Characterization of novel TCNQ and TCNE 1:1 and 1:2 salts of the tetrakis(dimethyamino)ethylene dication, $[\{(CH_3)_2N\}_2C{-}C\{N(CH_3)_2\}_2]^{2+}$

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Addition of TCNQ to a solution of tetrakis(dimethylamino)ethylene in MeCN produces the salt $[TDAE][TCNQ]_2$; the dipositive cation, $[\{(CH_3)_2N\}_2C{-}C\{N(CH_3)_2\}_2]^{2+}$, is *nonplanar*, with a dihedral angle of 63.9°, while the TCNQ anions crystallize as $[TCNQ]_2^{2-}$ dimers with an interplanar separation of 3.16 Å. The complex [TDAE][TCNE] was prepared in a similar manner; the $[TDAE]^{2+}$ cation and $[TCNE]^{2-}$ anion are nonplanar, with dihedral angles of 71.3 and 76.6°, respectively. The four CN groups in the $[TCNE]^{2-}$ anion each accept three C–H···N hydrogen bonds. In each case, one C–N···H angle is in the range 134–156°, while the other two are near 90° (81–100°).

Donor–acceptor (D–A) complexes have been studied for many decades.[1] Extension to studies of electron-transfer salts[2,3,4] led to the discovery (1960) of molecular-based, metal-like conductors,[2–6] and the later discoveries of molecular-based materials exhibiting cooperative phenomena, *e.g.* superconductivity[7] and ferromagnetism.[8,9] With the commercial uses of some of these materials already achieved,[10,11] the anticipation of finding additional examples of materials exhibiting cooperative phenomena, and the promise of improved physical properties including higher critical temperatures, new donors and acceptors continue to be the subject of intense study.

Although many donors, principally those based on the tetrathiafulvalene framework, have been exhaustively studied,[12] electron-rich tetraaminoethylenes have received comparatively little attention.[13–15] The prototypical tetraaminoethylene, tetrakis(dimethylamino)ethylene (TDAE), is a strong electron donor with an ionization potential of 6.13 eV.[13] TDAE undergoes two one-electron oxidations to $[TDAE]^{+}$ and $[TDAE]^{2+}$ at −0.53 and −0.68 V *vs.* SCE in MeCN (Fig. 1).[13,16] A few electron-transfer salts of TDAE have been reported. The reaction of TDAE and TCNE (TCNE = tetracyanoethylene) was reported to form only the violet–black 1:2 $[TDAE]^{2+}[TCNE]_2^{2-}$.[13,17]

More recently, the 1:1 complex with C_{60} has been reported to exhibit unusual ferromagnetic coupling, albeit with a low saturation magnetization.[15] However, the reported structure was obtained by using the results of molecular mechanics to obtain trial coordinates for *neutral* TDAE; these were then used in a series of Rietveld refinements of the powder diffraction data. While the observed ferromagnetism indicated that TDAE had been oxidized, the structural consequences of that event were not discussed. When TDAE is oxidized from the neutral to the dipositive oxidation state, the twist angle about the central C–C bond changes from 28° to 67–76°.[14]

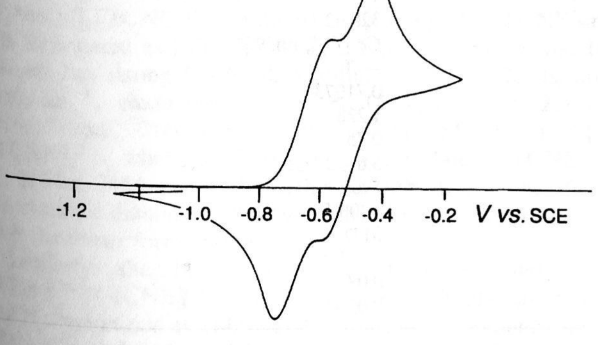

Fig. 1 Cyclic voltammogram of TDAE in MeCN

In order to understand the structure of TDAE as a function of oxidation state and crystal environment, we have reinvestigated the reaction of TDAE with TCNE and studied the reaction with TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane). Both acceptors react with TDAE to form both 1:1 and 1:2 electron transfer salts in high yield. The oxidation states of TDAE in these salts are uncertain, since 1:1 [TDAE][TCNX] (X = E, Q) can be formulated, for example, as $[TDAE]^{2+}[TCNX]^{2-}$ or $[TDAE]^{+}[TCNX]^{-}$, while 1:2 $[TDAE][TCNX]_2$ can be formulated as $[TDAE]^{2+}[TCNX]_2^{2-}$ or $[TDAE]^{+}\{[TCNX]^{-}\}\cdot[TCNX]$. Crystals of the 1:1 salt with TCNE and the 1:2 salt with TCNQ were obtained, and have been studied by single crystal X-ray and infrared spectroscopic analyses.

Experimental

Microanalyses were carried out by Microanalytical Laboratory, Mountain View, CA. The purity and elemental analyses are typical of this class of electron-transfer salts. Detailed analyses of the purity were not undertaken. Conductivities of the TCNQ salts were measured by the four-probe method on compacted pellets; conductivities of the TCNQ salts are *ca.* 10^{-8} S cm^{-1}. Conductivity measurements were not carried out on the TCNE salts.

Synthesis

$[TDAE][TCNQ]_2$ **1** was prepared in an inert atmosphere glove box from TDAE (Aldrich, 68 mg; 0.34 mmol) dissolved in 2 ml of acetonitrile. To this was added a solution of TCNQ (140 mg; 0.69 mmol) in 20 ml acetonitrile; the resulting mixture became an emerald green colour. The solution was allowed to stand overnight. During this time purple crystals precipitated; these were collected by vacuum filtration (150 mg; 73% yield). Elemental analysis: Calc. for $C_{34}H_{32}N_{12}$; C, 67.09; H, 5.30; N, 27.61. Found: C, 66.85, 66.93; H, 5.09, 4.89; N, 28.17, 28.21%.

[TDAE][TCNQ] **2** was prepared by analogy with the preparation of **1** using equimolar amounts of the donor and acceptor. Elemental analysis: Calc. for $C_{22}H_{28}N_8$; C, 65.32; H, 6.98; N, 27.70. Found: C, 65.39; H, 7.07; N, 27.71%.

[TDAE][TCNE]$_2$ **3** was prepared by analogy with the preparation of **1** using a molar ratio of 1:2 for the donor and acceptor, respectively. Elemental analysis: Calc. for $C_{22}H_{24}N_{12}$: C, 57.88; H, 5.30; N, 36.82. Found: C, 58.28; H, 5.53; N, 37.08%.

[TDAE][TCNE] **4** was prepared by analogy with the preparation of **1** using equimolar amounts of the donor and acceptor. Elemental analysis: Calc. for $C_{16}H_{24}N_8$: C, 58.52; H, 7.37; N, 34.12. Found: C, 58.50; H, 7.42; N, 34.61%.

X-Ray diffraction

Structure determination of 1. Routine operations were performed as described previously (Syntex P2$_1$ diffractometer at Brandeis University).[18] The structure was refined by using anisotropic displacement parameters for N and C atoms; H atoms were fixed at calculated positions. Crystallographic data are presented in Table 1 and selected bond distances and angles appear in Table 2.

Structure determination of 4. Routine operations were performed as described previously (Enraf-Nonius CAD4 diffractometer at Du Pont).[8b] The structure was refined by using anisotropic displacement parameters for N and C atoms and isotropic displacement parameters for H atoms. Crystallographic data appear in Table 1 and selected bond distances and angles are in Table 3. Atomic coordinates, thermal parameters and bond lengths and angles for structures **1** and **4** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/8.

Results and Discussion

The molecular structure of the tetrakis(dimethylamino)ethylene moiety is shown in Fig. 2. Bond lengths and angles, as well as torsion angles, are very near to the values found for the [TDAE]$^{2+}$ cation in [TDAE]$X_2\cdot 2H_2O$ (X=Cl, Br).[14a] For **1**, the observed values for ν_{CN} (2186s, 2176s, 2158m and 2117vw cm^{-1}) are comparable to those observed for $[Cr(C_6H_6)_2]_2[TCNQ]_2$ (2182s, 2175s, 2156m cm^{-1})[19a] and $[Fe(C_5Me_5)_2]_2[TCNQ]_2$ (2184s, 2176s, 2157s cm^{-1}).[19b] On this basis we formulate the salt as $[TDAE]^{2+}[TCNQ]_2^{2-}$.

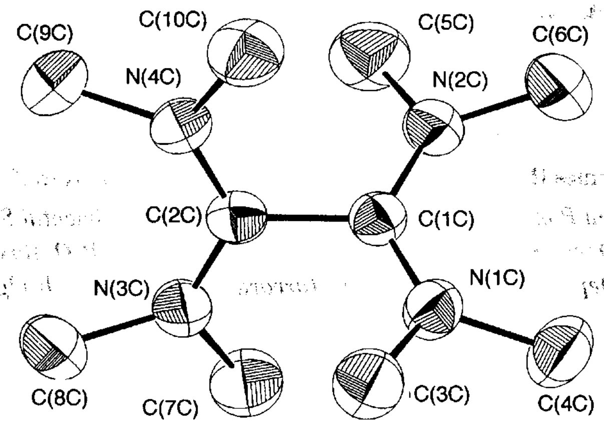

Fig. 2 A view of the cation $[\{(CH_3)_2N\}_2C=C\{N(CH_3)_2\}_2]^{2+}$ in **1** (50% probability ellipsoids shown). Selected bond distances and angles include: C(1C)–C(2C), 1.515(3); C(sp^2)–N, 1.305–1.320(3) Å; dihedral angle between two CN$_2$ planes, 63.9°; average C–N–C–C torsion angle, 22.8°.

The crystal structure (Fig. 3) lends additional support to this formulation, as the structure clearly contains $[TCNQ]_2^{2-}$ dimers. Bond lengths observed for each TCNQ anion in the dimer are in excellent agreement with those observed previously.[19c,20] Further, the dihedral angles between the C_6 and $C(CN)_2$ moieties in the anionic TCNQ species range from 6.6 to 10.6°, consistent with the assignment of each TCNQ as a monoanion.[20] The interplanar distance between pairs of anions is 3.16 Å, with an interplanar angle of 0.9°.

Salt **2** is formulated as $[TDAE]^{2+}[TCNQ]^{2-}$, based upon

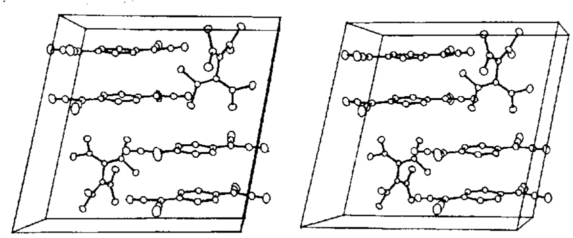

Fig. 3 Stereoscopic view of the crystal structure of **1** (*a* vertical, *c* horizontal)

Table 1 Data for the X-ray diffraction studies of **1** and **2**[a]

	1	2
chemical formula	$[C_{10}H_{24}N_4]^{2+}[C_{12}H_4N_4]_2^{2-}$	$[C_{10}H_{24}N_4]^{2+}[C_6N_4]^{2-}$
a/Å	8.161(2)	10.542(2)
b/Å	14.393(3)	14.877(3)
c/Å	14.514(4)	11.670(4)
α (°)	78.22(3)	90
β (°)	79.51(3)	103.89(1)
γ (°)	82.34(3)	90
V/Å^3	1632.8	1776.7
Z	2	4
formula mass	608.71	328.42
space group	$P\bar{1}$ [C_i^1; no. 2]	Cc [C_s^4; no. 9]
T/°C	21(1)	−70
λ (Mo-Kα)/Å	0.71073	0.71073
ρ_{calc}/g cm^{-3}	1.238	1.228
μ/cm^{-1} (Mo-Kα)	0.74	0.75
2θ range	$2\le 2\theta \le 46°$	$3.6\le 2\theta \le 52°$
no. of reflections measured	4804	1909
no. of refections used	3580 [$I\ge 1.96\sigma(I)$]	1203 [$I\ge 3\sigma(I)$]
number of parameters	416	311
transmission factors	0.879–1.00	—
R	0.049	0.036
R_w	0.065	0.030

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w=\{\Sigma w[|F_o|-|F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$.

Table 2 Bond lengths (Å) and angles (°) for $[C_{10}H_{24}N_4]^{2+}[C_{12}H_4N_4]_2^{2-}$

bond lengths			
C(1A)–C(2A)	1.417(3)	C(1B)–C(7B)	1.421(4)
C(1A)–C(6A)	1.415(3)	C(2B)–C(3B)	1.354(4)
C(1A)–C(7A)	1.408(4)	C(10B)–C(12B)	1.413(4)
C(2A)–C(3A)	1.357(4)	C(10B)–C(11B)	1.415(3)
C(3A)–C(4A)	1.413(3)	C(12B)–N(4B)	1.154(4)
C(4A)–C(5A)	1.422(3)	C(11B)–N(3B)	1.147(3)
C(4A)–C(10A)	1.414(4)	C(7B)–C(9B)	1.411(3)
C(5A)–C(6A)	1.357(4)	C(7B)–C(8B)	1.416(4)
C(7A)–C(8A)	1.416(4)	C(9B)–N(2B)	1.146(3)
C(7A)–C(9A)	1.420(3)	C(8B)–N(1B)	1.142(4)
C(8A)–N(1A)	1.148(4)	C(1C)–N(1C)	1.309(3)
C(9A)–N(2A)	1.144(3)	C(1C)–N(2C)	1.318(3)
C(10A)–C(11A)	1.412(3)	C(1C)–C(2C)	1.515(3)
C(10A)–C(12A)	1.405(4)	N(1C)–C(3C)	1.472(3)
C(11A)–N(3A)	1.152(3)	N(1C)–C(4C)	1.477(3)
C(12A)–N(4A)	1.143(4)	N(2C)–C(5C)	1.467(3)
C(4B)–C(5B)	1.416(3)	N(2C)–C(6C)	1.466(3)
C(4B)–C(3B)	1.419(3)	C(2C)–N(3C)	1.305(3)
C(4B)–C(10B)	1.413(4)	C(2C)–N(4C)	1.320(3)
C(5B)–C(6B)	1.360(4)	N(3C)–C(7C)	1.474(3)
C(6B)–C(1B)	1.409(3)	N(3C)–C(8C)	1.473(3)
C(1B)–C(2B)	1.416(3)	N(4C)–C(9C)	1.467(3)
N(4C)–C(10C)	1.469(3)		
bond angles			
C(2A)–C(1A)–C(6A)	116.7(2)	C(3B)–C(4B)–C(10B)	121.9(2)
C(2A)–C(1A)–C(7A)	121.4(2)	C(4B)–C(5B)–C(6B)	121.6(2)
C(6A)–C(1A)–C(7A)	121.9(2)	C(5B)–C(6B)–C(1B)	121.5(2)
C(1A)–C(2A)–C(3A)	121.8(2)	C(6B)–C(1B)–C(2B)	117.2(2)
C(2A)–C(3A)–C(4A)	121.5(2)	C(6B)–C(1B)–C(7B)	121.6(2)
C(3A)–C(4A)–C(5A)	116.8(2)	C(2B)–C(1B)–C(7B)	121.2(2)
C(3A)–C(4A)–C(10A)	120.8(2)	C(1B)–C(2B)–C(3B)	121.4(2)
C(5A)–C(4A)–C(10A)	122.4(2)	C(4B)–C(3B)–C(2B)	121.7(2)
C(4A)–C(5A)–C(6A)	121.5(2)	C(4B)–C(10B)–C(12B)	122.2(2)
C(1A)–C(6A)–C(5A)	121.7(2)	C(4B)–C(10B)–C(11B)	121.6(2)
C(1A)–C(7A)–C(8A)	121.7(2)	C(12B)–C(10B)–C(11B)	115.8(2)
C(1A)–C(7A)–C(9A)	122.4(2)	C(10B)–C(12B)–N(4B)	179.7(6)
C(8A)–C(7A)–C(9A)	115.7(2)	C(10B)–C(11B)–N(3B)	179.1(3)
C(7A)–C(8A)–N(1A)	179.4(3)	C(1B)–C(7B)–C(9B)	120.6(2)
C(7A)–C(9A)–N(2A)	178.9(3)	C(1B)–C(7B)–C(8B)	122.8(2)
C(4A)–C(10A)–C(11A)	123.1(2)	C(9B)–C(7B)–C(8B)	116.4(2)
C(4A)–C(10A)–C(12A)	120.6(2)	C(7B)–C(9B)–N(2B)	178.3(3)
C(11A)–C(10A)–C(12A)	116.3(2)	C(7B)–C(8B)–N(1B)	177.7(3)
C(10A)–C(11A)–N(3A)	178.4(3)	N(1C)–C(1C)–N(2C)	126.0(2)
C(10A)–C(12A)–N(4A)	178.1(3)	N(1C)–C(1C)–C(2C)	117.0(2)
C(5B)–C(4B)–C(3B)	116.7(2)	N(2C)–C(1C)–C(2C)	117.0(2)
C(5B)–C(4B)–C(10B)	121.5(2)	C(1C)–N(1C)–C(3C)	121.7(2)
C(1C)–N(1C)–C(4C)	123.1(2)	N(3C)–C(2C)–N(4C)	126.2(2)
C(3C)–N(1C)–C(4C)	115.1(2)	C(2C)–N(3C)–C(7C)	121.9(2)
C(1C)–N(2C)–C(5C)	121.3(2)	C(2C)–N(3C)–C(8C)	123.2(2)
C(1C)–N(2C)–C(6C)	123.2(2)	C(7C)–N(3C)–C(8C)	114.9(2)
C(5C)–N(2C)–C(6C)	115.3(2)	C(2C)–N(4C)–C(9C)	123.2(2)
C(1C)–C(2C)–N(3C)	116.9(2)	C(2C)–N(4C)–C(10C)	121.7(2)
C(1C)–C(2C)–N(4C)	117.0(2)	C(9C)–N(4C)–C(10C)	115.0(2)

IR evidence. The observed ν_{CN} for **2** (2156s, 2117m, 2105s cm^{-1}) is suggestive of $[TCNQ]^{2-}$ (*cf.* 2164s, 2096s cm^{-1} for Na_2TCNQ[21] and 2150s, 2105s cm^{-1} for $[Co(C_5Me_5)_2]_2[TCNQ]$[19c]). Similarly, the orange 1:2 TCNE salt **3** is formulated as $[TDAE]^{2+}[TCNE]_2^{2-}$. The observed IR (Nujol) has strong C≡N absorptions at 2193m, 2174s, and 2163s cm^{-1}, characteristic[22] of π-$[TCNE]_2^{2-}$ (*cf.* 2190m, 2169s, and 2160s cm^{-1} for $\{[Cr^I(C_6Me_xH_{6-x})_2]^+\}_2$-$[TCNE]_2^{2-}$, where $x=0$, 3), but not isolated $[TCNE^{\cdot}]^-$ (*cf.* 2184m, 2154s cm^{-1}).[8b] Further confirmation comes from the observed diamagnetism of the salt, which is only consistent with the dimer formulation.

Similarly, the brown 1:1 salt **4** is formulated as $[TDAE]^{2+}[TCNE]^{2-}$. The observed IR (Nujol) has strong C≡N absorptions at 2143m and 2078s cm^{-1}, characteristic of $[TCNE]^{2-}$ (cf. 2140 and 2069s cm^{-1} for isolated $[TCNE]^{2-}$ in $\{[Co(C_5Me_5)_2]^+\}_2[TCNE]^{2-}$).[23] Again, this salt is diamagnetic, which excludes a possible assignment as $[TCNE^{\cdot}]^-$. Fig. 4 shows the dianion/dication pair. Bond lengths and angles for $[TDAE]^{2+}$ are near the values reported for **1** and other structures, while those for $[TCNE]^{2-}$ parallel those found previously[23,24] for $[TCNE]^{2-}$. Variations in the single bond torsion angles are less than 13°, and probably arise from differences in packing or hydrogen bonding. Close inspection of the crystal structure of **4** reveals unusual hydrogen bonding patterns. The hydrogen bonding patterns, as delineated in Table 4 and Fig. 5, show that the anion receives an unusual number of donor hydrogen bonds. For each N atom in the anion, there is one donor H atom which approaches the anion at a C–N···H angle within expected ranges (134–156°, Table 4), *plus two others which approach the CN$^-$ group at nearly orthogonal positions.* The hydrogen bonding pattern is related

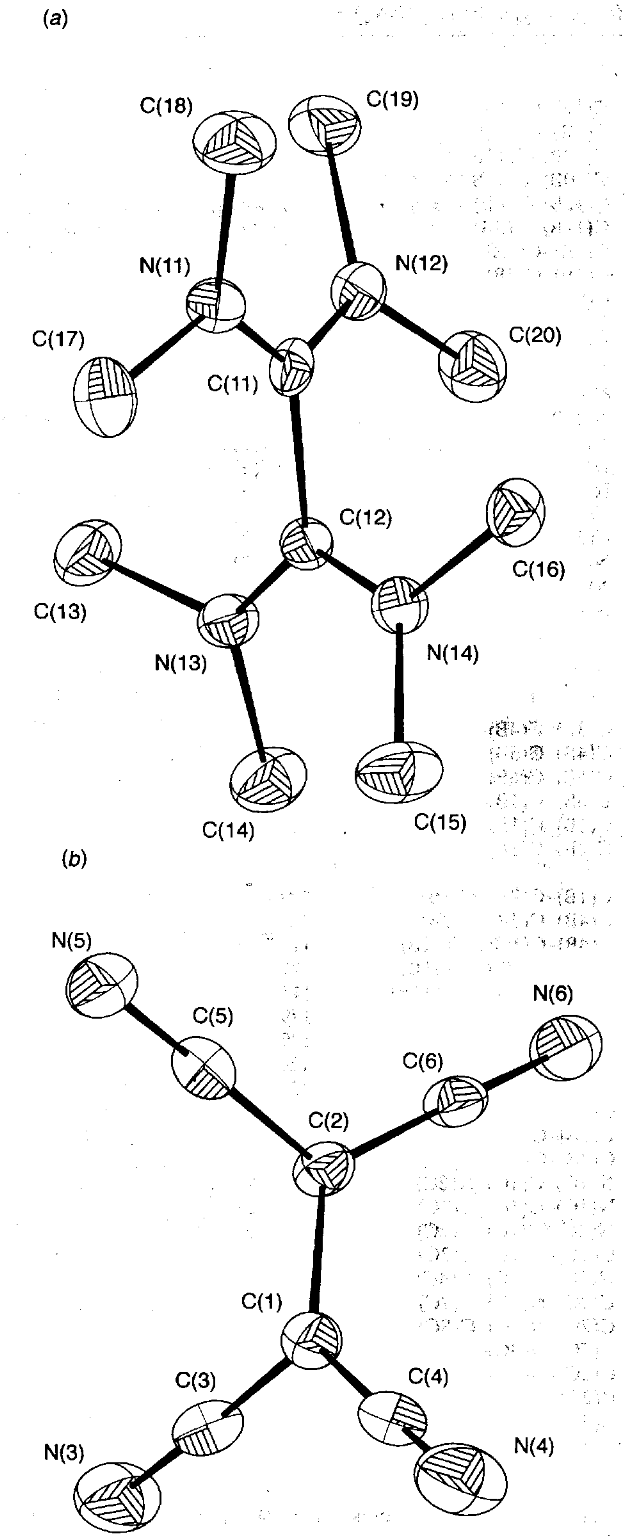

Fig. 4 A view of the anion and cation in **4** (50% probability ellipsoids shown). *Selected bond distances and angles*: (*a*) cation; C(11)–C(12), 1.516(4), C(sp^2)–N, 1.311–1.323(5) Å; dihedral angle between two CN_2 planes, 71.3°; (*b*) anion; C(1)–C(2), 1.488(4) Å; dihedral angle between two $C(CN)_2$ planes, 76.6°.

to the C–H··· π interactions observed in two ethynylgold complexes.[25] However, the shortest approach of the hydrogen bond is *not* to the centre of the C≡N π bond, but rather to the more electronegative N atom. Inspection of the other structures containing the $[TCNE]^{2-}$ ion does not reveal similar patterns. It would appear that the relatively compact $[TDAE]^{2+}$ has the correct combination of size and H-donor ability to produce this highly unusual structure.

Table 3 Bond lengths (Å) and angles (°) for $[C_{10}H_{24}N_4]^{2+}[C_6N_4]^{2-}$

bond lengths			
N(3)–C(3)	1.163(5)	N(13)–C(13)	1.475(5)
N(4)–C(4)	1.161(5)	N(13)–C(14)	1.473(5)
N(5)–C(5)	1.162(5)	N(14)–C(12)	1.316(5)
N(6)–C(6)	1.150(5)	N(14)–C(15)	1.471(5)
N(11)–C(11)	1.323(4)	N(14)–C(16)	1.468(5)
N(11)–C(17)	1.459(5)	C(1)–C(2)	1.488(4)
N(11)–C(18)	1.476(5)	C(1)–C(3)	1.396(6)
N(12)–C(11)	1.311(4)	C(1)–C(4)	1.406(6)
N(12)–C(19)	1.483(5)	C(2)–C(5)	1.402(5)
N(12)–C(20)	1.470(5)	C(2)–C(6)	1.391(5)
N(13)–C(12)	1.315(5)	C(11)–C(12)	1.516(4)
bond angles			
C(11)–N(11)–C(17)	121.4(3)	N(3)–C(3)–C(1)	177.9(5)
C(11)–N(11)–C(18)	124.6(3)	N(4)–C(4)–C(1)	178.3(4)
C(17)–N(11)–C(18)	114.1(4)	N(5)–C(5)–C(2)	178.8(5)
C(11)–N(12)–C(19)	124.1(3)	N(6)–C(6)–C(2)	179.0(5)
C(11)–N(12)–C(20)	121.7(3)	N(11)–C(11)–C(12)	116.3(3)
C(19)–N(12)–C(20)	114.2(3)	N(12)–C(11)–C(12)	117.2(3)
C(12)–N(13)–C(13)	121.5(3)	N(13)–C(12)–C(11)	117.4(4)
C(12)–N(13)–C(14)	124.8(3)	N(14)–C(12)–C(11)	116.3(3)
C(13)–N(13)–C(14)	113.8(3)	C(2)–C(1)–C(3)	121.2(4)
C(12)–N(14)–C(15)	124.0(3)	C(2)–C(1)–C(4)	121.2(4)
C(12)–N(14)–C(16)	122.4(3)	C(3)–C(1)–C(4)	117.4(3)
C(15)–N(14)–C(16)	113.6(3)	C(1)–C(2)–C(5)	121.1(4)
N(11)–C(11)–N(12)	126.5(3)	C(1)–C(2)–C(6)	121.7(3)
N(13)–C(12)–N(14)	126.3(3)	C(5)–C(2)–C(6)	117.3(3)

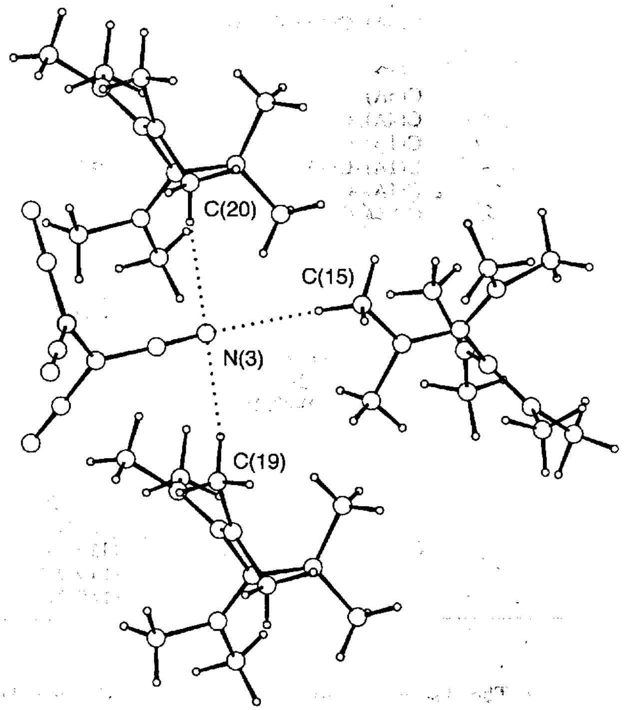

Fig. 5 A view of a portion of the crystal structure of **4**, showing the orthogonal H-bonding pattern. Three C–H···N(3) interactions are shown; the arrangement of hydrogen bonds about the other three cyano N atoms is similar (Table 4).

The facile preparation of these TDAE salts suggests that many other interesting salts and/or D–A complexes of TDAE await discovery; in particular efforts are underway in our laboratories to isolate and characterize the elusive $[TDAE]^{\cdot +}$.

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Table 4[a] Hydrogen bonds in $[C_{10}H_{24}N_4]^{2+}[C_6N_4]^{2-}$

atoms N···H–C	distance/Å N···C	distance/Å N···H	distance/Å C–H	angle/degrees N···H–C	angle/degrees C–N···H
N(3)···H(152)–C(15)[b]	3.404	2.45	0.99	164.4	155.5
N(3)···H(192)–C(19)[c]	3.352	2.71	1.05	119.3	95.1
N(3)···H(202)–C(20)[d]	3.417	2.45	1.04	154.5	92.7
N(4)···H(142)–C(14)[e]	3.461	2.80	0.98	125.5	150.5
N(4)···H(171)–C(17)[f]	3.328	2.75	1.01	116.8	91.5
N(4)···H(181)–C(18)[c]	3.473	2.75	1.00	129.5	100.2
N(5)···H(133)–C(13)[g]	3.426	2.45	1.01	161.9	133.5
N(5)···H(161)–C(16)[d]	3.407	2.51	1.03	145.2	93.2
N(5)···H(203)–C(20)[d]	3.443	2.93	0.91	117.3	80.8
N(6)···H(131)–C(13)[f]	3.280	2.44	0.92	153.1	99.6
N(6)···H(153)–C(15)[c]	3.469	2.61	1.04	139.9	92.8
N(6)···H(163)–C(16)[g]	3.410	2.50	0.93	167.0	136.5

[a] N–C distances have estimated standard deviations in the range 0.005–0.007 Å; N–H and C–H distances have estimated standard deviations in the range 0.04–0.05 Å, and are uncorrected for centroid errors: M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213. [b–g] Symmetry operations: (*b*) $x, -y, z-\frac{1}{2}$; (*c*) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (*d*) x, y, z; (*e*) $x+1, -y, z+\frac{1}{2}$; (*f*) $x+1, y, z$; (*g*) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

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