

Four-Center Carbon—Carbon Bonding[†]

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Received June 14, 2006

ABSTRACT

The 2.89-Å intradimer separation for cofacial [TCNE]₂²⁻ (TCNE = tetracyanoethylene) dimers is twice that of conventional C—C bonds but ~0.6 Å shorter than the sum of the van der Waals radii. Experimental and computational studies best characterize the intradimer bonding as a 2e⁻-4-center (2e⁻-4c) C—C bonding interaction (or bond). This nonconventional bonding exhibits unique spectroscopic properties (new, lower energy electronic absorption, new ν_{CC} and new and shifted ν_{CN} and δ_{CCN} vibrational absorptions, and characteristic ¹³C NMR chemical shifts) and is diamagnetic. [TCNE]₂²⁻ is a prototype of a growing number of organic compounds that are best described by multicenter C—C bonding.

Introduction

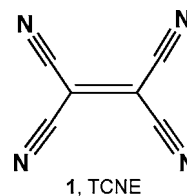
Chemical bonds, as first invoked by Gilbert N. Lewis,¹ involve a shared pair of electrons and are the basis of directional covalent bonding that today permeates all

After a postdoctoral fellowship at Stanford University and several positions in industry including Central Research & Development Department at Du Pont, Joel S. Miller joined the faculty at the University of Utah in 1993 where he is currently a Distinguished Professor in the Department of Chemistry. He has been a Visiting Scientist at the Weizmann Institute, a Visiting Professor of Chemistry at the University of Pennsylvania and University of Barcelona, and Professeur Invité, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université Louis Pasteur, among other institutions. He is on the advisory board of *Advanced Materials* and *Chemistry—a European Journal* and a member of the Inorganic Synthesis Corporation. His research interests focus on the solid state magnetic, electrical, and optical properties of molecular (organic, organometallic, and inorganic coordination) compounds and electron transfer complexes as well as the surface modification of solids. Currently he is actively involved in synthesis and characterization of organic/molecule-based magnets. He has edited 17 monographs and published over 450 papers in these and other areas and was recipient of the 1996 Pinguin Foundation's Wilhelm Manchot Research Professorship at the Technische Universität München, the 2000 American Chemical Society Award for *Chemistry of Materials*, and the 2007 American Physical Society's *James C. McGroddy Prize for New Materials*, among several other awards.

Juan J. Novoa received his B.Sc. (1977) and Ph.D. (1981) degrees from the University of Barcelona, where he also received a degree as a Scientific Applications Analysis (1986). After postdoctoral stays with Ramón Carbó (IQS; Barcelona, Spain; 1981–1982) and Michael A. Robb (Queen Elizabeth College; London, United Kingdom; 1983), he joined the University of Barcelona, where he had various faculty positions until being appointed Professor of Physical Chemistry in 1997. He has been visiting researcher or visiting professor at the North Carolina State University (1989–1991, 1993), Cray Research (1994), IBM Zurich Research Laboratory (2003, 2004, 2005) and Clark University (2006). He is also member of the Advisory Editorial Board of *CrystEngComm*. His research field has been always on Quantum Chemistry. In recent years, his main field of research has been on the theoretical study of the crystal packing and electronic properties of solids of technological interest, with particular interest on the properties of molecular-based magnets.

aspects of chemistry, particularly organic and biochemistry. Lewis' paradigm-shifting perspective and subsequent more detailed analyses and extension to include resonance by Linus Pauling² (among many others) dictate that orbital overlap is essential for bond formation. The discovery of electron-deficient boranes led to the appreciation of three-center (3c) BHB 2e⁻ bonds,³ which explained the bonding and structures of now innumerable boranes and related compounds but not carbon-based bonding.

Three-center (3c) bonds, being a significant departure from the overwhelming number of two-center bonds, are a last resort when conventional 2c bonding descriptions fail, as occurs for boranes. In contrast, the structures and bonding for all organic compounds, even esoteric and exotic examples, are well described by 2c bonding. Recently, however, the description of the structure of [TCNE]₂²⁻ (TCNE = tetracyanoethylene, **1**) dimer dianion



with a substantial sub-van der Waals intradimer separation required multicenter C—C bonding interactions (or bonds) to describe the structure, bonding, and spectroscopic properties and is prototypical of a growing number of organic compounds that are best described by multicenter bonding.

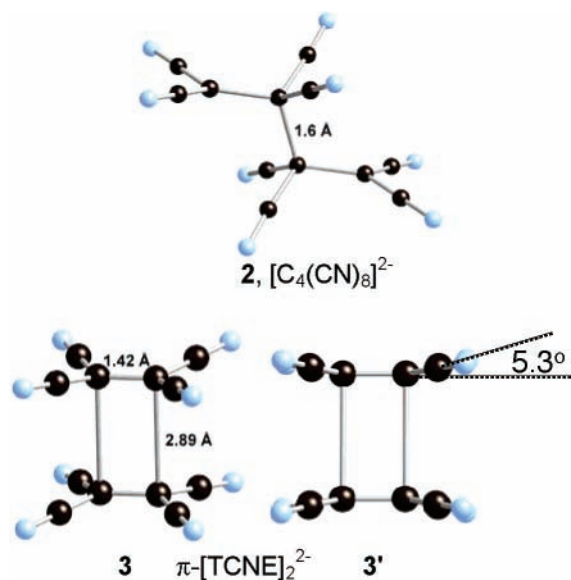
The understanding of the nature of these sub-van der Waals multicenter interactions and their associated bonding, *which cannot be described in a conventional manner*, is a specific focus of this Account. Clearly other groups worldwide have and continue to make important contributions in the understanding multicenter C—C bonding; however, due to the nature of this journal, work from our laboratory is primarily dwelled upon.

Four-Center (4c) Bonding in [TCNE]₂²⁻

TCNE (**1**) and [TCNE]^{•-} (**1^{•-}**) are planar, and their structures as well as electronic structures, are well characterized.⁴ Most notably, addition of an electron to the TCNE antibonding LUMO yields the [TCNE]^{•-} SOMO and concomitant reduction of the sp²-C—C bond order from 2 to 1.5 in accord with the distance increasing from 1.349(6) to 1.394(11) Å.⁵ {Reduction to [TCNE]²⁻ further reduces the bond order to 1 in accord with its longer 1.488(4) bond length, and due to the free rotation expected for a single bond, it is nonplanar.⁵}

In addition to **1^{•-}**, [TCNE]^{•-} can form its σ -dimer octacyanobutanediide, [C₄(CN)₈]²⁻, **2**, and as focused upon in this Account, its π -dimer [TCNE]₂²⁻, **3**. Albeit rarer than the π -dimer **3**, **2** can be stabilized with di- or trivalent cations bound to the four terminal nitriles, and although

[†] Dedicated to Edel Wasserman on the occasion of his 75th birthday.



the central C–C bond is relatively long (~ 1.6 Å), it can be described as a weak $\text{sp}^3\text{-C-C}$ bond.⁶

In contrast, the π -dimer $[\text{TCNE}]_2^{2-}$, **3**, has respective 1.42 and 2.89 Å intra- and inter-TCNE C–C bond lengths. First crystallographically characterized in 1981,⁷ 17 structures with different cations have been reported to date. Although the cations range from being covalently bonded to the $[\text{TCNE}]^{\bullet-}$ {as occurs for $[\text{Cu}^{\text{I}}(\text{PPh}_3)_3(\text{TCNE})]_2^8$ } to those with strong electrostatic interactions {as occurs for $\text{Tl}_2[\text{TCNE}]_2^9$ } to those with distant, weak electrostatic interactions {as occurs for $[\text{Fe}(\text{C}_5\text{H}_4)_2\text{C}_3\text{H}_6]_2[\text{TCNE}]_2^7$ and $[\text{Ni-Pr}_4]_2[\text{TCNE}]_2^{10}$ }, the cations do not affect the structure of the $[\text{TCNE}]_2^{2-}$ dimer. Large single crystals are frequently formed (Figure 1).

The 2.89-Å intradimer C–C distance far exceeds 1.54 Å found in the diamond allotrope of carbon—the length of a single bond between sp^3 -hybridized carbons and the longest of all common C–C bonds, although elongated sp^3 -hybridized C–C bonds as great as 2.0 Å have been reported.¹¹ Nonetheless, this distance is also substantially less than sum of the van der Waals radii for aromatic organic compounds (3.45 ± 0.05 Å),^{2c,12} indicative of bonding. These self-assembled cofacial dimers may be considered as supramolecular aggregates with intradimer C–C distances nearly twice that of typical C–C bonds. In addition to the 2.89 Å intradimer separation, the nitriles



FIGURE 1. Single crystal (114 mg) of $[\text{MeNC}_5\text{H}_5]_2[\text{TCNE}]_2$.

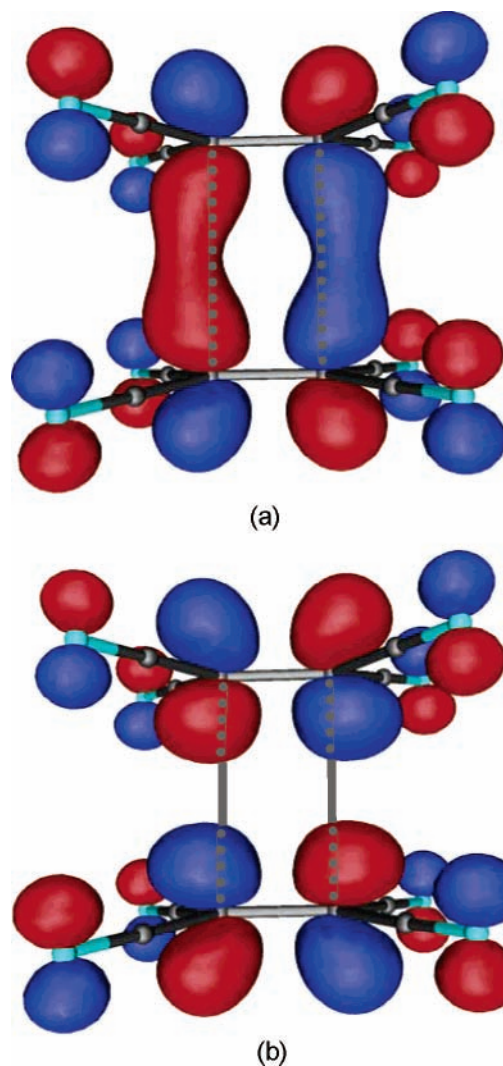


FIGURE 2. b_{2u} HOMO (a) and b_{1g} LUMO (b) of $[\text{TCNE}]_2^{2-}$.

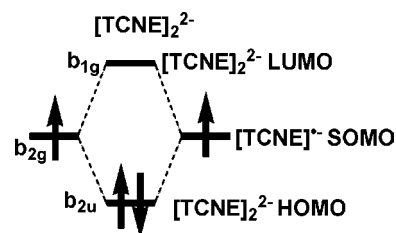


FIGURE 3. MO diagram arising from the overlap of two b_{2g} SOMOs on each $[\text{TCNE}]^{\bullet-}$ forming the $[\text{TCNE}]_2^{2-}$ b_{2u} HOMO and b_{1g} LUMO.

bend away from the nominal plane of the central C–C bonds by 5.3° (**3'**) suggestive that something is holding the two $[\text{TCNE}]^{\bullet-}$ fragments together, in addition to admixing of sp^3 hybridization to the sp^2 C atoms.

These observations piqued our curiosity and led to investigations (experimental and computational) aimed at unraveling the nature of the intradimer interactions. From DFT calculations at the UBLYP/6-31+G(2d,2p) level, the bonding for **3** can be described as the b_{2g} SOMOs on the two $[\text{TCNE}]^{\bullet-}$ fragments interacting to form dimer b_{2u} HOMO bonding and b_{1g} LUMO antibonding orbitals (Figures 2 and 3).^{13,14} Hence, the $[\text{TCNE}]_2^{2-}$ HOMO has the $2e^-$ distributed equally over the four central C atoms.

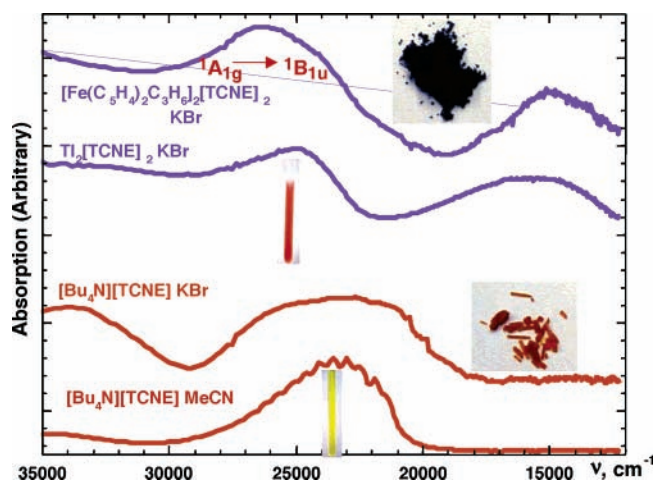


FIGURE 4. UV-vis spectra of $[\text{TCNE}]^{2-}$ in MeCN solution and as a KBr pellet (orange), and representative $[\text{TCNE}]_2^{2-}$ as the Tl^+ and $[\text{Fe}(\text{C}_5\text{H}_4)_2\text{C}_3\text{H}_6]^+$ salts in the solid state as KBr pellets. The yellow and red colored solution are the $[\text{NET}_4]_2[\text{TCNE}]_2$ dissolved in CH_2Cl_2 ; at room temperature $[\text{TCNE}]^{*-}$ is present, while at ca. -90°C , due to the $2[\text{TCNE}]^{*-} = [\text{TCNE}]_2^{2-}$ shifting to the right, $[\text{TCNE}]_2^{2-}$ is present. The orange crystals are $[\text{NBu}_4][\text{TCNE}]$, while the purple crystals are $[\text{NET}_4]_2[\text{TCNE}]_2$.

What is the nature of this—a $2e^-$ – $4c$ bond or bonding interaction? In fact, it begs the question of what is a bond. If the MO diagram (Figure 3) describes the bonding, then it provides a basis to predict several experimentally testable spectroscopic as well as magnetic properties.

The MO diagram (Figure 3) predicts that $[\text{TCNE}]_2^{2-}$ should exhibit a new (allowed) electronic transition (UV-vis) not observed for $[\text{TCNE}]^{*-}$. In addition, $[\text{TCNE}]_2^{2-}$, being an independent 20 atom species, should exhibit IR allowed absorptions that differ with respect to that observed for $[\text{TCNE}]^{*-}$. Finally, the MO diagram predicts a singlet 1A_g ground state for $[\text{TCNE}]_2^{2-}$, and hence it should be diamagnetic and exhibit sharp NMR resonances typical of diamagnetic compounds. These data should be self-consistent, in accord with expectations, thus validating the MO description that $[\text{TCNE}]_2^{2-}$ is best described by a $2e^-$ – $4c$ bond. The triplet state lies higher in energy than the single state.^{13,14}

The MO diagram predicts an allowed 1A_g ($b_{2u}^2b_{1g}^0$) \rightarrow $^1B_{1u}$ ($b_{2u}^1b_{1g}^1$) (or $S_0 \rightarrow S_1$) electronic transition that is not present for $[\text{TCNE}]^{*-}$.⁴ $[\text{TCNE}]^{*-}$ has an absorption at $23\,400\text{ cm}^{-1}$ (428 nm , 2.90 eV) that possesses 17 vibrational overtones⁴ and is orange in color (and yellow in solution) (Figure 4). In contrast, salts possessing $[\text{TCNE}]_2^{2-}$ exhibit a new, lower energy absorption, $\sim 17\,150\text{ cm}^{-1}$ (583 nm , 2.13 eV), which varies by $\sim 7\%$ depending on the cation, that accounts for the purple color these crystals have when viewed with reflected light (Figure 4). This new absorption is attributed to the MO-predicted $^1A_g \rightarrow ^1B_{1u}$ transition, consistent with bond formation.

Dissolution of purple crystals of $[\text{NET}_4]_2[\text{TCNE}]_2$ in CH_2Cl_2 yields a yellow solution of $[\text{TCNE}]^{*-}$ (Figure 4) due to the equilibrium $2[\text{TCNE}]^{*-} = [\text{TCNE}]_2^{2-}$ being shifted to the left. In accord with Le Châtelier's principle, reducing the temperature shifts the equilibrium to the right, and the absorption spectrum of red ($18\,940\text{ cm}^{-1}$, 528 nm , 2.35 eV) $[\text{TCNE}]_2^{2-}$ is observed at lower temperature (Figure 4).^{13b} Jay K. Kochi's group carefully studied the temperature dependence of this equilibrium constant ($\sim 7 \times 10^{-4}\text{ mol}^{-1}$ at 298 K in CH_2Cl_2) by UV-vis spectroscopy and determined $-\Delta H$, nominally the dimer bond dissociation energy, to be $42.4 \pm 4\text{ kJ mol}^{-1}$ ($8.8 \pm 1\text{ kcal mol}^{-1}$) and entropy to be -41 eu .¹⁵ Hence, expectedly the $2e^-$ – $4c$ bond is a weak bond.

Twenty-atom $[\text{TCNE}]_2^{2-}$ should exhibit a different IR spectrum with respect to ten-atom $[\text{TCNE}]^{*-}$. Planar $[\text{TCNE}]^n$ ($n = 0, 1$) should exhibit two ν_{CN} and one δ_{CCN} IR-allowed absorptions, while the ν_{CC} absorption is forbidden due to symmetry.⁴ The ν_{CN} absorptions occur at 2262 and 2228 and at 2183 and 2144 cm^{-1} for TCNE and $[\text{TCNE}]^{*-}$, respectively,⁵ while the δ_{CCN} absorptions occur at 522 cm^{-1} for both TCNE and $[\text{TCNE}]^{*-}$.^{13b} In contrast, as a result to a computational analysis,¹³ $[\text{TCNE}]_2^{2-}$ should exhibit a ν_{CC} , three ν_{CN} , and three δ_{CCN} IR-allowed absorptions. These seven absorptions occur at $1364(2)$, $2191(2)$, $2173(2)$, $2161(2)$, $549(3)$, $529(4)$, and $515(2)\text{ cm}^{-1}$ (Figure 5), respectively. The predicted (a) presence of the formally symmetry-forbidden ν_{CC} absorption and (b) splitting of both the δ_{CCN} and ν_{CN} absorptions with respect to $[\text{TCNE}]^n$

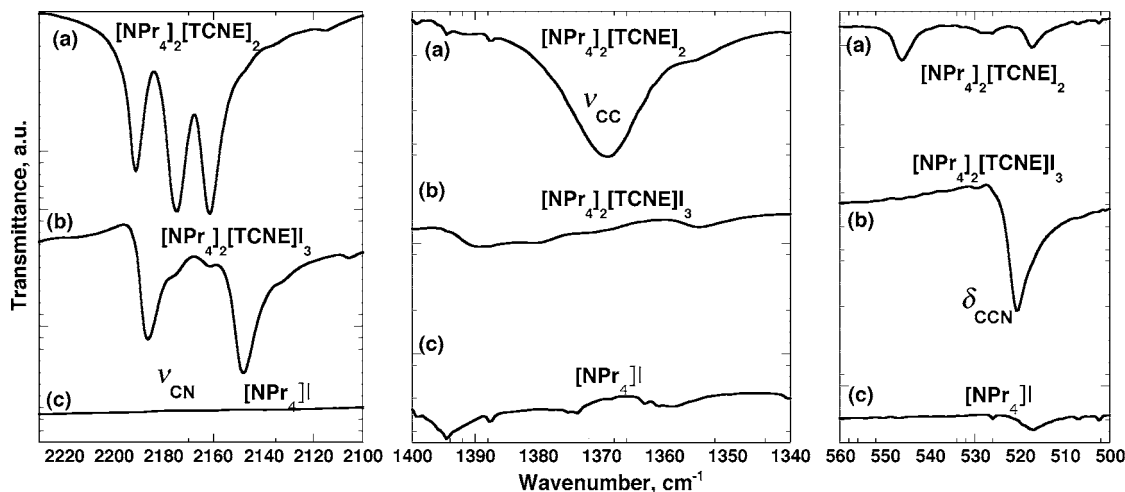


FIGURE 5. IR spectra of $[\text{NPr}_4]_2[\text{TCNE}]_2$ possessing $[\text{TCNE}]_2^{2-}$ (a), $[\text{NPr}_4]_2[\text{TCNE}]_3$ possessing $[\text{TCNE}]^{*-}$ (b), and $[\text{NPr}_4]$ in the ν_{CN} , ν_{CC} , and δ_{CCN} absorption regions.¹⁰

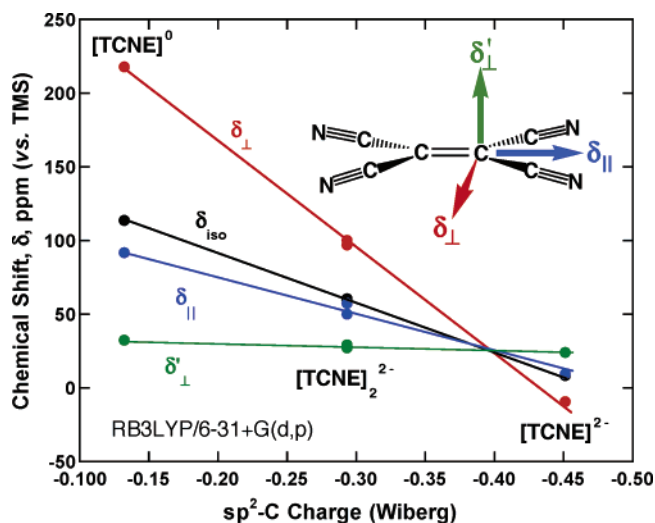


FIGURE 6. Chemical shifts of $\delta_{||}$, δ_{\perp} , δ'_{\perp} , and average δ_{iso} tensors for TCNE, $[\text{TCNE}]^{2-}$, and $[\text{TCNE}]_2^{2-}$ as a function of charge (Wiberg) on the central sp^2 C atom.¹⁶

indicates a geometry change consistent with $[\text{TCNE}]_2^{2-}$ being a stable species possessing $2e^- - 4c$ bonding.

The $2e^- - 4c$ bonding described by the MO diagram (Figure 3) predicts that unlike doublet $[\text{TCNE}]^{\bullet-}$, $[\text{TCNE}]_2^{2-}$ is closed shell and has a singlet 1A_g ground state. The 1A_g ground state is in accord with the temperature dependence of the magnetic susceptibility, which in conjunction with higher temperature EPR data, does not reveal evidence for either doublet or triplet states, in agreement with computational results.^{13b} The diamagnetic nature and $2e^- - 4c$ bonding for $[\text{TCNE}]_2^{2-}$ is further in evidence from the ^{13}C magic angle spinning (MAS) NMR spectra.¹⁶ The $\delta_{||}$, δ_{\perp} , δ'_{\perp} , and average δ_{iso} tensors for $[\text{NET}_4]_2[\text{TCNE}]_2$ {and $[\text{TDAE}][\text{TCNE}]_2$ [TDAE = tetrakis(dimethylamino)ethylene]} lie midway between the values for $[\text{TCNE}]^n$ ($n = 0, 2^-$) and in accord with the computed Wiberg charge for the central C atoms (Figure 6).

Thus, the structural (2.89-Å intradimer separation, and 5.3° bending away of the nitriles from the nominal plane of the central sp^2 -like carbon atoms), spectroscopic (new lower energy electronic absorption, new ν_{CC} and new and shifted ν_{CN} and δ_{CCN} vibrational absorptions, and characteristic ^{13}C NMR $\delta_{||}$, δ_{\perp} , δ'_{\perp} , and average δ_{iso} chemical shifts), and magnetic (diamagnetic ground state) data in addition to the results from DFT MO calculations support the existence of $[\text{TCNE}]_2^{2-}$ being an independent species composed of two $[\text{TCNE}]^{\bullet-}$'s bonded via a $2e^- - 4c$ bond. But is it really a bond, or perhaps more generally what is a bond?

What is a Chemical Bond?

The evolution of the concept of a chemical bond is discussed in the introduction. Linus Pauling, the most quoted definer of a bond, states^{2b}

...there is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to an aggregate with

sufficient stability to make it convenient for the chemist to consider it as an independent molecular species.

But always bear in mind Robert Mulliken's insight that "The chemical bond is not so simple as people think."¹⁷ One might argue that Pauling's definition tells us nothing, because it is untestable via experiment, and the convenience clause opens the door to kooks (me?) and other fringe groups to peddle their "bonds". Alternatively, Pauling's definition can be viewed as a deep clairvoyant insight into chemistry. Is the $2e^- - 4c$ "bond" discussed above a bond, or as suggested, is it a bonding interaction (etc.)? I, and others, see this as a semantic difference. I prefer to call it a bond due to the unique properties associated with the dimer making it both *convenient* and necessary to invoke the term bond to explain the new structural, spectroscopic, and magnetic properties associated with this interaction and formation of $[\text{TCNE}]_2^{2-}$, in addition to its directional nature. While I prefer the term bond, this preference is not as important as the exciting new chemistry that has evolved.

I would be remiss not to point out Richard F. W. Bader's testable, at least computationally, definition:

The existence of a (3,−1) critical point and its associated atomic interaction line indicates that electronic charge density is accumulated between the nuclei that are so linked...a necessary condition if two atoms are to be bonded to one another.¹⁸

Suffice it to say that $[\text{TCNE}]_2^{2-}$ exhibits two (3,−1) bond critical points^{13b} in accord with this definition. However, the lively contemporary discourse¹⁹ on whether the existence of a bond critical point is a necessary and sufficient condition of a chemical bond has not been resolved; thus, it is not being presented herein as evidence (primary or supporting) of bond formation.

As noted earlier, $\text{Cu}^{\text{I}}(\text{PPh}_3)_3(\text{TCNE})$ (**5**) crystallizes with formation of $[\text{TCNE}]_2^{2-}$ dimers, albeit one N from each monomer bonds to a Cu(I) site.^{8a} In contrast, $\text{Mn}^{\text{II}}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{TCNE})$ (**6**), also with one N bonded to a Mn(II) site,²⁰ unlike **5**, has an IR spectrum (and structure) that differs from that which is typical of $[\text{TCNE}]_2^{2-}$. A computational study targeting why $\text{Mn}^{\text{II}}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{TCNE})$ does not form the $[\text{TCNE}]_2^{2-}$ dimer led to the revelation that due to the electron spin on the low-spin Mn(II) site (Figure 7b), which is lacking for Cu(I) (Figure 7a), the Mn(II) spin couples to the $[\text{TCNE}]^{\bullet-}$ weakening the $[\text{TCNE}]^{\bullet-} \cdots [\text{TCNE}]^{\bullet-}$ interaction needed to form $[\text{TCNE}]_2^{2-}$. Hence, it is useful for the design of new $[\text{TCNE}]^{\bullet-}$ -based molecule-based magnets, where such dimerization is to be avoided, or π -dimers with $2e^- - 4c$ bonds.

Four-center bonding, albeit rare, has been established for several second row elements. Oxidation of, for example, S_4N_4 forms $[\text{S}_3\text{N}_2]^+$, which dimerizes to $[\text{S}_6\text{N}_4]^{2+}$. The 2.00-Å intradimer S \cdots S distance in $[\text{S}_6\text{N}_4]^{2+}$ is ~ 0.7 Å less than the sum of the van der Waals S radii and in accord with a $2e^- - 4c$ S–S bond.²² Likewise, reaction of

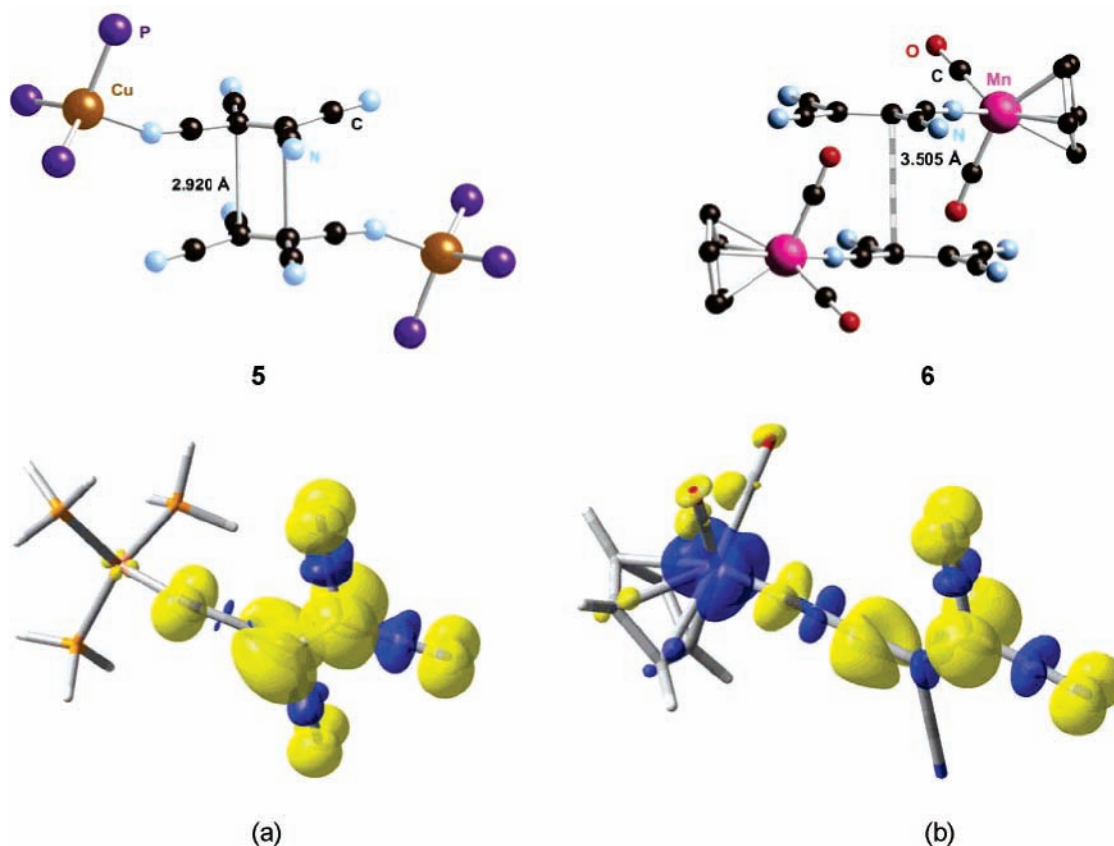


FIGURE 7. Spin density distribution for $\text{Cu}^{\text{I}}(\text{PPh}_3)_3(\text{TCNE})$ [represented by $\text{Cu}^{\text{I}}(\text{PH}_3)_3(\text{TCNE})$] (a) and $\text{Mn}^{\text{II}}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{TCNE})$ (b) (isosurface of $0.002 \text{ e}^-/\text{bohr}^3$ showing positive spin (blue) and negative (yellow) density regions).²¹

$\text{P}_2\text{CN}(i\text{-Pr})_2$ with BF_3 forms dimeric $[\text{P}_2\text{CN}(i\text{-Pr})_2]_2$ possessing sub-van der Waals $2\text{e}^- - 4\text{c}$ P–P bonds.²³

Multicenter C–C bonding

In addition to the $2\text{e}^- - 4\text{c}$ C–C bonding for $[\text{TCNE}]_2^{2-}$, multicenter π bonding or interactions have been described in the literature, although not characterized in detail as for $[\text{TCNE}]_2^{2-}$. Both $2\text{e}^- - 3\text{c}$ and $2\text{e}^- - 4\text{c}$ C–C bonds have been invoked for the successive one-electron -78°C oxidation products of [2.2.2.2]pagodane with $\text{SbF}_5/\text{SO}_2\text{-ClF}$;²⁴ however, $\{[2.2.2.2]\text{pagodane}\}^n$ ($n = 1+, 2+$) are unstable with rearrangements occurring.

The paucity of characterization undoubtedly arises in part from the computational complexity of larger systems, of which $[\text{TCNE}]_2^{2-}$ is the smallest, and thus its conceptual simplicity enables a $2\text{e}^- - 4\text{c}$ C–C bond to be drawn via two straight lines (**3** and **3'**). Dimeric examples of compounds exhibiting multicenter bonding include other dianions {e.g., 7,7,8,8-tetracyano-*p*-quinodimethanide, $[\text{TCNQ}]^{\bullet-}$,^{15,25} perfluoro-TCNQ $[\text{TCNQF}_4]^{\bullet-}$,^{25b,26} 2,3-dichloro-4,5-dicyanobenzoquinonide, $[\text{DDQ}]^{\bullet-}$,^{15,27}}, dications {e.g., tetrathiafulvalenium, $[\text{TTF}]^+$,²⁸ tetramethylphenylenediaminium, $[\text{TMPD}]^+$,²⁹ and octamethylbiphenylenium³⁰}, and neutral radicals (e.g., phenalenyl).³¹ These dimers all have sub-van der Waals intradimer separations and greater than four centers ($2\text{e}^- - n\text{c}$; $n > 4$), and frequently have slipped, not eclipsed, cofacial structures as solely occur for $[\text{TCNE}]_2^{2-}$. Being far more complex systems, they have not been characterized in detail but warrant further

theoretical and experimental studies, as is ongoing in our laboratories.

Besides dimers possessing multicenter C–C bonding, the electronic structure for several materials with extended linear chains exhibiting metal-like electrical conductivity have been described via a delocalized electron energy band (partially oxidized or reduced) that in reality is based on nearest neighbor multicenter C–C (π) bonding. This occurs for uniform segregated chains of reduced TCNQ exhibiting metal-like electrical conductivity. $[\text{TTF}][\text{TCNQ}]$ is a particularly excellent example because multicenter C–C bonding occurs for both the uniform segregated slipped chains of partially oxidized TTF and partially reduced TCNQ.³²

Recently the reaction of tetrakis(dimethylamino)ethylene, TDAE, with 1,2,4,5-tetracyanobenzene, TCNB, was reported to form $[\text{TDAE}][\text{TCNB}]_3 \cdot \text{MeCN}$.³³ The oxidation state of $[\text{TDAE}]^n$ ($n = 0, 1+, 2+$) was ascertained from the 1.511-Å central C–C bond distance, the 73.8° NCCN dihedral angle, and the ν_{NCN} doublet at 1671 and 1648 cm^{-1} that are expected for $n = 2+$.³⁴ Hence, from charge conservation $[\text{TDAE}]^{2+}[\text{TCNB}]_3^{2-}$ is present.

The intratrimer charge distribution was experimentally and computationally investigated to distinguish among the following formal distributions: (i) $[\text{TCNB}]^-[\text{TCNB}]^-[\text{TCNB}]^0$ {and $[\text{TCNB}]^-[\text{TCNB}]^0[\text{TCNB}]^-$ }, (ii) $[\text{TCNB}]^0[\text{TCNB}]^0[\text{TCNB}]^2-$ {and $[\text{TCNB}]^0[\text{TCNB}]^2-[\text{TCNB}]^0$ }, or delocalized (iii) $[\text{TCNB}]^{2/3-}[\text{TCNB}]^{2/3-}[\text{TCNB}]^{2/3}$, or (iv) $[\text{TCNB}]^{1/2-}[\text{TCNB}]^-[\text{TCNB}]^{1/2-}$, and iv was identified to be

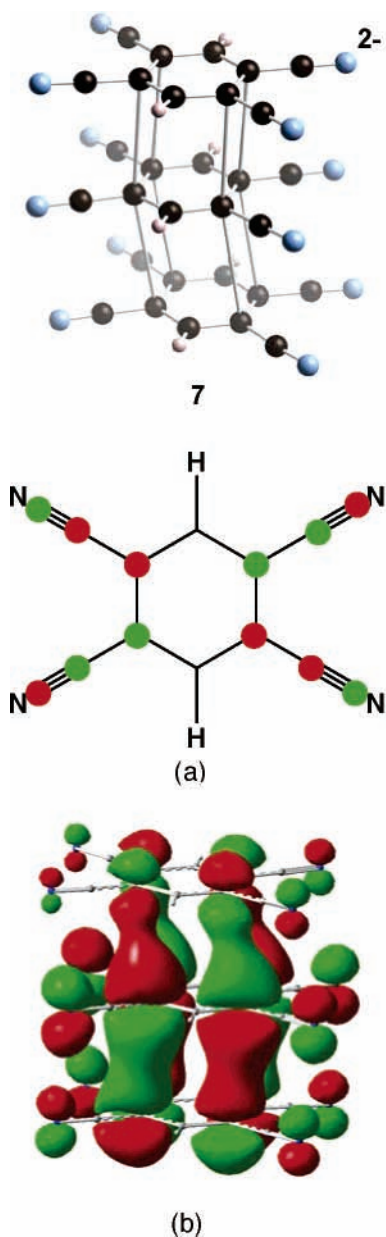


FIGURE 8. a_u $[\text{TCNE}]^{\cdot-}$ SOMO (or TCNE LUMO) (a) and a_u $[\text{TCNE}]_3^{2-}$ HOMO (b) with $2e^-$ –16c C–C bonding.

the best formal description.³³ Hence, the dianion is composed of an isolated triad of reduced TCNEs, **7**, with the 2- charge delocalized over the entire triad. DFT calculations at the MP2/6-31g(d) level indicate that the bonding for **7** is best described as the frontier a_u MOs on three TCNEs interacting to form a trimer a_u HOMO bonding orbital (Figures 8 and 9). It should be noted that the a_u $[\text{TCNE}]^{\cdot-}$ SOMO and consequently the a_u $[\text{TCNE}]_3^{2-}$ HOMO have nodes at the CH carbon atoms that are nonbonding components of the wavefunction and thus do not contribute to the overall bonding.^{35a} Hence, the $2e^-$ a_u HOMO of $[\text{TCNE}]_3^{2-}$ formed from three a_u TCNE MOs involves 12 sub-van der Waals C–C distances (**7**) and can be described as a $2e^-$ –24c C–C bonding orbital. However, due to the nodes at the CH carbon atoms, those four pairs of carbon atoms cannot contribute to the

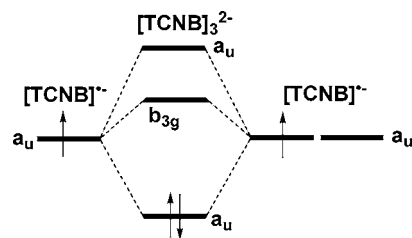


FIGURE 9. MO diagram arising from the overlap of three a_u MOs on each of three TCNEs forming the $[\text{TCNE}]_3^{2-}$ a_u HOMO.

overlap; hence, $[\text{TCNE}]_3^{2-}$ is best described as a $2e^-$ –16c C–C bonding interaction and represents a complex multicenter bonded system.

Conclusion and Future

Two-electron, four-center ($2e^-$ –4c) C–C bonding interactions (or bonds) have been established for $[\text{TCNE}]_2^{2-}$, and it is the prototype for other compounds and ions exhibiting multicenter C–C bonding. This is an embryonic area of organic chemistry where synthesis will undoubtedly lead to unexpectedly new examples with new attributes. Examples of multicenter bonding exist for cation, neutral radical, and anion dimers, as well as trimeric and extended chains. New examples are needed to develop a detailed understanding and exploitation of multicenter C–C bonding.

We wish to thank J. D. Bagnato, D. H. Barich, R. E. Del Sesto, D. M. Grant, P. Lafuente, R. Pugmire, W. W. Shum, J. P. Simons, M. Stromeier, and M. L. Taliaferro for their crucial contributions to various aspects of the work reported in this Account, as well as continued support from the U.S. Department of Energy (Grant No. DE FG 03-93ER45504).

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AR068175M