Cyanocarbon Compounds

DOI: 10.1002/ange.200601070

The Structure of Fractionally Charged Tetracyanobenzene^{n-} Present in $[TCNB]_3^{2-}$**

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Cyanocarbons are electron poor and form numerous Mulliken donor–acceptor complexes,[1] whereas their radical anions are stabilized by charge and spin delocalization, and form numerous stable electron transfer salts. As a consequence of their unpaired electrons and planar topology, these salts enabled the discovery and development of molecule-based materials exhibiting metal-like electrical conductivity,[2]

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[**] We thank Jack Simons and Henry S. White for helpful discussions and the continued partial support by the Department of Energy Division of Materials Science (Grant Nos. DE-FG03-93ER45504, and DE-FG03-94ER14452). Computer resources were provided by the Center for High Performance Computing at the University of Utah. $n_{average} \approx 2/3-$, TCNB = Tetracyanobenzene

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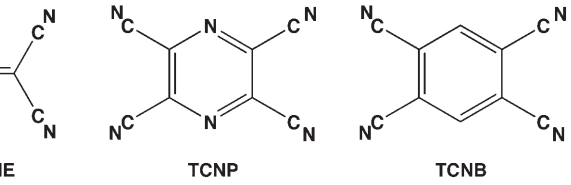
superconductivity,[3] and ferromagnetic ordering.[4] In particular, the reduction chemistry of numerous cyanocarbons has been studied with the objective of identifying new acceptors to stabilize magnetically ordered molecule-based materials. These include 2,4,6-tricyano-1,3,5-triazine (TCT) and 2,4,6-tricyanobenzene (TCB)[5] in addition to tetracyanoethylene (TCNE)[6] and others.

The reactions of $[V(CO)_6]$ with several cyanocarbon electron acceptors form organic-based magnets. These cyanocarbons include TCNE, TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane), tetracyanopyrazine, and recently, 1,2,4,5-tetracyanobenzene (TCNB), which magnetically order below approximately 400,[7] 56,[8] 200,[9] and 325 K,[10] respectively.

TCNB undergoes a reversible one-electron reduction at −0.64 V versus the saturated calomel electrode (SCE) in MeCN[11] and was reduced with tetrakis(dimethylamino)ethylene (TDAE). TDAE is a strong electron donor with an ionization potential of 6.13 eV,[12] and undergoes two reversible one-electron oxidations to $[TDAE]^+$ and $[TDAE]^{2+}$ at −0.68 and −0.53 V vs. SCE, respectively, in MeCN.[12b]

The reaction of one equivalent of TDAE with two equivalents of TCNB in MeCN led to the isolation of dark green crystals of composition $[TDAE][TCNB]_3 \cdot MeCN$ (**1**).[13] The IR spectrum of **1** exhibits several $\tilde{\nu}_{C\equiv N}$ absorptions with a sharp peak at 2170 cm^{-1} and broad peak at 2130 cm^{-1} (half-width at half-height ≈ 60 cm^{-1}; Figure 1). These absorptions are shifted to lower energy by more than 75 cm^{-1} with respect to the sharp 2245 cm^{-1} $\tilde{\nu}_{C\equiv N}$ absorption observed for TCNB and are thus indicative of its reduction in the formation of **1**.



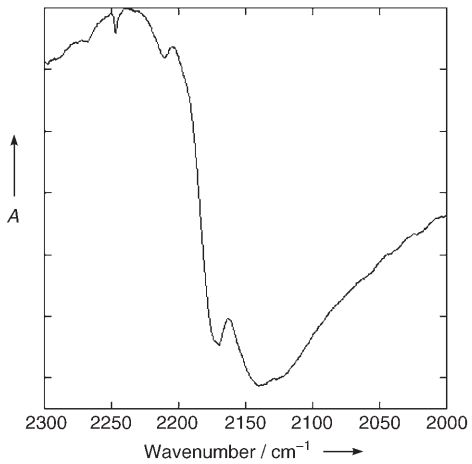


Figure 1. $\tilde{\nu}_{C\equiv N}$ IR (KBr) absorptions for **1** (the peak at 2245 cm^{-1} is due to MeCN).

Single-crystal X-ray diffraction analysis[13] of **1** reveals the presence of $[TDAE]^{2+}$ in addition to three nominally eclipsed TCNB moieties per unit cell (Figure 2), and an acetonitrile of solvation. The oxidation state of $[TDAE]^n$ ($n = 0, 1+, 2+$) is ascertained from both the central C–C bond length, which is 1.36 (for $n = 0$), 1.42 ($n = 1+$), and 1.52 Å ($n = 2+$),[14] owing to a decreasing bond order upon oxidation, and the NCCN dihedral angles that are approximately 26°,[15] ≈ 42°, and ≈ 76° respectively for $n = 0$, $1+$, $2+$,[14] as well as spectroscopic data. The TDAE in **1** has a central C–C bond distance of 1.511(6) Å and an average NCCN dihedral angle of 73.8° characteristic of $[TDAE]^{2+}$. The $[TDAE]^n$ oxidation state can also be distinguished by the IR $\tilde{\nu}_{NCN}$ absorptions that respectively occur at 1340, 1518, and a doublet at 1659/1675 cm^{-1} for $[TDAE]^n$ $n = 0$, $1+$, $2+$.[14] The observed doublet at 1671 and 1648 cm^{-1} (not shown; and the lack of absorptions at ≈ 1340 and ≈ 1518 cm^{-1}) are again consistent with the presence of $[TDAE]^{2+}$. Additionally, **1** is diamagnetic, and the solid-state ^{13}C NMR chemical shift for the TDAE central carbon atoms occurs at δ = 156.4 ppm (relative to tetramethyl silane (TMS) by a secondary external reference to the upfield peak of adamantane at δ = 38.6 ppm) in accord with the previously reported values of δ = 155.7 and 157.2 ppm for $[TDAE]^{2+}$.[16]

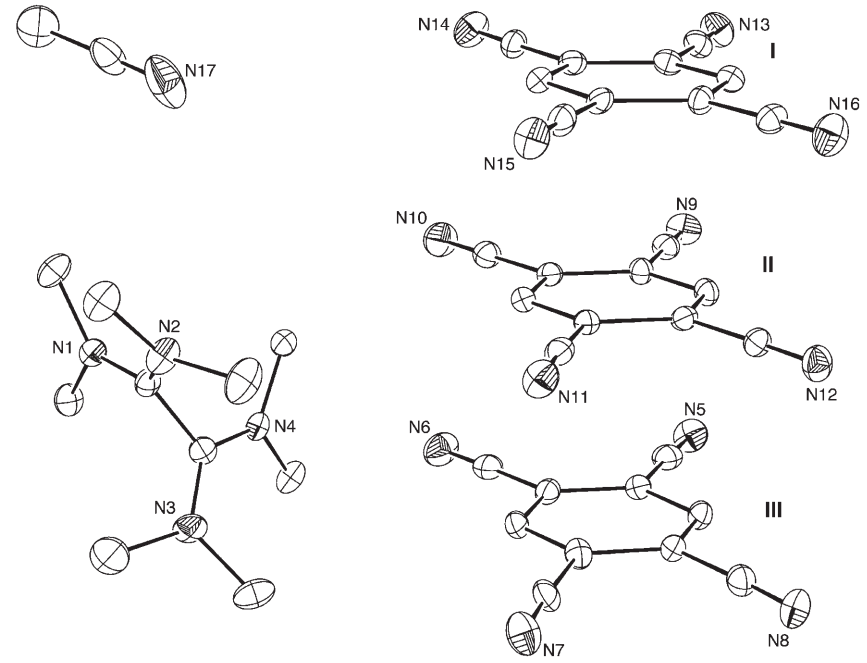


Figure 2. ORTEP plot (thermal ellipsoids set at 30% probability) for **1**. Unlabeled atoms are C.

Each TCNB is planar and each of the 42 atoms in the TCNB triad is unique; hence, all C–C distances are unique (Table 1). Although there are some small fluctuations, the NCC–CCN distances average 1.442 and 1.445 Å for TCNBs (**II** and **III**) (Figure 2, Table 1), while the HC–CCN distances average 1.384 and 1.387 Å for the same TCNBs. Hence, the NCC–CCN distance exceeds the HC–CCN distance by

Table 1: CC and CN bond lengths observed for **1**.

Moiety in **1**[a]	NCC-CCN [Å]	HC-CCN [Å]	C-CN [Å]	CN [Å]
TCNB **I**	1.446(6)	1.373(6)	1.428(6)	1.151(6)
	1.438(5)	1.390(6)	1.431(6)	1.155(6)
		1.383(6)	1.431(6)	1.165(6)
		1.391(6)	1.431(6)	1.142(6)
TCNB **II**	1.438(5)	1.398(6)	1.430(6)	1.150(6)
	1.452(5)	1.395(6)	1.434(6)	1.149(6)
		1.370(6)	1.421(6)	1.156(6)
		1.384(6)	1.423(6)	1.155(5)
TCNB **III**	1.432(6)	1.381(7)	1.436(6)	1.153(6)
	1.412(6)	1.400(6)	1.430(7)	1.148(6)
		1.397(6)	1.437(7)	1.153(6)
		1.442(6)	1.442(6)	1.148(5)
TCNB **I** Ave	1.442(6)	1.384(8)	1.430(2)	1.153(10)
TCNB **II** Ave	1.445(10)	1.387(13)	1.427(6)	1.153(4)
TCNB **III** Ave	1.422(14)	1.405(26)	1.436(5)	1.151(3)
Ave	1.436(14)	1.392(18)	1.431(6)	1.152(6)

[a] Structure determined at 150(1) K.

0.058 Å. This result is indicative of loss of the aromaticity that is present for $TCNB^0$, which has essentially equivalent NCC–CCN and HC–CCN distances of 1.398 and 1.385 Å,[17] respectively. TCNB **I** has a somewhat longer average NCC–CCN distance of 1.405 Å, and somewhat shorter average HC–CCN distance of 1.426 Å, but these are still less equivalent to that observed for $TCNB^o$. In addition, the average C–CN distance of 1.428 Å is 0.017 Å shorter than that observed for $TCNB^o$, while the C–N distance is 0.085 Å longer. While each TCNB in **1** differs, they are more similar to each other than to $TCNB^0$.

The TCNB units form columns composed of triads, with an average inter-triad separation of 3.6 Å that exceeds the van der Waals separation (> 1.5 Å[18]). The two average intra-triad separations are 3.3 and 3.4 Å, and are below the van der Waals separation. Hence, from structural and charge balance considerations the TCNB units form a trimeric dianion, $[TCNB]_3^{2-}$. The structural differences between the TCNB units are attributed to their different electrostatic environments with respect to the $[TDAE]^{2+}$. Each triad is surrounded by four $[TDAE]^{2+}$ ions. TCNB **II** is closer to all four surrounding $[TDAE]^{2+}$ ions than the TCNB **I** and **III**. TCNB **I** and **III** are close to two $[TDAE]^{2+}$ ions, albeit **III** is slightly closer than **I**. Thus, each TCNB is in a different electrostatic environment, which should effect their charge distributions and structure as observed.

The charge distribution within a trimer was experimentally and computationally investigated to evaluate the importance of the following formal distributions: **a**) $[TCNB]^{1-}$-$[TCNB]^{1-}[TCNB]^0$ {or $[TCNB]^{1-}[TCNB]^0[TCNB]^{1-}$}, **b**) $[TCNB]^0[TCNB]^{2-}[TCNB]^0$ {or $[TCNB]^{2-}[TCNB]^0$-$[TCNB]^0$}, or delocalized **c**) $[TCNB]^{2/3-}[TCNB]^{2/3-}[TCNB]^{2/3-}$, or **d**) $[TCNB]^{1/2-}[TCNB]^{1-}[TCNB]^{1/2-}$. Based upon the reversible first and second one-electron reduction potentials for TCNB,[11] conproportionation of **b** to **a** is disfavored by approximately 1 V; hence, the presence of $[TCNB]^{2-}$ is unlikely.

Localized distributions **a** and **b** should exhibit spectroscopic and structural evidence for the presence of $TCNB^0$. From the above structural data, $TCNB^0$ is not present; however, spectroscopy is a more incisive probe. As noted above, $TCNB^0$ has a characteristic $\tilde{\nu}_{C\equiv N}$ absorption at 2245 cm^{-1} that is not observed[19] and thus is suggestive of distributions **c** or **d**. Likewise, the ^{13}C NMR spectroscopy resonances for CH ($\delta = 139.5$ and 135.2 ppm), *C*CN ($\delta =$ 122.7 ppm), and CN ($\delta = 115.8$ ppm) that occur for $TCNB^0$ (Figure 3) are not observed for **1**, in which these resonances occur at $\delta = 144.8$, 111.8, and 125.5 ppm, respectively.[20] In addition, the two ^1H NMR spectroscopy resonances observed at $\delta = 7.1$ and 6.2 ppm for $TCNB^o$ are not present in **1** for which three resonances occur at $\delta = 5.3$, 6.3, and 8.2 ppm. The observed shifts and the presence of a third ^1H resonance are assumed to arise from the complex chemical environments (six different protons) that are present.

Density functional theory molecular orbital (DFT MO) calculations[21] on $[TCNB]_3^{2-}$ indicate an up field shift of the

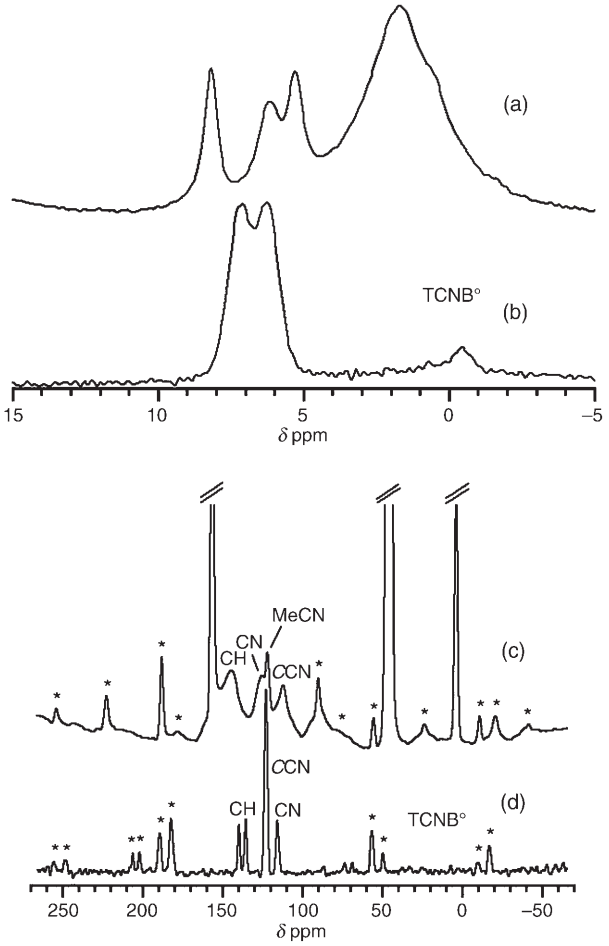
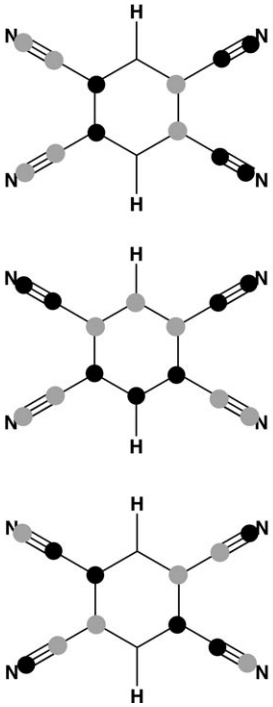


Figure 3. Single pulse magic-angle spinning (MAS) ^1H NMR spectrum for **1** (a) and $TCNB^0$ (b) and cross-polarization (CP)-MAS ^{13}C NMR spectrum for **1** (c) and $TCNB^0$ (d). The ^{13}C and ^1H NMR chemical shift scales are given relative to TMS; spinning sidebands are indicated by asterisks. For the CP-MAS experiments cross polarization from ^1H and TPPM (TPPM = two-pulse phase modulation) ^1H decoupling was used. The spinning speed was 10 kHz in all experiments. Referencing for ^{13}C NMR resonance signals was achieved by a secondary external reference to the upfield peak of adamantane at $\delta = 38.6$ ppm and for ^1H NMR signals to liquid DMSO at $\delta = 2.5$ ppm.

CH and CN carbon isotropic chemical shifts, whereas the CCN carbon shifts down field as observed in the ^{13}C NMR spectrum.[22] The presence of diamagnetic $[TCNB]^{2-}$ ions is unlikely as MO calculations predict *C*CN to have an isotropic shift of $\delta \approx 68$ ppm, however, there is no resonance observed in this region. As the NMR spectroscopy data does not support the presence of TCNB^{o}, it is in accord with distributions **c** or **d** with each TCNB being fractionally reduced.

The electronic structure of [TDAE][TCNB]$_3$·MeCN was calculated by using an ab initio method.[21] Natural bond orbital analysis[21] revealed charge delocalization over all three TCNB units in $[TCNB]_3^{2-}$ in accord with distribution **d**. TCNB has different computed charge distribution, that is, $[TCNB]^{0.25-}[TCNB]^{1.11-}[TCNB]^{0.61-}$.[21] The non-uniform charge distribution is a consequence of the differing electrostatic environments for each TCNB unit, which leads to differences in the contributions from the p_y orbitals (perpendicular to the TCNB plane). The *C*CN p_y orbital contribution of TCNB **II** and TCNB **III** are 12 to 19% and are 5 to 8% higher than TCNB **I**, respectively. Since the electron density is the square of the wavefunction, the orbital contribution qualitatively relates to the charge distribution. The triads form as a result of the delocalized bonding of the $[TCNB]_3^{2-}$ ion. The overlapping of the singly occupied molecular orbital (SOMO) of $[TCNB]^{\bullet -}$ gives the bonding orbital of $[TCNB]_3^{2-}$, the highest occupied molecular orbital (HOMO) of a_u symmetry (Figure 4).



The detailed understanding of multicenter C–C bonding has only recently garnered attention, but is evident for several systems that include dimeric $[TCNE]_2^{2-}$ and the trimeric system reported herein. Related systems that presumably exhibit similar mutlicentered bonding over a trimeric units include examples of $[TCNQ]_3^{2-}$,[23] as well as a extended chains that stabilize metallic conductivity, such as spirobiphenalenyl radicals.[24]

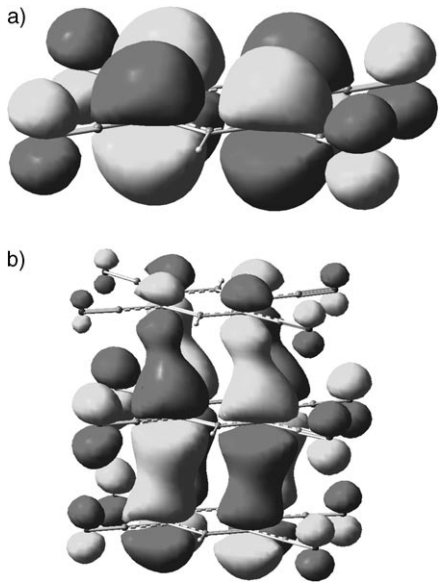


Figure 4. Calculated SOMO for $[TCNB]^{-}$ (a) and HOMO for $[TCNB]_3^{2-}$ (b).

Received: March 17, 2006
Published online: July 17, 2006

Keywords: cyanocarbon compounds · electron transfer · ions · partial charges · structure elucidation

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[13] Elemental analysis (%) calcd for $[TDAE][TCNB]_3 \cdot MeCN$: C 65.02, H 4.29, N 30.69; Found: C 64.82, H 3.98 N 30.39. A $0.23 \times 0.13 \times 0.03$ mm crystal mounted on a glass fiber with traces of a viscous oil was studied at 150(1) K on a Nonius KappaCCD diffractometer [$Mo_{K\alpha}$ ($\lambda = 0.71073$ Å)]. A total of 12534 reflections ($\theta_{max} = 25.07°$) were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using DENZO-SMN and SCALEPAC. Monoclinic space group $P2_1/c$: $a = 16.0115(7)$, $b = 10.1304(5)$, $c = 24.8810(8)$ Å, $\beta = 96.224(2)°$, $V = 4012.0(3)$ Å^3. $R1 = 0.0850$, $wR2 = 0.2062$, and $S = 1.04$ for 3783 reflections with $I > 2\sigma(I)$, and $R1 = 0.1623$, $wR2 = 0.2493$, and $S = 1.04$ for 7048 unique reflections and 620 parameters. The final difference-Fourier map ranged from -0.306 to 0.449 e Å^3. CCDC-299545 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[19] The absorption observed at 2245 cm^{-1} is due to MeCN present in the structure.

[20] Unfortunately, the spread of isotropic shifts for each position in the asymmetric unit of **1** deteriorates the resolution and prevents the measurement of the chemical shift principal values that are an even more sensitive probe of electronic structure.

[21] Electronic structures of TCNB^o, $[TCNB]^{\bullet -}$, and $[TDAE][TCNB]_3 \cdot MeCN$ were calculated by using ab initio Hartree–Fock (HF) method followed by second-order Møller–Plesset (MP2) correlation energy correction (*S1*) with Gaussian type 6-31g(d) basis set. Geometry optimization was performed for both TCNB^o (spin restricted) and $[TCNB]^{\bullet -}$ (spin unrestricted), single-point energy calculation for $[TDAE][TCNB]_3 \cdot MeCN$ (spin restricted) taken from the crystal structure and subsequent natural bond orbital (NBO) analysis (*S1-S1*). DFT calculation for the NMR chemical shift was performed at the B3LYP/D95** level on $[TCNB]_3^{2-}$. C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618; E. D. Glendening, et al. *NBO 5.0* (Theoretical Chemistry Institute, Univerity of Wisconsin, Madison, **2001**. Gaussian 03 (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.

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