

Doped Dialkylated Phenazines: A Novel Series of Highly Conducting Organic Solids

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Abstract

Doped dialkylated phenazines: a novel series of highly conducting organic solids. Dietz, K.;¹ Flandrois, S.;² Keller, H. J.;¹ Koch, P.;² Queckbörner, J.;¹ Schweitzer, D.³ (Anorganisch-Chemisches Institut, Universität Heidelberg,¹ Im Neuenheimer Feld 270, 6900 Heidelberg, Germany; Centre de Recherche Paul Pascal,² Domaine Universitaire, 33405 Talence, France and Max-Planck-Institut für Medizinische Forschung,³ Abteilung für Molekulare Physik, D-6900 Heidelberg, Federal Republic of Germany.

Doping dimethylphenazine (M_2P)–TCNQ and diethylphenazine (E_2P)–TCNQ with phenazine gave rise to new conducting compounds with segregated stacks: $(M_2P)_{0.5}(P)_{0.5}$ TCNQ (1) and $(E_2P)_{0.55}(P)_{0.45}$ TCNQ (2). The room temperature electrical conductivities are in the range 10 – $100 \Omega^{-1}cm^{-1}$ for (1) and 1 – $10 \Omega^{-1}cm^{-1}$ for (2). The paramagnetism of both compounds could be separated into contributions from TCNQ and Phenazine stacks. The structural, electrical and magnetic similarities of (1) with the well-known N-methylphenazinium (NMP)–TCNQ led to a reexamination of its magnetic properties. It was shown that an estimate of the charge transfer can be obtained from the temperature dependence of the magnetic susceptibility.

Introduction

Phenazine derivatives are able to form many charge transfer complexes with TCNQ [1]. One of them, NMP–TCNQ, was for a decade the best organic conductor and has received considerable attention. However some questions still remain concerning for example the degree of charge transfer from NMP to TCNQ, the nature of its conductivity or the interpretation of its magnetic properties. Recent progress in the understanding of this system was obtained by doping NMP–TCNQ with neutral phenazine [2]. NMP molecules can easily be substituted by phenazine molecules, to give compounds of formula $(NMP)_x(P)_{1-x}$ TCNQ with $0.5 < x < 1$. As it is reasonable to assume no charge transfer from phenazine to TCNQ, the effect of doping is a reduction of the charge transfer and hence a reduction of the band filling.

Our purpose was to replace NMP by other phenazine derivatives. Dimethylphenazine (M_2P) and Diethylphenazine (E_2P) were chosen. They are known to form with TCNQ mixed stack complexes of –ADAD– type. However by doping with Phenazine, segregated stack complexes are obtained. Moreover, whereas NMP⁺ is diamagnetic, M_2P^+ and E_2P^+ are cation-radicals, so that the amount of charge transfer can be obtained directly from magnetic measurements, if we are able to distinguish the respective contributions to χ_p of TCNQ and M_2P^+ or E_2P^+ . In this paper we show that this separation is possible and can be extended to NMP–TCNQ.

Sample preparation and characterization

By cooling down to room temperature hot acetonitrile solutions of M_2P (or E_2P), Phenazine and TCNQ, crystals of $(M_2P)_x(P)_{1-x}$ TCNQ or $(E_2P)_x(P)_{1-x}$ TCNQ precipitated. We tried to vary x by changing the ratio $[M_2P]/[P]$ or $[E_2P]/[P]$ in the solution. However our analyses by UV spectroscopy and high pressure liquid chromatography showed us that only one phase could be obtained: $(M_2P)_{0.5}(P)_{0.5}$ TCNQ for M_2P or $(E_2P)_{0.55}(P)_{0.45}$ TCNQ for E_2P compound.

The crystal structure of $(M_2P)_{0.5}(P)_{0.5}$ TCNQ was recently determined [3]. Regular segregated stacks of phenazine species and TCNQ molecules are present in the crystal. The interplanar distance is 3.44 \AA in the phenazine stack, where the distribution of M_2P and P is random, and 3.26 \AA in the TCNQ stack, compared to 3.36 and 3.26 \AA respectively for NMP–TCNQ [4]. The crystal structure determination of E_2P compound is in progress. Preliminary results show that segregated stacks are also present, but probably not regular [5].

Results and Discussion

1) Conductivity

The d. c. electrical conductivities of single crystals were measured by a standard four-probe method. The room temperature values are 50 – $100 \Omega^{-1}cm^{-1}$ for $(M_2P)_{0.5}(P)_{0.5}$ TCNQ and 1 – $10 \Omega^{-1}cm^{-1}$ for $(E_2P)_{0.55}(P)_{0.45}$ TCNQ. The temperature dependences given in figure 1 show that E_2P compound has a semi-conducting behavior, whereas M_2P compound behaves metal-like at high temperature. The maximum ratio $\sigma/\sigma_{R.T.} \sim 1.1$ has the value generally found in conducting TCNQ ion-radical salts. At low temperature the compound becomes insulating.

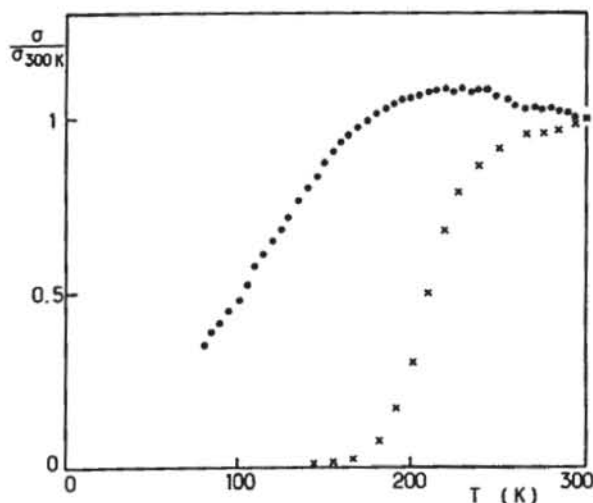


Fig. 1. Single crystal electrical conductivities of $(M_2P)_{0.5}(P)_{0.5}$ TCNQ (dots) and $(E_2P)_{0.55}(P)_{0.45}$ TCNQ (crosses).

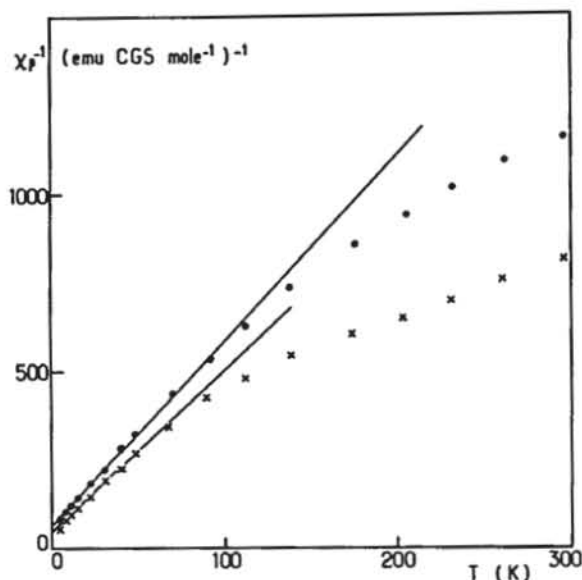


Fig. 2. Paramagnetic susceptibility of $(M_2P)_{0.5}(P)_{0.5}$ TCNQ (dots) and $(E_2P)_{0.55}(P)_{0.45}$ TCNQ (crosses).

2) Magnetism

The magnetic susceptibility investigations were carried out by using the Faraday method. The paramagnetism was obtained by subtracting from the measured values the core diamagnetism calculated from Pascal constants or measured on separate constituents. The temperature dependences of the molar paramagnetic susceptibility χ_p are shown in figure 2, where $1/\chi_p$ is plotted versus temperature. For both compounds a Curie-Weiss law is obeyed from about 100 K down to 10 K. Moreover the Curie constants, determined from the slopes of the straight lines below 100 K, correspond within the accuracy to 0.50 and 0.55 mole of spins respectively for M_2P and E_2P compound, i.e. to the stoichiometric coefficient of M_2P and E_2P . This result means that below 100 K the paramagnetic behavior is dominated by phenazine stacks and that the charge transfer is total from M_2P or E_2P to TCNQ. A weak antiferromagnetic interaction between the spins of phenazine stacks exists, as shown by the small negative Curie-Weiss temperature: $\theta \sim -10$ K.

For $T > 100$ K the paramagnetism deviates from Curie-Weiss behavior. This is due to the contribution of TCNQ stacks. By subtracting from the total susceptibility the Curie-Weiss susceptibility due to phenazine stacks it is possible to obtain the TCNQ contribution to χ_p . The results are shown in figure 3. Although the accuracy is probably not very good in particular at low temperature, the room

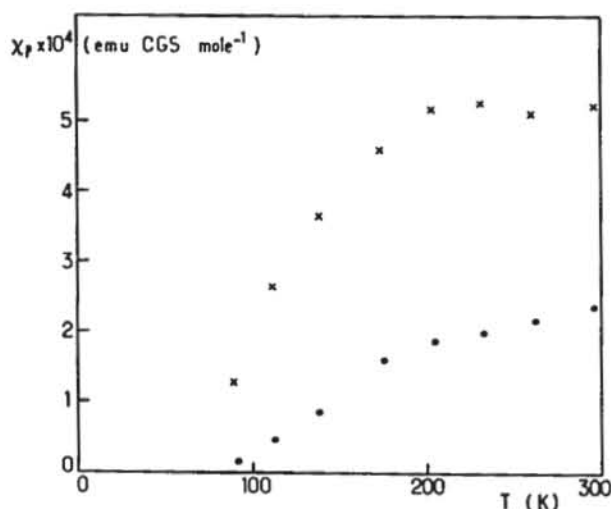


Fig. 3. Paramagnetic susceptibility of TCNQ stacks in $(M_2P)_{0.5}(P)_{0.5}$ TCNQ (dots) and $(E_2P)_{0.55}(P)_{0.45}$ TCNQ (crosses).

temperature values have the expected order of magnitude, compared with other TCNQ ion-radical salts.

Finally these results allow us to reinterpret the magnetic behavior of NMP-TCNQ, whose crystal structure is very similar to that of $(M_2P)_{0.5}(P)_{0.5}$ TCNQ. The magnetic susceptibility of NMP-TCNQ has been measured by many authors including ourselves. Severe discrepancies exist from one author to another, particularly at low temperature, which have been explained by the presence in the NMP stacks of neutral phenazine molecules or $NMPH^+$ ion-radicals. Nevertheless the examination of published (and non-published) data leads to the conclusion that in the range 10–100 K a Curie-Weiss law is obeyed like in our M_2P compound. This Curie-Weiss law was already pointed out by earlier workers [6]. For all the data the Curie-Weiss constants are in the range corresponding to 0.2–0.4 mole of spins, i.e. to a back charge transfer of 0.2 to 0.4 electrons from TCNQ to NMP, so that the ionicity of TCNQ in NMP-TCNQ deduced from χ_p would be 0.6–0.8. This result is in good agreement with recent C. T. determination by X-ray scattering experiments [7] which gave a value of 0.66 electron per TCNQ.

References

1. Soos, Z. G., Keller, H. J., Moroni, W. and Nöthe, D., *Ann. N. Y. Acad. Sci.* 1978, 313, 442.
2. Epstein, A. J. and Miller, J. S., *The Physics and Chemistry of Low-Dimensional Solids* (Ed. L. Alcacer), p. 339, Reidel, Dorchester, 1980.
3. Endres, H., Keller, H. J., Moroni, W. and Nöthe, D., to be published.
4. Fritchie, C. J., *Acta Cryst.* 1966, 18, 892.
5. Endres, H., private communication.
6. Epstein, A. J., Etemad, S., Garito, A. F. and Heeger, A. J., *Phys. Rev. B* 1971, 5, 952.
7. Pouget, J. P., *Chemica Scripta* 1981, 17, 85.

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