Paper

$[Et_4N]_2[TCNE]_2$ (TCNE = tetracyanoethylene) – an example of an exceptionally long 2.827 Å CC bond

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The reaction of $[Et_4N]I$ and tetracyanoethylene (TCNE) forms $[Et_4N]_2[TCNE]_2$, which possesses $[TCNE]_2^{2-}$ with a 2.827(3) Å intradimer CC bond distance and exhibits ν_{C-N} at 2191, 2170 and 2163 cm^{-1}, ν_{C-C} at 1365 cm^{-1}, and UV-Vis bands at 26 150 and 16 850 cm^{-1}.

Introduction

Interest in organic compounds exhibiting unusually long CC bonds has been the subject of several recent studies.[1–3] The longest sp^3–sp^3 C–C single bond reported to date is 1.73 Å,[1,2] whereas several $[TCNE]_2^{2-}$ (TCNE = tetracyanoethylene) dimers have been recently reported to form cation-assisted, long, two-electron π*–π* CC bonds involving four carbon atoms. These CC bonds range from 2.833 to 3.09 Å. The cations range from electrostatically bonded Tl^+ [4] and K^+ [5] to large, bulky, non-coordinating cations such as $[Cr(C_6H_6)_2]^+$,[6] $[Fe(C_5H_4)_2C_3H_6]^+$,[7] and $[TDAE]^{2+}$ [TDAE = $(Me_2N)_2C{=}C(NMe_2)_2$].[4,8] Herein we report the structure, IR and UV-Vis spectroscopic properties of $[Et_4N]_2[TCNE]_2$, a new example of the $[TCNE]_2^{2-}$ dimer, which exhibits the shortest π*–π* CC bond for this family of compounds.

Experimental

Synthesis

A solution of $[Et_4N]I$ [385 mg (1.5 mmol) in 10 mL hot MeCN] was slowly added to a rapidly stirring solution of TCNE [128 mg (1.0 mmol) in 5 mL of hot MeCN]. The solution was allowed to stir for one hour, and then placed in a freezer at −30 °C. The resulting crystals were filtered out and recrystallized twice more from MeCN. IR (KBr/cm^{-1}): ν_{C-N} 2191 (m), 2170 (s), 2163 (s); ν_{C-C} 1365 (s). UV-Vis (KBr/cm^{-1}): 26 150, 16 850.

Crystal structure determination

A crystalline sample of $[Et_4N][TCNE]$ was prepared by slow evaporation of a MeCN solution under nitrogen. A suitable crystal was selected and mounted on a thin glass fiber using silicone grease. Preliminary unit-cell determinations were obtained by harvesting reflections from three orthogonal sets of 20 frames, using −0.3° ω scans. These results were confirmed by refinement of unit-cell parameters during integration. Crystallographic information is summarized in Table 1. The structure was solved using direct methods. Non-hydrogen atoms were located by difference Fourier synthesis and were refined anisotropically. Hydrogen atoms were added at calculated positions and treated as isotropic contributions with thermal parameters defined as 1.2 or 1.5 times that of the parent atom. The ethyl groups of the $[Et_4N]^+$ are unequally disordered over two orientations (*vide infra*). All software and sources of scattering factors are contained in the SHELXTL-97 program library (version 5.10, G. Sheldrick, Bruker-AXS, Madison, WI, 1997).

Spectroscopic studies

Infrared spectra were taken using a Bio-Rad FTS-40 FTIR spectrophotometer with ±1 cm^{-1} resolution, and scanned in the range 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) for both experiments.

Table 1 Crystallographic data for $[Et_4N]_2[TCNE]_2$[a]

Parameter	
Empirical formula	$C_{14}H_{20}N_5$
M	258.35
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	7.17860(10)
b/Å	17.8246(3)
c/Å	12.0348(2)
β/°	105.6190(10)
V/Å^3	1483.06(4)
Z	4
T/K	135(2)
D_c/g cm^{-3}	1.157
μ/cm^{-1}	0.73
λ(MoKα)/Å	0.71073
Max. transmission coefficient	0.9956
Min. tramsmission coefficient	0.9437
Reflections collected	12 213
Unique reflections	3935 (R_{int} = 0.0361)
Reflections observed	3028
R index[b] [$I > 2\sigma(I)$]	$R_1 = 0.0828$
R indices[b] (all data)	$R_1 = 0.1073$
	$wR_2 = 0.1868$
Weighting coefficients[c]	$a = 0.0391$
	$b = 1.5207$
Goodness-of-fit[d] on F^2	1.168

[a]Click here for full crystallographic data (CCDC 170964). [b]$R_1 = \frac{\sum ||F_o|-|F_c||}{\sum |F_o|}$; $wR_2 = \sqrt{\frac{\sum [w(F_o^2-F_c^2)^2]}{\sum [w(F_o^2)^2]}}$. [c]$w^{-1} = [\sigma^2(F_o^2)+(aP)^2+bP]$, where $P = \frac{(F_o^2+2F_c^2)}{3}$. [d]$\mathrm{GoF} = S = \sqrt{\frac{\sum [w(F_o^2-F_c^2)^2]}{(M-N)}}$, where M = number of reflections, N = number of parameters refined.

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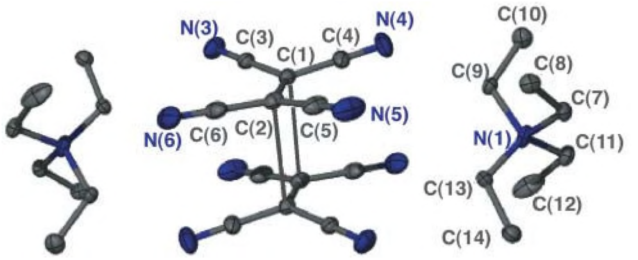

Fig. 1 Atom labeling and thermal ellipsoid (40%) plot of [Et$_4$N]$_2$[TCNE]$_2$. H atoms and disordered alkyl chains are omitted for clarity. Key bond distances (Å) and angles (°) are: C(1)–C(2) 1.418(3), C(1)–C(2)′ 2.827(3), C(1)–C(3) 1.424(3), C(1)–C(4) 1.418(3), C(2)–C(5) 1.425(3), C(2)–C(6) 1.432(3), C(3)–N(3) 1.149(3), C(4)–N(4) 1.145(3), C(5)–N(5) 1.146(3), C(6)–N(6) 1.150(3); C(1)–C(2)–C(1)′ 90.2(2), C(2)–C(1)–C(2)′ 89.8(2), C(3)–C(1)–C(4) 118.5(2), C(5)–C(2)–C(6) 117.3(2), C(1)–C(2)–C(5) 120.7(2), C(1)–C(2)–C(6) 120.7(2), C(2)–C(1)–C(3) 120.3(2), C(2)–C(1)–C(4) 119.9(2); C(4)–C(1)–C(2)–C(6) 169.0(2), C(3)–C(1)–C(2)–C(5) 164.6(2).

Results and discussion

The reaction of [Et$_4$N]I and TCNE leads to the formation of [Et$_4$N]$_2$[TCNE]$_2$, eqn. (1),

$$3[\mathrm{Et_4N}]^+ + 3\mathrm{I}^- + 2\mathrm{TCNE} \rightarrow [\mathrm{Et_4N}]\mathrm{I_3} + [\mathrm{Et_4N}]_2[\mathrm{TCNE}]_2 \quad (1)$$

whose structure consists of the π-[TCNE]$_2^{2-}$ dimer, Fig. 1. The two halves of the [TCNE]$_2^{2-}$ dimer are related by inversion. Close approach between the two [TCNE]$^-$ anions results in an eclipsed dimer with a separation of 2.827(3) Å between olefin carbons. The central CC bond on each [TCNE]$^-$ moiety is 1.418(3) Å, and the cyano groups bend away from the center of the dimer to accommodate this interaction. The CN groups move out of the [TCNE]$^-$ plane by 6.6 ± 1.1°.[9] Thus, C(3), C(4), C(5), C(6) deviate from the nominal plane that contains C(1) and C(2) by 0.266 Å. Each alkyl group of the [Et$_4$N]$^+$ cation displays 65/35 disorder over two positions. The occupancy of the two alkyl chain orientations were refined using free variables. The solid state structure consists of dimerized zigzag chains of [TCNE]$_2^{2-}$ with intra- and inter-dimer separations of 2.827(3) and 3.26(3) Å, respectively, Fig. 2.

[TCNE]$_2^{2-}$ is a π dimer with a two-electron four-centered bond between the [TCNE]$^-$ monomer moieties as reported earlier.[3] The intradimer CC bond distance is 2.827(3) Å, comparable to those reported that range from 2.833 to 3.09 Å.[3] Another manifestation of the intradimer CC bonding is the change in hybridization of the central carbons, which leads to the *trans*-NC–C–C–CN angle increasing from 0° for planar [TCNE]$^-$ to 6.6° for [Et$_4$N]$_2$[TCNE]$_2$. This value is in accord with those reported that range from 3.6 to 6.5°.[3]

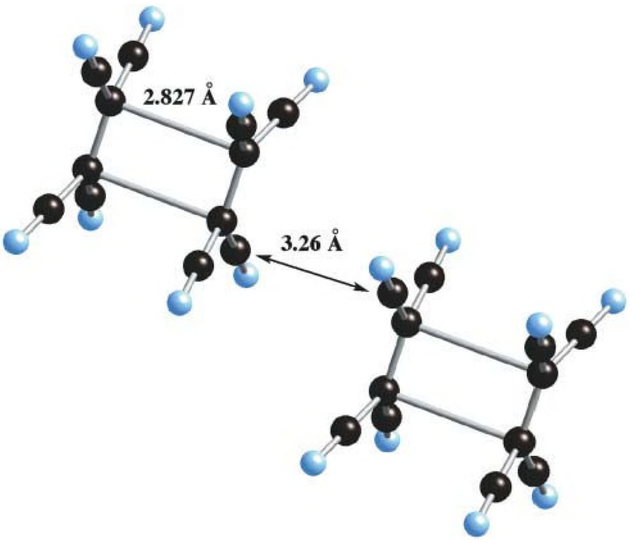

Fig. 2 Intra- and inter-dimer [TCNE]$_2^{2-}$ interactions in [Et$_4$N]$_2$-[TCNE]$_2$. Click image or here to access a 3D representation.

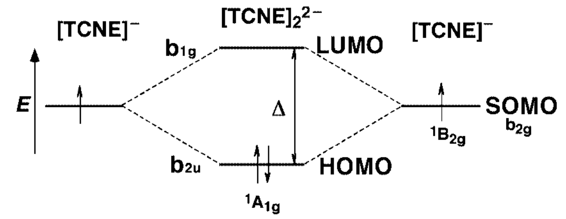

Fig. 3 Schematic diagram of the b_{2g} SOMO [TCNE]$^-$ orbitals overlapping to form bonding and antibonding orbitals of b_{2u} and b_{1g} symmetry, respectively, for the [TCNE]$_2^{2-}$ dimer.

Dimerization of [TCNE]$^-$ leads to overlap of the b_{2g} singly occupied molecular orbital (SOMO) on each moiety to form bonding and antibonding orbitals of b_{2u} and b_{1g} symmetry (Fig. 3), respectively, with a $^1A_{1g}$ ($b_{2u}^2b_{1g}^0$) ground state electronic structure for the dimer.

Intradimer [TCNE]$_2^{2-}$ bond formation also leads to a change in the IR spectrum, which differs with respect to its fragments, *i.e.* [TCNE]$^{\bullet-}$. For the single anion moiety, $\nu_{\mathrm{C\equiv N}}$ IR absorptions occur at 2183 and 2144 cm^{-1},[10] and the ν_{CC} absorption is inactive and not observed. In contrast, the as reported π-[TCNE]$_2^{2-}$ exhibits three $\nu_{\mathrm{C\equiv N}}$ vibrations, at 2191 ± 2 (m), 2172 ± 2 (s), and 2161 ± 2 (s) cm^{-1}, and $\nu_{\mathrm{C=C}}$ at 1360 (s) cm^{-1}.[3] The solid state spectrum of [Et$_4$N]$_2$[TCNE]$_2$ (Fig. 4) shows that new IR bands, arising from the intradimer bonding, occur at 2191 (m), 2170 (s), 2163 (s) ($\nu_{\mathrm{C\equiv N}}$), and 1365 (s) cm^{-1} ($\nu_{\mathrm{C=C}}$). The *ca.* 1360 cm^{-1} absorption is due to the antisymmetric combination of the intrafragment CC stretches of each fragment's central CC bond, which becomes allowed and gains intensity due to electron-vibrational coupling.[11]

The electronic absorption spectrum of [TCNE]$^{\bullet-}$ has an absorption at 23 375 cm^{-1} (428 nm; 2.89 eV) in solution, which has 17 vibrational overtones.[10] This $^2B_{2u} \rightarrow {}^2B_{3g}$ transition broadens in the solid state (Fig. 5). [TCNE]$_2^{2-}$ exhibits this broad absorption at 26 150 cm^{-1} (382 nm; 3.24 eV) as well as a new absorption at 16 850 cm^{-1} (593 nm; 2.09 eV) (Fig. 5). The latter absorption is assigned to the $b_{2u}^2b_{1g}^0$ ($^1A_{1g}$) → $b_{2u}^1b_{1g}^1$ ($^1B_{1u}$) transition and gives these dimeric compounds the observed dark blue–purple color. This value is higher in energy than the 15 300 cm^{-1} (654 nm, 1.90 eV) reported for

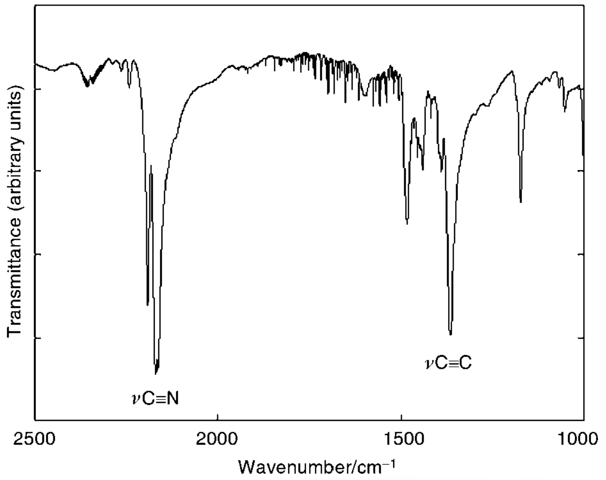

Fig. 4 Solid state IR spectrum of [TCNE]$_2^{2-}$ in [Et$_4$N]$_2$[TCNE]$_2$.

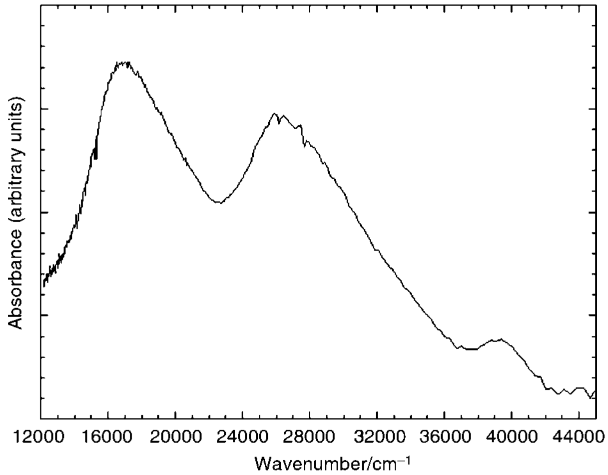

Fig. 5 Solid state UV-Vis spectrum of $[TCNE]_2^{2-}$ in $[Et_4N]_2[TCNE]_2$.

$Tl_2[TCNE]_2$, $[(Me_2N)_2CC(NMe_2)_2][TCNE]_2$, and $Cr^I(C_6H_6)]_2$-$[TCNE]_2$.[3]

Intradimer bond formation also affects the magnetic properties. When doublet $S = 1/2$ $[TCNE]^-$ fragments approach each other to form the π-$[TCNE]_2^{2-}$ dimer, Fig. 3, the spins interact to form an $S = 0$ singlet ground state and an $S = 1$ triplet excited state (or *vice versa*). Strong antiferromagnetic coupling between the spins leads to the singlet ground state. However, upon warming, thermal population of the triplet excited state may be achieved, as has frequently been reported.[12] As noted for related $[TCNE]_2^{2-}$ dimers,[3] diamagnetic-like behavior is observed for $[Et_4N]_2[TCNE]_2$ due to population of only the singlet state at and below room temperature.

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