Comments on the Preparation of the One-dimensional Conductor *N*-Methylphenazinium 7,7,8,8-Tetracyanoquinodimethanide

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Summary E.s.r. and mass spectral data prove that the green paramagnetic ion NMPH$^+$ is produced upon irradiation of solutions of NMP$^+$ using solvents like EtOH, MeCN, MeOH, or water; polycrystalline samples of NMP$^+$–TCNQ$^-$ prepared under daylight therefore contain appreciable amounts of NMPH$^+$–TCNQ$^-$.

N-Methylphenazinium 7,7,8,8-tetracyanoquinodimethanide (NMP–TCNQ) is a 'classic' in the history of one-dimensional 'metals',[1] and it has been claimed that it crystallizes in three different modifications. Two of the known phases contain segregated stacks with ordered[2] and disordered[3] NMP cations. Recently we have prepared[4] 5,10-dihydro-5-methylphenaziniumyl–TCNQ (NMPH$^+$–TCNQ$^-$) which was shown[5] to be identical with the 'second modification of NMP–TCNQ.' Nevertheless a number of recent papers describe the properties of 'high purity NMP–TCNQ' and its 'second modification,' while overlooking the complicated chemical problems involved in the preparation of the compounds. In an attempt to clarify the situation, we now report investigations on solutions of *N*-methylphenazinium compounds. Our results cast at least some doubt upon the physical results obtained for *polycrystalline* samples so far.

Investigations were carried out using 5-methylphenazinium methosulphate (from EGA) and 5-methylphenazinium perchlorate as starting materials. The latter compound was obtained by mixing 40 ml of a hot saturated solution of $NaClO_4$ in ethanol with a hot solution of 740 mg of $NMP^+MeSO_4^-$ in 180 ml of ethanol. The slightly greenish solutions (presence of small quantities of NMPH$^+$) turn to a light orange-yellow after addition of a few drops of bromine and yellow crystals of $NMP^+ClO_4^-$ are obtained on cooling.† The yellow solutions of *both* NMP$^+$ salts in solvents such as methanol, ethanol, acetonitrile *etc.* rapidly turn green upon exposure to daylight. This photochemical process, which can be enhanced appreciably by using a high-pressure xenon or mercury lamp, also takes place if the solution is kept under dry N_2. It even occurs in water. E.s.r. evidence (Figure 1) clearly suggests that the green species resulting in the reaction is NMPH$^+$. The type of spectra and hyperfine splittings are identical with those obtained earlier for this species.[6] The photoinduced reduction of ethanolic or methanolic solutions of NMP methosulphate to the phenaziniumyl radical NMPH$^+$ was pointed out earlier[7] but has not been considered in the preparation of NMP–TCNQ. In deuteriated solvents like D_2O or CD_3OD deuterium is transferred (e.s.r. spectrum, Figure 2) and 5,10-dihydro-5-methyl-10-deuteriophenaziniumyl results.

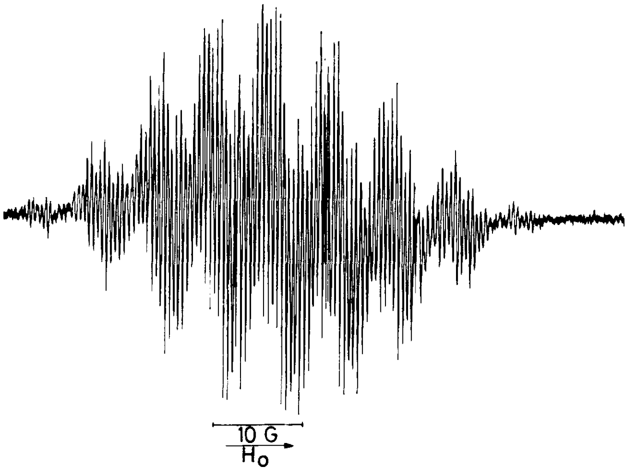

Figure 1. E.s.r. spectrum of NMPH$^+$ produced upon exposure of NMP$^+$ to daylight.

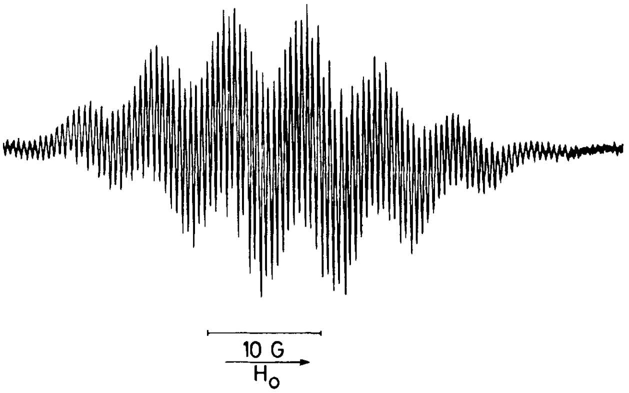

Figure 2. E.s.r. spectrum of NMPD$^+$.

Irradiation of NMP perchlorate in CD_3CN does *not* lead to a deuteriated phenaziniumyl radical but to the protonated species only. This indicates that hydrogen can be abstracted from NMP$^+$ under these conditions.

Addition of acetonitrile solutions[8–10] of LiTCNQ to NMP$^+$ solutions using the previously described procedures under common conditions (not in a dark room) thus inevitably leads to the formation of a mixture of NMPH–TCNQ and NMP–TCNQ. The former compound was erroneously claimed to be a 'second modification' of NMP–TCNQ by several groups.[8,11,12] *All* solid samples prepared under light show an unusual intense peak for mass 196 (NMPH$^+$) or 197 (NMPD)$^+$ for samples prepared in D_2O.

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† Analytical data for C, H, and N are within ±0·2% of the calculated values.

Since an additional peak with mass 210 is observed (5,10-dimethylphenazinium cation) which evidently comes from a mass spectrometer reaction the production of $NMPH^+$ also in the spectrometer cannot be excluded. The 196 mass peak is thus not strong evidence for impure samples but the $NMPD^+$ peak is.

Therefore, we believe that all the earlier investigated polycrystalline samples prepared under the same (daylight) conditions might contain considerable amounts of NMPH–TCNQ as well. In any case the extensive purification procedures often used to purify the starting materials[6a,10] do not lead to better materials since the main impurity in the finally isolated solid is generated during the preparation.

There is every reason to expect some $NMPH^+$ contamination in single crystals of NMP–TCNQ prepared in the standard way, even when direct structural data show segregated stacks of NMP^+ and of $TCNQ^-$. Only a small percentage of paramagnetic impurities is needed to rationalize the different low-temperature magnetic properties observed by various groups.[1c] The remaining structural problem for NMP–TCNQ is concerned with the preparation[2,8a] of a phase with ordered NMP molecules, in contrast to the more common[3] highly conducting phase with disordered NMP molecules. Whether NMPH-admixtures are also responsible for these single crystal properties is under investigation and will be reported elsewhere.

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