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CONDUCTING AND INSULATING SALTS OF PHOSPHINIMINIUM CATIONS WITH 7,7,8,8-TETRACYANO-p-QUINODIMETHANE (TCNQ)

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Abstract: A new series of cation-TCNQ salts is described: phosphiniminium cations (1) and (2) form 1:2 salts with TCNQ that are organic conductors (σ_{rt} 0.05-0.15 S cm^{-1}) whereas cations (3) and (4) form insulating 1:1 salts; variable temperature conductivity, magnetic susceptibility and FTir data are described.

A large number of complexes of TCNQ with ammonium and phosphonium cations have been thoroughly studied; they are the prototypes of segregated stack TCNQ salts and they provide classical examples of organic metals, semiconductors and insulators.[1,2,3] For example, semiconducting salts of TCNQ with $[Ph_3P{=}N{=}PPh_3]^+$ cations[4] and $[Ph_2(Me)PCH_2P(Me)Ph_2]^{2+}$ dications[5] have recently been characterised by a range of solid state techniques. In this communication we describe a new class of cations, viz. phosphiniminium cations (1)-(4), that form both conducting and insulating salts with TCNQ. Methyl- and ethyl-derivatives, (1) and (2), form conducting 1:2 salts, while, in marked contrast, under the same conditions, propyl- and butyl-derivatives,

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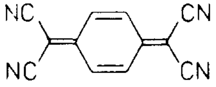
(3) and (4), form insulating 1:1 salts with TCNQ.[6] It is most unusual for such a change in properties to occur upon simple variation of alkyl substitution in a series of cation-TCNQ salts. This new series of salts has been characterised by variable temperature conductivity data, magnetic susceptibility data and spectroscopic techniques.

Room temperature values of conductivity (σ_{rt}) for salts (1)-(4) are shown in the Table. Predictably, the 1:2 salts are more conducting than the 1:1 congeners; this is well-established as a consequence of the partially-filled energy band present in the 1:2 salts.[1] The values of σ_{rt} for salts (1) and (2) are at the upper end of the range for most ammonium- or phosphonium-TCNQ salts (10^{-2}-10^{-5} S cm^{-1}).[1] Both salts (1) and (2) show semiconductor behaviour over the temperature range 300-80 K, with activation energies E_a 0.047 and 0.050 respectively. Pressure dependence of conductivity was studied for needles of salt (1); a maximum value, σ_{rt} 0.32 S cm^{-1}, was reached at 1.5 kBar.

All four salts (1)-(4) are paramagnetic. The temperature dependence of the paramagnetic susceptibility has been studied by e.s.r. spectroscopy; the variation of the total integrated signal intensity for salts (1)-(4) over the temperature range 300-90 K obeys Curie law behaviour, implying a major contribution with localised electrons on the TCNQ molecules.

Infrared and solid state ultraviolet-visible spectra provide structural information on salts (1)-(4). The presence of the TCNQ radical anion in salts (1)-(4) is confirmed by a strong absorption at λ_{max} 840 nm in the u.v. spectra. FTir spectra of powdered samples of conducting salts (1) and (2) have been obtained over the temperature range 300-15 K. At frequencies below a well-defined value [salt (1): 1975; salt (2) 2268 cm^{-1}] absorption coefficients increase with increasing temperature, while at frequencies above this value, absorption coefficients increase with decreasing temperature. This phenomenon has recently been reported for other conducting TCNQ salts and correlated with Peierls distortions in these materials.[7] Salts (1) and (2) both exhibit a broad charge-transfer absorption band, centred at 3400 cm^{-1}, which is characteristic of an organic conductor; this is absent in the

Cation $Ph_3P{=}\overset{+}{N}PhR$ TCNQ



Complex	R	Stoichiometry Cation : TCNQ	σ_{rt} (S cm^{-1})
(1)	Me	1 : 2	0.15[a]
(2)	Et	1 : 2	0.05[a]
(3)	n-Pr	1 : 1	1×10^{-8} [b]
(4)	n-Bu	1 : 1	2×10^{-7} [b]

[a] single crystal, 4 probe measurement

[b] compressed pellet, 2 probe measurement

Table

insulating salts (3) and (4). A noteworthy feature of the i.r. spectra of salts (1)-(4) is the stretching frequency of the nitrile absorptions; this is reported, for many TCNQ salts, to be linearly correlated with the degree of charge transfer and to occur between that of neutral TCNQ (2227 cm^{-1}) and that of fully-ionic metal-TCNQ salts (2185 cm^{-1}).[8] However, salts (1)-(4) all absorb[6] with moderate or strong intensity at significantly lower frequencies; in particular, the values of 2149 and 2160 cm^{-1} for the 1:1 salts (3) and (4) respectively, are remarkably low.

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6. Complexes were obtained by cooling acetonitrile solutions of equimolar amounts of alkylphosphiniminium iodide and TCNQ. Salts (1)-(4) gave satisfactory microanalytical data (C, H and N). Salt (1), (48%) mp 184-187°C (dec), ν_{max} 2168(s), 2176(s), 2191(m) cm^{-1}. Salt (2), (45%) mp 207-208°C (dec) ν_{max} 2176(s), 2194(m) cm^{-1}. Salt (3), (36%) mp 183-185°C (dec), ν_{max} 2149(m), 2176(s) cm^{-1}. Salt (4), mp 156-158°C (dec) ν_{max} 2160(s), 2196(m) cm^{-1}.
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