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

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H. J. Keller [a], W. Moroni [a] & D. Nöthe [a]

[a] Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69, Heidelberg, Germany

Version of record first published: 12 Oct 2011.

To cite this article: H. J. Keller , W. Moroni & D. Nöthe (1979): Magnetic Properties of N-Alkylated Phenazine Type Radicals, Molecular Crystals and Liquid Crystals, 52:1, 239-240

To link to this article: http://dx.doi.org/10.1080/00268947908071739

Mol. Cryst. Liq. Cryst., 1979, Vol. 52, pp. 239–240

Printed in Holland

Magnetic Properties of N-Alkylated Phenazine Type Radicals

H. J. KELLER, W. MORONI, and D. NÖTHE

Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69 Heidelberg, Germany

(*Received June 16, 1978*)

Phenazine and its derivatives are known for their pronounced ability of taking up electrons and forming semiquinoid and dihydro forms. Depending on the conditions one obtains neutral or cationic radicals.[1] As the different forms even the radicalic ones are relatively stable they are well suited for the investigation of the solid state properties of the corresponding charge transfer or radicalic salts.[2] This class of compounds is of special interest because NMP-TCNQ is one of the first organic metals found in it.

For NMP-TCNQ we could show that the interpretation of physical measurements at least of polycrystalline samples are rather doubtful.[3] Dissolving NMP methosulfate or perchlorate in methanol, ethanol or water and exposing to daylight leads to the rapid formation of the semiquinone $NMPH^+$. This can be seen from the development of the typical green colour and from the EPR spectrum. Using the corresponding deuterated solvents one obtains $NMPD^+$. In CD_3CN one does not get the deuterated but the protonated form. One has to assume that hydrogen transfer occurs between different NMP^+ molecules.

These facts show that all samples which had been prepared under daylight necessarily contain $NMPH^+$ impurities independently of the purity of the starting material.

Similar in composition to NMP-TCNQ is dimethyldihydrophenazine TCNQ (M_2P-TCNQ). Nevertheless the latter is totally different in structure[4] and properties. Donor and acceptor form mixed stacks, but from EPR one can clearly see the presence of triplet excitons. This is the first case where the two correlating electrons are located on chemically different molecules. On rising the temperature one observes that in addition to the usual line broadening the fine structure lines approach one another. This points to a change in charge transfer ($M_2P\text{-}TCNQ \rightarrow M_2P^+TCNQ^-$) which finally leads to phase transition above 390 K.

This is in accordance with the observation that in polar solvents like alcohols the green colour of the ionic form and in nonpolar solvents like toluene the brown colour of the neutral form can be seen.

The donor properties of the phenazine can be improved by substituting the two methyl groups in M_2P by higher alkyl groups. Introducing for instance propyl groups lowers the temperature of the phase transition from 390 K to room temperature. The dialkyldihydrophenazines readily react with iodine to give products with varying iodine content.[5] By elementary and structural analysis we could identify M_2PI_3,[6] Et_2PI_3[6] and $Et_2PI_{1.6}$[7] (Et = ethyl). In contrast to the perchlorate and TCNQ salts do these compounds show one single broad line in the EPR.[8] For M_2PI_3 for instance the line width varies between 24 Gauss at room temperature and 41 Gauss at 160 K. Thus exchange interaction between neighbouring radical ions must be rather weak. This is also seen from the EPR intensity which follows a Curie law and from the magnetic moment which is 1.78 B.M. at room temperature. Crystal structures indeed show intermolecular distances of > 3.75 Å.

It is interesting to note that the bending of the M_2P about the N-N axis is very similar in the triiodide and the TCNQ compound. This is rather disturbing since the radical would be expected to be planar as in the case of the diethyl derivative.[7]

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