# Three-Electron Bond Valence-Bond Structures for the Ditetracyanoethylene Dianion

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ABSTRACT: Using valence-bond structures of the types $\dot{A} \cdot \dot{B}$ and $A \therefore B$ or $A \!-\! B$ to represent diatomic three-electron bonds, two types of valence-bond structures are constructed for the cyclic 6-electron 4-center bonding unit that is present in the ditetracyanoethylene dianion. These latter valence-bond structures, which are obtained by singlet spin-pairing the antibonding electrons of two three-electron bonds, are examples of increased-valence structures. It is shown that increased-valence structures that use the $\dot{A} \cdot \dot{B}$ three-electron bond structure, which relate easily to their component Lewis structures, should be preferred to those that involve the $A \therefore B$ or $A \!-\! B$ three-electron bond structures. STO-6G weights are reported for the two 6-electron 4-center increased-valence structures for the $[C_2]_2^{2-}$ component of the ditetracyanoethylene dianion.
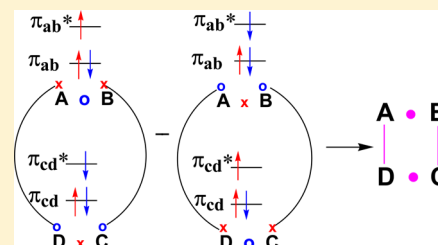
INTRODUCTION

In a recent paper,[1] Braida, Hiberty, and co-workers elucidated the nature of the multicenter bonding that arises in the central, rectangular C_4 component of the ditetracyanoethylene dianion complex $[TCNE]_2^{2-}$. They used *ab initio* valence-bond (VB) theory coupled with Quantum Monte Carlo methods. The analysis is interesting because as Schemes 2, 4, and 7 of ref 1 show, the C_4 component of $[TCNE]_2^{2-}$ involves a cyclic 6-electron 4-center bonding unit, i.e. six electron distributed among four overlapping atomic orbitals (AOs), as shown in Scheme 2 of ref 1. This bonding unit helps to bind together the two $[TCNE]^-$ radicals,[1] each of which possesses a diatomic three-electron bond (or three-electron two-orbital bond), symbolized as $A \therefore B$ in ref 1.

The authors of ref 1 did not realize that, since 1980, VB and related molecular orbital (MO) theories for rectangular, square, and extended 6-electron 4-center bonding units had been published on a number of occasions,[2] and it had been noted in ref 2e that the intermolecular C−C bonding for $[TCNE]_2^{2-}$ (with three-electron bonds as components) can be similarly described.

Each of the ref 2 publications uses $\dot{A} \cdot \dot{B}$ as the VB structure for a three-electron bond, whose orbital occupations differ (see below) from those for $A \therefore B$. The 6-electron 4-center VB structures of ref 2 are examples of "increased-valence" structures,[2−5] for which more electrons participate in bonding than does occur in the Lewis structures **1−10** in Scheme 4 of ref 1, or Figure 3 below.

In this Letter, I show why the increased-valence structures of ref 2 for 6-electron 4-center bonding units should be preferred to the 6-electron 4-center bonding VB structures of Scheme 7 of ref 1, which involve the $A \therefore B$ type three-electron bond structures.

This preference to use $\dot{A} \cdot \dot{B}$ as the three-electron bond structure is all-important because increased-valence structures for electron-rich molecules, with three-electron bonds as diatomic components, are considered to be part of the "intellectual heritage" of qualitative VB theory.[3] Therefore, increased-valence structures should use the best type of VB symbolism to represent them.

To illustrate aspects of theory, the results of some STO-6G VB calculations are reported for the $Na_2^{2+}[C_2]_2^{2-}$ component of $Na_2^{2+}[C_2H_4]_2^{2-}$ of ref 1.

VALENCE BOND STRUCTURES FOR THE DIATOMIC THREE-ELECTRON BOND

For the central, rectangular C_4 component of $[TCNE]_2^{2-}$, in Scheme 7 of ref 1 there are four (homopolar) three-electron bonds of the type $(\pi)^2(\pi^*)^1 = \overset{(-)}{\overset{\bullet\bullet}{C}} \overset{\bullet}{C} \leftrightarrow \overset{\bullet\bullet}{C} \overset{(-)}{\overset{\bullet}{C}}$, as in Scheme 3 of ref 1, in which π and π^* are bonding and antibonding MOs. Generalizing (for simplicity, without atomic formal charges), we have $(\pi_{ab})^2(\pi_{ab}^*)^1 = \dot{A} \ddot{B} \leftrightarrow \ddot{A} \dot{B} = (a)^1(b)^2 + (a)^2(b)^1$, in which a and b are overlapping $2p\pi$ atomic orbitals (AOs), and $\pi_{ab} = a + b$ and $\pi_{ab}^* = a - b$ are the resulting bonding and antibonding MOs.

In Scheme 7 of ref 1, the $A \therefore B$ type of VB structure is used to symbolize each $(\pi_{ab})^2(\pi_{ab}^*)^1$ three-electron bond configuration, in which the top dot is the antibonding electron. On occasions, $A \therefore B$ is also written as $A \!-\! B$.[2d,3−5] Each of $A \therefore B$ or $A \!-\! B$ (as well as the earlier Pauling VB structure[6] $A\cdots B$, which has been used recently in refs 7 and 8) is of course equivalent to the $\dot{A} \ddot{B} \leftrightarrow \ddot{A} \dot{B}$ bonding resonance. In Scheme 7 of ref 1, the two antibonding electrons in the two three-electron bonds for $[TCNE]_2^{2-}$ have opposed spins. Because their orbitals overlap,[1] the ground-state involves singlet spin-pairing for these electrons.

In 1960, Green and Linnett[9] transformed the $(\pi_{ab})^2(\pi_{ab}*)^1$-type MO configuration to show that it is proportional to the $(a)^1(\pi_{ab})^1(b)^1$ configuration,[2-5,9] with the spins of the a and b electrons opposed to that of the π_{ab} electron, as in Figure 1.
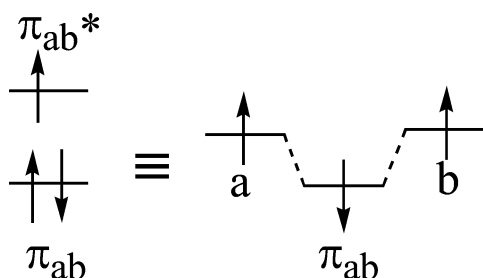

Figure 1. $(\pi_{ab})^2(\pi_{ab}*)^1 \propto (a)^1(\pi_{ab})^1(b)^1$ (for $S = S_z = 1/2$ electron spin quantum numbers).

Using crosses and circles (**x** and **o**) to represent electrons with s_z spin quantum numbers of $+1/2$ and $-1/2$, the resulting Green-Linnett VB structure is $\overset{x}{A}\,o\,\overset{x}{B}$ and $\overset{o}{A}\,x\,\overset{o}{B}$ when the antibonding $\pi_{ab}*$ electron has $s_z = +1/2$ and $-1/2$, respectively. If electron spins are not indicated, the Green-Linnett VB structure is $\dot{A}\cdot\dot{B}$.

VALENCE BOND STRUCTURES FOR CYCLIC 6-ELECTRON 4-CENTER BONDING UNIT

(a). Using $\dot{A}\cdot\dot{B}$ Type VB Structures for Three-Electron Bonds. Using the $\dot{A}\cdot\dot{B}$ type VB structure for a three-electron bond, it was shown in refs 2a–2d that when the antibonding electrons of two three-electron bond structures are singlet spin-paired, as in Figure 2, the cyclic 6-electron 4-center VB
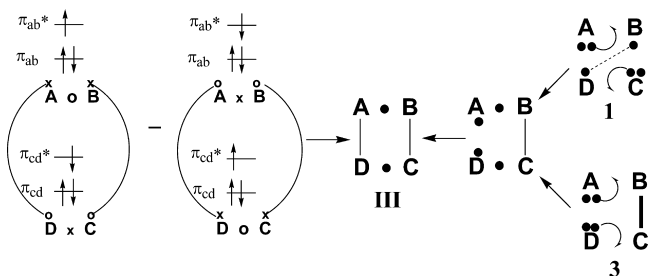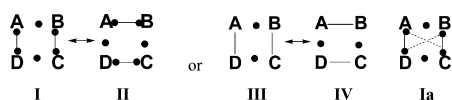

Figure 2. Construction of VB structure **III** (or **I**) by (i) singlet spin-pairing the antibonding electrons of the $(\pi_{ab})^2(\pi_{ab}*)^1$ and $(\pi_{cd})^2(\pi_{cd}*)^1$ three-electron bond configurations; (ii) delocalization of lone-pair electrons of the Lewis structures **1** and **3** of Scheme 4 of ref 1 (or Figure 3 here) into the π_{ab} and π_{cd} bonding MOs. The **A–B** and **C–D** bonds are in-plane π bonds (using $2p_y$ AOs), whereas the **A–D** and **B–C** bonds are σ-bonds.[1]

structures of the types $\mathbf{I}^{2d}$ and $\mathbf{II}^{2d}$ or $\mathbf{III}^{2a-c}$ and $\mathbf{IV}^{2a-c}$ are obtained. (In **III** and **IV**, the electrons that form the electron-pair bonds in **I** and **II** are not indicated.)

These VB structures involve fractional[10] (see below) nearest-neighbor and non-neighbor electron-pair bonds,[2,3] as well as one-electron bonds. For simplicity in representation of VB structures of this type, only the nearest-neighbor (**B–C**, **A–D**,

A–B, and **C–D**) electron-pair bonds are indicated.[2-5,10] However, if the non-neighbor **A–C** and **B–D** bonds are also included, structure **I** for example becomes structure **Ia**.

The lower-energy resonance between VB structures **I** and **II** or **III** and **IV** corresponds to the covalent component of a MO-configuration interaction wave function[2b-d,11] constructed from the four AOs.

Using identities of the type $\dot{A}\cdot\dot{B} = \dot{A}\ddot{B} \leftrightarrow \ddot{A}\dot{B}$ and Heitler-London AO wave functions for electron-pair bonds (for example, $a(1)b(2) + b(1)a(2)$ for the **A–B** electron-pair of VB structure **II** (or **IV**)), it is easy to deduce[2] that **I** (or **III**) and **II** (or **IV**) are equivalent to the $1 \leftrightarrow 2 \leftrightarrow 3 \leftrightarrow 4$ and $1 \leftrightarrow 2 \leftrightarrow 5 \leftrightarrow 6$ Lewis structure resonances, respectively, for which the Lewis VB structures **1–6** are displayed in Scheme 4 of ref 1 or Figure 3 here.
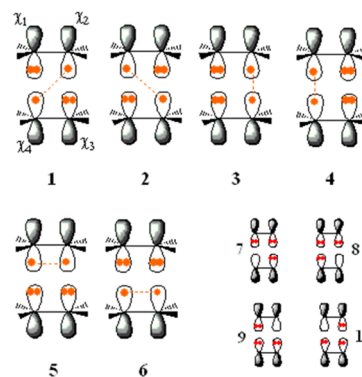

Figure 3. Lewis VB structures **1–6**. The χ_1, χ_2, χ_3, and χ_4 of ref 1 correspond to the a, b, c, and d AOs of this Letter. Structures **7–10** were not included in the VB calculations of ref 1 for the unsubstituted $Na_2^{2+}[C_2H_4]_2^{2-}$ diethylene complex. Reprinted with permission from ref 1. Copyright 2013 American Chemical Society.

Because each of the Lewis structures **3–6** has a nearest-neighbor (**B–C**, **A–D**, **A–B**, or **C–D**) electron-pair bond, and these bonds are absent from the "long-bond" Lewis structures **1** and **2**, the nearest-neighbor electron-pair bonds in VB structures **I–IV** are fractional[2,3,10] when structures **1** and **2** participate in resonance with either **3** and **4** or **5** and **6**.

(b). Weights for VB Structures 1–6, I or III and II or IV. In Table 2 of ref 1, the Coulson-Chirgwin weights[12] for structures **1–6** of Table 1 are reported again here in Table 1 for

Table 1. Coulson-Chirgwin Weights for Structures 1–6 of Figure 3 and I and II (or III and IV)

	1,2	3,4	5,6	I	II
ref 1, Table 2	0.219	0.211	0.071		
$[C_2]_2^{2-}$ STO-6G, 10 electrons	0.237	0.203	0.060	0.733	0.267
$[C_2]_2^{2-}$ STO-6G, 26 electrons	0.253	0.209	0.038	0.795	0.205

the unsubstituted $Na_2^{2+}[C_2H_4]_2^{2-}$ diethylene complex. Here we report the results of two sets of STO-6G VB calculations for the $Na_2^{2+}[C_2]_2^{2-}$ component of $Na_2^{2+}[C_2H_4]_2^{2-}$ (see the Appendix for methodology) in order to focus attention on the cyclic 6-electron 4-center bonding unit:

(a) including only the electrons that form the $[C_2]_2^{2-}$ 6-electron 4-center bonding unit, together with four electrons that form the two C–C σ-bonds of the diethylene; (b)

including the remaining 16 electrons of $[C_2]_2^{2-}$ in 1s and 2s AOs.

The STO-6G weights for structures **1–6** (Table 1) are similar to those reported in ref 1, which implies that increased-valence structure **I** ($\equiv$ **1** $\leftrightarrow$ **2** $\leftrightarrow$ **3** $\leftrightarrow$ **4**) should have a substantially larger weight than has increased-valence structure **II** ($\equiv$ **1** $\leftrightarrow$ **2** $\leftrightarrow$ **5** $\leftrightarrow$ **6**). The results of the STO-6G calculations (Table 1) show that structure **I** is dominant.

Two reasons account for the larger weights for structures **3**, **4**, and **I** compared with those for structures **5**, **6**, and **II**.

(i) To first order in AO overlap

$$\langle\Psi_1|\Psi_3\rangle = \langle\Psi_1|\Psi_4\rangle = \langle\Psi_2|\Psi_3\rangle = \langle\Psi_2|\Psi_4\rangle \propto S_{ab} = S_{cd}$$
$$= 0.43^1$$

$$\langle\Psi_1|\Psi_5\rangle = \langle\Psi_1|\Psi_6\rangle = \langle\Psi_2|\Psi_5\rangle = \langle\Psi_2|\Psi_6\rangle \propto S_{ad} = S_{bc}$$
$$= 0.19^1$$

i.e. the Ψ_1 and Ψ_2 wave functions for structures **1** and **2** overlap better with Ψ_3 and Ψ_4 than they do with Ψ_5 and Ψ_6.

(ii) Like atomic formal charges are better separated for structures **3** and **4** than they are for structures **5** and **6**.

Because there are three nonequivalent types of VB structures in Figure 3, the **1** $\leftrightarrow$ **2** $\leftrightarrow$ **3** $\leftrightarrow$ **4** $\leftrightarrow$ **5** $\leftrightarrow$ **6** resonance involves two independent variational parameters. The $\Psi = \Psi_I + \lambda\Psi_{II}$ involves only one variational parameter (λ). Therefore, the energy for the **I** $\leftrightarrow$ **II** resonance must lie above the energy for the **1** $\leftrightarrow$ **2** $\leftrightarrow$ **3** $\leftrightarrow$ **4** $\leftrightarrow$ **5** $\leftrightarrow$ **6** resonance.

(c). Using A∴B Type VB Structures for Three-Electron Bonds. Scheme 7 of ref 1 uses **A∴B** as the three-electron bond type of VB structure. When the antibonding electrons for each pair of **A∴B** (or **A∸B**)$^{2d,3-5}$ three-electron bonds are singlet spin-paired, VB structures **V** and **VI** or **VII** and **VIII** are obtained.
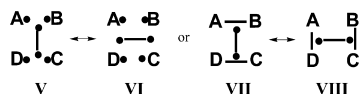
Because the wave functions for $\dot{A} \cdot \dot{B}$ and **A∴B** (or **A∸B**) are equivalent (cf. Figure 1), the VB structures of **V–VIII** can also be considered to be examples of "increased-valence" structures. However, structures **V–VIII** show less clearly the nature of the bonding between pairs of atoms than do VB structures **I–IV**.

The use of the identity $\dot{A} \cdot \dot{B} = \dot{A}\,\ddot{B} \leftrightarrow \ddot{A}\,\dot{B}$ relates the increased-valence structures **I–IV** more immediately to their component Lewis VB structures **1–6** than do either **A∴B** or **A∸B** $= \dot{A}\,\ddot{B} \leftrightarrow \ddot{A}\,\dot{B}$ for increased-valence structures **V–VIII**. The location of the electron-pair bond that links the two three-electron bonds in each of the structures **V–VIII** does not occur in any of its component Lewis structures.

CONCLUSION

Three-electron bond structures of the $\dot{A} \cdot \dot{B}$ type occur extensively as components of easily constructed increased-valence structures.$^{2-5}$ These types of increased-valence structures help to provide qualitative VB representations of the electronic structures for a large number of triatomic and polyatomic electron-rich molecules.$^{2-5}$ In ref 13, these types of increased-valence structures are displayed for the cyclic and extended 6-electron 4-center bonding units that arise in spiral chain O_4 polymers. Some of the earlier publications that also

use increased-valence structures of types **I** and **II** (or **III** and **IV**) include those of refs 14 and 15.

APPENDIX

Method for STO 6G VB Calculations

The $Na^+-[C_2]_2^{2-}-Na^+$ geometry of ref 1 for $Na^+-[C_2H_4]_2^{2-}-Na^+$($C_A-C_B = C_C-C_D = 1.46$ Å, $C_A-C_D = C_B-C_C = 2.75$ Å, $Na^+-Na^+ = 6.93$ Å) was used in the STO 6G VB calculations, for which the AOs a, b, c, and d are $2p_y$ AOs. The Na^+ ions were replaced by H^+ ions. The four electrons that form the C_A-C_B and C_C-C_D electron-pair σ bonds were accommodated in two $\sigma 2p_x$ bonding MOs, with no $2s-2p_x$ hybridization. Each of the 2s and 2p AOs was assigned a $C^{-1/2}$ Slater orbital exponent of 1.5375, and a Slater orbital exponent of 5.7 was used for the 1s AOs.

For the cyclic 6-electron 4-center bonding unit of $[C_2]_2^{2-}$, the (unnormalized) $\Psi(I) \equiv \Psi(III)$ and $\Psi(II) \equiv \Psi(IV)$ are given by eqs 1–6 (see for example eqs 1–6 of ref 14d, with $k = l = 1$ in the MOs)

$$\Psi(I) = |\psi_{ab}\bar{\psi}_{ab}\psi_{cd}\bar{\psi}_{cd}\psi^*_{ab}\bar{\psi}^*_{cd}| + |\psi_{ab}\bar{\psi}_{ab}\psi_{cd}\bar{\psi}_{cd}\psi^*_{cd}\bar{\psi}^*_{ab}| \tag{1}$$

$$\propto |a\,\bar{\psi}_{ab}\psi_{cd}\bar{c}\,b\,\bar{d}| + |\psi_{ab}\bar{a}\,c\,\bar{\psi}_{cd}d\,\bar{b}| \tag{2}$$

$$\propto \Psi_1 + \Psi_2 - \Psi_3 - \Psi_4 \tag{3}$$

$$\Psi(II) = |\psi_{ad}\bar{\psi}_{ad}\psi_{bc}\bar{\psi}_{bc}\psi^*_{ad}\bar{\psi}^*_{bc}| + |\psi_{ad}\bar{\psi}_{ad}\psi_{bc}\bar{\psi}_{bc}\psi^*_{bc}\bar{\psi}^*_{ad}| \tag{4}$$

$$\propto |a\,\bar{\psi}_{ad}\psi_{bc}\bar{c}\,d\,\bar{b}| + |\psi_{ad}\,\bar{a}\,c\,\bar{\psi}_{bc}b\,\bar{d}|) \tag{5}$$

$$\propto \Psi_1 + \Psi_2 - \Psi_5 - \Psi_6 \tag{6}$$

in which $\psi_{ab} = a + b$, $\psi_{cd} = c + d$, $\psi_{ad} = a + d$, and $\psi_{bc} = b + c$. The presence or absence of a bar ($^-$) over the orbital specifies a β or α electron spin wavefunction.

The calculations were performed using Roso's *ab initio* VB program as used in refs 2c and 16, for example.

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Notes
The authors declare no competing financial interest.

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(10) A fractional electron-pair bond has a bond number less than unity[2−5] and is represented by a thin bond line in the VB structures.[2−5] With two homopolar one-electron bonds in each of the VB structures **I**−**IV**, the fractional **A**−**C**, **A**−**D**, **B**−**C**, and **B**−**D** bond numbers are 0.25 in structures **I** and **III**. In structures **II** and **IV**, the bond number for each of the fractional **A**−**B**, **A**−**C**, **B**−**D**, and **C**−**D** bonds is also equal to 0.25 (cf. refs 2a,2b).

(11) The three lowest-energy ^1A_g MO configurations are $\Phi_1 = (a_g)^2(b_{3u})^2(b_{2u})^2$, $\Phi_2 = (a_g)^2(b_{3u})^2(b_{1g})^2$, and $\Phi_3 = (a_g)^2(b_{2u})^2(b_{1g})^2$, each of which has been expressed as a Ψ(covalent) + Ψ(ionic) type wave function.[2b−d] There are two Ψ(covalent) type wave functions, which relate to structures **1** and **2** and either **3** and **4** or **5** and **6** of Figure 3. For the Ψ(ionic) type wave functions, structures **7**−**10** of Scheme 4 of ref 1 replace structures **1** and **2**. The a_g, b_{3u}, b_{2u}, and b_{1g} MOs are those of Scheme 2 of ref 1. Other theorems, which are not needed here, can also be developed.

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■ NOTE ADDED IN PROOF

See ref 2d and ref 36 therein for diatomic three-electron bond theory with three or more AOs. It has also been concluded that the three-electron bond "probes the ultimate limits of valence for electron-rich molecules."[17]