Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: Munir M. Ahmad & Martin R. Bryce (1985): A Complex of Bis(Triphenylphosphoranylidene)Cations with TCNQ: $(PPN)_2(TCNQ)_3(CH_3CN)_2$, Molecular Crystals and Liquid Crystals, 120:1, 361-363

To link to this article: http://dx.doi.org/10.1080/00268948508075820

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 361-363
0026-8941/85/1204-0361/$10.00/0

Printed in the United States of America

A COMPLEX OF BIS(TRIPHENYLPHOSPHORANYLIDENE)CATIONS WITH TCNQ: $(PPN)_2(TCNQ)_3(CH_3CN)_2$

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Abstract PPN forms a 2:3 complex with TCNQ that contains acetonitrile in the crystal lattice; the material is a semiconductor with activation energy 160 meV.

Complexes of TCNQ with ammonium cations continue to play a central role in the search for new materials with unusual solid state properties.[1] We chose PPN because (i) there is renewed interest[2] in large phosphorous-containing cations and dications e.g. $[Ph_2(Me)PCH_2P(Me)Ph_2]^{2+}$; (ii) PPN is known to form highly-crystalline complexes with anions,[3] e.g. S_4N^-; (iii) compounds containing a nitrogen-phosphorous bond have not been complexed with TCNQ.

$Ph_3P{=}\overset{+}{N}{=}PPh_3$ = PPN

Mixing equimolar solutions of PPN iodide and TCNQ in hot, dry acetonitrile followed by cooling to -15°C yielded black crystals of complex in 70% yield. [Found: C, 76.1; H, 4.6; N, 11.9; $C_{116}H_{78}P_4N_{16}$ requires C, 76.6; H, 4.3; N, 12.3%; m.p. 183-188°C; e.s.r. (powder) strong singlet g 2.005, 1.8G wide; λ_{max} (CH_3CN) 394, 743, 760, 820, 842 nm]. X-ray crystallography confirms the stoichiometry of the complex as $(PPN)_2(TCNQ)_3(CH_3CN)_2$ [Crystals are triclinic, 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)°]. The TCNQ stacks are trimerised with intratrimer distance 3.30Å and ring-over-bond overlap. A most unusual feature of the structure is a very large intertrimer distance (9.85Å).

The complex is a semi-conductor [σ_{rt} lies between 4.6 x 10^{-4} and 7.5 x 10^{-5} $(\Omega\ cm)^{-1}$]. The temperature dependence of conductivity over the range 190-310K was measured on four crystals from two different preparations. There is a linear drop in conductivity with temperature without any observable transitions (Figure). This behaviour is typical of a semi-conductor with energy of activation 160 meV. The mechanism of conductivity most likely involves hopping of electrons from the TCNQ trimers onto phenyl rings of PPN in order to bridge the very large intertrimer gaps.

It is worth noting that there are very few cases in which CH_3CN, the commonest solvent for crystallising TCNQ complexes, has been found in the crystal lattice.[4]

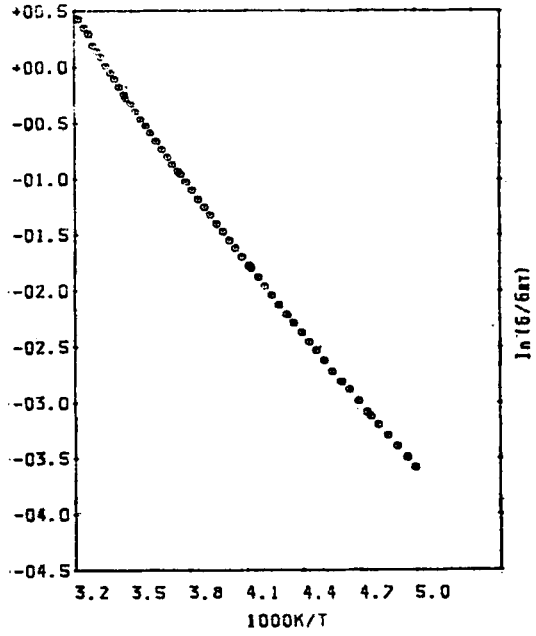

Figure Variable temperature conductivity of $(PPN)_2(TCNQ)_3(CH_3CN)_2$

ACKNOWLEDGEMENTS

We thank Dr. J. Halfpenny for X-ray data, Professor L. Weiler for initial experiments, and Professor A. Underhill for use of equipment for conductivity measurements.

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