Reaction Products of Benzimidazole with Tetracyanoethylene. Mechanism of Formation and ^{13}C NMR Spectroscopy of the Anions $C_{16}N_8H_5^-$, Dicyano(3,4-dicyano-5-benzimidazol-1-yl-2H-pyrrol-2-ylideneamino)methanide (1) and $C_{18}N_9H_4^-$, 1,2,4,5-Tetracyano-3,6,7,12,13-penta-aza-5H-indeno[1,2-d]-acenaphthylen-5-ide (2). Crystal and Molecular Structure of their Tetraphenylarsonium Salts

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The anions (1) and (2) have been synthesized by the reaction of benzimidazole with tetracyanoethylene. They have been characterized by X-ray crystallography and ^{13}C NMR spectroscopy. The molecular structures of their tetraphenylarsonium salts have been determined. The charge delocalization and mechanism of formation are discussed.

In the course of our studies on the synthesis of new poly-cyano-substituted molecules, derived from tetracyanoethylene (TCNE),[1] suitable for the preparation of molecular materials such as charge-transfer salts, we investigated the reaction of benzimidazole with TCNE, about which no information is reported in the literature, though TCNE has been made to react with a number of analogous heterocyclic nuclei.[2]

Results and Discussion

From the title reaction in THF we isolated two products (1) (33%) and (2) (trace amounts) as benzimidazolinium ($C_7N_2H_7^+$) salts, according to Scheme 1.

Scheme 1.
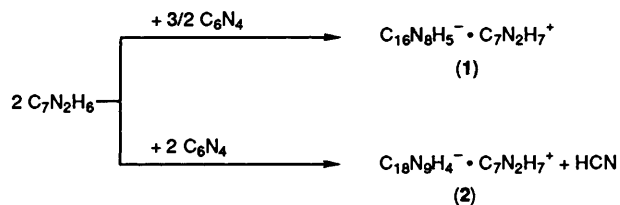
The anion (2), which results from a double deprotonation of benzimidazole, is obtained in a higher yield (25%) as the benz-imidazolinium salt from the reaction of sodium benzimidazolide in THF† [equation (1)]; (1) is not formed at all in the last

$$NaC_7N_2H_5 + 2 C_6N_4 + C_7N_2H_6 \longrightarrow$$
$$C_{18}N_9H_4^- \cdot C_7N_2H_7^+ + NaCN \quad (1)$$
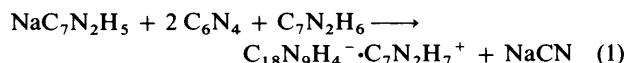
reaction. The molecular formulae of (1) and (2) are shown in Scheme 2. A substantial fraction of the negative charge is associated with three carbon atoms in both the anions, as illustrated by the mesomers (*a*), (*b*), (*c*), according to X-ray and ^{13}C NMR findings. Formulae (*a*) and (*b*) are well substantiated by structural parameters (see below), while the formula (*c*) is possible only in solution.

Both the compounds are dyes and electron-acceptors and have been covered by a patent protection for their potential technological applications.[3] Here we report the mechanism of formation, the ^{13}C NMR spectra and their X-ray crystal structures as [AsPh₄]⁺ salts.

Description of the Structures.—In both structures the tetra-hedral geometry of [AsPh₄]⁺ is regular, with As–C$_{Phenyl}$ distances as expected (see Tables 1 and 2). A drawing of the cation, with the atom labels has been deposited as supplementary material.

[As(C₆H₅)₄]⁺[C₁₆N₈H₅]⁻. The structure of anion (1) is shown in Figure 1; Table 1 reports selected bond lengths and angles. The molecule consists of a benzimidazolic system *N*-bonded to a substituted methyleneaminopyrrole ring. The benz-imidazolic and pyrrolic systems, if taken separately, are almost planar with a dihedral angle of 8.4° between them; the cyano groups move away from the pyrrolic rms plane with a maximum displacement of 0.20 Å for N(22). No π–π interactions between anions are present, as may be seen from the projection on the *b*–*c* plane of the anions packing reported in Figure 2. The only significant van der Waals interactions in the range 3.31–3.47 Å involving atoms of symmetry-related molecules, are N(18)···C(8′), N(18)···N(7′), N(20)···C(13′), N(20)···N(20″).‡

On the basis of the observed bond distances, two mesomeric formulations with the negative charge localized on the C(14) or C(16) atoms can be derived (Scheme 2 and Figure 1). The distances C(12)–N(15) and C(16)–N(15), 1.33(1) and 1.29(1) Å, respectively, agree with the value typical of an sp^2 hybridized carbon–nitrogen bond with a bond order of 1.5.[4]

[As(C₆H₅)₄]⁺[C₁₈N₉H₄]⁻. The structure of (2) is shown in Figure 3; it consists of well-separated tetraphenylarsonium AsPh₄⁺ cations, and of 'slipped stacked' dimers of faced anions $(C_{18}N_9H_4^-)_2$.

A high degree of planarity characterizes the anion, the largest deviation from the rms plane being 0.05 Å. The cyano groups are essentially coplanar with the system, the maximum displacements from the plane being −0.22 Å [N(23)] and 0.17 Å [N(27)]. Such distortions are attributable to intradimeric π–π interactions between faced molecules (see below), rather than to hydrogen bonds, because the only significant CH···N inter-

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† Nitrogen bases other than $C_7N_2H_6$ (*e.g.* pyridine) act as proton acceptors in this reaction, but only benzimidazole is convenient to use, because the benzimidazolinium salt is insoluble and therefore easily separable from the reaction mixture.

‡ The superscripts ′ and ″ refer to the equivalent positions $1 + x, y, z$ and $-x, -y, 1 - z$, respectively.
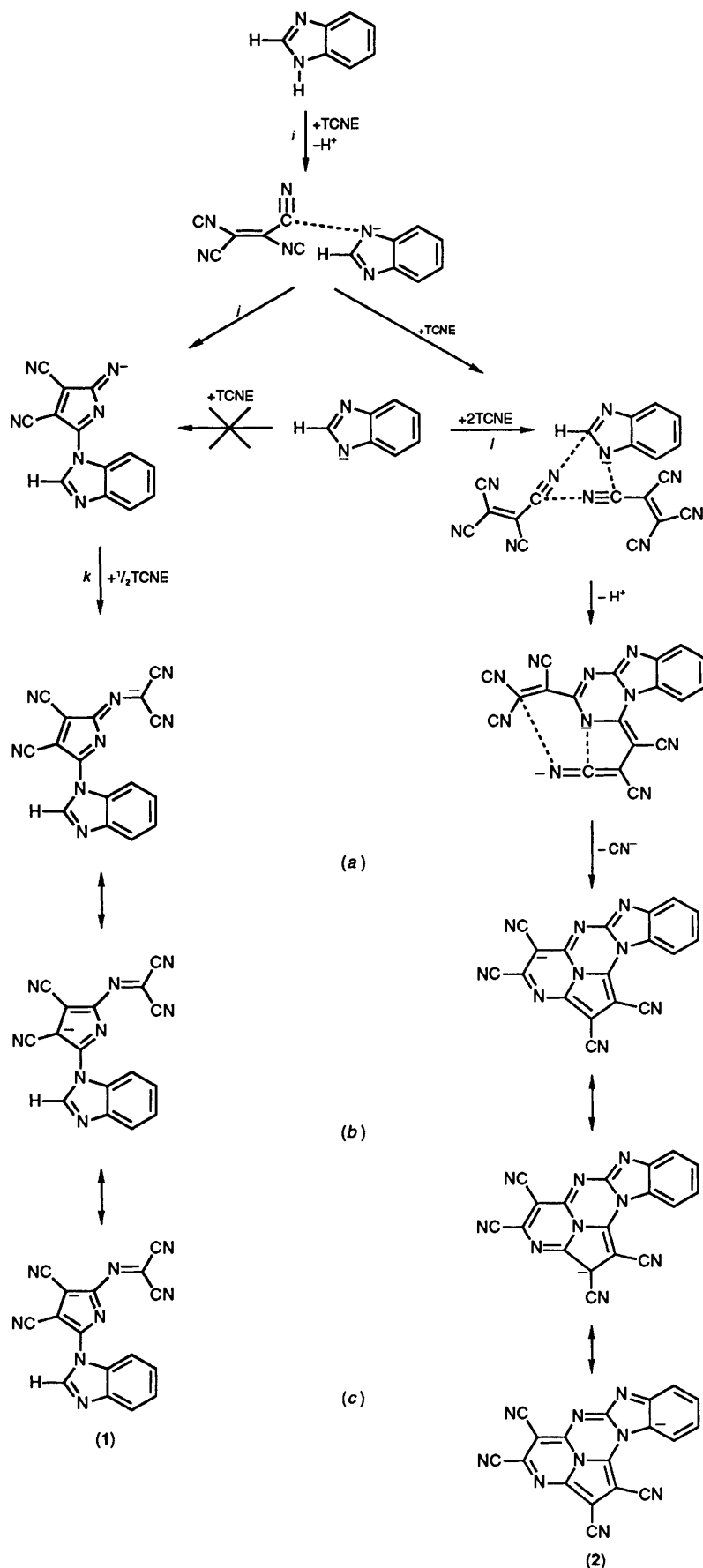
Scheme 2. Hypothetical reaction scheme between benzimidazole and TCNE explaining the formation of the title anions (top), and canonical planar formulae representing the anions with the negative charge on carbon atoms (bottom).

Table 1. Selected bond lengths (Å) and angles (°) with esds in parentheses for $[As(C_6H_5)_4]^+[C_{16}N_6H_5]^-$.

As–C(101)[a]	1.890(4)	C(8)–N(9)	1.30(1)
As–C(107)	1.891(4)	C(10)–N(11)	1.33(1)
As–C(113)	1.896(4)	C(10)–C(14)	1.42(1)
As–C(119)	1.895(4)	N(11)–C(12)	1.38(1)
		C(12)–C(13)	1.41(1)
		C(12)–N(15)	1.33(1)
C(1)–C(2)	1.36(2)	C(13)–C(14)	1.38(1)
C(1)–C(6)	1.39(1)	C(13)–C(21)	1.41(1)
C(2)–C(3)	1.39(1)	C(14)–C(23)	1.43(1)
C(3)–C(4)	1.39(1)	N(15)–C(16)	1.29(1)
C(4)–C(5)	1.36(1)	C(16)–C(17)	1.45(1)
C(5)–C(6)	1.40(1)	C(16)–C(19)	1.43(1)
C(5)–N(7)	1.43(1)	C(17)–N(18)	1.15(1)
C(6)–N(9)	1.40(1)	C(19)–N(20)	1.13(1)
N(7)–C(8)	1.39(1)	C(21)–N(22)	1.15(1)
N(7)–C(10)	1.39(1)	C(23)–N(24)	1.14(1)

C(107)–As–C(101)	109.2(2)	N(11)–C(10)–N(7)	120.2(7)
C(113)–As–C(101)	108.9(2)	C(14)–C(10)–N(7)	127.8(7)
C(113)–As–C(107)	110.1(2)	C(14)–C(10)–N(11)	112.0(7)
C(119)–As–C(101)	109.3(2)	C(12)–N(11)–C(10)	105.9(6)
C(119)–As–C(107)	110.4(2)	C(13)–C(12)–N(11)	110.0(7)
C(119)–As–C(113)	109.0(2)	N(15)–C(12)–N(11)	128.1(7)
C(6)–C(1)–C(2)	118.6(9)	N(15)–C(12)–C(13)	121.9(7)
C(3)–C(2)–C(1)	120.4(9)	C(14)–C(13)–C(12)	106.7(7)
C(4)–C(3)–C(2)	122.7(9)	C(21)–C(13)–C(12)	123.9(7)
C(5)–C(4)–C(3)	115.9(8)	C(21)–C(13)–C(14)	129.3(8)
C(6)–C(5)–C(4)	122.6(8)	C(13)–C(14)–C(10)	105.3(7)
		C(23)–C(14)–C(10)	129.3(7)
N(7)–C(5)–C(6)	105.8(8)	C(23)–C(14)–C(13)	125.4(8)
C(5)–C(6)–C(1)	119.8(9)	C(16)–N(15)–C(12)	125.2(7)
		C(17)–C(16)–N(15)	128.0(7)
N(9)–C(6)–C(5)	108.6(8)	C(19)–C(16)–N(15)	117.8(7)
C(8)–N(7)–C(5)	105.6(7)	C(19)–C(16)–C(17)	114.1(7)
C(10)–N(7)–C(5)	127.6(7)	N(18)–C(17)–C(16)	175.2(8)
C(10)–N(7)–C(8)	126.8(8)	N(20)–C(19)–C(16)	177.7(9)
N(9)–C(8)–N(7)	112.6(9)	N(22)–C(21)–C(13)	176.4(8)
C(8)–N(9)–C(6)	107.3(8)	N(24)–C(23)–C(14)	179(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.

Table 2. Selected bond lengths (Å) and angles (°) with esds in parentheses for $[As(C_6H_5)_4]^+[C_{18}N_9H_4]$.

As–C(101)[a]	1.907(5)	C(11)–C(14)	1.43(1)
As–C(107)	1.894(5)	N(12)–C(13)	1.38(1)
As–C(113)	1.906(5)	N(12)–C(17)	1.389(9)
As–C(119)	1.893(5)	C(13)–C(19)	1.38(1)
C(1)–C(2)	1.38(1)	C(14)–C(15)	1.41(1)
C(1)–C(6)	1.39(1)	C(14)–C(20)	1.43(1)
C(2)–C(3)	1.38(1)	C(15)–N(16)	1.33(1)
C(3)–C(4)	1.37(2)	C(15)–C(22)	1.47(1)
C(4)–C(5)	1.39(1)	N(16)–C(17)	1.35(1)
C(5)–C(6)	1.40(1)	C(17)–C(18)	1.37(1)
C(5)–N(7)	1.39(1)	C(18)–C(19)	1.45(1)
C(6)–N(9)	1.38(1)	C(18)–C(24)	1.43(1)
N(7)–C(8)	1.30(1)	C(19)–C(26)	1.42(1)
C(8)–N(9)	1.42(1)	C(20)–N(21)	1.14(1)
C(8)–N(10)	1.38(1)	C(22)–N(23)	1.13(1)
N(9)–C(13)	1.389(9)	C(24)–N(25)	1.14(1)
N(10)–C(11)	1.290(9)	C(26)–N(27)	1.13(1)
C(11)–N(12)	1.39(1)		

C(107)–As–C(101)	109.7(2)	C(13)–N(12)–C(11)	123.6(6)
C(113)–As–C(101)	111.5(2)	C(17)–N(12)–C(11)	125.4(7)
C(113)–As–C(107)	107.8(2)	C(17)–N(12)–C(13)	111.0(6)
C(119)–As–C(101)	108.0(2)	N(12)–C(13)–N(9)	114.8(6)
C(119)–As–C(107)	110.3(2)		
C(119)–As–C(113)	109.6(2)	C(19)–C(13)–N(12)	107.4(6)
C(6)–C(1)–C(2)	117.0(8)	C(15)–C(14)–C(11)	119.4(7)
C(3)–C(2)–C(1)	122(1)	C(20)–C(14)–C(11)	118.6(7)
C(4)–C(3)–C(2)	121.0(9)	C(20)–C(14)–C(15)	121.9(8)
C(5)–C(4)–C(3)	118.1(9)	N(16)–C(15)–C(14)	127.0(8)
C(6)–C(5)–C(4)	120.7(9)	C(22)–C(15)–C(14)	118.4(7)
		C(22)–C(15)–N(16)	114.4(7)
N(7)–C(5)–C(6)	111.0(7)	C(17)–N(16)–C(15)	113.8(6)
C(5)–C(6)–C(1)	121.3(8)	N(16)–C(17)–N(12)	122.6(7)
		C(18)–C(17)–N(12)	106.3(7)
N(9)–C(6)–C(5)	105.4(7)		
C(8)–N(7)–C(5)	105.2(7)	C(19)–C(18)–C(17)	108.3(6)
N(9)–C(8)–N(7)	112.1(8)	C(24)–C(18)–C(17)	125.1(7)
		C(24)–C(18)–C(19)	126.6(7)
N(10)–C(8)–N(9)	124.0(7)	C(18)–C(19)–C(13)	106.9(7)
C(8)–N(9)–C(6)	106.2(6)	C(26)–C(19)–C(13)	129.9(7)
		C(26)–C(19)–C(18)	123.2(6)
C(13)–N(9)–C(8)	118.6(7)	N(21)–C(20)–C(14)	178(1)
C(11)–N(10)–C(8)	115.8(7)	N(23)–C(22)–C(15)	179(1)
N(12)–C(11)–N(10)	123.1(7)	N(25)–C(24)–C(18)	178.8(8)
		N(27)–C(26)–C(19)	176.6(9)
C(14)–C(11)–N(12)	111.7(6)		

[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.

actions[5] between the cation phenyl rings and the cyano groups, CH(103)–N(6) and CH(104)–N(5), are 2.50 and 2.59 Å, respectively.

Interatomic distances and angles are reported in Table 2. On the basis of the known correlation between bond distance and bond order for C–C and C–N,[4] N(7)–C(8) and N(10)–C(11) bonds, with distances of 1.31(1) and 1.29(1) Å, respectively, can be regarded as localized double bonds. The distances and angles within the condensed system imply mesomeric formulation in the solid state in which the negative charge is possibly localized onto C(14) or C(18) carbon atoms (Scheme 2 and Figure 3).

Pairs of centrosymmetric ($\bar{I}$ at 0, 0, 1/2) anion molecules face at a distance of 3.34 Å with a degree of superposition that suggests interactions through the molecular π-system (see Figure 4). In contrast with that found in $As(C_6H_5)_4^+ \cdot C_{15}N_6H_3^-$ crystal structure, where infinite stacks of superimposed anions are present,[1a] in this case centrosymmetric dimers ($\bar{I}$ at 1/2, 0,

1/2) are shifted from each other in a way such that they are no longer facing and π-interactions are no longer possible. Figure 5 shows the sequence of centrosymmetric dimers developing along the x direction.

Mechanism of Formation.—The reactions involved in the formation of (1) and (2) are reported in Scheme 2.* The initial nucleophilic attack at the nitrile carbon atom is the crucial factor (step i); in the step j a similar inner attack occurs on the same TCNE to form the methyleneaminopyrrole ring;[6] a double nucleophilic attack at the alkenic carbon atoms of another TCNE then occurs leading to the homolytic cleavage of the C=C bond and the dicyanomethylene fragment[7] is incorporated (step k) into the final product (1).

The formation of (2) is more complex; it is accounted for by the bifunctional character (acid–base) that the benzimidazole anion shows towards TCNE in co-ordinating two units through the cyano groups (step l).[8] A sequence of well-known inter-
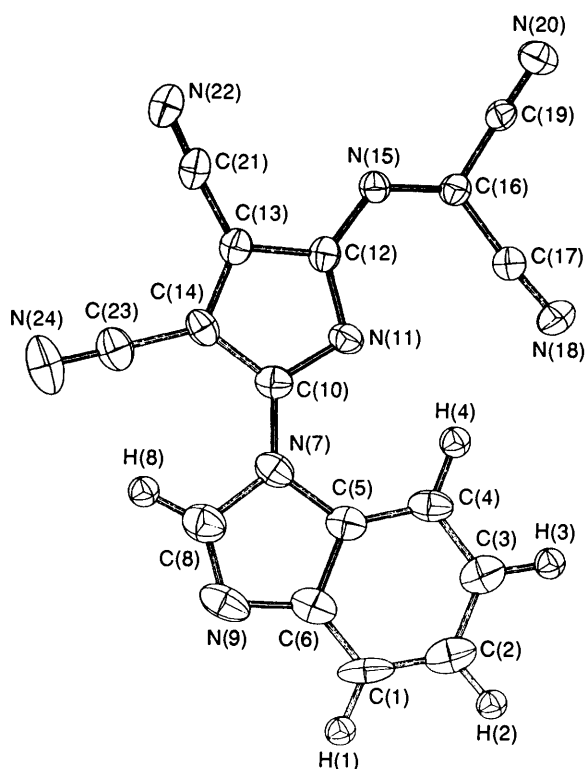
* Other reactions occur in these systems; most probably, electrophilic substitution at carbon or nitrogen, with elimination of HCN, to afford the corresponding C- (or N-) tricyanovinyl compounds, soluble in the reaction mixture. For this reason the yields of (1) and (2) cannot be improved much above 25–30%. In spite of this, we succeeded in isolating the title anions as pure benzimidazolinium salts because they are completely insoluble in THF.

Figure 1. A perspective view of the anion (1) with thermal ellipsoids (30% of probability level) and the numbering scheme.
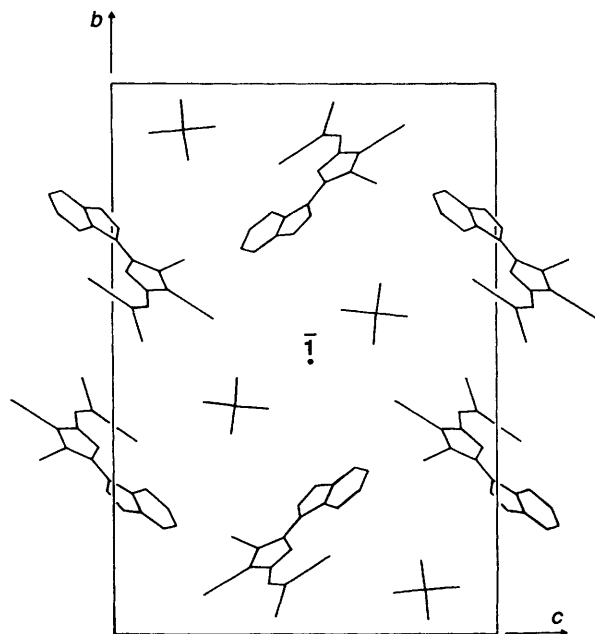

Figure 2. $[As(C_6H_5)_4]^+[C_{16}N_8H_5]^-$: projection of the unit cell onto the b–c plane.

Figure 3. A perspective view of the anion (2) with thermal ellipsoids and the numbering scheme.
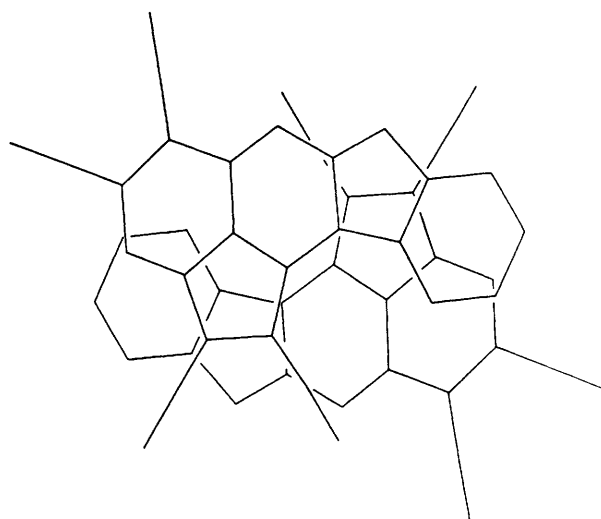
Figure 4. $[As(C_6H_5)_4]^+C_{18}N_9H_4^-$: projection of the superimposed anions (2) onto the molecular plane.
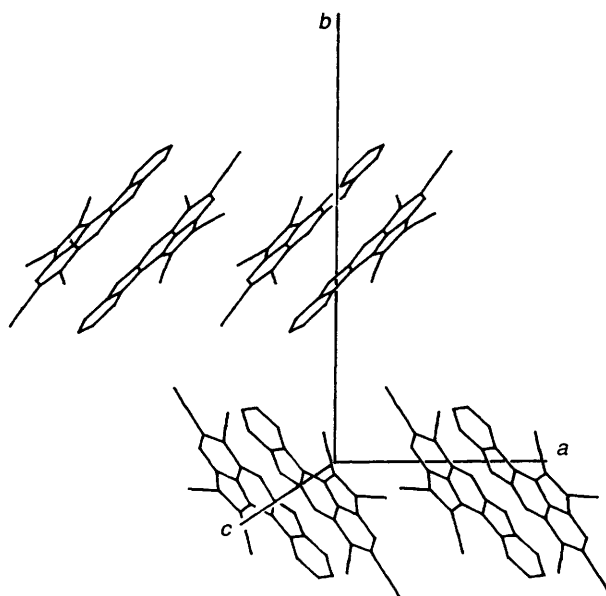
Figure 5. View of the anion (2) sequence along the x-axis.

actions thus occurs between the two TCNEs, brought into close proximity, which entails incorporation of three nitrile groups into the final product (2).

Recently we have synthesized and characterized the heterocyclic percyano-anion (3),[1b] which is very similar to (2), obtained from the self-condensation of TCNE, promoted by Lewis acids [M] (M = $ZnCl_2$, $AlCl_3$), Scheme 3.
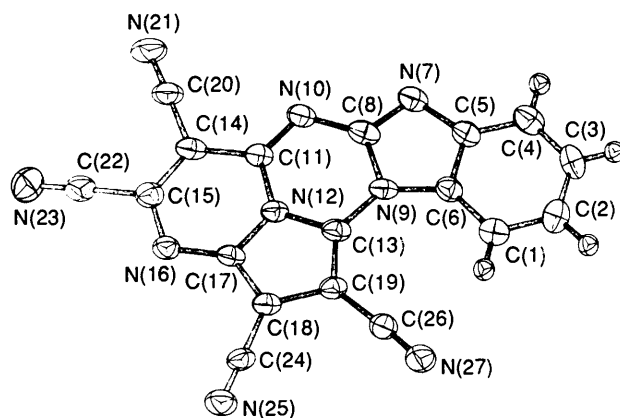
$$2\,C_6N_4^{-\bullet} + C_6N_4 \xrightarrow{[M]} \text{(structure 3)} + CN^-$$

(3)

Scheme 3.

Table 3. ^{13}C NMR spectral data [δ (ppm) from Me$_4$Si] of the anions (1)^a and (2)^a (B_0 4.7 T; T 300 K).

Assignment^b	$C_{16}N_8H_5^-$	$C_{18}N_9H_4^-$
C(1)	117.20^c	111.54^g
C(2)	120.45^c	118.08^g
C(3)	125.15^c	123.15^g
C(4)	126.20^c	124.32^g
C(5)	143.94^d	126.94
C(6)	133.83^d	76.36^h
C(8)	141.36	150.02
C(10)	148.05^e	
C(11)		128.64^i
C(12)	145.36^e	
C(13)	91.10^f	141.29^i
C(14)	107.08^f	79.65^h
C(15)		138.96^j
C(16)	94.98^f	
C(17)		150.95^i
C(18)		81.34^h
C(19)		140.90^j
CN groups	114.32	114.16
	114.56	113.87^k
	116.06	112.24
	117.20	

^{a} As the sodium salt in C$_2$D$_5$OD. ^{b} For the numbering scheme see Figures 1 and 3. $^{c-j}$ May be interchanged. ^{k} Double intensity.

The anions (2) and (3) have a common structural feature (the pyrimidine–pyrrole fused rings), derived from the condensation of two TCNE molecules; a parallel mechanism must operate in the formation of both. In the latter system the first species formed is the adduct M←N̄=Ċ–C(CN)=C(CN)$_2$, which behaves as a bifunctional system serving as acid–base sites for the binding of two TCNE units, exactly as benzimidazolide does, and as schematically summarized below in Scheme 4.
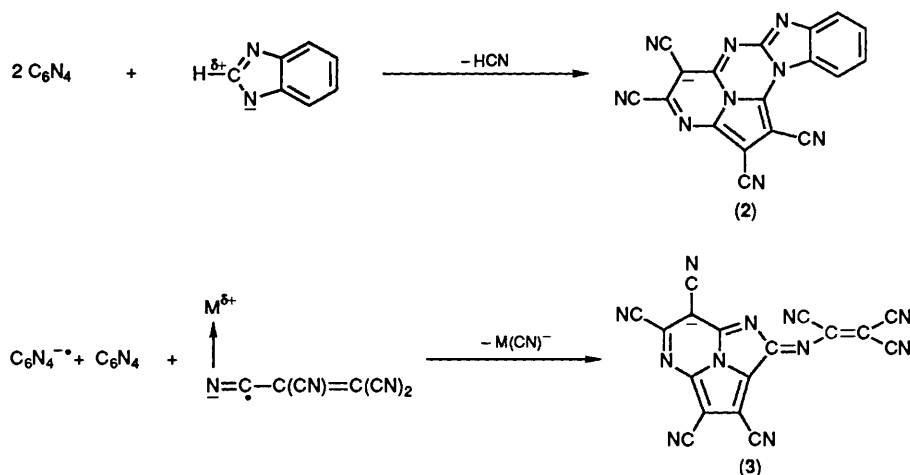
^{13}C *NMR Spectra.*—The ^{13}C NMR spectra are reported in Table 3. Only partial assignment is achievable; the location of the signals representing the protonated carbons [C(1), C(2), C(3), C(4) in (1) and (2) and C(8) in (1) at 141.36 ppm (cf. 141.46 in benzimidazole^9)] is straightforward.

All the nitrile carbon atoms are readily identified from the spectra of (1) and (2), made by using [cyano-^{13}C$_4$]TCNE: the four unaltered cyano groups and the other condensed nitriles [C(10) and C(12) in (1) and C(11), C(13), C(17) in (2)] show enhanced intensity in this case.
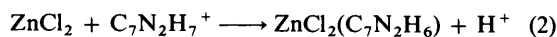
Three resonances are present in the high-field region indicating the existence of the same number of negatively charged carbon atoms in both compounds; these are the three carbon atoms which can accommodate one negative charge in the preferred patterns of electron delocalization shown in Scheme 2. The residual resonances in (1) (133.83 and 143.94 ppm) can be assigned to the bridgehead carbon atoms of benzimidazole [C(5) and C(6)] by exclusion, while in (2) the two close resonances at 138.96 and 140.90 ppm can tentatively be assigned to C(15) and C(19), which have similar electronic surroundings, the lowest-field resonance at 150.02 ppm to C(8) bonded to three nitrogen atoms, and finally the resonance at 126.94 ppm to C(5) by elimination.

Experimental

General.—Details of the physico-chemical measurements (analysis, IR, ^{13}C NMR, and UV spectra, cyclic voltammetry), are given in ref. 1(a).

Reagents.—Benzimidazole, TCNE, K^{13}CN were commercial products, used as received. ^{13}CN-labelled TCNE was prepared as outlined in the literature.^{10} The preparations of the anions (1) and (2) as C$_7$N$_2$H$_7$$^+$ or [AsPh$_4$]$^+$ or Na$^+$ salts have been reported.^{3} The anion (2) was also isolated as the acid C$_{18}$N$_9$H$_4$$^-$·H$^+$, completely ionized even in the solid state, prepared as follows.

Synthesis of C$_{18}$N$_9$H$_4$$^-$·H$^+$.—Anhydrous ZnCl$_2$ (1.5 g, exc.) was added to a suspension of C$_{18}$N$_9$H$_4$$^-$·C$_7N_2H_7$$^+$·THF (0.16 g, 1.12 mmol), in THF (30 cm^3) under N$_2$. After ca. 10 min the salt dissolved completely at room temperature to give a red–violet solution. After a few minutes purple crystals of the acid C$_{18}$N$_9$H$_5$ began to precipitate; in two hours the precipitation was complete (0.3 g, 77%) (Found: C, 61.15; H, 1.85; N, 36.55. C$_{18}$N$_9$H$_5$ requires C, 62.25; H, 1.45; N, 36.29). Both the UV and IR spectra of this compound are superimposable on those of C$_{18}$N$_9$H$_4$Na; the reaction involved is simply that given in

$$2\,C_6N_4 + \text{(benzimidazole structure)} \xrightarrow{-HCN} \text{(structure 2)}$$

(2)

$$C_6N_4^{-\bullet} + C_6N_4 + \begin{array}{c} M^{\delta+} \\ \uparrow \\ \underline{N}{=}\underset{\bullet}{C}{-}C(CN){=}C(CN)_2 \end{array} \xrightarrow{-M(CN)^-} \text{(structure 3)}$$

(3)

Scheme 4.

$$ZnCl_2 + C_7N_2H_7{}^+ \longrightarrow ZnCl_2(C_7N_2H_6) + H^+ \quad (2)$$

equation (2): the salt dissolves; then H^+ combines with the anion (2) to give the acid $C_{18}N_9H_5$, which is only slightly soluble in THF.

Relevant Spectroscopic and Electrochemical Data of (1) *and* (2) *as Sodium Salts.*—$C_{16}N_8H_5Na$: ν_{max}(Nujol) 3 060 cm^{-1} (NH); $\delta_H(C_2D_5OD)$ 8.86 [1 H, s, C(8)H]; λ_{max}(acetone) 482 nm (ε 32 300 dm^3 mol^{-1} cm^{-1}); E_p (rev., cat.) -0.865 V (*vs.* SCE). $C_{18}N_9H_4Na$: λ_{max}(acetone) 586 (2 800 dm^3 mol^{-1} cm^{-1}), 540 (4 740), and 502 nm (4 230); E_p (rev., cat.) -1.43 V (*vs.* SCE); E_p (rev., an.) $+1.2$ V (*vs.* SCE).

Crystal Data for $[As(C_6H_5)_4]^+[C_{16}N_8H_5]^-$.—$C_{40}H_{25}AsN_8$, $M = 692.61$, monoclinic, space group $P2_1/c$, $a = 6.544(2)$, $b = 28.136(7)$, $c = 17.750(5)$ Å, $U = 3\,259(1)$ Å^3, $Z = 4$, $D_c = 1.412$ g cm^{-3}, $F(000) = 1\,415$, λ(Mo-K_α) $= 0.710\,69$ Å, μ(Mo-K_α) $= 11.07$ cm^{-1}.

Data were collected at room temperature on a Nicolet automated four-circle diffractometer with graphite-monochromated Mo-K_α radiation using a crystal with dimensions $0.2 \times 0.3 \times 0.5$ mm. Cell parameters were determined by a least-squares fit of the setting angles of 15 reflections. A total of 5 833 intensities ($3° \leqslant 2\theta \leqslant 60°$) were collected by the θ–2θ scan technique and corrected for Lorentz and polarization effects; a semiempirical absorption correction, based upon a $360°$ scan around the scattering vector of a selected reflection, was applied (ratio between maximum and minimum values 1.13). Only 2 862 independent reflections having $I \geqslant 3\sigma(I)$ were used in the refinement.

The structure was solved by Patterson and Fourier methods. 274 parameters were refined by full-matrix least-squares analysis to a final conventional R ($= \Sigma|\Delta|/\Sigma|F_o|$) $= 0.058$, R_w ($= [\Sigma w|\Delta|^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$) $= 0.055$, the quantity minimized being $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$) with the weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\,650\,F_o{}^2]$.

Anisotropic thermal parameters were used for C and N atoms of the anion and for the As atom; the phenyl rings of the $[AsPh_4]^+$ cation were refined isotropically as rigid groups. All 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. 13.

Crystal Data for $[As(C_6H_5)_4]^+[C_{18}H_4N_9]^-$.—$C_{42}H_{24}AsN_9$, $M = 729.63$, red–violet monoclinic prisms, space group $P2_1/c$, $a = 9.291(1)$, $b = 21.901(3)$, $c = 17.952(2)$ Å, $\beta = 108.12(1)°$, $U = 3\,471.7(8)$ Å^3, $D_m = 1.41(2)$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.40$ g cm^{-3}, $F(000) = 1\,488$, λ(Cu-K_α) $= 1.5418$ Å, graphite monochromated, μ(Cu-K_α) $= 18.24$ cm^{-1}; a crystal $0.15 \times 0.15 \times 0.5$ mm was selected.

Details of the procedure of intensities collection and refinement are as given above for the previous structure analysis. 5 190 intensities ($4° \leqslant 2\theta \leqslant 110°$) were collected by the θ–2θ scan technique on a Nicolet diffractometer with Cu-K_α radiation, and corrected for Lorentz and polarization effects; a semiempirical absorption correction was applied (ratio max/min values 1.48). 2 544 independent reflections with $I \geqslant 3\sigma(I)$ were used in the refinement. The 58 and 244 parameters were alternately refined by blocked full-matrix least-squares to final values 0.056 and 0.059 for R and R_w, respectively.

Calculations were performed on an IBM 4361/4 computer, using the SHELX-76 system of crystallographic programs.[12] Supplementary data with atomic co-ordinates and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the CCDC deposition scheme, see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 2*, 1990, issue 1.