Electronic and Structural Properties of Novel Cyanocarbon Dyes based on Tetracyanoethylene

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Four novel cyanocarbon dyes derived from tetracyanoethylene (TCNE) have been studied. They are carbanions isolated as tetraphenylarsonium salts of formula $C_{11}N_7H_2^-$ (**1**), $C_{15}N_6H_3^-$ (**2**), $C_{14}N_7H_2^-$ (**3**), and $C_{13}N_8H^-$ (**4**). Compound (**1**) was obtained by a condensation reaction of TCNE promoted by $Ti(bpy)_3$ and its structure has already been reported. Compounds (**2**)—(**4**) are the 1,3-bistricyanovinyl derivatives of cyclopentadienyl, pyrrolyl, and imidazolyl anions, respectively. The tetraphenylarsonium salt of anion (**3**) gives crystals isomorphous with the crystals of the analogous salts of anions (**2**) and (**4**), whose crystal structures are reported here. Structural and electronic properties of the four anions are discussed on the basis of ^{13}C n.m.r., i.r., u.v., and electrochemical data; electrical and magnetic properties of their radical salts with the tetrathiafulvalenium cation ($TTF^{\cdot+}$) are also reported and discussed.

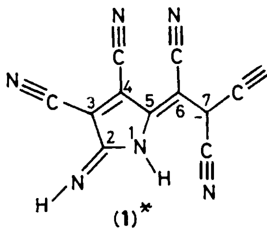
Cyanocarbon derivatives attract great interest for their electron-acceptor and chromophoric properties, often involving large molar absorptivities.[1] As organic dyes they have been used for many purposes in traditional applications;[2] furthermore, some years ago, new potential applications have been proposed;[3] very recently a radical-anion salt with the properties of a multidimensional organic metal with extremely high electrical conductivity has been obtained from *NN′*-dicyanoquinone di-imines.[4]

In the course of a project on materials with unusual electrical and/or magnetic properties, we have synthesized and characterized new cyanocarbons by using tetracyanoethylene (TCNE) as starting material. We have tried two new reactions of TCNE leading to new cyanocarbon anions. First, the novel heterocyclic anion, $C_{11}N_7H_2^-$, was obtained from a condensation reaction of TCNE promoted by $Ti(bpy)_3$ (bpy = bipyridyl).[5] Then we discovered a new substitution reaction of TCNE by using $Ticp_2(bpy)$ (cp = cyclopentadienyl) instead of $Ti(bpy)_3$ as promoter, the 1,3-bistricyanovinylation of cyclopentadienyl anion. This reaction has been extended to the analogous heterocyclic pyrrolyl and imidazolyl anions.[6] Here we report the structural and electronic properties of the four diamagnetic anions as the $(AsPh)_4^+$ and $(TTF)^{\cdot+}$ (TTF = tetrathiafulvalene) salts.

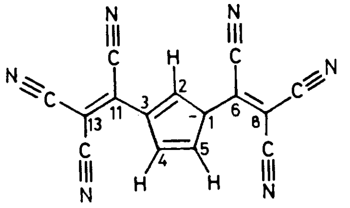
Results and Discussion

We have synthesized and characterized four new air-stable cyanocarbons isolated as tetraphenylarsonium salts. The results of both *X*-ray and ^{13}C n.m.r. measurements point to the carbanionic structures (**1**)—(**4**). These carbanions exhibit, to a greater or lesser extent, marked double-bond fixation. Compound (**1**) is non-aromatic and behaves as an alternant hydrocarbon (**a**) with an odd number of carbon atoms. The others are best described by the mesomeric formula (**b**) with the negative charge localized in positions 1 and 3.

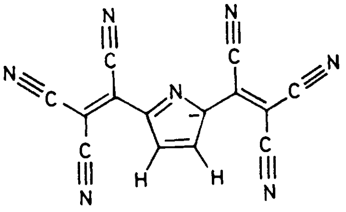
Synthesis.—Compound (**1**) was obtained by the reaction of TCNE with $Ti(bpy)_3$ followed by protonation; TCNE is first reduced to a dianion, then two molecules of the dianion condense, *via* a metal-promoted mechanism, to give, after protonation and elimination of HCN, the new heterocycle: 1,1,2-tricyano-2-(3,4-dicyano-5-imino-2,5-dihydro-1*H*-pyrrol-2-ylidene)ethanide.



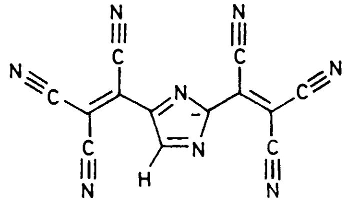
(**1**)*



(**2**)†



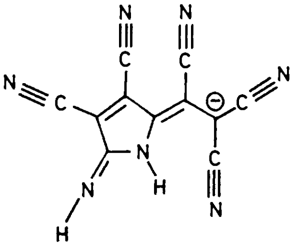
(**3**)



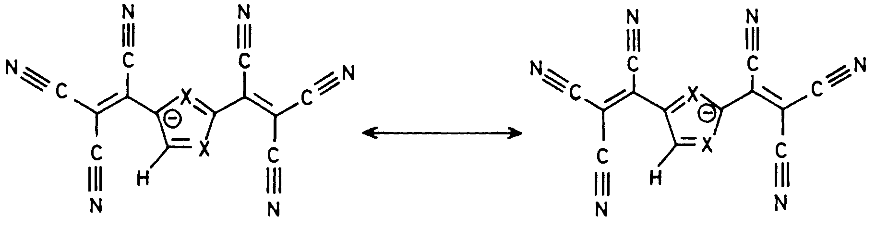
(**4**)

* IUPAC numbering. † Crystallographic numbering.

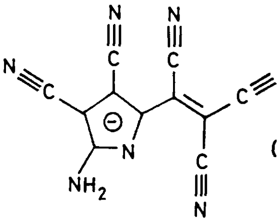
The same product, in different yields, was obtained by varying the transition metal complex, *e.g.* using $Ti(Me_2bpy)_3$, $Ti(o\text{-}phen)_3$ (*o*-phen = *o*-phenanthroline), $Zr(bpy)_3$, $V(bpy)_3$, and $Ticp_2(bpy)$. With the cyclopentadienyl titanium complex, together with compound (**1**), another violet product, readily separable by silica chromatography, was formed, which was identified as compound (**2**), 1,3-bis(tricyanovinyl)cyclopentadien-1-ide. This can be made in higher yield (see Experimental section) by reaction of one mole of NaCp with two



(a)



(b) (X = N, CH)



(c)

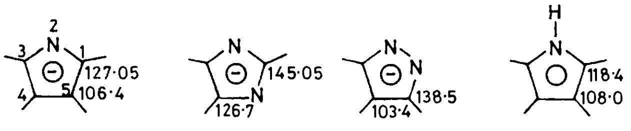


Figure 1. ^{13}C δ values from ref. 9

moles of TCNE. If this reaction is stopped after adding one mole of TCNE, an air-sensitive solution is obtained; with two moles of TCNE the solution turns to violet and became air-stable. Obviously, the stepwise reaction (1) takes place. This reaction

$$C_5H_5^- \xrightarrow[-HCN]{+TCNE} [C_5H_4C_2(CN)_3]^- \xrightarrow[-HCN]{+TCNE} [C_5H_3\{C_2(CN)_3\}_2]^- \quad (1)$$

amounts to the bistricyanovinylation of an anion.

We observe that (i) only the 1,3- and not the 1,2-disubstituted isomer is obtained, probably because of the steric hindrance of the tricyanovinyl group and (ii) no geometrical isomers can be isolated, in agreement with known facts,[7] which sustain rotation in solution around the C(1)–C(6) or C(3)–C(11) bonds.

The bistricyanovinylation of nitrogen-containing heterocyclic anions (pyrrolyl, imidazolyl, pyrazolyl) raises some questions. (1) The bistricyanovinylation of pyrrolyl anion affords only isomer (**3**), while the unsymmetrically substituted isomer has not been detected at all. (2) The bistricyanovinylation of the pyrazolyl anion does not occur though the yield of the bistricyanovinylation of the imidazolyl anion attains 25%.

Taking into account the fact that the bistricyanovinylation proceeds in a stepwise manner and that the second group enters the other available position, the problem reduces to explaining the direction of monotricyanovinylation. It is known that tricyanovinylation is an electrophilic substitution reaction occurring at the carbon position with the highest electron density.[8] The electron density distribution can be empirically derived from the ^{13}C chemical shift values. These data are reported in Figure 1 for the pyrrolyl, imidazolyl, and pyrazolyl anions and pyrrole.[9]

In the pyrrolyl anion monotricyanovinylation does not occur at position 5, in breach of the highest electron density rule, otherwise the 3,5-disubstituted isomer should be obtained, whereas the only product is the 1,3-disubstituted isomer. These facts can be explained by an initial attack of TCNE at the negatively charged nitrogen atom, followed by a 1,2-shift with concerted elimination of HCN. In the imidazolyl and pyrazolyl anions the nitrogen atoms are less negatively charged than in the pyrrolyl derivative and thus the initial attack occurs at the fourth carbon position, more likely in the pyrazolyl compound, where this position is electron rich; after this step another $C_2(CN)_3$ group cannot enter the pyrazolyl function because there is no CH function in the alternant position. The disubstituted derivative of pyrazolyl was not obtained at all, but the pentacyanopropenide anion was isolated as the only stable product under the reaction conditions (see Experimental section) where the base-catalysed hydrolysis of TCNE occurs.[10] It is pertinent here to recall that monotricyanovinylation of pyrrole (a well known reaction[11]) occurs at position 1 as for any other electrophilic substitution of pyrrole; in this case neither the electron density rule nor the attack at nitrogen are involved, but rather the minimum-energy principle of the carbocation intermediate is to be considered; this principle does not work in our case where the substrate is an anion.

N.m.r. Studies.—^{13}C N.m.r. spectral data are collected in Table 1. The most characteristic feature of the spectra (Figure 2) is the presence of one or two resonances in the region between δ 65 and 85 p.p.m., at considerably higher field than expected for either TCNE or the penta-atomic ring carbon atoms. This highfield shift is connected with the existence of localized

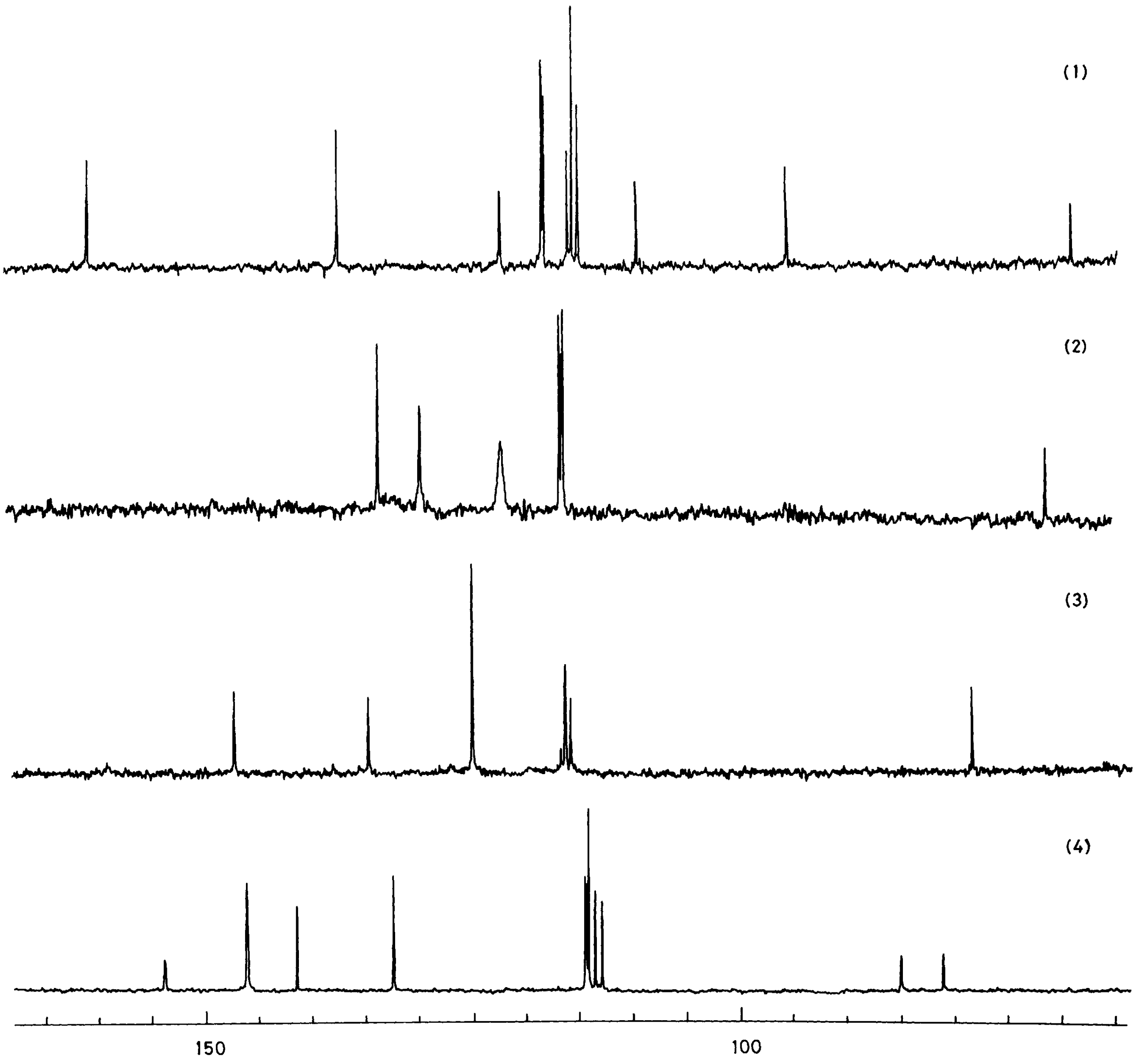


Figure 2. ^{13}C N.m.r. spectra of carbanions (**1**)—(**4**)

Table 1. ^{13}C N.m.r. spectral data for the sodium salts of the carbanions (**1**)—(**4**) (B_0 4.7 T; T 300 K; solvent ethanol)

	δ (p.p.m.)									
Carbanion		C(2)	C(3)	C(4)	C(5)	C(6)	C(7)			CN groups
$C_{11}N_7H_2^-$		161.10	121.79[b]	137.34[b]	94.62	108.91	67.76			114.43; 115.02; 115.37; 117.68; 117.84
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(8)	C(11)	C(13)	
$C_{15}N_6H_3^-$[a]	69.83	130.84	69.83	121.19	121.19	132.62[b]	128.79[b]	132.62[b]	128.79[b]	115.14; 115.57
$C_{14}N_7H_2^-$	77.67		77.67	124.66	124.66	147.04	134.33	147.04	134.33	115.26; 115.35; 115.75
$C_{13}N_8H^-$	80.42[b]		84.38[b]	145.97		153.68	132.10	141.17	132.10	112.42; 113.06; 113.68; 113.86; 114.00

[a] T 333 K; Cs^+ salt. [b] May be interchanged.

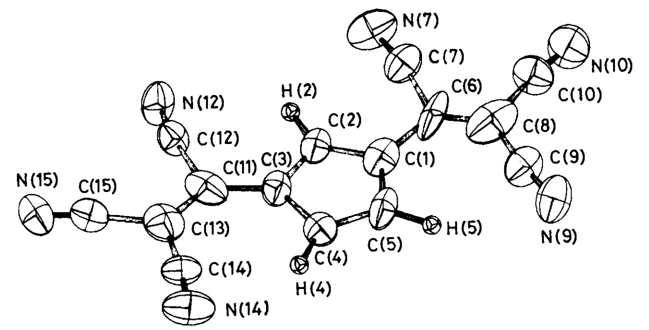


Figure 3. A perspective drawing of anion (**2**) with thermal ellipsoid view and the numbering scheme

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound (**2**)

C(1)–C(2)	1.36(2)	C(2)–C(1)–C(5)	106(1)
C(1)–C(5)	1.45(3)	C(1)–C(2)–C(3)	109(1)
C(1)–C(6)	1.54(4)	C(2)–C(3)–C(4)	108(1)
C(2)–C(3)	1.41(2)	C(3)–C(4)–C(5)	104(1)
C(3)–C(4)	1.46(2)	C(1)–C(5)–C(4)	110(1)
C(3)–C(11)	1.42(2)	C(1)–C(6)–C(7)	115(1)
C(4)–C(5)	1.36(2)	C(1)–C(6)–C(8)	124(2)
C(6)–C(7)	1.56(3)	C(7)–C(6)–C(8)	120(2)
C(6)–C(8)	1.20(3)	C(6)–C(7)–N(7)	168(2)
C(7)–N(7)	1.12(2)	C(6)–C(8)–C(9)	124(2)
C(8)–C(9)	1.42(3)	C(6)–C(8)–C(10)	115(2)
C(8)–C(10)	1.55(4)	C(9)–C(8)–C(10)	119(1)
C(9)–N(9)	1.09(2)	C(8)–C(9)–N(9)	172(2)
C(10)–N(10)	1.07(3)	C(8)–C(10)–N(10)	169(2)
C(11)–C(12)	1.58(3)	C(3)–C(11)–C(12)	119(1)
C(11)–C(13)	1.29(3)	C(3)–C(11)–C(13)	127(1)
C(12)–N(12)	1.07(2)	C(12)–C(11)–C(13)	112(1)
C(13)–C(14)	1.45(2)	C(11)–C(12)–N(12)	171(1)
C(13)–C(15)	1.56(3)	C(11)–C(13)–C(14)	123(1)
C(14)–N(14)	1.11(2)	C(11)–C(13)–C(15)	120(1)
C(15)–N(15)	1.11(2)	C(14)–C(13)–C(15)	115(1)
		C(13)–C(14)–N(14)	173(1)
		C(13)–C(15)–N(15)	170(1)

negative charges, namely with the presence of carbanionic carbon atoms.

Compound (**1**), which has been shown to be a non-aromatic alternant hydrocarbon,[5] bears the negative charge on C(7) (42 p.p.m. upfield shift relative to TCNE) and the resonances of C(6) and C(5) are shifted as expected for open-chain delocalized carbanions.[12]

According to the ^{13}C n.m.r. data, the negative charge is located on C(1) and C(3) for compounds (**2**)—(**4**), and the structure of the carbanions is described by the mesomeric formula (**b**). However, the structure is symmetric for (**2**) and (**3**) and gives rise to one upfield-shifted resonance only, while two carbanionic carbon resonances are observed for compound (**4**) because positions 1 and 3 are non-equivalent.

The total upfield shift of the ^{13}C resonances upon deprotonation of the ring to the corresponding anion is expected to be 56 p.p.m. for cyclopentadiene[13] and is 14.1 p.p.m. for pyrrole, where the negative charge is mainly located on the nitrogen atom (Figure 1). For our carbanions, the observed total upfield shift is 57.4 p.p.m. in the case of (**2**) (if an average value of 570.3 p.p.m. is taken as the sum of the ^{13}C chemical-shift values for the ring carbons of 1,3-disubstituted neutral cyclopentadienes)[14] and 41.3 p.p.m. for (**3**). These results indicate that the charge is indeed located on the ring and that the fraction of the negative charge on the ring carbons of compound (**3**) is larger than in the pyrrolyl anion itself.

Localization of the negative charge in the positions 1 and 3 is indicated by the large upfield shift of the corresponding resonances, which in the case of (**2**) is much larger than the values reported for the 1,3-disubstituted cyclopentadienyl anions, where the negative charge is delocalized over the whole ring.[14] Also the *X*-ray findings for compound (**4**) (see Figure 6 and Table 3) suggest that the C(1)–C(6) and C(3)–C(11) bonds are single, in agreement with the negative charge located on C(1) and C(3).

Only minor changes have been observed for the spectral position of the cyano resonances, indicating lack of charge delocalization for these carbons, in agreement with the *X*-ray data available (see below). The assignments of the other ^{13}C resonances are based essentially on the spectral positions and proton-undecoupled spectra.

It is worth noting that in the room temperature spectrum of the carbanion (**2**), the C(2) appears as a barely perceptible broad resonance at δ *ca.* 133 p.p.m. and the C(4), C(5) resonance is considerably broadened (see Figure 2). An increase in the temperature leads to a sharpening of the lines of these proton-bearing atoms. A marked temperature effect is also observed on the proton spectra of (**2**); however, the process responsible for this kinetic behaviour has not been identified and is currently under study.

Description of Structures.—The structure of anion (**1**) has already been reported.[5] The tetraphenylarsonium salt of the anion (**3**) gives crystals isomorphous with those of the analogous salt of anions (**2**) and (**4**), whose crystal structures are reported here. They consist of well separated tetraphenylarsonium cations $[AsPh_4]^+$, and of stacked anions. In both structures the geometry of the tetrahedral $[AsPh_4]^+$ is regular, with As–C_{phenyl} bond distances and angles as expected [1.888(5)—1.897(7) Å, and 106.7(2)—112.9(2)°]. For the sake of clarity, no representation of the well known cation has been reported here.

The structure of anion (**2**) is shown in Figure 3. Table 2 reports selected bond lengths and angles. The molecule is essentially planar, but it can be better described by taking into account the high planarity of the central ring and of each tricyanovinyl group. A noteworthy aspect is the aggregation of the anions into infinite stacks developing along the *z* axis (see Figure 4). Two columns of superimposed anions are present in the cell, while the $[AsPh_4]^+$ cations (not shown in Figure 4) fill the intercolumnar space. The Figure 5 shows one such column projected onto the *a*–*b* plane: the four symmetry-related anions, spaced by *ca.* 3.5 Å (range 3.4—3.6 Å), interact with each other essentially through the Cp π-system. The stack spacing value, compared with that of 3.2—3.5 Å generally recognized as indicating the presence of π–π interaction,[15] or with the value of 3.17 Å between stacked TCNQ$^-$,[16] confirms the aromatic character, although slightly weakened, of (**2**). To our knowledge, this is the first example of such crystal packing for the cyclopentadienyl system; in the case of tetramethyl-*p*-phenylenediamine–pentacyanocyclopentadienide[17] mixed stacking has been observed.

The structure of the anion (**4**) is shown in Figure 6; Table 3 reports selected bond lengths and angles. Owing to the isomorphism of the two crystals, the molecule is quite similar to (**2**) described above. The main difference is the positional disorder involving two carbon atoms of one tricyanovinyl group which occupies either the positions C(61), C(81) (56%) or C(62), C(82) (44%). In an unexpected way, the other atoms of the group do not appear perturbed by the disorder: this is probably due to the strong π–π interaction between the anions forming the columnar stacks as in the previous compound. The tricyanovinyl groups are quite planar and are almost coplanar with the imidazole ring. A singular characteristic of both structures is the very small value of the bond length C(6)–C(8)

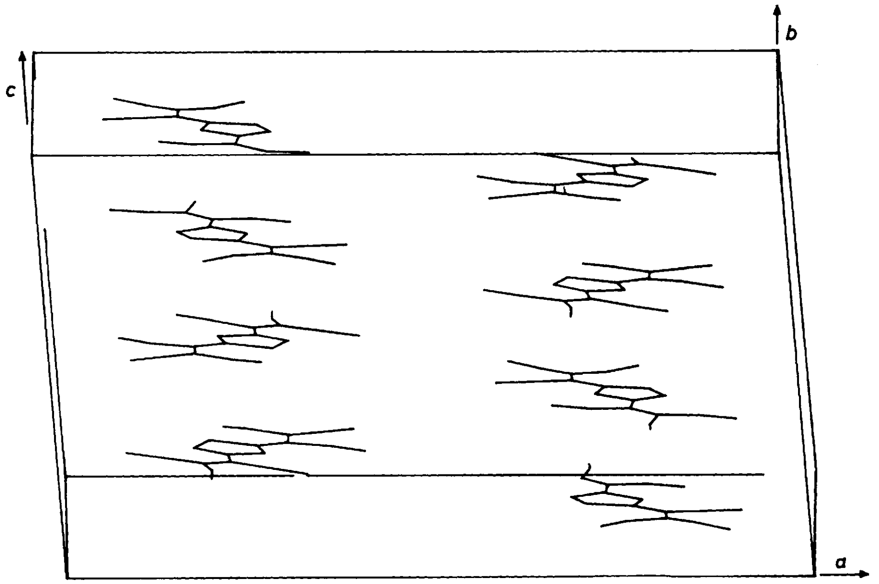


Figure 4. View of anion stacks along the *z*-axis

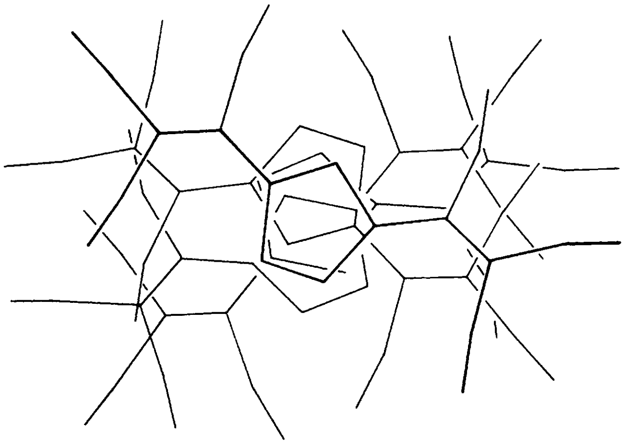


Figure 5. Projection of superimposed anions on the *a*–*b* plane

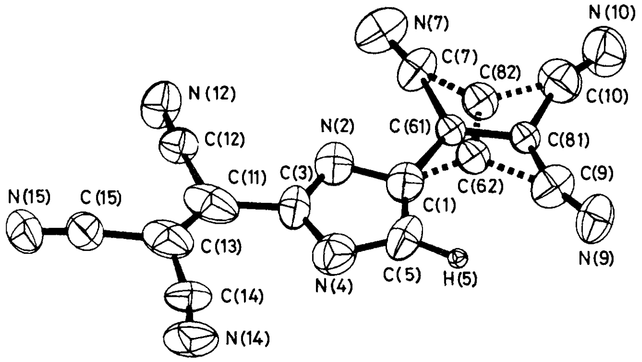


Figure 6. A perspective drawing of anion (4) with thermal ellipsoid view and the numbering scheme. The low probability one of the two disordered tricyanovinyl groups is bonded by interrupted lines

(1.20 Å) found in the first one, and of C(11)–C(13) (1.18 Å) in the second. These bond lengths appear considerably shorter than the double bond expected in such positions, as discussed before: we think that the very high anisotropy of the carbon atoms mentioned (see Figures 3 and 6) could be interpreted as librational motion leading to an apparent shortening of the bond lengths. The instability of the atomic positions in this region can be the cause of the disorder observed in one of the tricyanovinyl groups.

I.r. Spectra.—For compound (**1**) information gained from the i.r. spectrum clarifies the molecular structure. The two protons can be located; tautomer (**c**) can be excluded because the i.r. spectrum shows only one N–H stretching (3 360 cm^{-1}), while the NH_2 group usually exhibits two absorptions in the N–H stretching region;[18] moreover the band at 1 620 cm^{-1}, absent in the other compounds, can be assigned to the stretching of the imine group C=N–H;[19] these two bands shift on deuteriation to 2 450 and 1 520 cm^{-1}, respectively. Apart from these bands, the spectrum is very similar to that of the pyrrolyl anion (**3**), characterized by two intense bands centred at 1 540 and 1 350 cm^{-1}. Compounds (**2**) and (**4**) show the characteristic patterns of disubstituted anions. The cyano stretch appears as a very sharp peak at 2 210 cm^{-1} for compounds (**2**)—(**4**), while for compound (**1**) it gives rise to a broader band at 2 220 cm^{-1} with a shoulder at 2 210 cm^{-1}.

Cyclic Voltammetry.—The reversible reduction wave in the cyclic voltammogram of (**1**) at E_p −0.94 V is characterized by an overall process yielding the trianion. The two-electron transfer is stepwise and the transient unstable radical species ($C_{11}N_7H_2^{2-}$) is formed and can be detected by e.s.r. spectroscopy when the electrolysis is performed *in situ*.[20] Compounds (**2**)—(**4**) show two monoelectronic reversible waves (Table 4). The radical formed in the first reduction step is stable under N_2.[20]

Solution and Reflectance Spectra.—Solution spectra are characterized by an intense absorption in the visible region (see Table 5). In the solid state compounds (**2**)—(**4**) show in addition to the absorption band of the solution another band at lower energy; keeping in mind the packing of the anions in the crystals, this band results from the interanionic charge-transfer transition confined within the stack. This stacking originates from the well known properties of dyes, associated with colour, to self-aggregate.[21] Compound (**1**) does not self-aggregate and, consequently, does not show the extra band in the solid state. This different behaviour of compound (**1**) in comparison with the others is accountable not only for a lower absorption coefficient but also for the inherent instability of the dianion

Table 3. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound (**4**)

C(1)–C(5)	1.41(2)	C(5)–C(1)–N(2)	109(1)
C(1)–C(61)	1.55(3)	N(2)–C(3)–N(4)	116(1)
C(1)–C(62)	1.38(3)	C(1)–C(5)–N(4)	109(1)
C(1)–N(2)	1.35(2)	C(1)–C(61)–C(7)	125(1)
C(3)–C(11)	1.49(2)	C(1)–C(61)–C(81)	115(2)
C(3)–N(2)	1.31(2)	C(7)–C(61)–C(81)	118(2)
C(3)–N(4)	1.38(2)	C(1)–C(62)–C(82)	123(1)
C(5)–N(4)	1.32(2)	C(1)–C(62)–C(9)	125(1)
C(61)–C(7)	1.58(3)	C(82)–C(62)–C(9)	110(1)
C(61)–C(81)	1.35(4)	C(61)–C(7)–N(7)	167(1)
C(62)–C(82)	1.36(3)	C(82)–C(7)–N(7)	159(1)
C(62)–C(9)	1.60(2)	C(61)–C(81)–C(10)	108(2)
C(7)–C(82)	1.38(3)	C(9)–C(81)–C(10)	132(1)
C(7)–N(7)	1.11(2)	C(62)–C(82)–C(7)	118(1)
C(81)–C(9)	1.34(3)	C(62)–C(82)–C(10)	116(1)
C(81)–C(10)	1.52(3)	C(7)–C(82)–C(10)	124(1)
C(82)–C(10)	1.55(3)	C(62)–C(9)–N(9)	160(1)
C(9)–N(9)	1.11(2)	C(81)–C(9)–N(9)	157(1)
C(10)–N(10)	1.11(2)	C(81)–C(10)–N(10)	157(1)
C(11)–C(12)	1.56(2)	C(82)–C(10)–N(10)	158(1)
C(11)–C(13)	1.18(2)	C(3)–C(11)–C(12)	116(1)
C(12)–N(12)	1.09(1)	C(3)–C(11)–C(13)	127(1)
C(13)–C(14)	1.50(2)	C(12)–C(11)–C(13)	116(1)
C(13)–C(15)	1.53(2)	C(11)–C(12)–N(12)	174(1)
C(14)–N(14)	1.09(2)	C(11)–C(13)–C(14)	124(1)
C(15)–N(15)	1.12(2)	C(11)–C(13)–C(15)	121(1)
		C(14)–C(13)–C(15)	113(1)
		C(13)–C(14)–N(14)	168(1)
		C(13)–C(15)–N(15)	172(1)
		C(1)–N(2)–C(3)	102(1)
		C(3)–N(4)–C(5)	102(1)

Table 4. Cyclic voltammetric data for anions (**2**)—(**4**) in DMF solution (10^{-3}M)

Compound	E_p^1(cat)/V	E_p^2(cat)/V	ΔE_p^1/V[a]	ΔE_p^2/V[a]
$C_{15}N_6H_3^-$	−0.560	−1.29	0.080	0.070
$C_{14}N_7H_2^-$	−0.435	−1.07	0.070	0.070
$C_{13}N_8H^-$	−0.370	−0.99	0.080	0.060

[a] Cathodic to anodic peak potential separation.

Table 5. Electronic spectra of anions (**1**)—(**4**) (shoulders in parentheses; solvent, acetone)

Compound		$\lambda_{max.}$/nm	ε/l mol⁻¹ cm⁻¹
$C_{11}N_7H_2^-$	Solution	546	30 175
	Reflectance	564	
$C_{15}N_6H_3^-$	Solution	574	59 065
	Reflectance	575; (650)	
$C_{14}N_7H_2^-$	Solution	572	62 000
	Reflectance	565; 654	
$C_{13}N_8H^-$	Solution	533; (504)	50 000
	Reflectance	(580); 490	

$C_{11}N_7H_2^{2-}$.* A dianion dimer (A_2^{2-}) is formed in concentrated aqueous solution (0.01M) for A = (**2**)—(**4**) but not for A = (**1**) as evident from molecular weight measurements in water (see Table 6).

Table 6. Molecular weights for the sodium salts of anions (**1**)—(**4**) in water. The theoretical values are calculated assuming complete dissociation of the sodium salt in water: $NaA \longrightarrow Na + A$; $Na_2A_2 \longrightarrow 2Na + A_2$

Compound	Mol. wt. calc. for NaA	Mol. wt. calc. for Na_2A_2	Mol. wt. found
$C_{11}N_7H_2Na$	127	170	111
$C_{15}N_6H_3Na$	145	193	199
$C_{14}N_7H_2Na$	145.5	194	171
$C_{13}N_8HNa$	146	194	210

Table 7. Electrical conductivity (σ) and activation energy (E_a) for $(TTF)A_{0.67}$ at different temperatures

Compound A	Temperature (K)	σ (ohm⁻¹ cm⁻¹)	E_a (eV)
$C_{15}N_6H_3^-$	289	0.88×10^{-3}	0.040
	77	1.03×10^{-5}	
$C_{14}N_7H_2^-$	287	6.9×10^{-2}	0.058
	82	2.13×10^{-4}	
$C_{13}N_8H^-$	290	1.27×10^{-1}	0.027
	80	7.6×10^{-3}	

Radical-cation Salts with $TTF^{\bullet +}$.—All four anions can be used as electron acceptors to make charge-transfer complexes. In combination with the donor tetrathiafulvalene (TTF) such charge-transfer complexes can be prepared in two ways, either reacting TTF with the neutral acid obtained after protonation of the anion or by metathesis of the sodium salt with the tetrathiafulvalenium cation. We tried both routes (see Experimental section), but only the metathesis was successful. Following the reaction $(TTF)_3(BF_4)_2 + 2NaA$, compounds of composition $(TTF)A_{0.67}$ are formed [for A = (**2**)—(**4**)]; anion (**1**) is not stable in solution in the presence of the radical $TTF^{\bullet +}$, from which it abstracts one proton to give the acid $C_{11}N_7H_3$, as determined by elemental analysis.

All the salts behave as semiconductors in the temperature range investigated, −180 to +30 °C. The d.c. conductivity at 25 °C (σ), measured for compacted samples, and activation energies (E_a) for electrical conduction, calculated from the equation $\sigma = \sigma_0 \exp(-E_a/KT)$, are summarized in Table 7. The magnitude of χ at room temperature (χ *ca.* 10^{-3} e.u.m.) is as large as that per $TTF^{+\bullet}$ unit. This behaviour is very close to that of analogous radical cation salts $(TTF)X_{0.67}$ with anions (X = halogen) of low nucleophilicity[22] and is similar to that of the radical anion salts $(TCNQ)_yK$ ($1 < y < 3$) with alkaline cations of low electrophilicity belonging to class I of Pope and Swemberg's classification.[23]

Experimental

General.—Microanalyses were by Malissa and Reuter Analytische Laboratorien, Elbach, West Germany and by Servizio Microanalisi del CNR, Area della Ricerca di Roma. Molecular weights were measured for the sodium salts cryoscopically in water using $NaB(C_6H_5)_4$ as standard. I.r. spectra were recorded on a Perkin-Elmer 983 G spectrometer on KBr pellets. The solution electronic spectra were recorded on a Perkin-Elmer 330 spectrometer. A Beckman DK 2A instrument was used to record diffuse reflectance spectra on MgO-diluted samples. Electrical conductivity measurements were performed on polycrystalline samples using the van de Paw method with the apparatus described previously.[24] Magnetic measurements were carried out using the Gouy method at room temperature. The n.m.r. spectra have been obtained with a Bruker WP-200 spectrometer (n.m.r. service of the Area della Ricerca di Roma, CNR) operating at 4.7 T. The deuteriated

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* An important contribution to the ground state of the dimer (A_2^{2-}) is given by the covalent dative structure of the electronic excited state in which one electron has been transferred from one component to the other ($A—A^{2-}$); for compound (**1**) the species A^{2-}, *i.e.* $C_{11}N_7H_2^{2-}$, is not thermodynamically stable (see later).

solvent was used as internal reference and for field-frequency lock. All chemical-shift data are reported relative to tetramethylsilane. The spectra were collected at 300 K, unless otherwise stated. Electrochemical potentials E (V *versus* s.c.e.) were obtained from cyclic voltammetric measurements under the conditions reported in the literature.[25]

Reagents.—All reagents were of Fluka analytical grade. Ti(bpy)$_3$,[26] Ti(Me$_2$bpy)$_3$,[26] Zr(bpy)$_3$,[27] V(bpy)$_3$,[28] Ticp$_2$(bpy),[29] NaCp,[30] and (TTF)$_3$(BF$_4$)$_2$[31] were prepared as outlined in the literature. The preparation of the tetraphenylarsonium salts of the anions $C_{11}N_7H_2^-$, $C_{14}N_7H_2^-$, and $C_{13}N_8H^-$ have been reported previously.[5,6] The reaction between Ti(bpy)$_3$ and TCNE described in ref. 5 was extended by using Ti(Me$_2$bpy)$_3$, Zr(bpy)$_3$, V(bpy)$_3$, and Ticp$_2$(bpy) as promoters: the same final product, $C_{11}N_7H_2^-$, was obtained in each case.

Synthesis of As(C$_6$H$_5$)$_4$C$_{15}$N$_6$H$_3$.—TCNE (0.96 g, 7.5 mmol) was added under stirring at −80 °C to a tetrahydrofuran solution (50 ml) of NaCp (0.33 g, 3.75 mmol) under N$_2$. The solution was allowed to warm to room temperature. The solvent was then evaporated under vacuum and the black-violet residue was washed with toluene. The solid was dissolved with acetone (300 ml) and, after adding As(C$_6$H$_5$)$_4$Cl (3.15 g, 7.5 mmol) in water (50 ml) and concentrating, a black-violet residue was obtained. Chromatography of this residue on silica gel (150 g; 70 cm column; 230—400 mesh) and elution with methylene dichloride–acetone (95:5) yielded As(C$_6$H$_5$)$_4$C$_{15}$N$_6$H$_3$, as air-stable black-violet crystals (0.105 g, 7%). This new compound can be obtained in lower yield (*ca.* 2%) by replacing NaCp with Ticp$_2$(bpy) in the same reaction described above (Found: C, 71.8; H, 3.7; N, 12.8; As, 11.35. C$_{39}$H$_{23}$AsN$_6$ requires C, 72.0; H, 3.6; N, 12.9; As, 11.5%).

Synthesis of the Sodium Salts.—The sodium salts of all four anions have been obtained in quantitative yield by simple metathetical reaction of the tetraphenylarsonium salt with NaB(C$_6$H$_5$)$_4$ in acetone–water.

Synthesis of Radical Salts with TTF$^{\bullet+}$.—The sodium salts (NaA) of the anions (**2**)—(**4**) gave the corresponding TTF$^{\bullet+}$ radical salts in quantitative yield by metathesis with (TTF)$_3$(BF$_4$)$_2$ in CH$_3$CN. The composition (TTF)A$_{0.67}$ of the final products was ascertained by elemental analysis [A = (**2**); Found: C, 52.1; H, 2.0; N, 14.7; S, 30.8. C$_{24}$H$_9$N$_6$S$_6$ requires C, 50.2; H, 1.6; N, 14.6; S, 33.5%. A = (**3**); Found: C, 48.4; H, 1.5; N, 17.95; S, 32.2. C$_{23}$H$_8$N$_7$S$_6$ requires C, 48.1; H, 1.4; N, 17.1; S, 33.5%. A = (**4**); Found: C, 45.1; H, 1.5; N, 18.4; S, 35.0. C$_{22}$H$_7$N$_8$S$_6$ requires C, 44.7; H, 1.25; N, 19.9; S, 34.1%].

Crystal Data for (**2**): $[As(C_6H_5)_4]^+[C_{15}N_6H_3]^-$.—C$_{39}H_{23}AsN_6$, M = 650.58, monoclinic, space group $I2/a$, a = 24.292(11), b = 19.216(9), c = 13.991(7) Å, β = 94.48(4)°, U = 6 511(5) Å^3, Z = 8, D_m = 1.32(2) g cm^{-3} (by flotation), D_c = 1.328 g cm^{-1}, $F(000)$ = 2 656, (Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 11.05 cm^{-1}. Intensity data were measured at room temperature on a Nicolet P2$_1$ four-circle diffractometer in the θ–2θ scan mode. 1 980 Independent reflections were obtained with $I > 3\sigma(I)$. Lorenz-polarization but not absorption correction was applied, given the low value of μ. The structure was solved and refined by standard methods, using anisotropic thermal parameters for the C and N atoms of the anion and for the As atom; the phenyl rings of the cation were refined isotropically as rigid groups and the hydrogen atoms were introduced at calculated positions with a fixed isotropic thermal parameter B = 5.0 Å^2. Final values for R and R_w were 0.0623 and 0.0692, respectively. Neutral scattering factors (f' and f'' values) were used for non-hydrogen atoms.[32]

Crystal Data for (**4**): $[As(C_6H_5)_4]^+[C_{13}N_8H]^-$.—C$_{37}H_{21}AsN_8$, M = 652.55, monoclinic, space group $I2/a$, a = 24.227(11), b = 19.109(7), c = 13.891(4) Å, β = 94.99(3)°, U = 6 406(4) Å^3, Z = 8, D_c = 1.354 g cm^{-3}, $F(000)$ = 2 655.86, (Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 11.25 cm^{-1}. Details of the procedure of collecting intensities and refinement as given above for the previous structure analysis. 2 142 Independent reflections were obtained, with $I > 4\sigma(I)$.

Fourier syntheses revealed disorder in two non-equivalent positions for the tricyanovinyl group linked to C(1): in consequence, we refined the occupancies of the interested atoms, using isotropic thermal parameters, at the final values 56(1) and 44(1)%. Final values for R and R_w were 5.61 and 5.53, respectively. Computations were performed on an IBM 4361/4 computer, using the SHELX-76 system of crystallographic programs.[33,*]

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