and this together with the low symmetry of the DMTCNQ molecule apparently has important consequences for the electronic behaviour of the compound.

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Molecular Configurations of the N-Hydro-N'-methylphenaziniumyl Cation (HMP+)*

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N-Hydro-N'-methylphenazinium perchlorate, $C_{13}H_{12}N_2 \cdot ClO_4$ (HMP–ClO$_4$), crystallizes in space group *Pcab* with $a = 17.286$ (4), $b = 17.964$ (3), $c = 8.0852$ (9) Å and $Z = 8$. HMP$^+$ ions stack in columns along the c axis, with such stacks forming layers separated by the ClO_4^- ion along the a axis. The molecular configuration of the ion involves a small twist, forming a propeller. The previous communication on MP–TCNQ (II), N-methylphenazinium 7,7,8,8-tetracyanoquinodimethanide, is shown to be actually on HMP–TCNQ, $C_{13}H_{12}N_2 \cdot C_{12}H_4N_4$.

Introduction

A sufficient number of cation radical salts of substituted phenazine have been studied so that a systematic comparison of the solid-state properties is becoming possible (Soos, Keller, Moroni & Nöthe, 1977). The close similarity of such 15-π-electron phenazine radicals with the organic conductor MP–TCNQ,† in which MP$^+$ is the diamagnetic, 14-π-electron cation N-methylphenazinium, together with the apparent different crystal phases of MP–TCNQ reported (Morosin, 1975, 1976; Fritchie, 1966; Kobayashi, 1975), suggested a need for clarification (Soos, 1976) and resulted in establishing MP–TCNQ (II)

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† Many authors employ the acronym NMP–TCNQ for this material rather than MP–TCNQ.

CH₃

[HMP structure]⁺

(HMP)⁺
H
H

CH₃
-e / +e

[HMP structure]
H

HMP

(bent, diamagnetic)

-H / +H

+P ↑↓ -P

CH₃

[MP· structure]

MP·

(paramagnetic)

-H / +H

CH₃

[MP⁺ structure]⁺
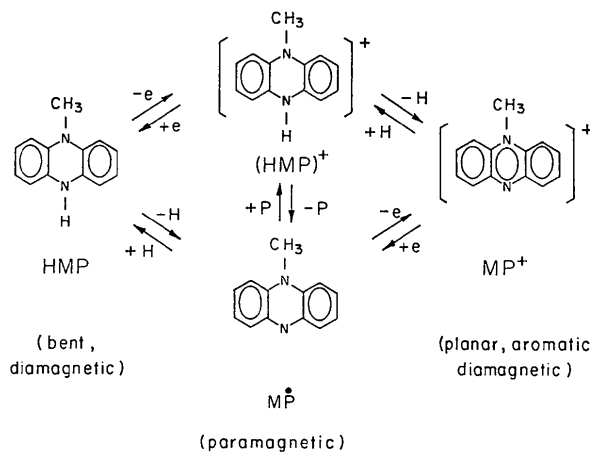
MP⁺

(planar, aromatic diamagnetic)

-e / +e

Fig. 1. Diamagnetic and paramagnetic species in the series HMP, HMP⁺, MP and MP⁺ (after Soos, 1977). The versatility and biochemical importance of phenazines is related to their ability to act as one-electron oxidants and reductants and also as proton donors and acceptors. Note that the MP⁺ ion is a 14-π-electron aromatic system isoelectronic with anthracene (methyl substituted) and that the addition of an electron or H atom (to form a neutral radical or cation radical, respectively) leads to a 15-π-electron system without aromatic character in the central ring. With a strongly ionic anion such as ClO_4^-, one clearly has a salt. With TCNQ, charge-transfer complexes are formed with the possibility of only partial charge transfer occurring; hence, other experimental evidence [such as NMR on MP–TCNQ showing a 0·94 charge transfer (Butler, Wudl & Soos, 1975)] may be necessary. Bond lengths from diffraction studies can also yield qualitative information on charge transfer in these as well as TCNQ radicals (see, for example, Flandrois & Chasseau, 1977).

data were measured with a scintillation detector employing pulse-height discrimination; the θ–2θ scan technique (to 50° 2θ) was used with a scan speed of 1° min⁻¹ over the interval $2\theta_{\lambda_1} - 1·25$ to $2\theta_{\lambda_2} + 1·25°$. Two octants of measured intensities yielded 902 observed and 1303 'less than' intensities. The 'less than' intensities were those in which the intensity value was less than $3\sigma_{ave}/n^{1/2}$, where σ_{ave} is the average σ for n measurements and where $\sigma = (N_{sc} + K^2 N_\beta)^{1/2}$ and N_{sc}, N_β and K are the total scan counts and background counts and the time ratio of the scan to background respectively. Scattering factors were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). The structure was determined by direct methods and refined by least-squares methods. The function $\Sigma w(F_o - F_c)^2$ was minimized with $w = 1/\sigma^2$; 'less than' intensities were included whenever the calculated value exceeded 3σ (there were 27 such intensities in the final cycle of least-squares refinement). From a difference Fourier synthesis, H positions were obtained, assigned the isotropic thermal parameter of the C atom to which they are bonded and these H positions with fixed thermal parameters were subjected to further least-squares refinement. A value of R equal to 0·047 with anisotropic parameters was

(Morosin, 1976) as actually HMP–TCNQ, containing the cation radical, N-hydro-N'-methylphenaziniumyl, HMP⁺. The interconversion of MP⁺ to the radical species HMP⁺ involves the addition of a H atom and has been overlooked in solid-state studies (Fig. 1); this should further increase the flexibility for designing phenazine-based organic salts.

In this communication, the molecular configurations of the HMP⁺ ion found in two different salts are reported. The portion of this study on the TCNQ salt serves as a correction to the previously published results.

Experimental details

(a) Crystal structure of HMP–ClO₄

Precision and Weissenberg photographs on needles of HMP–ClO₄ were consistent with systematic absences l odd for $0kl$, h odd for $h0l$, and k odd for $hk0$, defining $Pcab$. Room-temperature lattice constants were determined by least-squares fitting of the 2θ values for 13 strong hkl reflections between 42 and 55° 2θ using Mo $K\alpha$ radiation ($\lambda = 0·710688$ Å) on a Picker diffractometer; these are $a = 17·286$ (4), $b = 17·964$ (3) and $c = 8·0852$ (9) Å. The Mo $K\alpha$ intensity

Table 1. *Positional parameters* ($\times 10^4$; *for* H $\times 10^3$)

	x	y	z
Cl	4865·7 (9)	1229 (1)	3800 (3)
N(1)	8670 (2)	1192 (3)	3754 (7)
N(8)	7092 (3)	1140 (3)	3808 (8)
C(2)	8259 (3)	1717 (3)	2858 (8)
C(3)	8602 (4)	2283 (4)	1913 (9)
C(4)	8156 (4)	2792 (4)	1102 (10)
C(5)	7353 (4)	2766 (3)	1183 (9)
C(6)	7002 (4)	2217 (4)	2056 (9)
C(7)	7435 (3)	1687 (3)	2917 (8)
C(9)	7492 (4)	608 (3)	4660 (8)
C(10)	7106 (4)	51 (4)	5519 (9)
C(11)	7517 (5)	−469 (4)	6407 (10)
C(12)	8323 (5)	−428 (4)	6434 (10)
C(13)	8710 (4)	113 (4)	5572 (10)
C(14)	8309 (3)	638 (4)	4650 (8)
C(15)	9528 (4)	1218 (6)	3705 (13)
O(1)	5500 (3)	818 (3)	4479 (9)
O(2)	5178 (3)	1867 (4)	3002 (10)
O(3)	4350 (4)	1432 (5)	5065 (8)
O(4)	4462 (4)	794 (4)	2641 (9)
H(3)	914 (4)	232 (4)	176 (9)
H(4)	841 (4)	319 (4)	48 (9)
H(5)	708 (4)	315 (4)	56 (9)
H(6)	650 (4)	215 (4)	209 (9)
H(8)	665 (4)	115 (4)	392 (10)
H(10)	659 (4)	3 (4)	539 (9)
H(11)	724 (4)	−86 (4)	686 (10)
H(12)	856 (4)	−76 (4)	715 (10)
H(13)	925 (4)	9 (4)	552 (9)
H(15)	967 (4)	69 (4)	301 (10)
H(16)	970 (5)	129 (4)	474 (10)
H(17)	966 (5)	176 (4)	368 (10)

Table 2. *Bond lengths and angles of the perchlorate ion*

O(1)—Cl	1·432 (6) Å	O(1)—Cl—O(2)	107·3 (4)°
O(2)—Cl	1·422 (7)	O(1)—Cl—O(3)	109·9 (4)
O(3)—Cl	1·404 (7)	O(1)—Cl—O(4)	110·4 (4)
O(4)—Cl	1·404 (7)	O(2)—Cl—O(3)	111·2 (5)
		O(2)—Cl—O(4)	109·5 (5)
		O(3)—Cl—O(4)	108·5 (4)

(a)

(b)
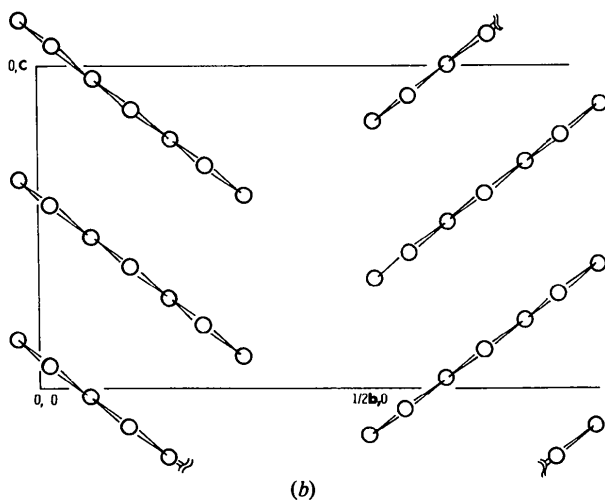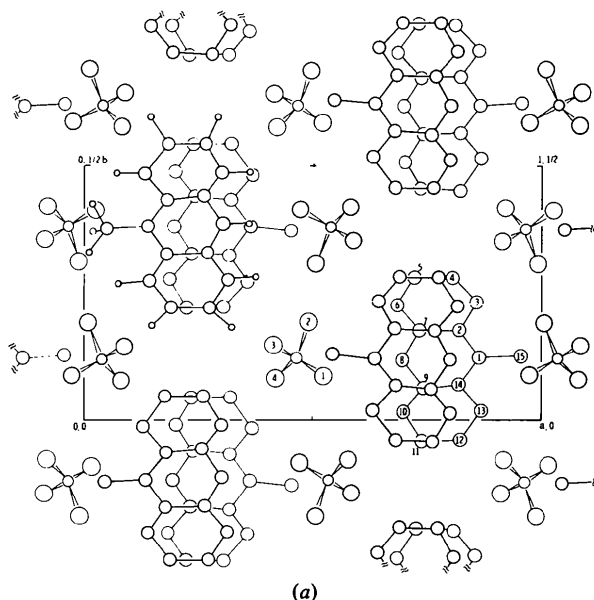
Fig. 2. (a) View along c of HMP–ClO₄. The labeling scheme employed in this communication is shown; N atoms are small circles 1 and 8, O atoms are larger circles 1–4 about the Cl atom. H atoms are shown only on one molecule. (b) Partial view along a; this projection shows the relative orientation of the HMP⁺ ions (at ¾ along x). The least-squares plane through the heavy atoms indicates that the deviation in a stack between HMP ions is only 0·9°; the adjacent stack (right) shown here is canted 72·7° to that near the origin (left).

obtained.* The final parameters are given in Table 1 using the labeling scheme shown in Fig. 2. The H atoms are labeled with the same number as the C atom to which they are bonded with the exception of the remaining methyl H atoms, H(16) and H(17). The values of the interatomic separations and angles for the perchlorate ion are given in Table 2. Values for the HMP⁺ ion in both structures are compared in Fig. 3 and discussed below. The computations were performed with the XRAY 76 system (Stewart, 1976).

(b) Crystal structure of HMP–TCNQ

It was pointed out (Soos, 1976) that the cation in MP–TCNQ (II) was non-planar whereas one would theoretically expect a 14-π-electron system such as the N-methylphenazinium cation to be planar. An examination of the final Fourier synthesis readily revealed the ignored, clearly visible peak (0·4 e Å⁻³). This peak was associated with the N atom labeled N(34). Hence MP–TCNQ (II) is, in fact, HMP–TCNQ.†

Employing the previous intensity data set and including four additional H atoms in the model previously employed (with fixed isotropic thermal parameters), least-squares refinement reduced R to 0·060 and produced an essentially flat difference Fourier map with less than 0·1 e Å⁻³ ripple. The refined hydrogen positions and corresponding distances are given in Table 3. The refined positional parameters are within one standard deviation of those given in the previous communication with the exceptions of C(35), $z = 0·0147$; N(34), $x = 0·7767$, $y = 0·3154$, $z = -0·0828$; H(6), $y = 0·053$; H(3), $y = 0·211$; H(25), y

† In order to attempt to understand the conditions which might lead to the formation of HMP–TCNQ, the so-called phase II, rather than MP–TCNQ, Coleman (1977) has reviewed his graduate work. It is believed that higher starting temperatures of acetonitrile solution favored phase II and it was apparent that the more pure the material and solvent were made, the more difficult it was to crystallize phase I. It was not established whether this was due to the methods used to clean up the acetonitrile, its absolute purity or the absolute purity of the TCNQ and MP.

Table 3. *Refined hydrogen positions* (×10³) *and corresponding distances* (Å)

	Bonded to	x	y	z	Distance
H(34)	N(34)	800 (5)	276 (2)	−135 (8)	1·12 (6)
H(36)	C(35)	809 (5)	490 (2)	−7 (8)	1·12 (6)
H(37)	C(35)	660 (5)	487 (2)	−113 (8)	1·10 (6)
H(38)	C(35)	669 (5)	481 (2)	126 (8)	0·97 (6)

= 0·441. (These parameters have also been deposited; see deposition footnote.)

Comments

(a) Molecular configuration of the HMP cations

These two crystal structure refinements yield different molecular configurations in the two compounds. A least-squares plane through the 14-membered-ring heavy atoms shows that the HMP$^+$ ion is bent in the TCNQ salt while it is twisted in the perchlorate case. In the TCNQ salt, the two least-squares planes through the heavy atoms and meeting at the N atoms in the middle of the ion form an angle of 5·6°; such a configuration can be compared to a pair of wings. In
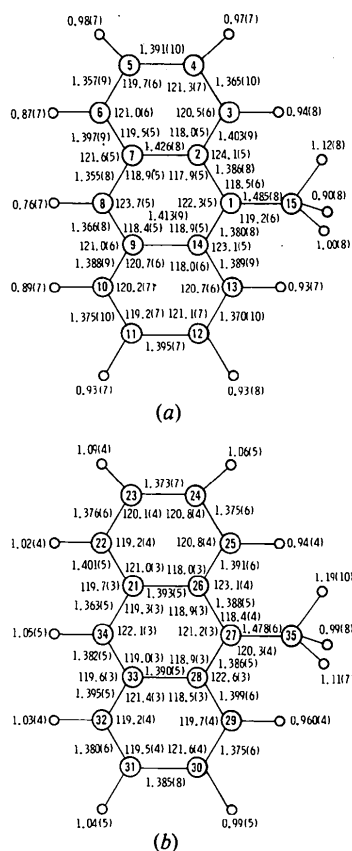
the case of the perchlorate salt, these two planes form a 'propeller' with the corresponding angle between the planes being 1·5°. (If only the C atoms are employed, the least-squares-plane fit is better and the 2·1° angle is slightly larger.)

The bond angles and lengths in the ion compare favorably (Fig. 3) even with the above-mentioned difference in molecular configuration. The average N—C length (1·385 Å) adjacent to the methyl group agrees well with the 1·383 (4) and 1·389 (4) Å lengths observed in the dimethyl analog (Goldberg & Shmueli, 1973a) and are longer than the 1·361 (4) and 1·352 (4) Å values observed in the ethyl analog (Morosin, Plastas, Coleman & Stewart, 1978) in which aromatic character is probably present. Similarly, the N—C lengths on the H side of the cation are longer than values found in analogs with aromatic character [1·338 (5) and 1·349 (4) Å in *α*-phenazine–TCNQ (Goldberg & Shmueli, 1973b) as well as 1·322 (5) and 1·326 (4) Å in the ethyl analog].

(b) Packing of ions in crystal structures

The packing arrangements for the two compounds are different (Figs. 2b and 4). In the perchlorate compound, this arrangement consists of HMP$^+$ ions stacked upon each other (segregated stack) and canted essentially with respect to the c axis. The least-squares plane through the heavy atoms of the HMP$^+$ ions within the stack indicates a slight 0·9° deviation between neighbors. The adjacent stack along the b axis is related by the glide operation so that the molecules in the two different stacks form an angle of 72·7°. The stacks are located so as to form layers of HMP$^+$ and ClO$_4^-$ ions along the **a** direction (Fig. 2a). The N(8)—O(1) separation is 2·86 Å with a H(8)—O(1) separation of 2·13 Å. The next closest O—H

(a)

(b)

Fig. 3. (a) Bond lengths and angles for the HMP$^+$ ion in the perchlorate compound. The molecular configuration of this ion is that of a 'propeller' with the angle between the least-squares planes through atoms 1–8 and through 9–14 plus 1 and 8 being 1·5°. (b) Bond lengths and angles for the HMP$^+$ ion in the TCNQ compound. The identical numbering sequence of the original study is employed. The least-squares planes through 21–27 and 34 and that through 27–34 form an angle of 5·6°; however, in this case the configuration is a 'wing'. Note that the values are in good agreement with those given in Fig. 2(a), even with the slightly different configurations, and that the N—C distances correspond to aliphatic rather than aromatic values (see text).
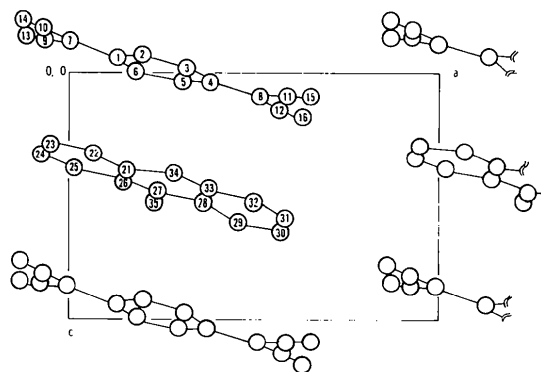

Fig. 4. Partial view of the HMP–TCNQ structure [this figure is a correction of Fig. 1(b) of our previous communication]. This view shows that in this material the two different ions stack alternately upon one another (mixed stack) whereas in the perchlorate compound, Fig. 2(b), the identical ions stack on top of each other (segregated stack).

separations are 0·3 Å longer: O(2)—H(6) of 2·46 Å and O(1)—H(10) of 2·47 Å. Thus the slight variation of the Cl—O distances (Table 2) probably results from the weak 2·86 Å hydrogen-bond interaction.

In HMP–TCNQ, the HMP^+ ions alternate with $TCNQ^-$ ions (mixed stacks) in columns parallel to the c axis. As mentioned in the previous communication, the least-squares planes through the main skeleton of the $TCNQ^-$ ion [i.e. through C(1)—C(8)] as well as the HMP^+ ion [i.e. through all but H and C(35)] indicate both ions to be slightly bowed. If this is ignored and such planes are employed to determine the relative orientation of ions in the lattice, the angle between the two ions within the stack is found to be 3·0°. Two HMP^+ ions in stacks related by the glide operation are canted 25·8° to each other.

(c) Implication of structure on magnetic properties

Both of these structures contain magnetically inequivalent stacks. In the perchlorate salt, the angle between the magnetically inequivalent stacks is 72·7° while in the TCNQ salt, it is 25·8°. Interestingly, in the perchlorate salt, only a single, exchange-narrowed, Lorentzian EPR line has been observed to date (Soos, Keller, Moroni & Nöthe, 1977), suggesting that the two-dimensional effects might be strong, in contrast to most $TCNQ^-$ salts with resolved EPR signals from inequivalent stacks (Soos & Klein, 1975). The large angle also supports the previous rough estimate of nearly orthogonal g tensors on this system. The case for the TCNQ salt appears to be slightly different.

The EPR spectra of HMP–TCNQ (Hughes, 1977) are quite similar to those previously reported for the N,N,N',N'-tetramethyl-p-phenylenediamine, TMPD, complex (Hughes & Hoffman, 1970). This is to be expected since the structures of both HMP–TCNQ and TMPD–TCNQ consist of mixed stacks. In HMP–TCNQ, the linewidths at Q band (35 MHz) are larger than for TMPD–TCNQ; normal to the a axis, the maximum linewidth at 1 G occurs along the c axis, with a linewidth minimum at about 50° from the c axis at 0·35 G, while along the b axis the linewidth is up to 0·7 G. As indicated in the previous section, the stacks are magnetically inequivalent in this plane and a small splitting (<0·3 G) in the line is observed at Q band at

intermediate angles. Thus HMP–TCNQ exhibits less two-dimensional behavior than $HMP–ClO_4$. The g factor anisotropy is small and consistent with a model in which the g tensors of the HMP^+ and $TCNQ^-$ ions are averaged.

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