

Preparation and Solid-state Characterization of the 7,7,8,8-Tetracyano-*p*-quinodimethanide Salt of the Bis(triphenylphosphoranylidinium) Cation: (PPN)₂(TCNQ)₃(MeCN)₂

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A 2:3 salt of the bis(triphenylphosphoranylidinium) cation (PPN) and TCNQ has been prepared in high yield and characterized in the solid state by a range of techniques. Single-crystal X-ray analysis reveals isolated TCNQ trimers with an intra-trimer separation of 3.27 Å and ring-over-bond overlap typical of TCNQ salts. A stoichiometric amount of solvent acetonitrile is occluded in the crystal lattice. The material is a semiconductor, σ_{rt} ca. 10^{-4} S cm⁻¹, with energy of activation 170 meV. Variable-temperature magnetic susceptibility measurements and e.s.r. data show that the material is paramagnetic and a singlet-triplet separation of 0.03 eV is observed associated with the TCNQ trimers. From Raman and i.r. spectra, we infer that two electrons are predominantly localized on two of the TCNQ molecules within the trimer, leaving the central molecule as neutral TCNQ.

TCNQ (1) is an electron acceptor of prime importance in the development of solid-state chemistry. Pioneering work at the DuPont Laboratories established that anion radical salts of TCNQ form readily with metal cations [e.g., Li⁺(TCNQ⁻)], complexed metal cations [e.g., Cu(2,2'-dipyridylamine)²⁺(TCNQ)₂⁻], and onium cations [e.g., R₄N⁺TCNQ⁻ and R₂P⁺TCNQ⁻ (R = H, alkyl or aryl)].¹ The solid-state properties of these materials have attracted considerable attention as many of them show semiconducting (σ_{rt} 10⁻⁶ – 1 S cm⁻¹) or metallic (σ_{rt} > 1 S cm⁻¹) behaviour with an associated range of interesting magnetic and spectroscopic properties. The anisotropy that is observed is so marked that these salts are quasi-one-dimensional.^{2,3} This is a result of crystallization in segregated stacks of cations and TCNQ where molecules are suitably spaced and orientated for efficient π -overlap and electron delocalization along the stacking axis only. Several groups have recently described new TCNQ salts of ammonium and phosphonium cations, e.g., *N,N*-dialkylmorpholinium,⁴ diethyldiphenylphosphonium,⁵ and 5,5-dimethyldibenzophospholium⁶ cations, and various dications.^{7,8} We have described, in a preliminary form, the first TCNQ salt of a cation that contains a phosphorus–nitrogen bond, viz. bis(triphenylphosphoranylidene)ammonium (PPN) (2),⁹ and we now present full details of the preparation, solid-state properties, and X-ray crystal structure of this salt.

We chose PPN as a starting point for our studies on conducting salts of phosphorus–nitrogen cations because PPN is noted for its ability to stabilize inorganic anions, e.g., S₄N⁻¹⁰ and H₂W₂(CO)₈²⁻,¹¹ with which it forms highly crystalline salts, yet PPN has been rarely used to complex organic anions. A high degree of symmetry in the cation is also generally a beneficial factor, although by no means a prerequisite, for the formation of conducting TCNQ salts;^{2,3} this is a consequence of the more highly ordered crystal structure that can be formed by a symmetrical cation in comparison with a non-symmetrical analogue.

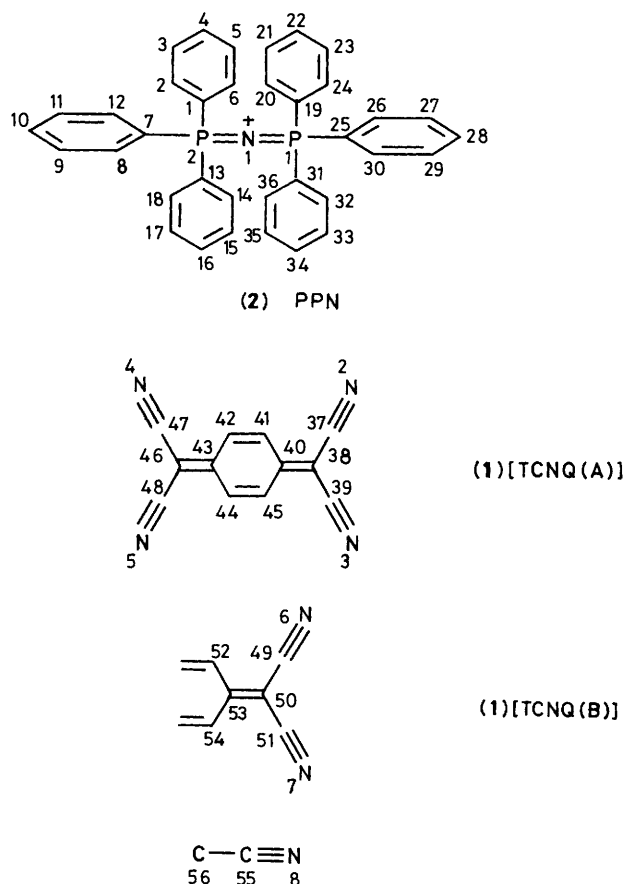


Figure 1. Atom-numbering scheme for compounds (1), (2), and acetonitrile

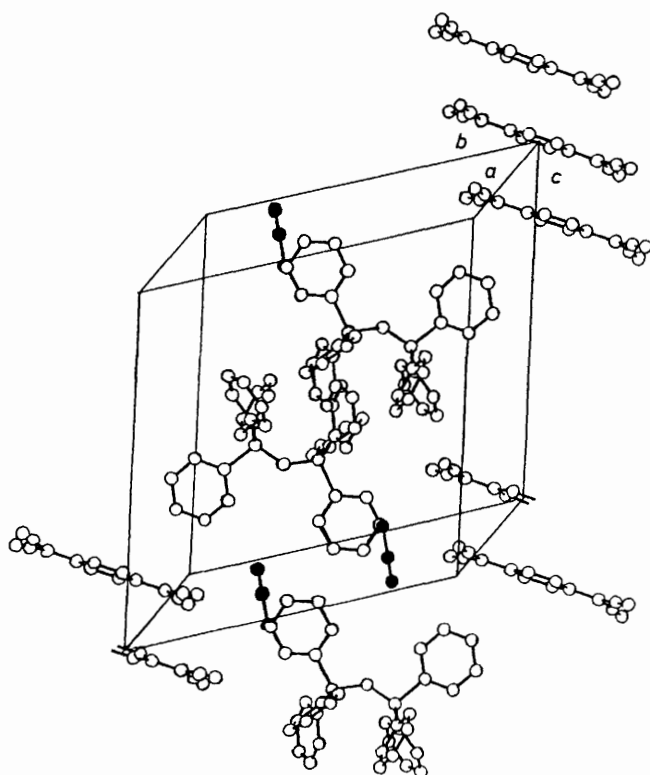


Figure 2. Unit cell of complex (1) showing complete TCNQ molecules that lie on the centre of inversion. The acetonitrile molecules are shaded

Results and Discussion

The crystalline complex $(\text{PPN})_2(\text{TCNQ})_3(\text{MeCN})_2$ [complex (1)] was prepared in high yield from the reaction of PPN iodide with TCNQ in acetonitrile. The stoichiometry of complex (1) was deduced from elemental analysis and confirmed by *X*-ray analysis. The PPN^+ cation exists in a bent configuration with a P–N–P angle of $137.6(4)^\circ$ [*cf.*, $143.1(2)^\circ$ for $\text{PPN}^+\text{S}_4\text{N}^-$ ¹⁰ and $139.4(4)^\circ$ for $[(\text{PPN})_2^+\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$;¹¹ this is the usual configuration although examples of a linear P–N–P backbone in PPN^+ salts are known [*e.g.*, $\text{PPN}^+\text{V}(\text{CO})_6^-$ ¹² and the salt of a novel molybdenum carbonyl cluster trianion¹³]. The P–N bond lengths in complex (1) are also typical of those reported previously for the cation.^{10,11}

A view of the unit cell of complex (1) is shown in Figure 2. The TCNQ molecules form isolated trimers (ABA) with molecule B, in the middle of the trimer, lying at the origin of the unit cell, giving rise to two crystallographically independent types of TCNQ. The packing diagram is shown in Figure 3 with PPN and acetonitrile molecules excluded for clarity. The nearest inter-trimer distance is the sideways separation of 8.84 Å, *i.e.*, the length of unit cell along the *a* axis. In the majority of complexes where TCNQ forms trimerized (or dimerized) stacks, the inter-trimer (dimer) separation along the stacking axis, *i.e.*, the axis perpendicular to the planes of the TCNQ rings, is only slightly longer than the intra-trimer (dimer) separation.^{2,3,14–17} This is not observed in complex (1) where the perpendicular distance between the mean molecular planes within the ABA trimer is 3.27 Å and the inter-trimer separation along the stacking axis is 9.85 Å. A view onto the plane of the TCNQ rings shows that phenyl rings of PPN occupy the inter-trimer space. Within the trimers of complex (1), the TCNQ molecules are displaced lengthways giving rise to a quinonoid ring over exocyclic C=C bond overlap typical of TCNQ salts.^{2,3}

The stoichiometry of complex (1) is uncommon, although *X*-

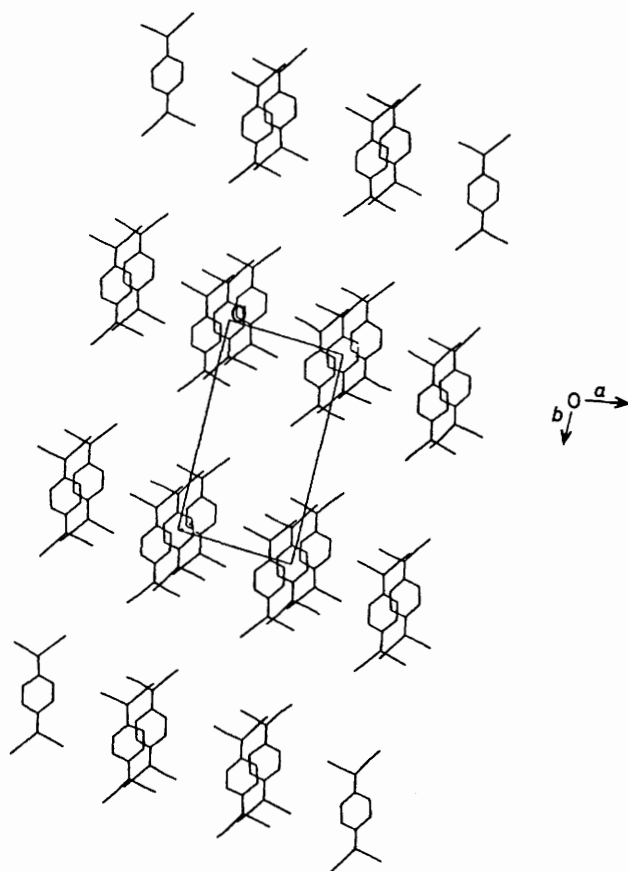


Figure 3. Molecular packing of TCNQ trimers viewed down the *c* axis. The PPN and acetonitrile molecules are excluded for clarity

ray structures of other complexes of stoichiometry $(\text{cation}^+)_2(\text{TCNQ}^-)_3$ have been determined, *e.g.*, (morpholinium)₂-(TCNQ)₃¹⁴ and (triethylammonium)₂-(TCNQ)₃,¹⁵ and for these structures a comparison of bond lengths of the TCNQ molecules with those of TCNQ⁰ and TCNQ⁻ suggests that the two negative charges are localized on two of the TCNQ molecules within each trimer, leaving the third molecule as neutral TCNQ. On the other hand, delocalization of charge throughout a trimer has been concluded by Ashwell *et al.*,¹⁶ for the 1:3 dication salt $[\text{N,N}'\text{-}(p\text{-phenylenedimethylene})\text{di}(\text{quinolinium})]^{2+}(\text{TCNQ})_3^{2-}$ and by Mathieu for a 2:3 salt of a 1,2-dithiolium cation and TCNQ.¹⁷ From the moderate quality of our *X*-ray data (R_w 0.056), it is not clear whether or not this is the situation in complex (1) where the bond lengths for TCNQ (A) and TCNQ (B), allowing for standard deviations, are all intermediate between those found for neutral TCNQ⁰ and the radical anion TCNQ⁻. However, spectroscopic data demonstrate that complex (1) does contain distinct TCNQ⁰ and TCNQ⁻ molecules within the trimer (see below).

Another feature of complex (1) that is revealed by the *X*-ray structure is the presence of acetonitrile. Acetonitrile is the commonest solvent for the crystallization of TCNQ salts, yet the instances are limited where the occlusion of acetonitrile into the lattice has been proved by structural studies. Chasseau and co-workers¹⁸ have described two TCNQ salts of benzimidazolium cations where acetonitrile is present, and a recent example is provided by a quinolinium salt.¹⁹ Other TCNQ salts are known to form stoichiometric complexes with the solvents benzene,²⁰ dichloromethane,²¹ and water,²² and in some cases the presence of these solvent molecules markedly affects the properties of the material.^{19,23} Recently, Ashwell and

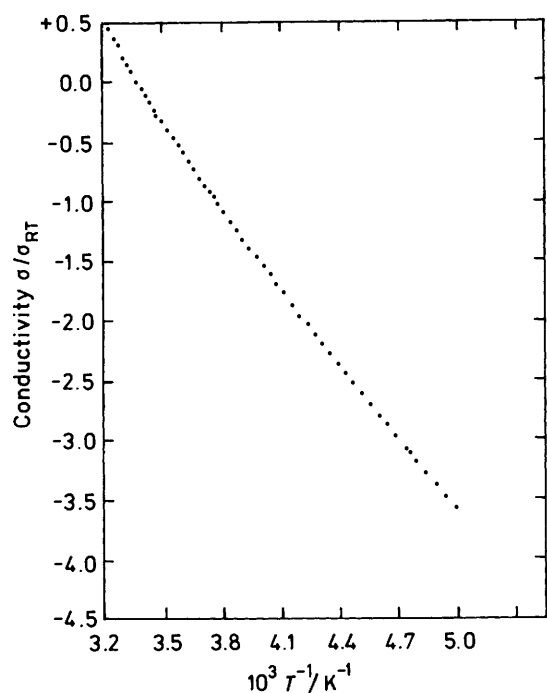


Figure 4. Variable-temperature conductivity of complex (1)

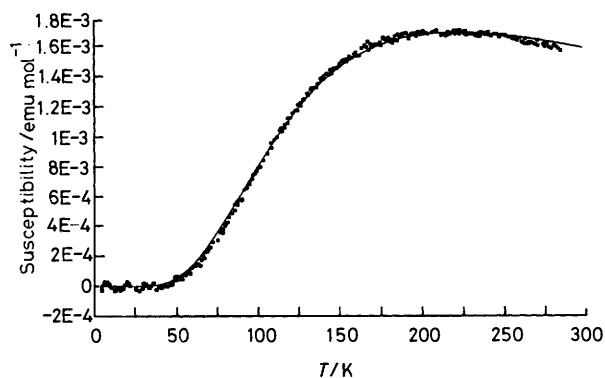


Figure 5. Total magnetic susceptibility of complex (1), corrected for a Curie spin contribution corresponding to 11 000 p.p.m. of $s = \frac{1}{2}$ spins

co-workers²⁴ have presented evidence that transitions observed by differential scanning calorimetry, and in conductivity and magnetic properties, for several TCNQ salts, are derived from isolated pockets of solvent acetonitrile trapped in the crystal lattice. Such transitions are not observed in the conductivity or magnetic behaviour of complex (1) (see below) nor would they be expected, since the acetonitrile molecules in complex (1) are isolated. The closest intermolecular contact involving acetonitrile in complex (1) is between the acetonitrile nitrogen atom and a phenyl ring carbon of PPN [N(8)–C(3) 3.377 Å]; Chasseau observed close contact (3.11 Å) of the methyl carbon of acetonitrile with a nitrogen atom of TCNQ in one of the benzimidazolium–TCNQ salts.¹⁸

Spectroscopic data clarify the electronic distribution within the trimers of complex (1). The i.r. spectrum of complex (1) exhibits two strong absorption bands derived from the nitrile group of TCNQ at 2180 and 2215 cm^{-1} with approximate relative intensities of 3:1. Bloch and co-workers have demonstrated that the degree of charge-transfer (ρ) in TCNQ salts

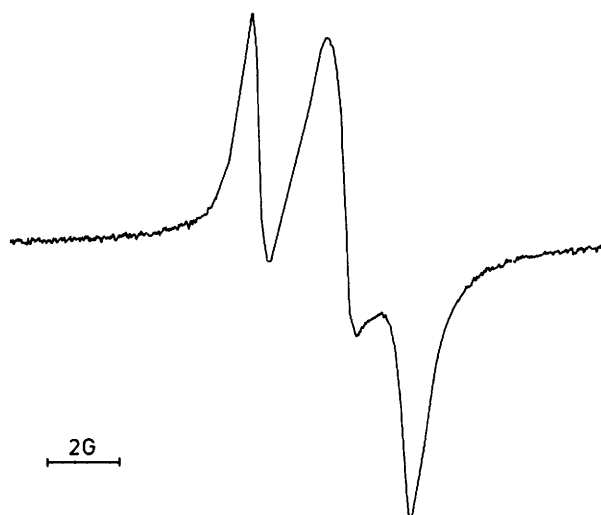


Figure 6. Solid-state e.s.r. spectrum (X-band) of the g -value ≈ 2 region of complex (1) at 295 K

shows a linear dependence upon the nitrile stretching frequency; ν_{max} . 2180 and 2225 cm^{-1} are characteristic of TCNQ^- and TCNQ^0 , respectively.²⁵ For certain non-integral salts, *e.g.*, Cs_2TCNQ_3 , the two absorption bands observed are assigned to distinct TCNQ^- and TCNQ^0 species within the trimer. For complex (1), the peak at 2180 cm^{-1} is clearly indicative of TCNQ^- , while the peak at 2215 cm^{-1} is characteristic of a TCNQ molecule bearing a fractional anionic charge (*ca.* 0.2 electrons) rather than neutral TCNQ^0 .²⁵ However, the presence of neutral TCNQ along with the fully charged TCNQ radical anion is implied from the Raman spectrum of complex (1) which exhibits strong peaks at both 1375 (TCNQ^-) and 1455 cm^{-1} (TCNQ^0) with no peaks at intermediate frequencies. On the basis of other work, these peaks can be assigned to the ν_4 mode (C=C ring str) of TCNQ and their frequencies are known to be very sensitive to ρ .²⁶ Taken together, these spectroscopic data strongly suggest that the two electrons are not delocalized over the TCNQ trimer in complex (1) but are (at least predominantly) localized on two of the TCNQ molecules. This conclusion is more reliable than that based on bond lengths determined by X-ray analysis (Table 2). Discrepancies in conclusions based on spectroscopic and X-ray data have been reported previously for 1:2 cation–TCNQ salts.²⁵ Since there is a symmetry relationship between the outer two TCNQ molecules in each ABA trimer of complex (1), we identify these as the two charged TCNQ molecules, leaving the central TCNQ neutral.

Complex (1) is a semiconductor; σ_{rt} lies between 4.6×10^{-4} – $7.5 \times 10^{-5} \text{ S cm}^{-1}$. The temperature dependence of conductivity over the range 190–310 K was measured using standard four-probe techniques for four crystals from two different preparations, and the plot of $\ln \sigma$ versus $1/T$ shows an almost linear drop in conductivity with temperature without any observable transitions (Figure 4). An activation energy of 170 meV is obtained from the slope of the plot shown in Figure 4. Conductivity measurements could be made only along the long axis of the crystals. On the basis of the crystal structure of complex (1), it is unlikely that transport properties are highly anisotropic. In particular the large separation of trimers along the stacking axis precludes direct interaction between the trimers contributing to electrical conductivity in this direction.

The total paramagnetic susceptibility (χ_{para}) of complex (1) was found to increase over the temperature range 50–220 K. The major component of this variation is consistent with the thermal population of a low-lying triplet state. If the inter-

Table 1. Crystal data and experimental parameters for complex (1)

<i>M</i>	885
Crystal system	Triclinic
Crystal habit	Elongated crystals
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	8.84 (1)
<i>b</i> /Å	16.70 (1)
<i>c</i> /Å	17.16 (1)
α /°	69.85 (7)
β /°	84.11 (9)
γ /°	85.26 (9)
<i>U</i> /Å ³	2 365 (6)
<i>Z</i>	2
<i>D_c</i> /g cm ⁻³	1.24
<i>F</i> (000)	966
<i>T</i> /K	293
λ /Å	0.7107
μ	0.105 mm ⁻¹
<i>R</i>	0.0625
<i>R_w</i>	0.056
Data recorded	7 604
Data	7 009
Data used	2 833 with <i>I</i> > 3 σ (<i>I</i>)
Crystal size/mm	0.4 × 0.5 × 0.05

actions between spins within each trimer (antiferromagnetic exchange $J = k_B b$) are much greater than those between trimers, the expected temperature dependence of χ is given by²⁷

$$\chi_{\text{para}} = \frac{2Ng^2\mu_B^2}{[\exp(J/kT) + 3]kT}$$

The experimental data and the best fit to this expression are given in Figure 5.

A singlet-triplet separation $k_B b$ of 0.03 eV and a μ_{eff} of 2.804 were estimated from the best values of the constants *a* and *b* (see Experimental section). A value of 2.83 for μ_{eff} is expected for one triplet state per formula unit.

The solid-state e.s.r. spectrum of complex (1) was examined between 100 and 360 K. The variation of total integrated signal intensity with temperature is in agreement with the static χ results discussed above and a reasonable fit to the data was obtained for a singlet-triplet separation of 0.026 eV. The major component of the e.s.r. spectrum arose from a signal with marked *g*-value anisotropy shown in Figure 6. Unfortunately, suitable single crystals were not obtained, zero-field splittings could not be resolved, and a half-field ($\Delta M_S \pm 2$) line was not detected. Several other semiconducting TCNQ salts have been discovered which exhibit singlet-triplet statistics of a similar magnitude.²⁸ In such materials, half-field lines have been difficult to detect and generally lower temperatures than 100 K are necessary before the effects of zero-field splitting can be observed. At higher temperatures spin exchange interactions between triplet entities broaden the dipole-dipole split lines until one broad resonance line is observed.

Experimental

Bis(triphenylphosphoranylidene) iodide (PPN⁺I⁻) was prepared from PPN⁺Cl⁻ (Aldrich) using a published procedure.²⁹ Acetonitrile was dried by distillation from P₂O₅ and TCNQ (Aldrich) was recrystallized from acetonitrile before use.

I.r. spectra were recorded on a Perkin-Elmer 577 instrument; Raman spectra on a Cary 82 spectrometer using the red line of

Table 2. Fractional atomic co-ordinates (× 10⁴)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	9 094(2)	3 868(1)	2 566(1)
P(2)	8 361(2)	2 078(1)	3 521(1)
N(1)	8 355(5)	2 971(3)	2 789(3)
N(2)	11 400(8)	2 904(5)	5 771(5)
N(3)	7 222(9)	3 877(5)	6 799(5)
N(4)	9 510(9)	-2 041(4)	8 927(5)
N(5)	5 302(9)	-1 002(5)	9 878(0)
N(6)	3 229(9)	1 840(5)	7 939(5)
N(7)	-900(9)	2 980(5)	8 767(5)
N(8)	4 297(14)	7 163(7)	-482(8)
C(1)	7 597(5)	1 331(2)	3 160(3)
C(2)	7 103(5)	1 595(2)	2 349(3)
C(3)	6 454(5)	1 021(2)	2 068(3)
C(4)	6 252(5)	184(2)	2 598(3)
C(5)	6 698(5)	-79(2)	3 408(3)
C(6)	7 346(5)	494(2)	3 689(3)
C(7)	10 211(5)	1 640(3)	3 825(3)
C(8)	10 919(5)	1 924(3)	4 365(3)
C(9)	12 439(5)	1 681(3)	4 513(3)
C(10)	13 252(5)	1 154(3)	4 122(3)
C(11)	12 544(5)	870(3)	3 582(3)
C(12)	11 024(5)	1 113(3)	3 434(3)
C(13)	7 266(5)	2 102(2)	4 452(3)
C(14)	6 158(5)	2 762(2)	4 386(3)
C(15)	5 266(5)	2 799(2)	5 093(3)
C(16)	5 483(5)	2 177(2)	5 866(3)
C(17)	6 591(5)	1 517(2)	5 932(3)
C(18)	7 483(5)	1 480(2)	5 225(3)
C(19)	8 617(5)	4 518(3)	1 546(3)
C(20)	7 752(5)	4 213(3)	1 082(3)
C(21)	7 403(5)	4 734(3)	285(3)
C(22)	7 919(5)	5 560(3)	-48(3)
C(23)	8 785(5)	5 865(3)	415(3)
C(24)	9 134(5)	5 344(3)	1 212(3)
C(25)	8 439(5)	4 427(3)	3 269(3)
C(26)	7 205(5)	5 019(3)	3 090(3)
C(27)	6 583(5)	5 381(3)	3 680(3)
C(28)	7 194(5)	5 150(3)	4 449(3)
C(29)	8 428(5)	4 557(3)	4 628(2)
C(30)	9 051(5)	4 196(3)	4 038(3)
C(31)	11 099(5)	3 786(3)	2 527(3)
C(32)	11 856(5)	3 155(3)	2 151(3)
C(33)	13 443(5)	3 085(3)	2 184(3)
C(34)	14 274(5)	3 646(3)	2 393(3)
C(35)	13 517(5)	4 277(3)	2 669(3)
C(36)	11 930(5)	4 347(3)	2 736(3)
C(37)	10 355(10)	2 788(5)	6 233(5)
C(38)	9 049(8)	2 604(5)	6 813(5)
C(39)	8 061(10)	3 313(6)	6 801(5)
C(40)	8 733(8)	1 784(5)	7 349(5)
C(41)	9 762(8)	1 068(5)	7 352(4)
C(42)	9 436(8)	259(5)	7 867(4)
C(43)	8 091(9)	102(5)	8 387(5)
C(44)	7 087(8)	809(5)	8 394(5)
C(45)	7 398(8)	1 607(5)	7 890(5)
C(46)	7 735(9)	-730(5)	8 920(5)
C(47)	8 718(10)	-1 467(6)	8 933(5)
C(48)	6 380(10)	-894(5)	9 461(5)
C(49)	2 135(11)	1 732(5)	8 385(6)
C(50)	763(9)	1 621(5)	8 914(5)
C(51)	-151(10)	2 382(6)	8 839(5)
C(52)	1 357(8)	69(5)	9 505(5)
C(53)	419(9)	816(5)	9 455(5)
C(54)	-974(9)	719(5)	9 971(5)
C(55)	4 535(13)	6 948(7)	198(9)
C(56)	4 841(12)	6 676(7)	1 064(7)

a He/Ne laser at a power of 8 mW; e.s.r. spectra were recorded on a Varian E109 spectrometer and signal intensities were measured by double integration of the derivative signal against an internal standard using double-cavity techniques.

Table 3. Bond distances (Å) and bond angles (°) for complex (1)

N(1)–P(1)	1.593(5)	C(43)–C(44)	1.421(11)
N(1)–P(2)	1.586(4)	C(43)–C(46)	1.415(10)
C(1)–P(2)	1.796(5)	C(44)–C(45)	1.349(10)
C(7)–P(2)	1.788(5)	C(46)–C(47)	1.443(12)
C(13)–P(2)	1.792(5)	C(46)–C(48)	1.442(11)
C(19)–P(1)	1.786(5)	N(4)–C(47)	1.147(12)
C(25)–P(1)	1.790(6)	N(5)–C(48)	1.121(11)
C(31)–P(1)	1.763(5)	N(6)–C(49)	1.155(12)
N(2)–C(37)	1.138(11)	C(49)–C(50)	1.424(12)
C(37)–C(38)	1.425(11)	C(50)–C(51)	1.422(13)
C(38)–C(39)	1.408(12)	C(50)–C(53)	1.383(10)
C(38)–C(40)	1.395(10)	N(7)–C(51)	1.121(12)
N(3)–C(39)	1.149(12)	C(52)–C(53)	1.422(12)
C(40)–C(41)	1.441(11)	C(54)–C(53)	1.429(11)
C(40)–C(45)	1.408(10)	C(55)–C(56)	1.444(18)
C(42)–C(41)	1.371(10)	N(8)–C(55)	1.134(17)
C(42)–C(43)	1.399(10)	C(52)–C(54)	1.368(12)

All C–C (ring) 1.395, all C–H 1.080 Å, constrained

C(40) ... C(50 ^b)	3.305	C(43) ... C(54 ^b)	3.414
C(40) ... C(51 ^b)	3.310	C(44) ... C(54 ^b)	3.304
C(41) ... C(49 ^b)	3.358	C(45) ... C(51 ^b)	3.416
C(41) ... C(50 ^b)	3.340	C(39) ... N(7 ^b)	3.345
C(42) ... C(52 ^b)	3.343	C(52 ⁱⁱ) ... C(46 ⁱⁱⁱ)	3.437
C(3 ⁱⁱ) ... N(8 ⁱⁱ)	3.377	C(53 ⁱⁱ) ... C(47 ⁱⁱⁱ)	3.473
C(42) ... C(53 ^b)	3.380	C(53 ⁱⁱ) ... C(46 ⁱⁱⁱ)	3.328
C(43) ... C(53 ^b)	3.420	C(54 ⁱⁱ) ... C(47 ⁱⁱⁱ)	3.446

P(2)–N(1)–P(1)	137.6(4)	C(7)–P(2)–C(13)	106.3(2)
C(19)–P(1)–N(1)	108.0(3)	N(2)–C(37)–C(38)	177.4(9)
C(25)–P(1)–N(1)	113.6(3)	C(37)–C(38)–C(39)	115.2(6)
C(31)–P(1)–N(1)	113.0(2)	C(38)–C(39)–N(3)	178.1(9)
C(19)–P(1)–C(25)	108.2(2)	C(37)–C(38)–C(40)	123.3(7)
C(25)–P(1)–C(31)	107.5(3)	C(39)–C(38)–C(40)	121.4(7)
C(1)–P(2)–N(1)	107.4(3)	C(41)–C(40)–C(45)	116.9(6)
C(7)–P(2)–N(1)	114.6(2)	C(40)–C(41)–C(42)	120.5(6)
C(13)–P(2)–N(1)	113.5(2)	C(41)–C(42)–C(43)	121.3(7)
C(1)–P(2)–C(7)	106.7(2)	C(42)–C(43)–C(44)	118.2(6)
C(43)–C(44)–C(45)	120.8(6)	N(6)–C(49)–C(50)	178.1(9)
C(44)–C(45)–C(40)	122.2(7)	N(7)–C(51)–C(50)	178.2(12)
C(42)–C(43)–C(46)	122.0(7)	C(49)–C(50)–C(51)	115.1(7)
C(44)–C(43)–C(46)	119.8(7)	C(49)–C(50)–C(53)	119.7(8)
C(43)–C(46)–C(47)	121.7(6)	C(51)–C(50)–C(53)	125.2(7)
C(43)–C(46)–C(48)	122.4(7)	C(50)–C(53)–C(54)	118.7(7)
C(47)–C(46)–C(48)	115.9(7)	C(50)–C(53)–C(52)	123.4(7)
N(4)–C(47)–C(46)	178.5(8)	C(52)–C(53)–C(54)	117.9(7)
N(5)–C(48)–C(46)	178.3(9)	N(8)–C(55)–C(56)	179.9(3)

All C–C–C (ring) 120.0°, constrained

Symmetry code: (i) $-1 + x, y, z$; (ii) $1 - x, -y, 2 - z$; (iii) $-x, -y, -z$; (iv) $1 - x, 1 - y, -z$

Static magnetic susceptibility data were obtained using a Faraday balance in two fields of 0.5 and 0.75 Tesla. The data were corrected for ferromagnetic impurities found to be 0.9 p.p.m. as a saturated iron impurity. Core correction applied to the data to zero the susceptibility at $T = 0 \text{ K} = -9.2 \times 10^{-4} \text{ emu mol}^{-1}$; core diamagnetism from Pascal's constants = $-9.8 \times 10^{-4} \text{ emu mol}^{-1}$. Errors in fitting parameters to the expression:²⁷

$$\chi(T) = \frac{2Ng^2\mu_B^2}{\left[\exp\left(\frac{J}{kT}\right) + 3\right]kT}$$

were $a/[\exp b/T + 3]T = 2.97 \pm 0.01$, $b = 353.1 \pm 0.6$; this gives values $g = 1.986 \pm 0.004$ and $J = 0.030 \pm 0.001 \text{ eV}$.

Data were corrected for a small Curie spin contribution equivalent to 11 000 p.p.m. $s = \frac{1}{2}$ spins.

Preparation of (PPN)₂(TCNQ)₃(MeCN)₂ [Complex (1)].—A hot solution of TCNQ (204 mg, 1 mmol) dissolved in acetonitrile (30 ml) was added to a hot solution of PPN iodide (2.0 g, 3 mmol) dissolved in acetonitrile (20 ml); the mixture was cooled to room temperature and then allowed to stand at -15°C for several days, to give black crystals of complex (1) (500 mg, 80%), m.p. 183–188 °C (Found: C, 76.1; H, 4.6; N, 11.9; P, 7.0. $\text{C}_{56}\text{H}_{35}\text{N}_8\text{P}_2$ requires C, 75.9; H, 4.4; N, 12.6; P, 7.0%; ν_{max} (Nujol) 2 215, 2 180, 1 560, 1 328, 1 120, 956, 728, 700, and 538 cm^{-1}).

Crystal Structure Determination.—Crystal data and experimental parameters for complex (1) are summarized in Table 1. Data were collected using a Stoe Stadi-2 two-circle diffractometer with Mo- K_α X-radiation (graphite monochromator). No absorption correction was applied. The structure was solved by Multan 78³⁰ and refined using SHELX 76.³¹ Co-ordinates for non-hydrogen atoms are presented in Table 2 and bond distances and angles in Table 3.*

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* Supplementary data (see section 5.6.3. of Instructions for Authors, in the January issue). Fractional atomic co-ordinates, hydrogen-atom co-ordinates, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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