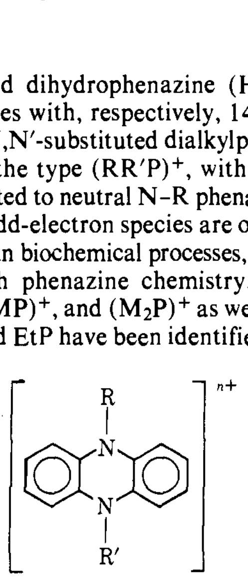
Cation Radical Salts of Phenazine

Z. G. Soos,* H. J. Keller, W. Moroni, and D. Nöthe

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540 and the Anorganisch-Chemisches Institut der Universitat Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, West Germany. *Received January 10, 1977*

Abstract: The cation radicals of dihydrophenazine $(H_2P)^+$, methylhydrophenazine $(HMP)^+$, and dimethylphenazine $(M_2P)^+$ form free radical salts with halide or perchlorate counterions. Single crystal EPR of HMP-ClO_4 and H_2P-ClO_4 indicates strong antiferromagnetic exchange interactions. HMP and M_2P also form 1:1 charge-transfer (CT) complexes with TCNQ. The former is a paramagnetic ionic solid which had previously been described as the "second phase" of *N*-methylphenazinium (MP)-TCNQ. The M_2P-TCNQ complex is largely neutral and diamagnetic at 300 K and undergoes an unusual, reversible transition to a paramagnetic state at 390 K, indicating that phenazine-TCNQ systems are close to the neutral to ionic separation of solid CT complexes.

Phenazine (P) and dihydrophenazine (H_2P) are stable diamagnetic molecules with, respectively, 14 and 16 π electrons. Oxidation of N,N′-substituted dialkylphenazines yields cation radicals **1** of the type $(RR'P)^+$, with 15 π electrons, which are closely related to neutral N-R phenazyl radicals like (RP). These stable odd-electron species are one-electron oxidants and reductants in biochemical processes, which have long been associated with phenazine chemistry.[1-3] The cation radicals $(H_2P)^+$ $(HMP)^+$, and $(M_2P)^+$ as well as the neutral radicals HP, MP, and EtP have been identified in solution by EPR,[4,5] optical,[6] or photochemical[7] studies. Et$\dot{P}$ (or NEP) also forms a stable neutral free-radical solid.[8] Various halogen salts of the cation radical $(H_2P)^+$ have been reported,[9] as has the perchlorate[10,11] of $(HMP)^+$ and of $(M_2P)^+$. These ion radical solids have narrow (~1 G) EPR lines and reduced magnetic susceptibilities $\chi(T)$, as expected for substantial antiferromagnetic exchange.[9-11] As anticipated from the far more widely studied anion radical salts[12,13] of tetracyanoquinodimethane (TCNQ), these planar cations probably form columnar structures. Melby[14] has prepared $(M_2P)I$ and related chlorides in his systematic study of the powder conductivity of TCNQ salts.



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$n = 1$, R = R′ = H $(H_2P)^+$
R = H; R′ = CH_3 $(HMP)^+$
R = R′ = CH_3 $(M_2\dot{P})^+$
$n = 0$, R = CH_3 MP
(no R′) R = CH_2CH_3 EtP

We report here the preparation and solid-state (EPR, IR) properties of two new phenazine cation radical salts, $(H_2P)^+ClO_4^-$ and $(HMP)^+(TCNQ)^-$, together with single crystal EPR results on $(HMP)^+ClO_4^-$ and powder EPR on $(M_2P)(TCNQ)$. There are two reasons for focusing on the solid-state properties of phenazine radicals, one general and one specific. The general reason has to do with the potential flexibility of closely related cation and neutral radicals in producing either interesting novel solids or in permitting systematic studies. No systematic comparisons have been reported on solid-state properties. The data collected in Table I nevertheless show that the cation radical salts of phenazine are fairly extensive. Other substituents, for example CN at one N or at the C-2 position, provide further possibilities, but will not be considered here. The specific interest in phenazine radicals is their close similarity to the organic conductor,[14,16] $MP^{\gamma+}$ $TCNQ^{\gamma-}$, where MP^+ is the diamagnetic, 14 π-electron cation *N*-methylphenazinium and $\gamma = 0.94$ is the degree of charge transfer.[17]

The paramagnetism of free radical salts based on phenazine cation radicals and closed-shell, diamagnetic counterions like ClO_4^- or X^- is clearly associated with the phenazine moiety. The situation is more complicated in charge-transfer (CT) solids[12] in which phenazine is a π-electron donor (D) and TCNQ is a π-electron acceptor (A). Weak D and A complexes are diamagnetic molecular solids which usually crystallize[13] in mixed stacks . . . DADA . . . Strong donors, with low ionization potential, and strong acceptors, with high electron affinity, stabilize an ion radical ground state based on mixed stacking . . . $D^+A^-D^+A^-$ . . . of open-shell species. Both D^+ and A^- contribute to the paramagnetism of ionic CT complexes.

The HMP-TCNQ synthesized here is paramagnetic at 300 K and is thus expected to show the mixed stacking of 1:1 ionic CT complexes.[12,13] Mixed stacking is also observed[15] in M_2P-TCNQ, which, however, is better described as largely neutral and diamagnetic at 300 K, and in the second phase[18] of MP-TCNQ. The possibility of three MP-TCNQ phases[18-20] needs clarification and in fact the "second phase" is actually HMP-TCNQ. The interconversion of diamagnetic MP^+ to the cation radical $(HMP)^+$ was overlooked in previous work. The possibility of both electron and proton transfers in phenazine-related molecules is another indication of their potential flexibility for producing novel organic solids.

The occurrence of closely related neutral [M_2P-TCNQ] and ionic [$(HMP)^+(TCNQ)^-$] CT complexes indicates that a suitably chosen phenazine-TCNQ system may provide the first observation of a neutral-ionic transition. In fact, we believe that the strong reversible paramagnetism of M_2P-TCNQ on heating is evidence for such a transition. Many *neutral* complexes (or . . . DADA . . . stacks) and a few *ionic* complexes (or . . . $D^+A^-D^+A^-$ . . .) have been reported.[12] None has yet shown a neutral-ionic transition, which requires that the electronic energies of the two forms be so nearly equal that thermal energies can interchange the ground state. A CT system which, like M_2P-TCNQ, has a reversible neutral-ionic transition would consequently be of great interest both theoretically and experimentally.

Experimental Section

5,10-Dihydro-5-Methylphenazine (HMP). HMP was prepared under pure nitrogen according to Morley[21] and recrystallized twice

Table I. Solid State Properties of Phenazine-Related Radical Salts

Substituents (R,R′)	Compds	Solid state properties, remarks, and references
	A. Cation Radicals	
R = R′ = H	$(H_2P)^+Cl^-$	Powder EPR; optical[a]
	$(H_2P)^+Br^-$	Several other hydrates and substituents are found[a]
	$(H_2P)^+ClO_4^-$	Powder EPR, single crystal EPR[d]
R = H, R′ = CH_3	$(HMP)^+ClO_4^-$	Single crystal EPR;[b,d]
	$(HMP)^+I^-$	EPR and additional compound with more I[b]
	$(HMP)^+TCNQ^-$	Powder EPR, IR[d]
R = R′ = CH_3	$(M_2P)^+ClO_4^-$	Powder EPR[b,d]
	$(M_2P)TCNQ$	Preparation; powder conductivity,[c] structure[e]
	$(M_2P)^+(TCNQ)_2^-$	Preparation; powder conductivity[c]
	B. Neutral Radical (R′ = 0)	
R = CH_2CH_3	NEP	Preparation, magnetism, and single crystal optical[f]

[a] Reference 9. [b] Reference 11. [c] Reference 14. [d] Present work. [e] Reference 15. [f] Reference 8.

from acetone. TCNQ (from Aldrich Chemical Co.) was used. All operations were carried out under nitrogen and only absolute solvents were used.

HMP-TCNQ. A filtered hot solution of 234 mg (1.17 mmol) of HMP in ca. 150 mL of 2-propanol was mixed with a hot, filtered solution of 239 mg (1.17 mmol) of TCNQ in ca. 1000 mL of 2-propanol. The mixture immediately turns dark green violet and after leaving it overnight at room temperature small purple needles precipitated. The crystals were filtered, washed with 2-propanol and ether, and dried in vacuo. Anal. Calcd: C, 74.98; N, 20.99; H, 4.03. Found: C, 74.45; N. 20.74; H, 4.10. Using benzene as a solvent, the same color change is observed on mixing the two solutions, yet the precipitate is more microcrystalline and the color is more blue than purple.

HMP-ClO$_4$. HMP$^+$ ClO$_4^-$ was prepared according to literature.[11] Needles of a length of ca. 1.5 cm were obtained by dissolving HMP$^+$ ClO$_4^-$ in hot ethanol, filtering, concentrating by evaporation, and slowly cooling down to room temperature within 3 days. Anal. Calcd: *C*, *52.79*; *H*, *4.09*; *N*, *9.48*. *Found*: *C*, *52.52*; *H*, 4.17; *N*, *9.28*.

H$_2$P-ClO$_4$. $LiClO_4 \cdot 2H_2O$ (500 mg, 3.13 mmol) are dissolved and 546 mg (3 mmol) of 5,10-dihydrophenazine are suspended in 25 mL of oxygen-free ethanol. To this mixture, 16 mL of freshly prepared 0.2 M ethanolic solution of bromine is added under cooling (ice/NaCl) and stirring. The color changes from gray to dark green. After the addition of 200 mL of ether a precipitate is obtained that is dissolved again in ethanol containing ca. 1 mL of $HClO_4$ (70%). The solution is filtered, concentrated by evaporation, and left overnight in a refrigerator. The precipitated, needle-like, dark green crystals are rather unstable and very fragile. Anal. Calcd: C, 51.06; H, 3.55; N, 9.93. Found: C, 50.69; H, 3.61; N, 9.39. In the range of 3100-3300 cm^{-1}, the IR spectrum shows the same characteristic N-H absorption band as MPH-ClO$_4$.

NMP-TCNQ, M$_2$P-ClO$_4$, and M$_2$P-TCNQ. MP-TCNQ(I) was prepared as described in the literature.[14] The EPR spectra were taken on a Bruker B-ER 418 X-band spectrometer. IR characterization on all samples were carried out on pressed pellets at 300 K on a Beckman 4240.

M$_2$P-ClO$_4$[11] and M$_2$P-TCNQ[14] were prepared as described earlier. These compounds were identified by their elemental analysis and/or their IR spectra.

Results

A. Powder IR. Since aromatic N-H vibration frequencies occur between 3000 and 3500 cm^{-1}, this region of the IR spectrum provides a simple test for the occurrence of $(H_2P)^+$ or $(HMP)^+$ in the solid. As shown in Figure 1, powdered $(H_2P)^+ClO_4^-$, $(HMP)^+ClO_4^-$, and $(HMP)^+(TCNQ)^-$ all have absorptions in this region, while MP-TCNQ(I) and M$_2$P-TCNQ, with no N-H bond, do not. The structure seen in several of the N-H absorbtions in Figure 1 probably arises from inequivalent N-H bonds.

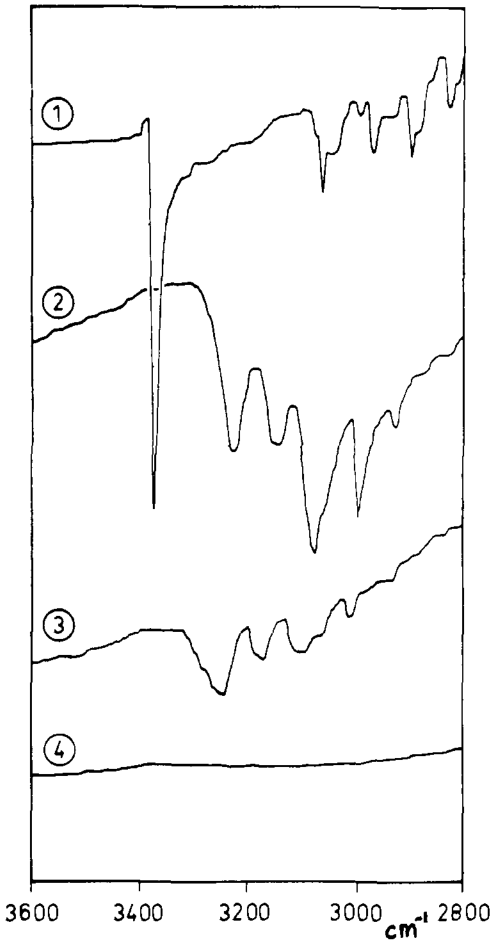

Figure 1. Powder IR in the aromatic NH region around 3200 cm^{-1}: (1) solid (neutral) HMP; (2) $(HMP)^+ClO_4^-$; (3) $(HMP)^+(TCNQ)^-$; (4) MP-TCNQ(I), which has no N-H bond.

The powder spectrum of the conducting MP-TCNQ(I) and of HMP-TCNQ are superimposed in Figure 2. The broad electronic absorption of the conductor yields a smaller signal to noise for the vibrational features. Except in the NH region, the very close correspondence between the two spectra in Figure 2 indicates that the phenazine compound is largely ionic, $(HMP)^+(TCNQ)^-$ This formulation is consistent with a paramagnetic solid and such IR spectra were early evidence for ionic organic solids.[22] In addition, the close correspondence of the spectra in Figure 2 demonstrates the relative insensitivity[23] of *molecular* properties to the crystal packing. MP-TCNQ(I) forms segregated stacks of MP$^+$ and TCNQ$^-$, with face-to-face chains of the same species. HMP-TCNQ forms a mixed stack,[24] as in M$_2$P-TCNQ[15] and in the vast majority of donor-acceptor systems, with an alternate arrangement of $(HMP)^+$ and $(TCNQ)^-$ along the chain. While the exact

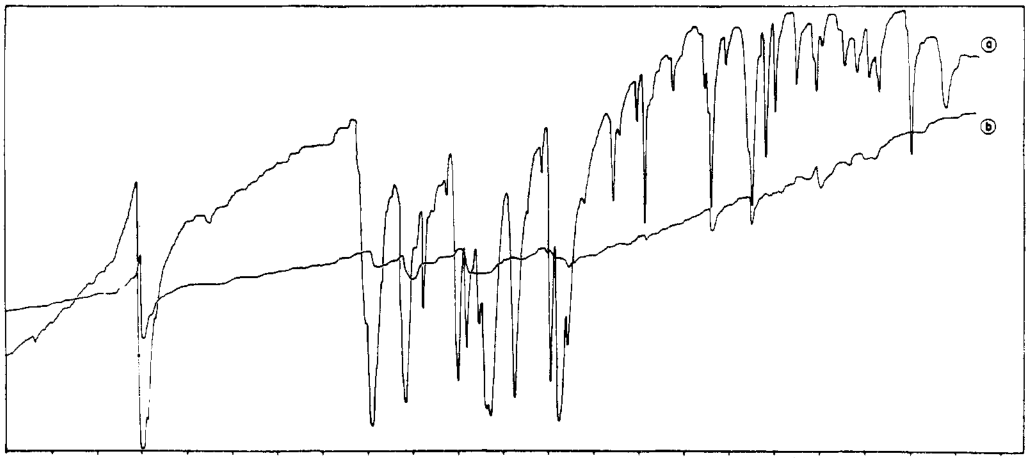

Figure 2. Comparison of the powder IR at 300 K of (a) the nonconductor HMP-TCNQ, with mixed stacks, and (b) the organic conductor MP-TCNQ(I), with segregated stacks.

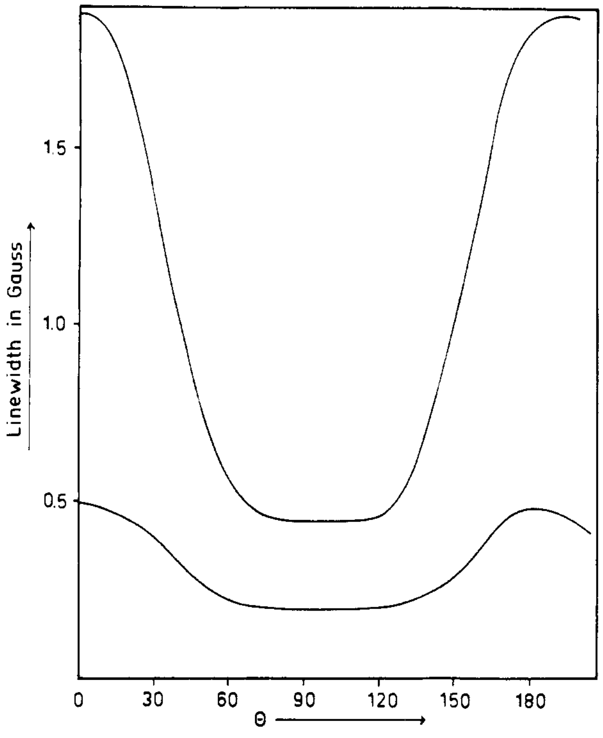

Figure 3. Peak-to-peak derivative line width of the EPR spectrum of single crystal $(HMP)^+ ClO_4^-$ at 300 (upper curve) and 110 K (lower curve) as a function of orientation, with $\theta = 0°$ corresponding to $g_\parallel$ and $\theta = 90°$ to $g_\perp$.

Table II

Sample	g factor (298 K)	Line width, G
HMP^+TCNQ^- powder	$\bar{g} = 2.0029$	0.83 symmetric
$HMP^+ClO_4^-$ single crystal	$g_x = 2.0025$ $g_y = 2.0028$ $g_z = 2.0037$	
$H_2P^+ClO_4^-$ single crystal	$g_x = 2.0028$ $g_y = 2.0029$ $g_z = 2.0030$	
$M_2P^+ClO_4^-$ powder	$\bar{g} = 2.0030$	2.5 slightly asymmetric

degree of ionicity is not known from IR or even from structural studies, the predominantly ionic character of $(HMP)^+(TCNQ)^-$ can be inferred at once from Figure 2.

B. EPR. A single, exchange-narrowed, Lorentzian EPR line was observed at X-band in these phenazine cation radical salts. The principal values of the g tensor for $(HMP)^+ClO_4^-$ are given in Table II and are independent of temperature between 100 and 300 K, the region of the measurement. The g tensor for $(H_2P)^+ClO_4^-$ (Table II) is more isotropic and is rather smaller than the 2.0049 reported[9] in $(H_2P)^+Cl^-$ or $(H_2P)^+Br^-$. The lower values are consistent with organic radicals with no heavy-atom substituents. However, we have not pursued the origin of the g-value discrepancy. The $(HMP)^+(TCNQ)^-$ powder spectrum at 300 K also corresponds to an exchange-narrowed line at $\bar{g} = 2.0029$. The line width of ~0.83 G apparently exceeds the g tensor anisotropy, since the absorption is symmetric; thus $|\Delta g|$ must be $<\sim 0.0005$.

The g tensor of $(HMP)^+ClO_4^-$ probably reflects the crystal average of magnetically inequivalent $(HMP)^+$ stacks. This follows from the observation that *planar* organic radicals are essentially axial, with $g_\perp^{mol} > g_\parallel^{mol} \sim 2.0023$, the free-electron value. The average of two such axial g tensors with an angle of ~90° between their axes is again axial, but now with $g_\perp = \frac{1}{2}(g_\perp^{mol} + g_\parallel^{mol}) < g_\parallel = g_\perp^{mol}$. The structure of $(HMP)^+ClO_4^-$ will be required for a detailed analysis. Similarly, the essentially isotropic g tensor of $(H_2P)^+ClO_4^-$ may represent either additional averaging in the crystal of magnetically inequivalent molecules or may indicate significant deviations from planarity in $(H_2P)^+$.

The angular dependence of the peak-to-peak derivative line width ΔH_{pp} for $(HMP)^+ClO_4^-$ is shown in Figure 3 at two temperatures. Other principal axes planes show similarly strong angular dependences and a substantial narrowing at 110 K. The anisotropy is greatly reduced in $(H_2P)^+ClO_4^-$, which at 300 K has $1.3\ G < \Delta H_{pp} < 2.1\ G$. The $(M_2P)^+ClO_4^-$ crystal, by contrast, has a slightly broader line (~4 G) at 80 K than at 300 K (~2.5 G). The occurrence of an exchange-narrowed line with width of ~1 G is thus a general feature of the perchlorate salts, of $(HMP)^+(TCNQ)^-$, and of the second phase[18] of MP(TCNQ). The relatively weak temperature dependence (compared to triplet exciton salts[12]) points to a regular (rather than dimerized) stack of cation radicals. The pronounced anisotropy and temperature dependence (Figure 3) of $(HMP^+ClO_4)^-$ offers a good test of models, for example, based on dipolar broadening, once the crystal structure is determined.

As discussed elsewhere,[12] the temperature dependence of $\chi(T)$, or of the EPR intensity $I \approx (\Delta H_{pp})^2$ h for a Lorentzian

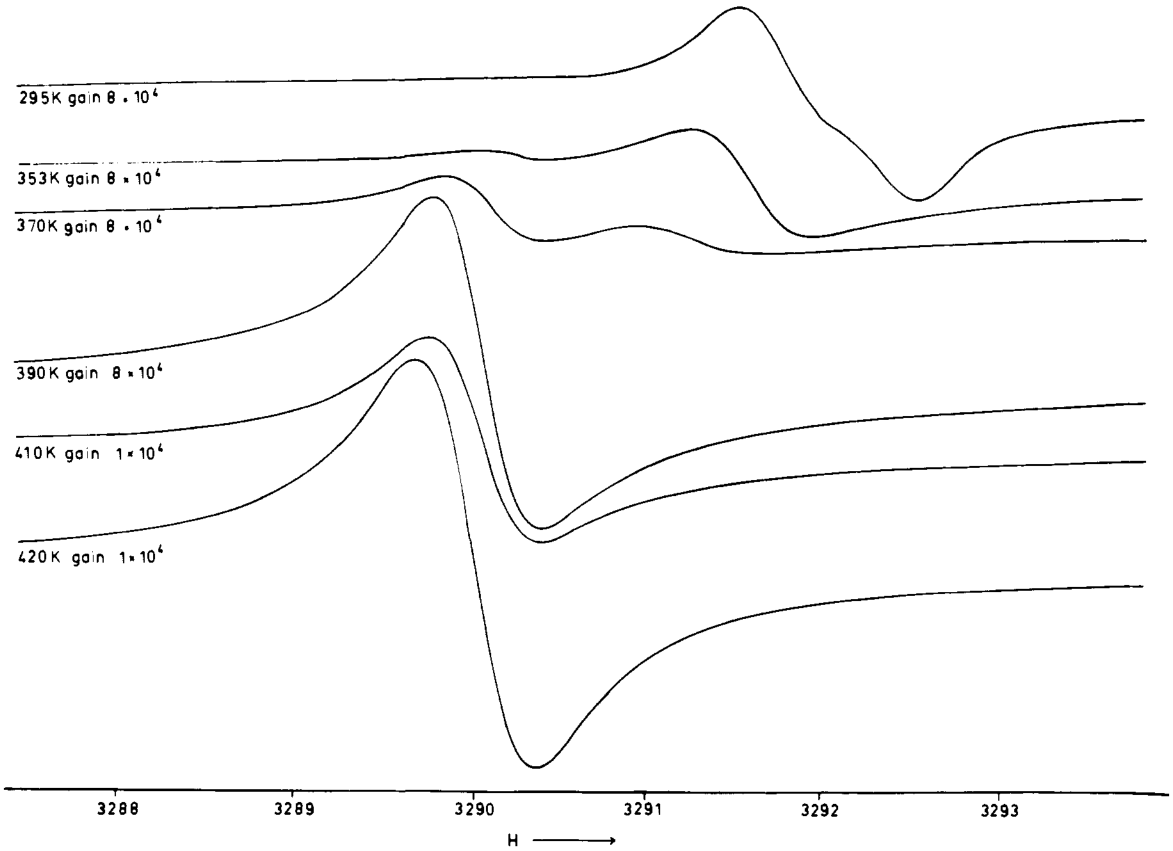

Figure 4. EPR of powder M_2P–TCNQ at several temperatures. Note the change in gain for the 410 K spectrum, which represents an order of magnitude more spins.

line of height h, is not well understood in organic solids based on regular stacks. Strongly alternating stacks have $\chi(T)T\alpha(1 + \frac{1}{3} \exp \Delta E_p/kT)^{-1}$, where ΔE_p is the activation energy for paramagnetism. Such systems show fine-structure splittings at low temperature and have strongly temperature-dependent ΔH_{pp}. The phenazine cation radical salts do not show fine structure and have rather weakly temperature-dependent ΔH_{pp}. However, the EPR intensity changes considerably more than the Bonner-Fisher result[25] for a regular chain. The analysis of slightly alternating chains is more difficult and requires several parameters. As in previous work,[11] we estimate the exchange J in a stack by fitting ΔE_p in the singlet-triplet model to the relative EPR intensity. This yields, roughly, $\Delta E_p \sim 0.03$ ev for $(HMP)^+ClO_4^-$ and is typical of such systems.[11]

At room temperature, M_2P–TCNQ powder shows (Figure 4) a very weak EPR line at $g = 2.0026$ which could be assigned to a small amount of $TCNQ^-$ impurities in the lattice. On heating the sample an additional exchange-narrowed signal at $g = 2.0035$ appears whose intensity increases rapidly with increasing temperature. The original smaller "impurity" signal merges with the more intense "high-temperature" signal, or more likely disappears at about 390 K. The temperature dependence of these EPR spectra is fully reversible between room temperature and 420 K. On cooling the sample from 420 K the intense signal disappears to give rise to the small absorption at $g = 2.0026$ at room temperature.

A similar but irreversible effect occurs on grinding the solid M_2P–TCNQ in a mortar. An intense EPR absorption is observed after a very short time of grinding, which grows in intensity if more care is taken to powder the sample. A strong signal at $g = 2.0030$ is recorded after the sample was ground for several minutes. The line width of this signal increases from 1.0 to 2.8 G with increasing time of grinding the crystalline sample. 2-Propanol solutions of M_2P–TCNQ in contact with the solid change their color from greenish to green on heating from room temperature to 70 °C. This effect may be explained with a $M_2P + TCNQ \rightleftharpoons M_2P^+ + TCNQ^-$ equilibrium in solution, which was postulated earlier by Melby,[14] and is now invoked for the solid state as well. The increase in radical concentration in these solutions was followed by EPR qualitatively over the temperature range from 298 to 370 K. In the more polar solvent CH_3CN the solutions are deep green, indicating higher $TCNQ^-$ concentrations. Toluene solutions are yellow.

Discussion

There are several crystal structures of phenazine-related TCNQ compounds: M_2P–TCNQ,[15] P–TCNQ,[26] MP–TCNQ(I),[19] MP–TCNQ(II),[18] MP–TCNQ(III),[20] and various phenothiazines.[27] In addition, TCNQ radical salts are well characterized structurally[12,13] as are a smaller number of cation radical salts. Thus structural aspects of the present salts can be discussed with some confidence. Unusual features typically merit further crystallographic studies, as not all new systems require such attention.

M_2P–TCNQ has[15] a bent M_2P molecule, with a dihedral angle of 165° between the two planes intersecting along the N–N line. The bond lengths further suggest a largely neutral structure at 300 K. The 14 π-electron cation MP^+ in MP–TCNQ(I) is a planar aromatic species,[19] while it apparently[18] is slightly bent (5.4°) in MP–TCNQ(II). The unusual properties of MP–TCNQ(II), including the bent MP^+ species, suggest strongly that the "second phase" is actually HMP–TCNQ, with the MP^+ cation inadvertently converted to the HMP^+ radical. Morosin[24] has confirmed this hypothesis by reexamining the "MP–TCNQ(II)" structure and by comparing it with our HMP–TCNQ samples. The exchange narrowed EPR of both systems is reminiscent of mixed stack ionic charge-transfer complexes,[12] as expected for a ...

$D^+A^-D^+A^- \ldots$ system in which $D^+ = (HMP)^+$.

The paramagnetism and IR spectrum (Figure 2) of HMP-TCNQ led us to postulate a largely ionic ground state, $(HMP)^+(TCNQ^-)$, in contrast to M_2P-TCNQ. The additional structural information[24] of mixed stacking, as in the largely neutral M_2P-TCNQ complex,[15] then indicates that both complexes must be close to the neutral-ionic boundary separating the known charge-transfer solids.[28,29] Additional evidence that phenazine-TCNQ systems are close to the neutral-ionic transition comes from the partial charge transfer in MP-TCNQ(I), which is probably associated with 6% localized $(MP)_2^+$ dimer radicals on the basis of NMR[17] and heat capacity studies.[30] Such sites arise naturally from structural disorder.[19] The energy change for a misoriented MP^+ must nevertheless be sufficient to transfer an electron to the $TCNQ^-$ stack, which indicates a rather close matching of the two electronic energies.

The structural and EPR data on M_2P-TCNQ at 300 K indicate a largely neutral, diamagnetic ground state. The reversible increase of the EPR intensity around 390 K shown in Figure 4 indicates a paramagnetic, ionic CT crystal. We believe that this is the first example of a reversible neutral-ionic transition in an organic CT crystal induced by changing temperature. Early theoretical work[28] emphasized that, in the limit of zero overlap between adjacent molecules, a solid state complex was either neutral or ionic. The degree of CT, γ, in the ground electronic state $\ldots D^{\gamma+}A^{\gamma-}D^{\gamma+}A^{\gamma-} \ldots$ is then constrained by the long range Madelung interactions to $\gamma = 0$ (neutral) or $\gamma = 1$ (ionic). Finite π-electron overlap along the DA stack is indicated by a survey[12] of optical, electric, magnetic, and structural data. Finite overlap does not alter the previous conclusion about the sharp separation of organic CT crystals into two classes, one largely neutral ($\gamma \approx 0$), the other largely ionic ($\gamma \approx 1$). But finite overlap allows[29] intermediate values of γ for crystals in which the Madelung energy M per D^+A^- pair is accidentally close to the energy $I_D - A_A$ for creating a D^+A^- pair by ionizing D and transferring the electron to A.

The thermodynamic properties and quantum mechanics for CT complexes near the neutral-ionic separation have yet to be found. The following simple argument merely shows that the ionic paramagnetic phase is favored at high temperature. We suppose that M_2P-TCNQ is more nearly approximated by the neutral diamagnetic form at 300 K, with energy E_n, as indicated by the absence of paramagnetism. The paramagnetic ionic form with energy E_i necessarily has a higher entropy $k \ln W_i$ arising from various spin orientations. Thus the molar free-energy difference can be approximated by:

$$\Delta G = G_i - G_n = E_i - E_n - RT \ln W_i$$

and shows that, for $E_n - E_i > 0$, the spin entropy can stabilize the ionic form at high temperature. We emphasize that $RT \ln 2$ is the *upper bound* for a mole of DA complex, since the spin degeneracy is at most 2 for noninteracting D^+ and A^- radical ions. In practice, strong exchange interactions,[12] as indicated by the narrow EPR line in Figure 4, reduce the entropy at finite T. Even the upper bound of $2RT \ln 2 \sim 1$ kcal/mol at 400 K shows that E_i and E_n must accidentally be almost degenerate for a neutral-ionic transition to be possible. Such near degeneracy appears to be characteristic of phenazine-TCNQ complexes and especially of M_2P- TCNQ. While additional experimental data on M_2P-TCNQ and improved theoretical treatments of the neutral-ionic transition are needed, the qualitative features of M_2P-TCNQ indicate a neutral-ionic transition around 390 K.

The flexibility of open-shelled molecular solids based on phenazine related cation and neutral radicals, as well as the nearness of several 1:1 phenazine-TCNQ charge-transfer systems to the neutral-ionic boundary, indicates that the solid state properties of these systems merit further work.

Note Added in Proof. B. Morosin (private communication) has obtained the $HMP^+ClO_4^-$ structure and finds an angle of 72° between the magnetically inequivalent HMP^+ stacks, in agreement with our g-value analysis.

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