Condensation Reactions of Tetracyanoethylene and its Monoanion Promoted by Lewis Acids: Synthesis and Crystal, Molecular, and Electronic Structure of a Novel Heterocycle, the 2,3,6,7-Tetracyano-5-(tricyanoethenylimino)-3*H*-1,4,7b-triazabenzo[*i,j*]pentalenide Ion

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From the condensation reaction of tetracyanoethylene (C_6N_4, TCNE) with its radical monoanion ($C_6N_4^{\bullet -}$) promoted by a Lewis acid [$ZnCl_2$, $AlCl_3$, or $V(bpy)_3^{+2}$], a novel heterocyclic carbanion ($C_{17}N_{11}^-$) has been synthesized and characterized by X-ray, ^{13}C NMR, IR, and UV spectroscopy and cyclic voltammetry measurements. The crystal and molecular structure of the title anion has been determined for the tetraphenylarsonium salt, and its electronic structure and the mechanism of formation are discussed.

Technological interest in polycyano compounds is growing because of the large variety of potential applications due to their chromophoric, electron-acceptor and metal-ligating propeties.[1]

We have been interested for a number of years in novel materials with unusual electrical and/or magnetic properties. We started to explore reactions of tetracyanoethylene (C_6N_4, TCNE) promoted by low-valent metal complexes, *viz.* $M(bpy)_3$ (M = Ti, V, Zr; bpy = 2,2′-bipyridine); first a novel heterocyclic carbanion, $C_{11}N_7H_2^-$, was obtained from the reaction of TCNE with $M(bpy)_3$ and structurally characterized;[2] this novel reaction has been thoroughly examined by varying the TCNE/$M(bpy)_3$ ratio and the reaction temperature. Another condensation hydrogen-free product has been recently characterized, $C_{17}N_{11}^-$, and we report on this ion and discuss its structural and electronic properties and mechanism of formation.

Results and Discussion

We have synthesized and characterized the novel heterocyclic carbanion, $C_{17}N_{11}^-$ [(**3**) in Scheme 2], isolated as the salt of the tetraphenylarsonium cation $[As(C_6H_5)_4]^+$, resulting from the condensation reaction in Scheme 1.

$$2\,C_6N_4^{\bullet -} + C_6N_4 \xrightarrow{\text{Lewis acid}} C_{17}N_{11}^- + CN^-$$

Scheme 1.

From X-ray and ^{13}C NMR spectroscopic results it seems that in the solid state this ion behaves as an aromatic system with the negative charge extensively delocalized, while in solution it can be regarded as a system in which a substantial fraction of the charge is associated with four carbon atoms, as illustrated by the four mesomers A–D in Figure 1.

Description of the Structure.—The solid-state molecular structure of the $C_{17}N_{11}^-$ anion, revealed by the X-ray analysis and shown in Figure 2, consists of three condensed rings (namely pyrimidine, imidazole, and pyrrole), tetracyano- and tricyanoethenylimino-substituted. This last substituting group, together with the C-4 atom, can be regarded as a C_6N_4 unit, in which a nitrile $\longrightarrow$ isonitrile isomerization $(CN)_2C{=}C(CN)_2 \longrightarrow (CN)_2C{=}C(CN)(NC)$ formally occurs. Such evidence comes from the refinement: the thermal parameters of atoms 3 and 4 become comparable with the rest of the molecule only by refining as nitrogen the former and carbon the latter.

The anion is on the whole planar, the mean deviation from the C(1)–C(14) r.m.s. plane being 0.14 Å for the atoms of the cyano groups, but only 0.02 Å for the internal atoms. Interatomic distances (Table 1) agree well with the sp^2 C–C and C–N reported values[3,4] and can be compared with those found in analogous heterocyclic compounds.[5–9] Within the limits of the accuracy available, their values are consistent with extensive conjugation over the whole C(1)–C(14) framework, which also involves the central N-7 atom, in agreement with the degree of aromaticity present in similar heterocyclic condensed systems with peripheral nitrogen atoms.[10] Several mesomeric formulae, some of which are shown in Figure 1, give an account of such a description.

The crystal structure of the title compound is reminiscent of that of the previously reported cyanocarbanions, the TCNE derivatives;[1a] it comprises well-separated tetraphenylarsonium cations $[AsPh_4]^+$ and stacks of anions developing along the *a*-axis, which form an angle of 30° with the normal to their r.m.s. planes (Figure 3).

The $[AsPh_4]^+$ tetrahedral geometry is regular, As–C_{Ph} bond distances and angles being in the range 1.889–1.895(4) Å and 105.4–112.5(2)° respectively. The anions are spaced by 3.30(1) and 3.33(1) Å alternately: this suggests a good degree of π–π interaction, the C(1)–C(4) frame being well superimposed onto the heterocyclic system (Figure 4).

Synthesis.—The title compound (**3**) was obtained by the reaction of TCNE with $M(bpy)_3$ in tetrahydrofuran (THF). In fact, several concomitant reactions are involved as illustrated in Scheme 2. By using a low temperature (*ca.* −30 °C) and a ratio TCNE/$M(bpy)_3$ = 1 the intermediate (**1**) is formed from which hydrolysis by air (H^+/O_2) furnishes the heterocycle (**2**).[2]

After treatment of the intermediate (**1**) with an excess of TCNE followed by prolonged heating in rigorously anaerobic conditions, the final product (**3**) was obtained in poor yield (10%). This product can be made more easily (35% yield) by starting the former reaction with a ratio TCNE/$M(bpy)_3$ = 3 and heating (see Experimental, route A); it is possible to isolate the intermediate (**4**), in a pure and crystalline form by using a ratio TCNE/$M(bpy)_3$ = 2 at room temperature. The role played by the metal complex is twofold: first the electron-rich $[M(bpy)_3]^0$ species behaves as a two-electron reductant toward TCNE by reducing it to dianion or to two radical monoanions; secondly the oxidized form $[M(bpy)_3]^{2+}$ acts as a Lewis acid in

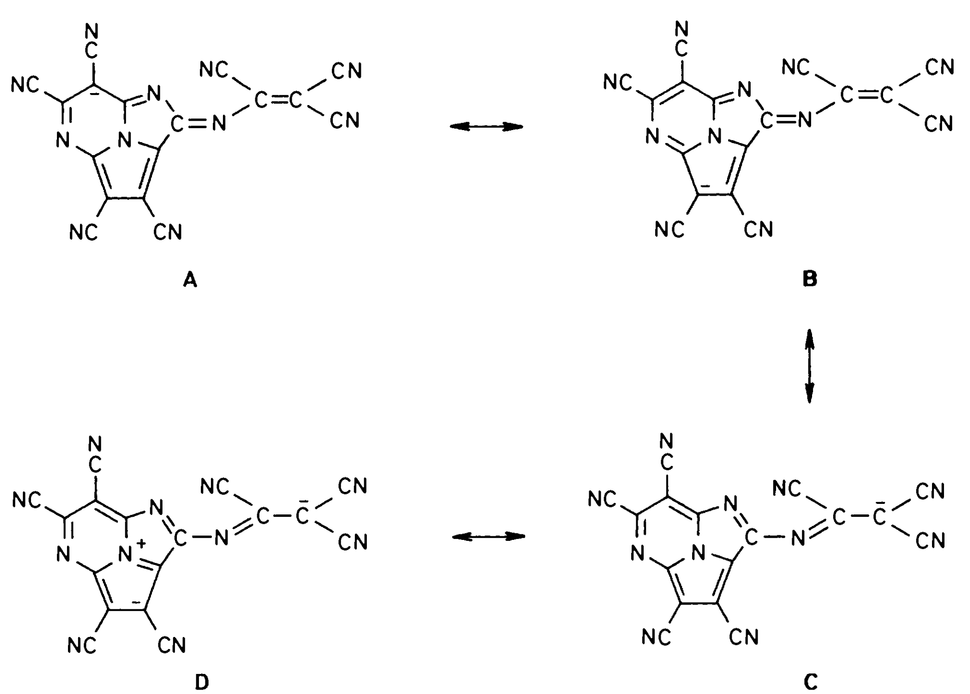


Figure 1. Preferred canonical planar formulae representing the anion (3) in solution, with the negative charge on the carbon atoms as deduced from ^{13}C NMR spectroscopy.

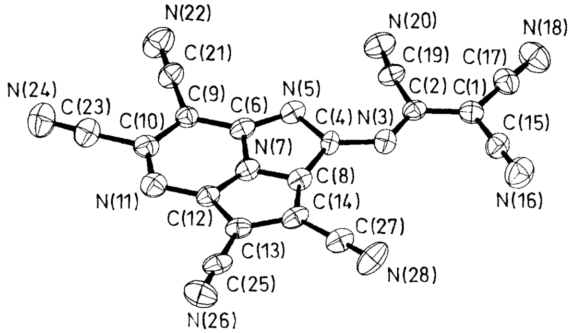


Figure 2. A perspective view of the $C_{17}N_{11}^-$ anion molecule, with thermal ellipsoid (30% probability level) and the labelling scheme.

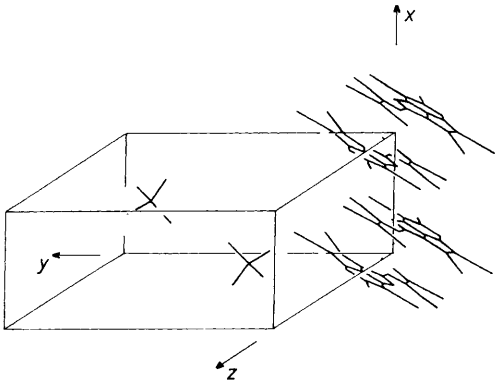


Figure 3. A partial representation of the unit-cell content showing the relative orientation of the anion molecules along the x direction. For sake of clarity, the phenyl rings of the $[AsPh_4]^+$ cation have been omitted, but only the As co-ordination tetrahedron has been shown.

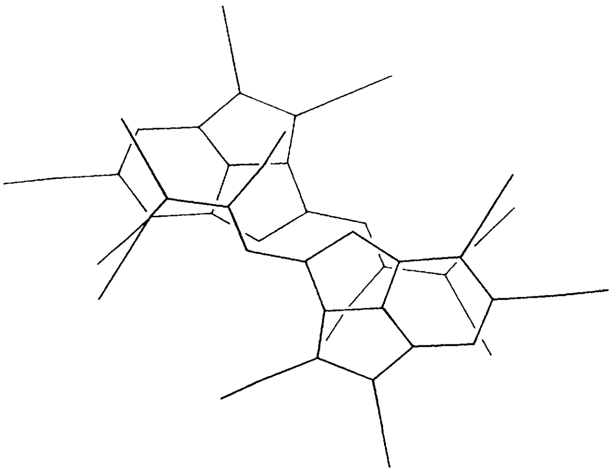


Figure 4. Stacked anions as viewed along the x-direction.

co-ordinating the anions TCNE$^{\cdot-}$ or TCNE^{2-}, after displacement of bpy. A mechanism which explains the formation of (2) has already been given;[2] in order to clarify the mechanism for the formation of (3), we have substituted the metal complex $M(bpy)_3$ for a simpler Lewis acid ($ZnCl_2$ or $AlCl_3$) and used KTCNE instead of TCNE (see Experimental, route B). Thus, when we performed the reaction in Scheme 3,

$$2\,C_6N_4^{\cdot-} + C_6N_4 + ZnCl_2 \longrightarrow C_{17}N_{11}^- + [ZnCl(CN)] + Cl^-$$

Scheme 3.

we prepared the same heterocyclic carbanion (3) plus the inorganic polymer $[ZnCl(CN)]_n$ (see Experimental). On the basis of these results we elaborated the reaction mechanism shown in Scheme 4, where [M] represents the Lewis acid.

In the first step (i) two radical mono-anions, $C_6N_4^{\cdot-}$, are co-ordinated by [M] *via* the negative nitrogen atoms. In the second step (ii) a cyano group of the neutral TCNE is attacked by the previous metal complex. In the third step (iii) electronic rearrangement occurs, the attacked cyano group opens and another constrained cyano group leaves as CN$^-$ and migrates

Table 1. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses[a]

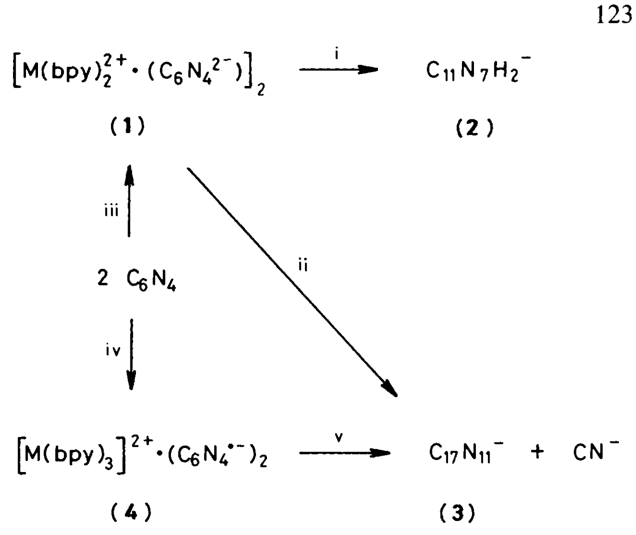
Bond lengths

As–C(101)	1.890(6)	C(8)–C(14)	1.41(1)
As–C(107)	1.890(8)	C(9)–C(10)	1.41(1)
As–C(113)	1.895(5)	C(9)–C(21)	1.44(2)
As–C(119)	1.889(6)	C(10)–N(11)	1.35(1)
C(1)–C(2)	1.38(2)	C(10)–C(23)	1.48(2)
C(1)–C(15)	1.41(2)	N(11)–C(12)	1.36(2)
C(1)–C(17)	1.42(1)	C(12)–C(13)	1.40(2)
C(2)–N(3)	1.35(1)	C(13)–C(14)	1.40(1)
C(2)–C(19)	1.45(2)	C(13)–C(25)	1.44(1)
N(3)–C(4)	1.32(2)	C(14)–C(27)	1.46(2)
C(4)–N(5)	1.38(2)	C(15)–N(16)	1.13(2)
C(4)–C(8)	1.47(1)	C(17)–N(18)	1.15(1)
N(5)–C(6)	1.33(1)	C(19)–N(20)	1.13(2)
C(6)–N(7)	1.37(1)	C(21)–N(22)	1.15(2)
C(6)–C(9)	1.38(2)	C(23)–N(24)	1.11(2)
N(7)–C(8)	1.33(1)	C(25)–N(26)	1.14(1)
N(7)–C(12)	1.33(1)	C(27)–N(28)	1.13(2)

Bond angles

C(107)–As–C(101)	105.8(3)	C(14)–C(8)–N(7)	103.2(8)
C(113)–As–C(101)	111.8(2)	C(10)–C(9)–C(6)	118(1)
C(113)–As–C(107)	110.5(3)	C(21)–C(9)–C(6)	122.3(8)
C(119)–As–C(101)	110.9(3)	C(21)–C(9)–C(10)	120(1)
C(119)–As–C(107)	112.5(3)	N(11)–C(10)–C(9)	128(1)
C(119)–As–C(113)	105.4(2)	C(23)–C(10)–C(9)	119(1)
C(15)–C(1)–C(2)	119.4(8)	C(23)–C(10)–N(11)	113.1(9)
C(17)–C(1)–C(2)	123(1)	C(12)–N(11)–C(10)	112.6(8)
C(17)–C(1)–C(15)	118(1)	N(11)–C(12)–N(7)	119.9(9)
N(3)–C(2)–C(1)	119(1)	C(13)–C(12)–N(7)	104.0(9)
C(19)–C(2)–C(1)	115.4(8)	C(13)–C(12)–N(11)	136.0(8)
C(19)–C(2)–C(3)	126(1)	C(14)–C(13)–C(12)	107.5(8)
C(4)–N(3)–C(2)	122.5(9)	C(25)–C(13)–C(12)	128(1)
N(5)–C(4)–N(3)	129.9(9)	C(25)–C(13)–C(14)	124(1)
C(8)–C(4)–N(3)	121(1)	C(13)–C(14)–C(8)	108(1)
C(8)–C(4)–N(5)	109(1)	C(27)–C(14)–C(8)	127.2(9)
C(6)–N(5)–C(4)	106.8(8)	C(27)–C(14)–C(13)	124.4(8)
N(7)–C(6)–N(5)	109(1)	N(16)–C(15)–C(1)	179(1)
C(9)–C(6)–N(5)	139.4(9)	N(18)–C(17)–C(1)	179(1)
C(9)–C(6)–N(7)	111.6(8)	N(20)–C(19)–C(2)	172(1)
C(8)–N(7)–C(6)	112.7(7)	N(22)–C(21)–C(9)	179(1)
C(12)–N(7)–C(6)	130(1)	N(24)–C(23)–C(10)	177(1)
C(12)–N(7)–C(8)	117.0(9)	N(26)–C(25)–C(13)	177(1)
N(7)–C(8)–C(4)	102(1)	N(28)–C(27)–C(14)	176(1)
C(14)–C(8)–C(4)	154(1)		

[a] The As–C bonds refer to the As tetrahedral group. A complete labelled drawing of the $[AsPh_4]^+$ cation together with a complete list of atomic co-ordinates have been deposited as supplementary material.



Scheme 2. *Reagents and conditions:* i, $-HCN$, $+3H^+/O_2$; ii, $+C_6N_4$, heat; iii, $-2bpy$, $+2M(bpy)_3$, $-30\,°C$; iv, $+M(bpy)_3$, room temperature; v, $+C_6N_4$, heat.

to [M]. In the fourth step (iv) a new pair of nucleophile $\rightleftharpoons$ electrophile concerted interactions occur on another cyano group. In the fifth step (v) the two [M]–N bonds are weakened by the co-ordination of CN^- to [M]; the two proximate nitrogen atoms, with different charges, interact; in the sixth step (vi) the deactivated Lewis acid separates (the reaction is not catalytic); and in the final step a rearrangement of the dipolar carbene intermediate* occurs, giving the more stable product (3).

Spectral and Physical Properties

NMR Spectrum.—The ^{13}C NMR spectral data are collected in Table 2. The sixteen peaks (one of which is doubly intense)—unchanged when gated proton-decoupled—can be subdivided into three groups:

(*a*) Seven central signals from the cyano groups, spread over the range 113.75–115.68 ppm, compared with the value 112.30 in the free TCNE.[11]

(*b*) Four high-field signals, which suggest the existence of the same number of carbon atoms bearing a negative charge (C-1, C-9, C-13, C-14). It is reasonable to assign the signal at 106.6 ppm to C-1, shifted upfield 1.6 ppm relative to TCNE.[11]

(*c*) Six low-field signals, which can be further subdivided into two groups: three signals arising from the condensed nitrile carbon atoms (C-6, C-8, C-12);* the remaining signals can be assigned to C-4 and to the carbon atoms originally of the type >C= in TCNE (C-2, C-10).

Solution and Reflectance Spectra.—Compound (3) is a magenta dye and the absorption responsible for the colour falls at 518 nm (ε = 49 000 dm^3 mol^{-1} cm^{-1}) with a shoulder at 544 nm (ε = 34 000). The reflectance spectrum shows the presence of an extra band at 750 nm in the solid state, probably originated by an interanionic charge-transfer transition within the stacks (Figures 3 and 4).

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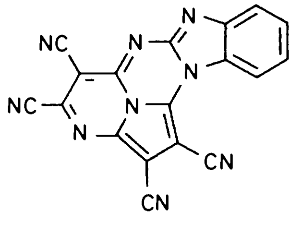
* M. Bonamico, V. Fares, A. Flamini, and P. Imperatori, work in progress. After the reaction of TCNE with benzimidazolyl anion

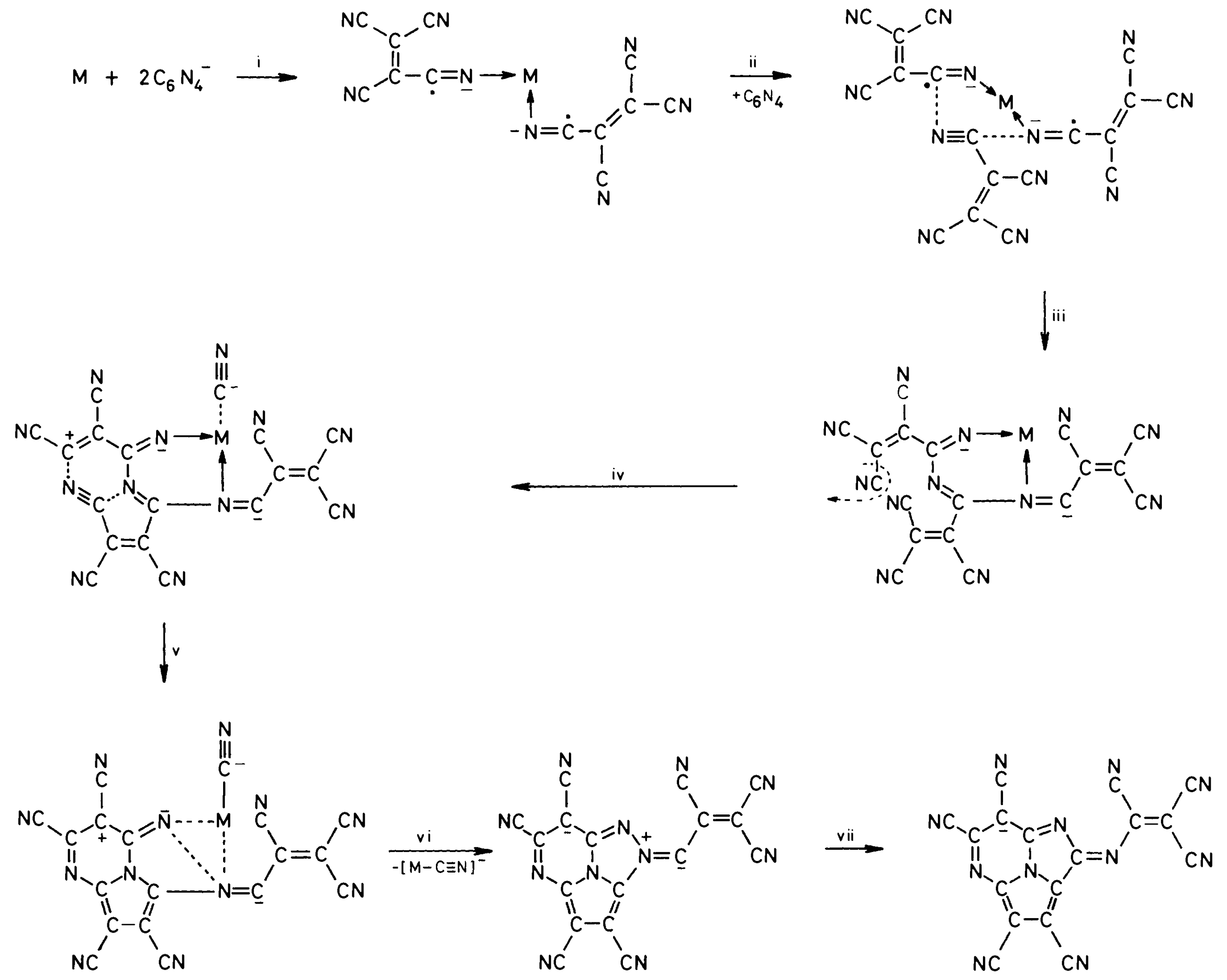
$$(2\,C_6N_4 + C_7N_2H_5^- \longrightarrow \underset{(5)}{C_{18}N_9H_4^-} + HCN)$$

heterocyclic fused rings are formed:



(5)

for which the ^{13}C NMR spectra have been assigned by using TCNE–^{13}CN labelled (O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, 1962, **84**, 3678), and the X-ray crystal structure determined. The anions (3) and (5) contain a common part (the pyrimidine–pyrrole fused system), derived from the condensation of two TCNE molecules. A parallel mechanism, with the formation of a carbene intermediate in the case of anion (3) can be therefore envisaged.



Scheme 4. Hypothetical reaction scheme explaining the formation of the title anion.

Table 2. ^{13}C Spectral data for the sodium salt of the title carbanion[a] (B_0 = 4.7 T; T = 300 K; solvent = C_2D_5OD).

C-1	C-2	C-4	C-6	C-8	C-9	C-10	C-12	C-13	C-14	CN groups
106.60	123.56[b]	137.64[b]	149.88[c]	163.16[c]	90.64[d]	145.39[b]	139.68[c]	98.47[d]	78.45[d]	113.75[e] 114.82 114.94 115.31 116.97 117.68

[a] For the numbering scheme see Figure 2. [b,c,d] May be interchanged. [e] Doubly intense.

Experimental

General.—Analytical data, details of IR, ^{13}C NMR, solution and reflectance spectroscopy and cyclic voltammetry data have been given earlier.[1a]

Reagents.—All the reagents were of Fluka analytical grade; $V(bpy)_3$ was made in good yield (85%) by the reduction of $VCl_3 \cdot 3THF$ with Li_2bpy. KTCNE,[12] $VCl_3 \cdot 3THF$,[13] $ZnCl_2$,[14] and $AlCl_3$[15] were prepared or dehydrated as outlined in the literature.

Synthesis of $As(C_6H_5)_4C_{17}N_{11}$.—*Route A.* TCNE (0.37 g, 2.89 mmol) was added to a THF solution (30 cm^3) of $V(bpy)_3$ (0.50 g, 0.96 mmol) kept under nitrogen in a vial; the vial was sealed under vacuum and opened after being heated for 24 h at 60 °C with stirring. The brick-red air-stable solution was diluted with acetone (20 cm^3), whereupon it became completely clear, and it was then poured into a solution of $As(C_6H_5)_4Cl$ (0.5 g, 1.19 mmol) in water (30 cm^3). A brown oil separated, the solution was decanted, and the oil was washed with toluene, leaving a black-brown residue. Chromatography of this residue on 150 g silica gel (70 cm column, 230/400 mesh) and elution with methylene chloride–acetone (95:5), yielded $As(C_6H_5)_4C_{17}N_{11}$ as an air-stable microcrystalline powder (0.25 g, 35%); it was then recrystallized from an acetone–heptane mixture giving red-brown crystals. (Found: C, 66.4; H, 2.9; N, 21.0; As, 9.65. $C_{41}H_{20}N_{11}As$ requires C, 66.40; H, 2.71; N, 20.78; As, 10.10%);

$\nu_{max.}$(KBr) 2 220 (CN), 1 595, 1 530, 1 475, 1 440, 1 385, 1 340, 1 240, 1 210, 1 180, 1 070, 820, and 740 cm^{-1}; E_p (rev, cat) − 0.41 and − 1.07 (V *vs.* SCE).

Route B. The same compound can be prepared in a comparable yield (40%) by performing the reaction above using KTCNE (0.46 g, 2.78 mmol), TCNE (0.18 g, 1.39 mmol), and $ZnCl_2$ (0.19 g, 1.39 mmol). At the end of this reaction we succeeded in isolating the inorganic component as follows. Acetone was added to the mixture; the solution did not become clear but a microcrystalline grey powder separated out (0.1 g) which was filtered and washed with acetone and water. (Found: C, 9.6; N, 9.2; Cl, 27.2. ZnCNCl requires C, 9.46; N, 11.04; Cl, 27.94%). This compound is probably the polymer $[ZnCl(CN)]_n$. $\nu_{max.}$(Nujol) 2 220s, 2 150m, and 460s cm^{-1}.

Crystal Data.—$As(C_6H_5)_4{}^+\cdot C_{17}N_{11}{}^-$, M = 741.61, red-brown triclinic prisms, space group $P\bar{1}$, a = 7.706(2), b = 15.491(5), c = 16.689(7) Å, α = 65.67(3)°, β = 98.61(3)°, γ = 91.61(3)°, U = 1 794(1) Å^3, D_m = 1.37(2) g cm^{-3} (by flotation), Z = 2, D_c = 1.374 g cm^{-3}, $F(000)$ = 752, Mo-K_α radiation, λ = 0.710 69 Å, graphite monochromator, μ(Mo-K_α) = 10.52 cm^{-1}.

A crystal 0.6 × 0.3 × 0.2 mm was selected; the data were collected at room temperature on a Nicolet *P*3*m* four-circle diffractometer by the $\theta - 2\theta$ scan mode. The cell dimensions were refined from a least-squares fit of the setting angles of 15 reflections ($20° \leqslant 2\theta \leqslant 28°$). The intensities of 3 202 independent reflections with $I \geqslant 3\sigma(I)$ were used, corrected for Lorentz and polarization effects. No absorption correction was applied given the low value of μ. The structure was solved by conventional Patterson and Fourier methods; 310 parameters were refined by full-matrix least-squares to a final conventional R $[= \Sigma|\Delta F|/\Sigma|F_o|] = 0.069$, R_w $[= \{\Sigma w(\Delta F)^2/\Sigma w F_o{}^2\}^{\frac{1}{2}}] = 0.075$, the quantity minimized being $\Sigma w(|F_o| - |F_c|)^2$, with the weighting scheme $w = 1/[\sigma(F_o)^2 + 0.010\,51\,F_o{}^2]$.

Anisotropic thermal parameters were used for the C and N atoms of the $C_{17}N_{11}{}^-$ anion and for the As atom, while the phenyl rings of the $AsPh_4{}^+$ cation were refined isotropically as rigid groups. The hydrogen atoms were introduced at calculated positions with a fixed thermal parameter U = 0.08 Å^2. Neutral-atom scattering factors (f' and f'' values) were taken from ref. 16. Computations were performed on a 4361/4 IBM Computer, using the SHELX-76 System of Crystallographic Programs.[17] Final atomic co-ordinates together with U_{eq} or U_{iso} thermal parameters, anisotropic u_{ij} values, and a drawing of the cation with the atom labels, have been deposited at the Cambridge Crystallographic Data Centre;* interatomic distances and angles for the anion atoms and for the As tetrahedral group are given in Table 1.

Acknowledgements

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* For details of the CCDC deposition scheme, see 'Instructions for Authors (1990)', *J. Chem. Soc., Perkin Trans. 2*, in the January issue.