyl-Qn molecules increases the alternation of TCNQ molecules, the singlet-triplet activation energy is increased, replacing the observability of triplet excitons from low temperatures to high ones. Applying hydrostatic pressure and reducing the lattice distances, the interaction between the spins in singlet state becomes stronger resulting bigger singlet-triplet activation energy, but the propagation of the excitons along the chain is more favorable.

ACKNOWLEDGMENT - We acknowledge the single crystals provided by Budapest-group, and the useful discussions with J.R.Cooper, A.Jánossy and L.Zuppiroli.One of us (L.F.) acknowledges the constant interest and help of Prof.Graja and Prof.Stankowski in performing these experiment on the Institute of Molecular Physics in Poznan.

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