Tetrahedron Letters,Vol.25,No.38,pp 4275-4278,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

PREPARATION, PROPERTIES AND X-RAY CRYSTAL STRUCTURE OF A COMPLEX OF BIS(TRIPHENYLPHOSPHORANYLIDENE)AMMONIUM IODIDE WITH 7,7,8,8-TETRACYANO-P-QUINODIMETHANE: $(PPN)_2(TCNQ)_3(CH_3CN)_2$

Munir M. Ahmad,[a] Martin R. Bryce,[a*] Joan Halfpenny[b] and Larry Weiler[c]

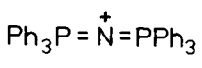
[a] Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, U.K.

[b] Department of Chemistry, Napier College, Colinton Road, Edinburgh, EH10 5DT, U.K.

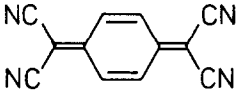
[c] Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada, V6T 1Y6.

Abstract: Bis(triphenylphosphoranylidene)ammonium iodide (PPN^+I^-) forms a 2:3 complex with TCNQ [$(PPN)_2(TCNQ)_3(CH_3CN)_2$] that provides an example of a TCNQ complex containing acetonitrile in the crystal lattice; the material is a semi-conductor with trimerised TCNQ stacks.

The central role of TCNQ complexes and ion radical salts in the quest for new organic materials with unusual semi-conducting and conducting properties is now well established.[1] By virtue of their crystalline packing arrangements these materials exhibit anisotropy of certain intensive variables including electrical, optical and magnetic properties. This one-dimensional character makes transport properties in these materials more susceptible to the influence of impurities or lattice defects than is the case for conventional three-dimensional semi-conductors or metals.



PPN



TCNQ

Amongst the most thoroughly studied TCNQ salts are those formed with alkyl- or aryl-substituted ammonium or phosphonium ions and they span almost all the typical properties of TCNQ salts. It is generally recognized that in complex charge-transfer salts there is a partially-filled TCNQ band, resulting in a narrow band gap semi-conductor or an organic metal. The presence of another electron acceptor in the lattice, e.g. iodine,[2] or occluded solvent,[3] is uncommon and may greatly affect the solid state properties. We now report the preparation, electrical properties and X-ray crystal structure of the title complex, which provides an example of a TCNQ salt that contains acetonitrile in the crystal lattice.

Bis(triphenylphosphoranylidene)ammonium (PPN), $(Ph_3P{=}N{=}PPh_3)^+$ was chosen as the cation because there is renewed interest in TCNQ complexes of large phosphorus-containing cations, e.g. 5,5-dimethyldibenzophospholium,[4] and dications[5] such as $[Ph_2(Me)PCH_2P(Me)Ph_2]^{2+}$. The title complex was prepared by cooling to -15°C an equimolar solution of PPN iodide and TCNQ in hot, dry acetonitrile and isolated in 70% yield (m.p. 183-188°C; λ_{max} (CH_3CN) 394, 743, 760, 820, 842 nm; e.s.r. (powder) strong singlet, g 2.005, 1.8 G wide). $(PPN)_2(TCNQ)_3(CH_3CN)_2$ forms thin, rectangular, black crystals. The electrical conduction properties were measured by the four-probe technique along the needle axis on six crystals from two separate preparations. The room temperature conductivity lies between 4.6×10^{-4} and 7.5×10^{-5} $(\Omega\ cm)^{-1}$, typical of a semi-conductor. This value is lower than that of many complex TCNQ salts,[1] a fact consistent with the X-ray crystal structure which shows TCNQ molecules stacked in trimers with an unusually large inter-trimer distance (9.85Å), while the intra-trimer distance is 3.30Å (Figure). (The crystals are triclinic with space group $P\bar{1}$; a = 8.843(1), b = 16.705(2), c = 17.163(2)Å, α = 69.85(2), β = 84.11(3), γ = 85.26(3)°, determined from 2833 independent reflections recorded on a Stoe Two-Circle Diffractometer using MoK_α radiation.) There is only one type of intra-trimer overlap, the 'ring-over-bond' overlap typical of highly conducting TCNQ complexes. The large cations are non-planar and non-symmetrical.

The temperature dependence of conductivity over the temperature range 190-310K was measured on four crystals from two different preparations.* There is a linear drop of conductivity with temperature without any observable transitions. This behaviour is typical of a semi-conductor with energy of activation 160 meV.

* We are thankful to Professor A.E. Underhill and his research group (Bangor) for their help and cooperation.

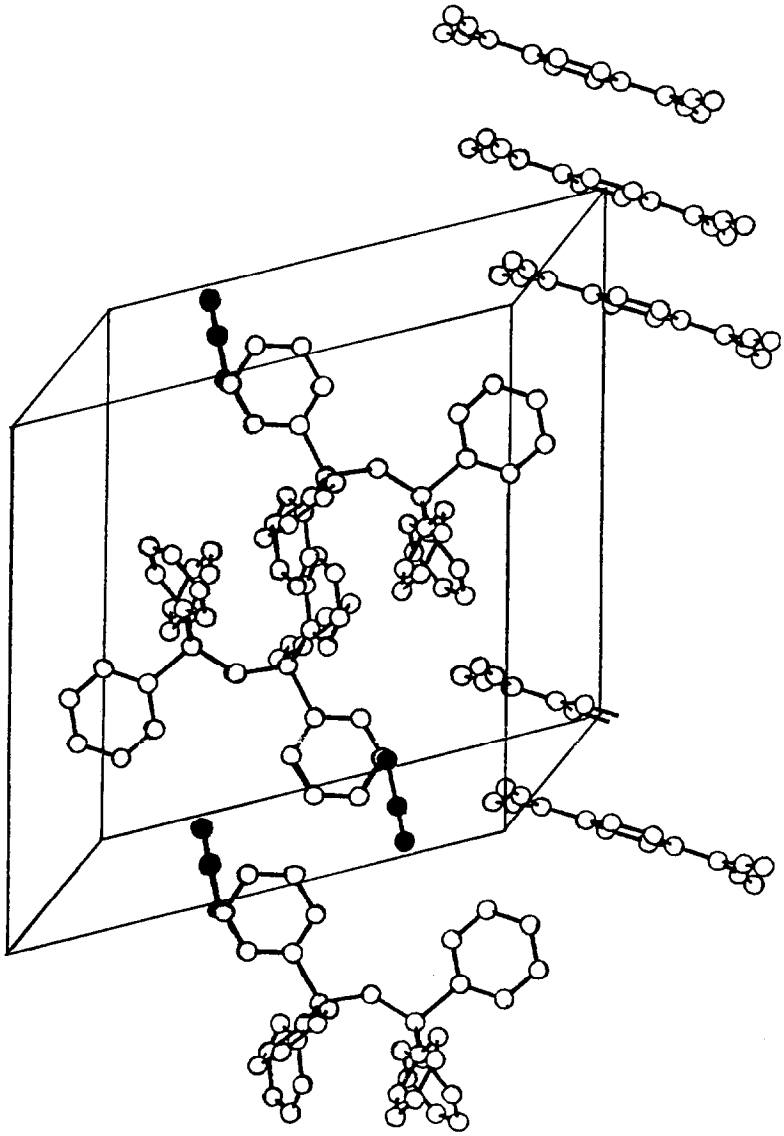


Figure. View of the unit cell showing three units of structure.

(The acetonitrile molecules are shaded.)

References

1. For recent reviews and monographs see J.B. Torrance, Accounts Chem. Res., 1979, 12, 79; 'The Physics and Chemistry of Low Dimensional Solids', ed. L. Alcacer, D. Reidel, Dordrecht, Holland, 1980; 'Extended Linear Chain Compounds', Vols. 1-3, Plenum, London, 1982 and 1983; M.R. Bryce and L.C. Murphy, Nature, 1984, 309, 119.
2. P. Dupuis, S. Flandrois, P. Delhaes and C. Coulon, J. Chem. Soc. Chem. Commun., 1978, 337;
3. G.J. Ashwell, Phys. Stat. Sol. (b), 1978, 86, 705; G.J. Ashwell, Nature, 1981, 290, 686; H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki and H. Inokuchi, J. Amer. Chem. Soc., 1983, 105, 297.
4. G.J. Ashwell, D.W. Allen, D.A. Kennedy and I.W. Nowell, Acta Crystallogr., 1982, B38, 2525.
5. M. Lequan, R.M. Lequan, P. Batail, J.F. Halet and L. Ouahab, Tetrahedron Lett., 1983, 24, 3107.

(Received in UK 29 June 1984)