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Highly Conducting Phenazine-Doped 5,10-Dihydro-5,10-dimethylphenaziniumyl-TCNQ. Physical Properties and Crystal and Molecular Structure

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Abstract

5,10-Dihydro-5,10-dimethylphenaziniumyl 7,7,8,8-tetracyano-*p*-quinodimethanide (M_2P -TCNQ) can be doped chemically with neutral phenazine (P). We investigated single crystals of a phase with composition $P_{0.4}(M_2P)_{0.6}TCNQ$, i.e. $(C_{12}H_8N_2)_{0.4}-(C_{14}H_{14}N_2)_{0.6}(C_{12}H_4N_4)$, $C_{25.2}H_{15.6}N_6$, $M_r = 402.44$, triclinic, $P\bar{1}$, $a = 3.843$ (3), $b = 7.730$ (6), $c = 16.028$ (11) Å, $\alpha = 91.93$ (6), $\beta = 93.56$ (6), $\gamma = 94.57$ (5)°, $V = 473$ Å³, $Z = 1$, $d_c = 1.41$ Mg m⁻³. The structure was solved by direct methods and refined by least squares to $R = 0.073$ for 704 independent diffractometer data. The structure consists of segregated regular stacks of TCNQ and of dimethyl-

phenazine doped with 40% phenazine. Interplanar distances are 3.26 (1) Å in the TCNQ and 3.44 (1) Å in the M_2P stacks. The structure, the EPR data between 100 and 380 K and the electrical conductivity at room temperature are all very similar to those of NMP-TCNQ.

Introduction

The structure and properties of the one-dimensional organic metal 5-methylphenazinium-TCNQ (NMP-TCNQ) are exceptional in the class of 1:1 charge-transfer complexes of heterocyclic donors with TCNQ (Keller, Moroni, Nöthe, Seifried & Werner, 1979;

Keller, Nöthe & Werner, 1979; Sandman, 1978, 1979). The chemical purity of the compound has been questioned (Keller, Nöthe, Moroni & Soos, 1978; Sandman, 1978, 1979; Keller, Moroni, Nöthe, Seifried & Werner, 1979) and 'accidental' doping of this material may well explain the different physical properties reported so far. It has been proven that directed doping of NMP with neutral phenazine may change the solid-state properties depending on the amount of phenazine in the crystal (Epstein & Miller, 1978; Miller & Epstein, 1978a, 1979). Additionally, it is well known that phenazine doping of phenazinium-TCNQ solids not only changes the band filling in segregated stacked materials but can also cause structural changes from a mixed to a segregated stacked crystal (Moroni, 1977; Sandman, 1978, 1979; Keller, Moroni, Nöthe, Seifried & Werner, 1979). So far only X-ray powder and preliminary single-crystal results have been presented as proof for these changes. Herein we report the first full structure of a new M_2P/P -TCNQ phase with a M_2P/P ratio of 3:2 and with segregated stacks.

Experimental

1. Preparation

A hot, concentrated solution of 5,10-dihydro-5,10-dimethylphenazine (M_2P) with about 40% phenazine (mmol quantities) in acetonitrile or acetone was added to a hot, concentrated solution of an equimolar amount of TCNQ. The hot mixture was allowed to cool down to room temperature. Black crystals with a steel-blue lustre were precipitated.

The growth of crystalline phases containing phenazine occurs simultaneously with the growth of pure M_2P -TCNQ crystals, the latter being black needles with a slight violet lustre. We found that the

rate of cooling was an important factor. Mostly we obtained big crystals of pure M_2P -TCNQ by slow cooling (longer than one day) while the phenazine-doped M_2P -TCNQ crystals were formed by cooling within a few hours. Thus, both compounds were very often precipitated together but with different crystal sizes.

Crystals of the two compounds are difficult to distinguish optically because of their very similar appearance (only a slight difference in the lustre). The differences in the C, H, N values of the elemental analyses are very small indeed and clearly within experimental error. Elemental analysis calculated for pure M_2P -TCNQ ($C_{26}H_{18}N_6$):

C 75.36% N 20.29% H 4.35%,

calculated for $P_{0.4}(M_2P)_{0.6}TCNQ$ ($C_{25.2}H_{15.6}N_6$):

C 75.22% N 20.90% H 3.88%,

found:

C 75.46% N 20.45% H 4.07%.

A thin-layer chromatogram is the best tool to check which compound has been obtained, for only the phenazine/ M_2P system gives a clearly discernible phenazine spot.

The doped and undoped compounds differ clearly in physical properties such as their infrared spectra (see Fig. 1), their conductivities, the EPR data and the Debye-Scherrer, rotation and Weissenberg photographs.

2. EPR and conductivity measurements

EPR spectra were taken on a Bruker B-ER 418 spectrometer equipped with a Bruker NMR Gaussmeter and an EIP 351 D microwave frequency counter. Four probe resistance measurements were made as described by Coleman, Cohen, Garito & Heeger (1973) on single crystals (2–3 mm long and 0.03–0.07 mm in diameter) along the needle axis which is parallel to the TCNQ stacks. Electrical contact was made by wetting the gold wires with a silver-paste paint. Experimental problems (fragility of the crystals) have so far precluded low-temperature measurements.

3. X-ray investigations

Weissenberg photographs of ten single crystals gave identical patterns. The photographs showed the crystal to be triclinic and gave an estimate for the lattice constants. One crystal ($0.5 \times 0.04 \times 0.05$ mm) was chosen for a full structure determination. Exact lattice constants (see *Abstract*) were calculated by least squares (Berdesinski & Nuber, 1966) from the θ values of 46 reflections centered on a diffractometer. Data collection on a computer-controlled single-crystal

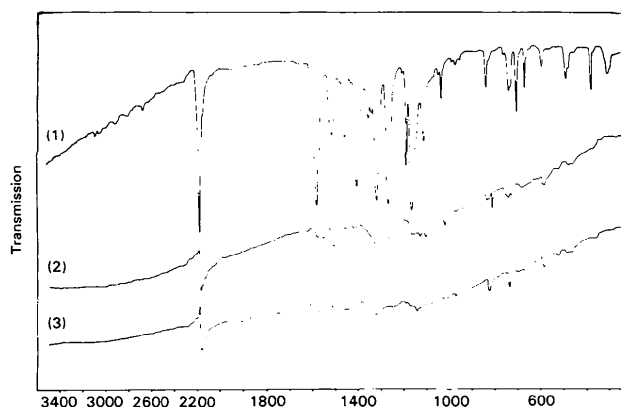


Fig. 1. IR spectra (KBr pellets) at room temperature. (1) Pure M_2P -TCNQ; (2) $P_{0.4}(M_2P)_{0.6}TCNQ$; (3) NMP-TCNQ.

diffractometer (Siemens AED, Mo $K\alpha$ radiation, θ - 2θ scans, five-value method, $4 < 2\theta < 50^\circ$) yielded 704 independent observed reflections with $I > 3.0\sigma(I)$. They were corrected for Lorentz and polarization factors. As the crystal contains only light atoms, no absorption correction was applied.

Calculations were carried out on an IBM 370/168 computer (Universitätsrechenzentrum Heidelberg) with programs from the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) and scattering factors from *International Tables for X-ray Crystallography* (1974). Plots were performed with ORTEP (Johnson, 1965).

3.1. Structure determination and refinement. The short a axis indicates that the structure consists of segregated stacks of the planar constituent molecules. With $Z = 1$ and centrosymmetric molecules, the choice of the centrosymmetric space group $P\bar{1}$ seemed favored and was verified by the successful solution and refinement of the structure. Application of direct methods (*MULTAN*: Main, Germain & Woolfson, 1971) revealed the positions of some of the non-hydrogen atoms, the rest of them were found on Fourier maps. Refinement with anisotropic temperature factors converged with $R = 0.101$. As the ratio of phenazine to M_2P was not known at the beginning, different population parameters ranging from 0.3 to 1.0 were inserted for the methyl C(13) and refined. In all cases, the population parameter was calculated as 0.60 (2). Relatively large thermal parameters were attributed to this C(13), their values and standard deviations being about four times those of the other nonhydrogen atoms. The positions of the H atoms attached to rings were detected on a difference-Fourier map and refined with individual isotropic temperature factors. The final R became 0.073. The H atoms of the partially occupied methyl group could not be detected.*

Results

1. Description of the structure

Atomic coordinates are listed in Table 1. The numbering scheme, bond distances and angles of the non-hydrogen atoms are given in Figs. 2 and 3. Bond distances to H range from 0.92 (9) to 1.12 (9) Å, angles from 101 (5) to 135 (5)°. The distribution of M_2P and phenazine is random, and no superstructure reflections or diffuse scattering could be observed in routine rotation and Weissenberg photographs. The refinement of the population parameter of the methyl

Table 1. Atomic coordinates ($\times 10^4$, H $\times 10^3$) and isotropic temperature factors equivalent to the refined anisotropic values

	x	y	z	U (Å ²)
N(1)	11622 (22)	4862 (10)	7587 (5)	0.064
N(2)	10103 (20)	118 (10)	6084 (5)	0.065
C(1)	6911 (20)	4150 (10)	5611 (5)	0.038
C(2)	3623 (21)	4058 (10)	4284 (5)	0.040
C(3)	5556 (22)	3272 (11)	4871 (5)	0.039
C(4)	8915 (21)	3339 (10)	6222 (5)	0.039
C(5)	10404 (22)	4211 (11)	6971 (6)	0.042
C(6)	9597 (20)	1549 (12)	6134 (5)	0.042
N(3)	-134 (18)	1785 (9)	68 (5)	0.047
C(7)	1530 (21)	-885 (12)	619 (5)	0.045
C(8)	3174 (23)	-1730 (12)	1285 (6)	0.053
C(9)	4532 (27)	-802 (16)	1973 (7)	0.066
C(10)	4487 (25)	1028 (15)	2046 (7)	0.061
C(11)	2899 (24)	1872 (14)	1408 (6)	0.052
C(12)	1431 (21)	943 (11)	699 (5)	0.042
C(13)	-127 (67)	3738 (24)	161 (14)	0.130
H(1)	552 (18)	211 (10)	470 (4)	0.043
H(2)	283 (18)	334 (9)	374 (5)	0.043
H(3)	252 (22)	312 (12)	148 (5)	0.072
H(4)	549 (22)	173 (11)	264 (6)	0.077
H(5)	436 (20)	105 (10)	753 (5)	0.058
H(6)	672 (18)	307 (10)	882 (4)	0.046

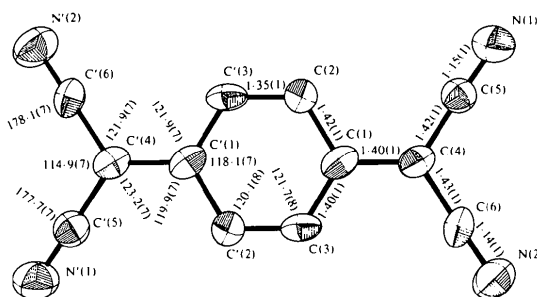


Fig. 2. Numbering scheme, bond distances (Å) and angles (°) in TCNQ.

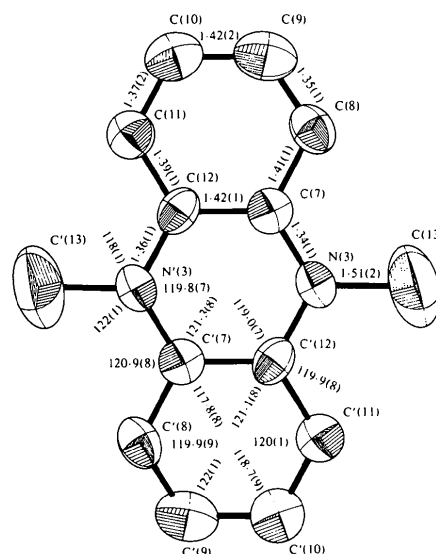


Fig. 3. Numbering scheme, bond distances (Å) and angles (°) in the averaged M_2P /phenazine species.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35125 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(13) showed the ratio $M_2P:P$ to be 60:40 with an uncertainty of 2.

The phenazine species lies at the inversion center at (0,0,0) and is completely planar. The maximum deviation of a ring atom from the least-squares plane is 0.01 (1) Å, the deviation of C(13) from this plane is insignificant: 0.02 (1) Å. There is no hint from the standard deviations and thermal ellipsoids of the phenazine C atoms that the planar configuration found is a statistical superposition of two bent species. If the population parameters of all the phenazine atoms are allowed to vary, they end up at values between 0.98 and 1.02. The molecules form regular stacks along *a*, and the interplanar distance in the phenazine stack is 3.44 (1) Å. A perpendicular projection of two adjacent molecules of one stack is shown in Fig. 4. The angle between the normal to the plane and the stacking axis is 27°. TCNQ lies at the inversion center at (0.5,0.5,0.5) and also forms regular stacks along *a*. The molecule is completely planar. The maximum deviation of an atom of the quinoid ring from the least-squares plane is 0.02 (1) Å. The dihedral angle between this plane and the plane through the terminal $C(CN)_2$ group (0.4°) is not significantly different from zero. The normal to the plane forms an angle of 32° with the stacking direction. The interplanar distance is 3.26 (1) Å. Fig. 5 shows a perpendicular projection of two adjacent TCNQ molecules of the same stack: the overlap is of the characteristic 'ring-external bond' type. TCNQ and

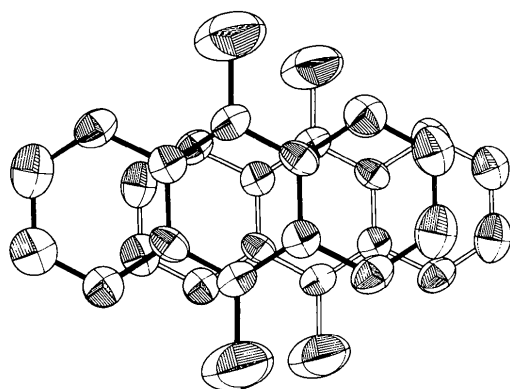


Fig. 4. A perpendicular projection of two adjacent M_2P species of one stack.

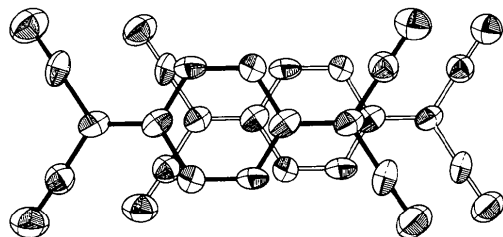


Fig. 5. A perpendicular projection of two adjacent TCNQ molecules of one stack.

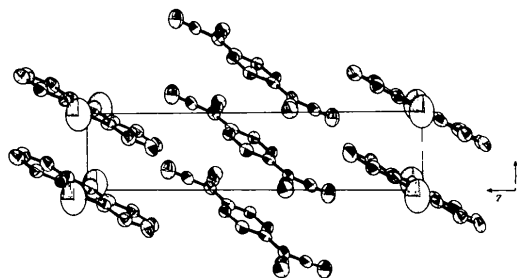


Fig. 6. Projection onto the *xz* plane.

the phenazine species form segregated stacks in the crystal.

The molecular planes in the donor and the acceptor stacks are inclined nearly in the same direction with respect to the stacking axis: the dihedral angle between the TCNQ and the phenazine planes is only 8°. This type of stacking is indicated in Fig. 6 with a projection onto the *xz* plane. Thus the typical 'herring-bone' type of stacking, often encountered in TCNQ charge-transfer salts with segregated stacks, is not formed in this case. There are no remarkable short intermolecular contacts: neglecting H, the shortest distances are from N(1) to C(10) and C(11), 3.42 (1) and 3.45 (1) Å respectively.

2. Electrical conductivity and EPR spectra of M_2P/P -TCNQ

The conductivity of five single crystals of doped M_2P -TCNQ was found to be between 5 and 10 $\Omega^{-1} \text{ mm}^{-1}$ along the stacking axis *a* at room temperature.

The EPR spectra show a single strong absorption. The *g* value varies between 2.0025 and 2.0037 for H_0 parallel and perpendicular to the needle axis of the crystals. The *g* anisotropy $(g_{\perp} - g_{\parallel})/g$ of 6×10^{-4} is thus similar to that found in NMP-TCNQ (4×10^{-4}). The peak to peak width ΔH_{pp} of the Lorentzian line is 0.34×10^{-4} T between 120 and 380 K and becomes slightly broader at lower temperatures, being 0.43×10^{-4} T at 100 K. The EPR intensity, as measured by the product of $(\Delta H_{pp})^2$ times peak height, follows a Curie-Weiss law between 100 and 380 K. Above that temperature the signal intensity decreases irreversibly (decomposition).

Discussion

It is well known that highly conducting compounds like TTF-TCNQ and NMP-TCNQ form segregated stacks and exist in a mixed-valence state. Compounds with mixed stacks, on the other hand, exhibit low conductivity (Keller, 1977; Miller & Epstein, 1978b; Hatfield, 1979). The important point in this investigation is the change of structure and physical proper-

ties achieved by 'doping' with a very similar species. The crystal structure of the 'doped' M_2P -TCNQ compound is nearly identical to the segregated stack structure of NMP-TCNQ (Fritchie, 1966; Kobayashi, 1975). The interplanar spacing in the TCNQ column is the same (3.26 Å) while the spacing in the phenazine- M_2P stack (3.44 Å) is a little larger (0.08 Å) than that of the NMP stack in NMP-TCNQ (3.36 Å). The latter value might be due to the number of methyl groups being about 10% less in NMP-TCNQ than in mixed phenazine/ M_2P -TCNQ.

The pure and 'doped' M_2P -TCNQ structures differ in the type of stacking. Also, the shape of the M_2P molecule seems to be different in the two structures. In the mixed stacked M_2P -TCNQ, the M_2P species is folded along the N---N axis with a dihedral angle of 165° (Goldberg & Shmueli, 1973). In the present segregated stacked 'doped' M_2P -TCNQ the $(M_2P)_{0.6}(P)_{0.4}$ species is planar by symmetry. One might expect a strictly planar structure for phenazine and a somewhat folded one for the M_2P^+ radical cation.

The present structure determination, although suffering from non-stoichiometry and from a relatively small ratio of the number of independent reflections to the number of atomic parameters, suggests planarity of the $P_{0.4}(M_2P)_{0.6}$ species. An attempt to refine the structure in the space group $P1$ did not yield statistically significant improvements. Also, the thermal ellipsoids do not suggest appreciable statistical disorder between two considerably bent structures. Therefore, the present structure solution favors the view that M_2P^+ can approach planarity.

To help to determine whether such an inference is reasonable we prepared two triiodide compounds of M_2P and determined their structures. One compound contained only M_2P^+ radical cations and triiodide anions (Keller, Moroni, Nöthe, Scherz & Weiss, 1978) and the other one beside these species contained, occupying different sites, neutral phenazine and dimethyl glycol ether (Scherz, 1977). In both cases there are M_2P^+ radical cations as proved by EPR (Curie-Weiss paramagnetism) and magnetic susceptibility but with different dihedral angles about the N---N line. In the first case the M_2P molecule is bent (165.5°) as in the M_2P -TCNQ structure while in the second case the M_2P^+ cation is almost planar (173.8°). Thus M_2P may be ionic both in pure M_2P -TCNQ and in doped M_2P -TCNQ.

As in the case of NMP-TCNQ, where the mixed-valence state is formed by neutral NMP and ionic NMP^+ species, the physical and structural properties of doped M_2P -TCNQ can be understood as arising from mixing ionic M_2P^+ and neutral phenazine in the stack. In NMP-TCNQ for example there is still considerable doubt (Megtert, Pouget & Comès, 1979) about the degree of charge transfer from the TCNQ anions to the NMP cation in the solid state. However, in doped

M_2P -TCNQ the 60% population of the methyl group seems to suggest a possible mixed-valence state along the M_2P stack (60% ionic M_2P^+ and 40% neutral phenazine) and a corresponding 60% ionicity along the TCNQ stack. Since the analytical proof of the composition of the sample is based only on the X-ray structure refinement and since other analytical tools to determine the correct amount of phenazine in the sample are not available, it cannot be ruled out that crystals with other compositions exist.*

The physical properties of the doped $P_{0.4}(M_2P)_{0.6}$ -TCNQ and the pure M_2P -TCNQ are completely different. The doped M_2P -TCNQ shows a conductivity at room temperature similar to that of NMP-TCNQ which is about six orders of magnitude higher than that of pure M_2P -TCNQ. The similarity of the IR spectrum (see Fig. 1) with that of NMP-TCNQ is also very impressive. The strong IR absorption is consistent with the high conductivity. The EPR properties reflect the resemblance between NMP-TCNQ and doped M_2P -TCNQ as well. While the pure, mixed stacked M_2P -TCNQ shows thermally activated triplet spin excitons (Nöthe, Moroni, Keller, Soos & Mazumdar, 1978), the segregated stacked phenazine-containing M_2P -TCNQ follows a Curie-Weiss law just as NMP-TCNQ does below 200 K. The observed line width is only very weakly temperature-dependent with a tendency of line broadening at low temperatures. The same behavior has been found in NMP-TCNQ in the low-temperature semiconducting region (Epstein, Etamad, Garito & Heeger, 1972). In doped M_2P -TCNQ the transition temperature from the semiconducting to the metallic state, if any, was too high to be accessible without decomposition of the compound around 400 K, at least for the three investigated crystals. From one of these crystals the X-ray structure was determined.

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* *Note added in proof:* The $M_2P:P = 60:40$ ratio reported here must be considered with caution: Examining this ratio in a crystal of a different batch, we became aware of the strong interdependence of site-occupation factor (s.o.f.) and temperature factor (t.f.). If the t.f. is held fixed at different reasonable values, the s.o.f. refines to values between 0.5 and 0.7. In the refinement described above, we refined the t.f. in one cycle and the s.o.f. in a subsequent one and so on. This procedure resulted in the values given in this paper.

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A Reinvestigation of the Structure of *S,S*-Dimethyl-*N*-methylsulphonylsulphilimine*

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Abstract

The structure of *S,S*-dimethyl-*N*-methylsulphonylsulphilimine ($\text{Me}_2\text{SNSO}_2\text{Me}$), $\text{C}_3\text{H}_9\text{NO}_2\text{S}_2$, has been reinvestigated with diffractometer data. The crystals are monoclinic, $a = 5.809$ (1), $b = 13.518$ (2), $c = 9.212$ (2) Å, $\beta = 105.17$ (2)°, $Z = 4$, space group $P2_1/c$. The atomic parameters obtained from film data ($R = 0.105$) have been refined by least squares to $R = 0.048$ for 1115 independent reflexions. The $\text{S}^{\text{IV}}\text{N}$ and $\text{S}^{\text{VI}}\text{N}$ bond lengths are discussed.

* IUPAC name: *S,S*-dimethyl-*N*-methylsulphonylsulphimide.

Introduction

An X-ray structure determination of the title compound was carried out (Kálmán, 1967) to study the chemical bonds and stereochemistry of organosulphur compounds of the *N*-sulphonylsulphilimine type ($\text{R}^1\text{R}^2\text{SNSO}_2\text{R}^3$). Later, the conclusions gained further support from subsequent X-ray investigations of related molecules: $\text{Me}_2\text{SNSO}_2\text{C}_6\text{H}_4\text{Me}$ (Cameron, Hair & Morris, 1973), $\text{Ph}_2\text{SNSO}_2\text{C}_6\text{H}_4\text{Me}$ (Kálmán, Duffin & Kucsmán, 1971), $\text{PrPhSNSO}_2\text{C}_6\text{H}_4\text{Me}$ (Kálmán & Sasvári, 1972) and $[\text{tert-BuC}_5\text{H}_9\text{SN}(\text{Et})\text{SO}_2\text{C}_6\text{H}_4\text{Me}]^+[\text{BF}_4]^-$ (Cook, Glick, Rigau & Johnson, 1971).