

Isolation of two salts from the reduction of TCNE with $[(n\text{-C}_3\text{H}_7)_4\text{N}]\text{I}$. A further example of long 2.87 Å $\pi\text{-C-C}$ bonding in $\pi\text{-}[\text{TCNE}]_2^{2-}$

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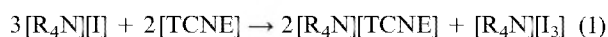
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Reduction of tetracyanoethylene, TCNE, with tetrakis(*n*-propyl)ammonium iodide, $[\text{Pr}_4\text{N}]\text{I}$, results in a new example of long $\pi^*\text{-CC}$ bonded $\pi\text{-}[\text{TCNE}]_2^{2-}$ dimers with a 2.870(4) Å intradimer CC bond, which is structurally and spectroscopically characterized. This reaction also results in isolation of $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$ possessing isolated $[\text{TCNE}]^{\cdot-}$ radical anions.

Introduction

In pursuit of new examples of the π -dimers of $[\text{TCNE}]^{\cdot-}$ (TCNE = tetracyanoethylene), $\pi\text{-}[\text{TCNE}]_2^{2-}$ to understand the nature of the long $\pi^*\text{-CC}$ bonding which exists in the crystalline materials, synthesis of the tetrakis(*n*-propyl)ammonium, $[\text{Pr}_4\text{N}]^+$, salt has been carried out. $[\text{Et}_4\text{N}]_2[\text{TCNE}]_2^{2-}$ and $[(n\text{-Bu})_4\text{N}][\text{TCNE}]_2^{2-}$ have been isolated, with the former having the $\pi\text{-}[\text{TCNE}]_2^{2-}$ dimer with a 2.827 Å long intradimer C–C bond, and the latter existing as the monomer $[\text{TCNE}]^{\cdot-}$. The general reaction for the synthesis of $[\text{Pr}_4\text{N}][\text{TCNE}]$ was used with $[\text{Pr}_4\text{N}]\text{I}$ [eqn. (1)].



Reaction (1) was carried out with $\text{R} = n\text{-Pr}$ in hot MeCN, and upon slow cooling to 0 °C and then to –30 °C, crystals of $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$ formed. Later, upon cooling the filtrate, $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$ was isolated. The structures of both were determined, and as the former contains $\pi\text{-}[\text{TCNE}]_2^{2-}$ dimers and the latter $[\text{TCNE}]^{\cdot-}$ monomers it presents the almost ideal system to compare the different spectroscopic properties of the two different structures of reduced TCNE.

Experimental

Synthesis

A solution of $[\text{Pr}_4\text{N}]\text{I}$ (310 mg, 1.0 mmol) in 10 mL hot MeCN was slowly added to a rapidly stirred solution of TCNE (85 mg, 0.67 mmol) in 5 mL of hot MeCN. The solution was allowed to stir for two hours; it was then placed in a 0 °C freezer for three hours, and then in a –30 °C freezer. The resulting crystals were filtered out and recrystallized from MeCN. IR (KBr/cm⁻¹): $\nu_{\text{C=N}}$ 2191 (m), 2175 (s), 2161 (s); $\nu_{\text{C=C}}$ 1369. UV/Vis (KBr/cm⁻¹): 26 400, 18 200.

The filtrate from the above solution was allowed to sit at room temperature overnight after which time approximately half of the solvent had evaporated. The solution was then cooled to –30 °C at which time a second batch of crystals resulted, and was determined as being $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$. IR (KBr/cm⁻¹): $\nu_{\text{C=N}}$ 2186 (s), 2148 (s); $\nu_{\text{C-CN}}$ 521 (s). UV/Vis (KBr/cm⁻¹): 34 000, 27 500, 22 000.

Crystal structure determination

A crystalline sample of $[\text{Pr}_4\text{N}][\text{TCNE}]$ was prepared by slow cooling of a hot MeCN solution under nitrogen. A single crystal of each compound was covered with a drop of vacuum grease, and mounted on a Nonius KapaCCD diffractometer and cooled to 150 K. Both crystals poorly diffract at high angle. Numerical absorption corrections were applied for the $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$. The crystal structures were determined with SHELXS-97 and refined with the SHELXL-97 computer program.⁴ Crystallographic information is summarized in Table 1

Spectroscopic studies

Infrared spectra were taken using a Bio-Rad FTS-40 FTIR spectrophotometer with ± 1 cm⁻¹ resolution, and scanned in the range of 400–4000 cm⁻¹. UV/Vis spectroscopy was carried out on a Hewlett Packard 8452A Diode Array Spectrophotometer, scanning from 190 to 820 nm. Samples were prepared as KBr pressed pellets (ca. 5% w/w) and in MeCN solution for both compounds.

Results and discussion

The dimer in $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$ has an intradimer central C–C distance of 2.870(4) Å, Fig. 1(top), with a center of inversion in the center of the $[\text{TCNE}]_2^{2-}$ unit. The dimers stack slightly off from the crystallographic *x*-axis and each dimer is offset by about 3/4 of a TCNE unit from the previous dimer, Fig. 1(bottom). The closest interdimer separation is 7.4 Å, which is much greater than observed for $[\text{Et}_4\text{N}]_2[\text{TCNE}]_2$ due to the longer propyl groups penetrating into the dimer stacks. The deviation angle of nitriles from the nominal TCNE plane is 5.21° based on half of the *trans*-NC–C–C–CN dihedral angles.

In contrast, $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$ (Fig. 2) lacks dimers and has isolated $[\text{TCNE}]^{\cdot-}$. The $[\text{TCNE}]^{\cdot-}$ is almost planar, with a slight twist about the central C–C bond of about 3°. The closest contact between two $[\text{TCNE}]^{\cdot-}$ radical anions is 7.3 Å. The geometrical parameters of the triiodide moiety – the I–I bond distance of 2.9201(7) Å, and I–I–I bond angle of 178.30(3)° – agree very well with the average geometry obtained from 44 organic salts containing triiodide moieties listed in the Cambridge crystallographic structural data base.⁵ The average I–I

Table 1 Crystallographic data for $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$ and $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]^d$

Parameter	$[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$	$[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$
Empirical formula	$\text{C}_{36}\text{H}_{56}\text{N}_{10}$	$\text{C}_{30}\text{H}_{56}\text{N}_6\text{I}_3$
<i>M</i>	628.91	881.53
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>Pbcn</i>
<i>a</i> /Å	18.199(4)	13.566(3)
<i>b</i> /Å	11.749(3)	20.082(4)
<i>c</i> /Å	19.534(5)	13.992(3)
β /°	114.450(11)	90
<i>V</i> /Å ³	3802.2(16)	3811.9(14)
<i>Z</i>	8	8
<i>T</i> /K	150(2)	150(2)
<i>D_c</i> /g cm ⁻³	1.099	1.536
μ /cm ⁻¹	0.068	2.486
λ (MoK α)/Å	0.71073	0.71073
Min., max. transmission coefficient	0.9682, 0.9826	0.65851, 0.79940
Reflections collected	20 093	30 154
Unique reflections	3348 (<i>R</i> _{int} = 0.0766)	3357 (<i>R</i> _{int} = 0.0730)
Reflections observed	1403	1651
<i>R</i> index ^b [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0578	<i>R</i> ₁ = 0.0389
<i>R</i> indices ^b (all data)	<i>R</i> ₁ = 0.1560	<i>R</i> ₁ = 0.1160
	<i>wR</i> ₂ = 0.1306	<i>wR</i> ₂ = 0.0595
Weighting coefficients ^c	<i>a</i> = 0.06041	<i>a</i> = 0.0078
	<i>b</i> = 0.0	<i>b</i> = 0.0
Goodness-of-fit ^d on <i>F</i> ²	0.896	0.826

^aClick here for full crystallographic data (CCDC 178430 and 178431).

$$^b R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad ^c wR_2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2}}; \quad ^d w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP],$$

where $P = \frac{(F_o^2 + 2F_c^2)}{3}$. ^dGoF = $S = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]^2}{(M - N)}}$, *M* = number of reflections, *N* = number of parameters refined.

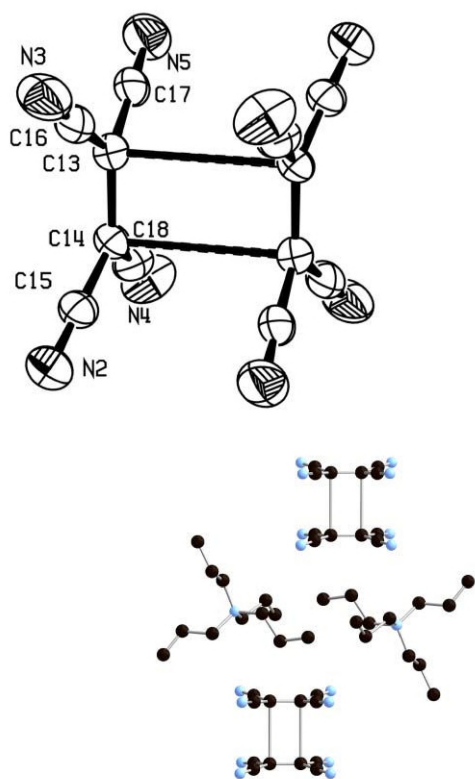


Fig. 1 ORTEP (50%) diagram of $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$. Bond lengths (Å) are 1.408(4) for C13–C14, 2.870(4) for C13–C14', 1.420(4) for C13–C16, 1.422(5) for C13–C17, 1.414(4) for C14–C15, 1.428(4) for C14–C18, 1.153(4) for C15–N2, 1.146(4) for C16–N3, 1.145(4) for C18–N4, and 1.144(4) for C17–N5. Click image or here to access a 3D representation.

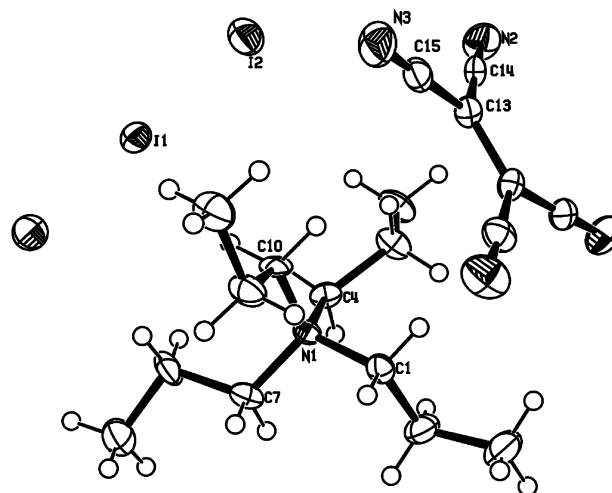


Fig. 2 ORTEP (50%) diagram of $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$. Bond lengths (Å) are 1.405(11) for C13–C13', 1.421(8) for C13–C14, 1.429(7) for C13–C15, 1.141(6) for C14–N2, 1.155(6) for C15–N3, and 2.9201(7) for I1–I2.

distance is 2.924(56) Å, and the average I–I–I bond angle is 178.3(2.1)°.

The IR spectrum for $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$ shows the typical three band pattern in the nitrile region at 2191, 2175, 2161 cm^{-1} , as previously reported for the family of π - $[\text{TCNE}]_2^{2-}$ dimers.¹ The nitrile region for $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$ is shifted to slightly lower energy and occurs as two absorptions, at 2186 and 2148 cm^{-1} . Additionally, the characteristic absorption at 1369 cm^{-1} due to the antisymmetric combination of the intradimer C–C bond of each $[\text{TCNE}]^-$ fragment is present in $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$, Fig. 3, but is not present in the spectrum of $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$ due to the symmetric nature of the central C–C bond. These differences are clearly visible in the comparison of the two $[\text{Pr}_4\text{N}]^+$ salts, Fig. 3(a,b). It is important to emphasize that the C–C stretching of the π - $[\text{TCNE}]_2^{2-}$ dimer at 1369 cm^{-1} is clearly absent from the monomeric species, and is an important fingerprint for the identification of the π - $[\text{TCNE}]_2^{2-}$ dimers.

UV/Vis spectra of $[\text{Et}_4\text{N}]_2[\text{TCNE}]_2$,² and $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$ are shown in Fig. 4(a) and (b), respectively. The peak maxima are observed at ca. 27 000 cm^{-1} for both dimers, whereas $[\text{Et}_4\text{N}]_2[\text{TCNE}]_2$ displays a second maximum at 17 000 cm^{-1} , and $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$ at 18 200 cm^{-1} . This absorption at 18 200 cm^{-1} is due to the dimer bonding–antibonding orbital transition. This is absent from the monomeric species

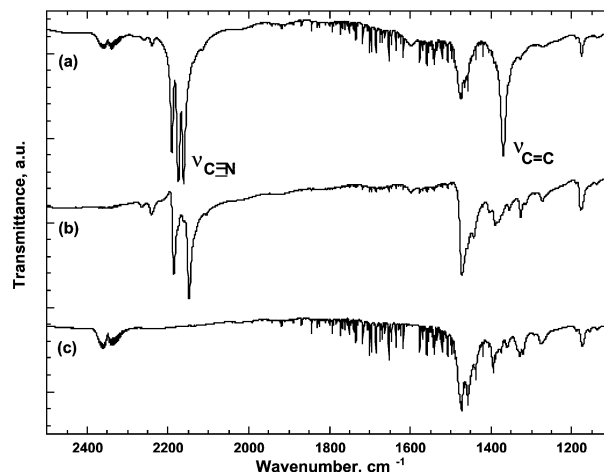


Fig. 3 IR spectra for (a) $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$, (b) $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$, and (c) $[\text{Pr}_4\text{N}]\text{I}$ in KBr pellets.

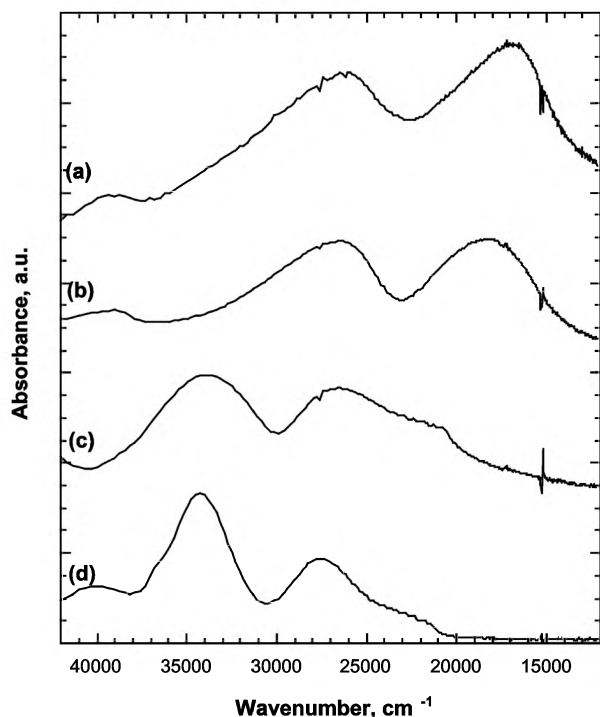


Fig. 4 UV spectra for $[\text{Et}_4\text{N}]_2[\text{TCNE}]_2^2$ (a), $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$ (b), and $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$ as a KBr pellet (c), and in MeCN (d).

$[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$, which does show the absorption for the monomer $[\text{TCNE}]^-$ π - π^* transition at *ca.* $22\,000\text{ cm}^{-1}$ in both the solid state, Fig. 4(c), and as a MeCN solution, Fig. 4(d),

similar to that observed in the $[\text{Bu}_4\text{N}][\text{TCNE}]$ salt.³ This peak is slightly obscured by the strong absorptions of the $[\text{I}_3]^-$ anion at $34\,000$ and $27\,500\text{ cm}^{-1}$.⁶

In summary, another example of long C–C bonding has been discovered in the $[\text{Pr}_4\text{N}]_2[\text{TCNE}]_2$ dimer, with a distance of $2.870(4)\text{ \AA}$. The spectroscopic properties are all consistent with the other materials in this class of dimers. These characteristic properties are distinguishable from those of the monomeric $[\text{TCNE}]^-$ species, as seen in comparison to the isolated and structurally characterized $[\text{Pr}_4\text{N}]_2[\text{TCNE}][\text{I}_3]$.

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