Electronic Structure



A New Conformation With an Extraordinarily Long, 3.04 Å Two-Electron, Six-Center Bond Observed for the π -[TCNE]₂²⁻ Dimer in [NMe₄]₂[TCNE]₂ (TCNE = Tetracyanoethylene)

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Dedicated to Professor Jack Simons on the occasion of his 70th Birthday

Abstract: $[NMe_4]_2[TCNE]_2$ (TCNE = tetracyanoethenide) formed from the reaction of TCNE and (NMe₄)CN in MeCN has v_{CN} IR absorptions at 2195, 2191, 2172, and 2156 cm⁻¹ and a v_{cc} absorption at 1383 cm⁻¹ that are characteristic of reduced TCNE. The TCNEs have an average central C-C distance of 1.423 Å that is also characteristic of reduced TCNE. The reduced TCNE forms a previously unknown noneclipsed, centrosymmetric π -[TCNE]₂²⁻ dimer with nominal C₂ symmetry, 12 sub van der Waals interatomic contacts < 3.3 Å, a central intradimer separation of 3.039(3) Å, and comparable intradimer C---N distances of 3.050(3) and 2.984(3) Å. The two pairs of central C---C atoms form a \leq C–C-C–C of 112.6° that is substantially greater than the 0° observed for the eclipsed $D_{2h} \pi$ -[TCNE]₂²⁻ dimer possessing a two-electron, four-center (2e⁻/4c) bond with two C···C components from a molecular orbital (MO) analysis. A MO study combining CAS(2,2)/MRMP2/cc-pVTZ and atoms-inmolecules (AIM) calculations indicates that the non-eclipsed,

Introduction

The concept and implications of chemical bonding are core aspects of chemistry^[1] that continue to attract attention even as we approach the centennial anniversary of G. N. Lewis' land-

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	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201501963. It contains Ortep drawings, HOMO and LUMO and optimum geometries of D_{2h} and $C_2 \pi$ -[TCNE] ₂ ²⁻ , and estimated energy gain induced by the overlap of two p orbitals of π symmetry placed each in one atom.

 $C_2 \pi$ -[TCNE]₂²⁻ dimer exhibits a new type of a long, intradimer bond involving one strong C---C and two weak C---N components, that is, a 2e⁻/6c bond. The $C_2 \pi$ -[TCNE]₂²⁻ conformer has a singlet, diamagnetic ground state with a thermally populated triplet excited state with $J/k_{\rm B} = 1000 \, {\rm K}$ (700 cm⁻¹; 86.8 meV; 2.00 kcal mol⁻¹; $H = -2JS_a \cdot S_b$); at the CAS(2,2)/MBMP2 level the triplet is computed to be 9.0 kcal mol⁻¹ higher in energy than the closed-shell singlet ground state. The results from CAS(2,2)/NEVPT2/cc-pVTZ calculations indicate that the C_2 and D_{2h} conformers have two different local metastable minima with the C_2 conformer being 1.3 kcalmol⁻¹ less stable. The different natures of the C_2 and D_{2h} conformers are also noted from the results of valence bond (VB) qualitative diagram that shows a 10e⁻/6c bond with one C···C and two C···N bonding components for the C_2 conformer as compared to the $6e^{-1/4c}$ bond for the D_{2h} conformer with two C-C bonding components.

mark description of covalent bonding.^[2] Organic chemistry has been exceptionally well served by this two-electron, twocenter ($2e^{-}/2c$) bonding description and the concept of resonance. The study of electron-deficient boranes expanded bonding concepts to more than two centers,^[3] but $2e^{-}/2c$ bonding suffices for the vast majority of C–C bonds.

The structure of D_{2h} eclipsed π -[TCNE]₂²⁻ (TCNE = tetracyanoethylene), Figure 1 a, possesses a substantial sub van der Waals intradimer separation of about 2.9 Å, and a 2e⁻/4c C–C molecular orbital (MO) bonding description is invoked.^[4] Albeit computed to be metastable, the isolated dimers share many of the features of a conventional 2e⁻/2c covalent bond,^[4–6] including a bond critical point from an atoms-in-molecules (AIM) analysis,^[5,7] although this is not always an accepted description of a bond as both false positive and false negative examples have been reported.^[8] This 2e⁻/4c C–C bonding is a new type of bond, first termed a long, multicenter bond.^[4,5] Alternatively, a valence bond (VB) study later described this as a 6e⁻/4c bond with three electrons placed in the p_z orbitals of the two central C atoms.^[9] This allows two equivalent resonance forms, each with a 2e⁻/2c bond between two of the overlapping cen-

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Figure 1. Perspective view (a) and a description of the electronic structure requiring two VB determinants having a $2e^{-}/2c$ bonds (b) and one determinants having two $3e^{-}/2c$ bonds (c) for $D_{2h} \pi$ -[TCNE]₂²⁻, as well as perspective (d) and top (e) views of the noneclipsed $C_2 \pi$ -[TCNE]₂²⁻ (the atoms with yellow surfaces are below) present in [NMe₄]₂[TCNE]₂.

tral C atoms of each fragment (Figure 1 b), and a third resonant form in which two 3e⁻/2c bonds form among the central C atoms (Figure 1 c). This 6e⁻/4c VB description is numerically equivalent^[10] to the results from a CASSCF(6,4) MO study,^[11] and also gives nearly identical orbital occupation numbers for the SOMO \pm SOMOs than does a CASSCF(2,2) study,^[12-14] and are in agreement with the results from RASSCF computations using very large active spaces of near-full configuration interaction (CI) quality for the dimer π orbitals.^[12]

The long, intradimer bond found for π -[TCNE]₂²⁻ is prototypical of a growing number of organic compounds that are best described by multicenter bonding.^[15-20] To date there are about 30 structural determinations of the eclipsed, D_{2h} π -[TCNE]₂²⁻ dimer (Figure 1 a) with cations that range from small with significant electrostatic interactions, for example, K⁺,^[4,5,21] to distant bulky cations with reduced electrostatic interactions, for example, [Cr(C₆H₆)₂]⁺.^[22] Geometrically, all examples (~30) of D_{2h} π -[TCNE]₂²⁻ are essentially identical with eclipsed, reduced TCNE moieties with a 2.895±0.047 Å intradimer separation, the C–CN moieties bend away from the nominal TCNE plane by on average 5.0° (thus, the central C atoms are slightly pyramidal and deviate from sp² character), and a \preccurlyeq C–C···C–C dihedral angle between the central CC bonds of 0° is found.^[4,5]

As part of a project aimed at enhancing our knowledge of unusually long multicenter CC bonds, and bonding in general, the systematic study of the physical properties of π -[TCNE]₂²⁻ has led to several examples possessing the aforementioned eclipsed geometry. [NMe₄]₂[TCNE]₂ reported herein is anomalous due to it lacking the robust eclipsed D_{2h} π -[TCNE]₂²⁻ structure, and it is the first example with local C_2 symmetry.

Results and Discussion

The reaction of TCNE and (NMe₄)CN^[23] in MeCN forms a purple crystalline solid^[24] with $\nu_{\rm CN}$ absorptions at 2195, 2191, 2172, and 2156 cm^{-1} that differ from the three absorptions at 2191, 2172, and 2162 cm⁻¹ that are typical of the eclipsed D_{2h} π -[TCNE]₂^{2-.[5]} Nonetheless, they are in the range attributed to monoreduced TCNE.[25] However, the absorption at 1383 cm⁻¹ is assigned to $\nu_{\rm CC}$, but it is 20 cm⁻¹ higher in frequency than is typically observed for D_{2h} π -[TCNE]₂²⁻. In accord with the indication that the reduced TCNE is neither the above D_{2h} π -[TCNE]₂²⁻ nor the σ-dimer, $[C_4(CN)_8]^{2-,[26]}$ its structure was elucidated, Figure 1 d,e and Figure S1 in the Supporting Infor-

mation.^[27] The TCNEs have average C--CN and central C--C and distances of 1.417 and 1.423 Å, respectively, in accord with D_{2h} π -[TCNE]₂²⁻. In sharp contrast, however, this new reduced TCNE forms dimers with local C_2 symmetry with twelve < 3.3 Å intradimer separations ranging from 2.947 to 3.168 Å, that average 3.048 ± 0.075 Å, Figure 1 d,e. The central, intradimer CC distance is 3.039(3) Å, while the two shortest intradimer C···N distances are 3.050(3) and 2.984(3) Å. The nitrile groups are slightly bent away from the nominal TCNE plane by about 4.5°; thus, the central C atoms are slightly pyramidalized, that is, mixing some sp³ into the dominant sp² character. This is in accord with an average out-of-the plane bending of 5.0° for $D_{2h} \pi$ -[TCNE]₂^{2-[4,5]} Furthermore, the 112.6° \leq C–C-C dihedral angle is substantially greater than 0° for the eclipsed D_{2h} π -[TCNE]₂²⁻. Except for different orientation, the geometrical features are similar to those for $D_{2h} \pi$ -[TCNE]₂²⁻, thus suggesting that a long, intradimer bond is also present for the noneclipsed $C_2 \pi$ -[TCNE]₂²⁻ conformer. Hence, it is a new type of long, multicenter bond with an intradimer CC distance of 3.039 Å; 5% longer than that observed for the eclipsed D_{2h} π - $[\text{TCNE}]_2^{2-}$ conformer (Figure 1 a).

Further support for the presence of a long, intradimer bond in $C_2 \pi$ -[TCNE]₂²⁻ comes from magnetic measurements. The magnetic susceptibility, $\chi(T)$, of [NMe₄]₂[TCNE]₂ was measured above 5 K in a 3 kOe applied magnetic field, Figure 2.^[28] [NMe₄]₂[TCNE]₂ exhibits a diamagnetic response in accord with its closed-shell, singlet ground state as occurs for the eclipsed $D_{2h} \pi$ -[TCNE]₂^{2-,[4,5]} and is inconsistent with the presence of S =1/2 [TCNE]⁻. However, for $D_{2h} \pi$ -[TCNE]₂²⁻ above about 250 K, $\chi(T)$ increases suggestive of thermal population of the triplet state. The $\chi(T)$ data were fitted to the Bleaney–Bower's expression [Eq. (1); for $H = -2JS_a \cdot S_b$] for coupled spins, in which $N_A =$ Avogadro's constant, k_B =Boltzmann's constant, g=Landé g-

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Table 1. Shortest inter-fragment C···C distance (Å) for the D_{2h} and $C_2 \pi$ -[TCNE]₂²⁻ conformers and computed orbital occupation number for the SOMO ± SOMOs (n_{b-SOMO} and $n_{ab-SOMO}$ in e⁻). Also given is the interaction energy, E_{intr} relative to the four ionic fragments, E_{int} (4), the interaction energy relative to two radical anions, E_{int} (2), and the energetic components of the latter [that is, exchange-repulsion, E_{er} electrostatic, E_{el} , dispersion, E_{disp} , and bonding, E_{bond} : $E_{er} + E_{el} + E_{disp} + E_{bond} = E_{int}$ (2)].^[31] The difference between the singlet, E(S), and triplet, E(T), total energy is computed as $E_{S-T} = E$ (S)–E(T). All energies were calculated at the MRMP2 level^[32] (as described in the Supporting Information) and are given in kcal mol⁻¹.

	r _{cc} [Å]	Method	n _b	n _{ab}	$E_{\rm int}(4)$	$E_{\rm int}(2)$	E _{er}	E _{el}	$E_{\rm disp}$	E _{bond}	E _{st}
D _{2h}	2.89 ^[a]	CAS(2,2)/MRMP2	1.63 ^[c]	0.37 ^[c]	-200.6	43.0	20.1	60.8	-25.8	-12.1	-14.1
	2.89 ^[a]	CAS(2,2)/NEVPT2	1.63	0.37		39.3				-12.1	-15.3
	2.63 ^[b]	CAS(2,2)/NEVPT2	1.81	0.19		36.4					[e]
C ₂	3.04 ^[a]	CAS(2,2)/MRMP2	1.54 ^[d]	0.46 ^[d]	-161.4	44.3	17.3	54.1	-21.0	-8.0	-9.0
	3.04 ^[a]	CAS(2,2)/NEVPT2	1.54	0.46		40.1				-8.0	-10.6
	2.82 ^[b]	CAS(2,2)/NEVPT2	1.67	0.33		39.6					[e]

[a] Geometry from the crystal. [b] Geometry optimized using CASSCF(2,2)/NEVPT2 calculations. [c] These values respectively become 1.70 and 0.32 using a CASSCF(6,4) calculation and 1.81 and 0.23 using a CASSCF(22,20) calculation. [d] These values respectively become 1.60 and 0.41 using a CASSCF(6,4) calculation. [e] When the optimum geometry of the triplet is computationally searched, starting from the experimental structure, the computed energy of the dimer exceeds that of the two [TCNE]⁻⁻ fragments and no minimum is found.

value, $\mu_{\rm B}$ = Bohr magneton, *S* = spin quantum number (i.e., 1/2), and θ is the intradimer coupling for the thermal population of the triplet state. (The second term of Equation (1) accounts for unpaired spin impurities arising from defects sites.^[29]) The data can be fit to Equation (1) with ρ = 0.01, θ = 0 K, and *J*/*k*_B = 1000 K (700 cm⁻¹; 86.8 meV; 2.00 kcal mol⁻¹), Figure 2.



Figure 2. $\chi(7)$ (x) for [NMe₄]₂[TCNE]₂ and the fit (-----) of the data to Equation (1).

$$\chi = (1 - \rho) \frac{2N_{\rm A}g^2\mu_{\rm B}}{k_{\rm B}(T - \theta)(3 + e^{\frac{2i}{k_{\rm B}T}})} + \rho \frac{N_{\rm A}g^2\mu_{\rm B}^2S(S + 1)}{3k_{\rm B}T}$$
(1)

The electronic structure of $C_2 \pi$ -[TCNE]₂²⁻ was computationally characterized by CAS(2,2)/MRMP2 and CAS(2,2)/NEVPT2 computations on the observed structure, using the cc-pVTZ basis set, Table 1, Figure 3. A MO analysis reveals that the $C_2 \pi$ -[TCNE]₂²⁻, akin to the D_{2h} conformer,^[5] has a non-negligible overlap between the SOMOs providing the type of MO diagram found for conventional covalent bonds. Thus, the ground electronic state^[30] is due to 1) the overlap of the two [TCNE]^{*-} fragments orbitals yielding a bonding and antibonding combination, and 2) double occupation of each of the bonding and antibonding combinations for the doubly occupied orbitals and the SOMO + SOMO combination of the fragments. Thus,



Figure 3. a) Side and b) top views of the HOMO, and c) side and d) top views of the LUMO for $C_2 \pi$ -[TCNE]₂^{2–} (cutoff of 0.02 atomic units). e) 3D and f) contour view of the [TCNE]⁺ SOMO, and g) three bond critical points identified from an AIM analysis of the closed shell singlet electron density for [NMe₄]₂[TCNE]₂.

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the ground state should be a diamagnetic, closed-shell singlet similar to the D_{2h} conformer,^[5] as observed. The first excited singlet state is computed to be open-shell and results from exciting one electron from the SOMO + SOMO combination to the SOMO – SOMO combination. According to the results from the CAS(2,2)/MRMP2 calculations (Table 1), the triplet states for the C_2 and D_{2h} conformers are 9.0 and 14.1 kcal mol⁻¹, respectively, above their closed-shell singlet ground states.

This multireferent character of the wavefunction describing these systems is manifested in the occupation number of the bonding and antibonding combinations of the SOMOs.^[33] For the C_2 conformer the computed orbital occupation numbers are 1.6 and 0.4 e⁻, respectively, which differ slightly from the values of 1.8 and 0.2 e⁻, respectively, found in the D_{2h} conformer (Table 1).^[5] Both sets of numbers significantly differ from



Figure 4. Potential energy curves for the D_{2h} and C_2 conformations of the π -[TCNE]₂²⁻ dimer computed at the CAS(2,2)/MRMP2 level (see Figure 1 d,e for the geometries).

that expected for a monoreferent closed-shell singlet state (i.e., 2 and 0 e⁻, respectively). The $C_2 \pi$ -[TCNE]₂²⁻ structure is also predicted to have a closed-shell singlet ground state 9.0 kcal mol⁻¹ below the lowest lying triplet state at the MBMP2 level, and is about 70% of the 14.1 kcal mol⁻¹ computed for $D_{2h} \pi$ -[TCNE]₂²⁻ by the same method.^[5]

Both conformations have a similar computed interaction energy (E_{int}) and stability with respect to dissociation into two [TCNE]^{•–} fragments (Table 1), but the D_{2h} conformer is slightly more stable than the C_2 conformer (by 1.3 and 0.8 kcal mol⁻¹ at the CAS(2,2)/MRMP2 and CAS(2,2)/NEVPT2 levels,^[34] respectively), and the results from the latter methodology have different local metastable minima in their potential energy surface (Figures 4 and 5).^[35] Hence, a polymorph possessing the more prevalent D_{2h} conformer might be observed, perhaps from a different solvent; however, this has yet to be noted.

The C_2 and $D_{2h} \pi$ -[TCNE]₂²⁻ conformers share the same metastable character with respect to its dissociation into two [TCNE]^{*-} fragments^[5] (i.e., $E_{int}(2) > 0$, Table 1; Figure 4).



Figure 5. Shape of the potential energy surface $E(d_x,d_y)$ for a) the D_{2h} and b) the C_2 conformations around the experimental geometry indicating c) the d_x (red) and d) the d_y (green) directions located at the center of the surface. The lower molecules are fixed and the upper ones move as indicated by the green (*y* axis) and red (*x* axis). In both surfaces the (0,0) point corresponds to the experimental geometry, that is, the dimer when the upper molecule is not displaced. c) and d): Movement along *x* in c) displaces the upper molecule along the central C–C bond versus the fixed molecule; thus, decreasing the energy. Movement along *y* induces a lateral motion of the molecule downward in d) and the energy increases, but then is slightly reduced (red region) when the two nitrile groups overlap. The curves were computed when the two fragments were at their experimental geometry.

However, although moderately repulsive, once formed the dimers do not dissociate due to the barriers with respect to dissociation, Figure 4. (These barriers were computationally identified to originate from the competition between the stabilizing E_{bond} and the destabilizing E_{el} components of $E_{\text{int}}(2)$.⁽³⁶⁾

Note that computationally both π -[TCNE]₂²⁻ conformers become energetically stable only when the cations are included, as the sum of the attractive cation⁺···anion⁻ interactions exceed the sum of the repulsive cation⁺···cation⁺ and anion⁻ ···anion⁻ interactions (that is, $E_{int}(4) < 0$, Table 1).^[5]



The nature of E_{int} for the C_2 and D_{2h} conformers was also quantitatively compared by looking at the relative strength of the E_{int} components, that is, $E_{\rm er}$, $E_{\rm el}$, $E_{\rm disp}$, and $E_{\rm bond}$, Table 1. $E_{\rm el}$ dominates for both conformations and destabilizes E_{int} , while for both conformers $E_{\rm disp} \approx 40\%$ $|E_{\rm el}|$ is stabilizing. For the closed-shell single state, the stabilizing Ebond is approximately equal to $E_{disp}/2$. Nonetheless, despite this small relative weight of the bonding component, it is the key component indicating the energetic preference for the singlet state. Note, that the energy differences in the com-



Figure 6. Qualitative VB illustration of a) the C(central)···C(central) and b) the two weaker C(central)···N $3e^{-/2c}$ bonding components for $C_2 \pi$ -[TCNE]₂²⁻.

ponents of E_{int} between the C_2 and D_{2h} conformers are not constant. Thus, while E_{el} is 6.7 kcal mol⁻¹ more repulsive for the D_{2h} with respect to the C_2 conformer (due to the eclipsed orientation of the two interacting fragments in the D_{2h} conformer), the E_{disp} and E_{bond} components are also 4.8 and 4.1 kcal mol⁻¹ more stable for the D_{2h} conformer.

The aforementioned MO results show that the C_2 conformer has the same electronic structure and $E_{int}(2)$ interaction energy as the D_{2h} conformer. Hence, in accord with all the criteria used before to determine the presence of an intradimer bond for the D_{2h} conformer, an intradimer bond is also present for C_2 π -[TCNE]₂²⁻.

The differing structures, however, lead to very important differences in their electronic properties. Their MO diagrams are similar with an identical occupation of the fragment SOMO+ SOMO and SOMO-SOMOs, and a predominantly closed-shell singlet ground state. However, due to their different geometries they have different bonding overlaps that impact their important electronic properties. The C_2 conformer has three short intradimer contacts: one C(central)...C(central) and two C(central)...N. A detailed analysis of the SOMO + SOMO combinations for the C_2 (Figure 3a-d,f) and D_{2h} (Figure S1 in the Supporting Information) conformers show regions in which the two SOMOs simultaneously maximize their in-phase overlap, with minimal out-of-phase overlap; thus, maximizing the net overlap, and the bonding energy component, E_{bond} . Also, the electrostatic repulsion is minimized (Table 1) creating a local minimum.

The MO diagrams and the orbital occupation numbers (Table 1) indicate that the HOMO involves two electrons, one from each fragment SOMO. Thus, in the MO methodology the long bond in the C_2 conformer is a 2e⁻/6c, bond, and thus, differs from the 2e⁻/4c description for the D_{2h} conformer.^[5] The AIM analysis of the electron density computed at the CAS(2,2)/MRMP2 level indicates that three intradimer bond critical points (bcps) are located in the three aforementioned regions for the C_2 conformer, and two for the D_{2h} conformer,^[5] Figure S2c in the Supporting Information.

The different intradimer bonding in the C_2 and D_{2h} conformers are also noted from a qualitative VB analysis. For the C_2 conformation the electronic distribution in each [TCNE]⁺⁻ fragment (Figures 1 b,c and 6) and the type of bonds that they allow (i.e., $1e^{-}/2c$, $2e^{-}/2c$, and $3e^{-}/2c$ types, Figure S2 in the Supporting Information) indicates that some [TCNE]⁺⁻ fragment resonant forms allow the simultaneous presence of a $3e^{-}/2c$ C(central)···C(central) bonding component (Figure 6a), and two $3e^{-}/2c$ C(central)···N bonding components for the C_2 conformer (Figure 6b) in agreement with the MO analysis. Thus, at the VB level the C_2 conformer has a $10e^{-}/6c$ bond with one central C···C and two weaker, lateral C···N bonding components.

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Conclusion

The C_2 conformation of π -[TCNE]₂²⁻ observed in [NMe₄]₂[TCNE] differs significantly from the eclipsed, D_{2h} conformation reported for about 30 other cations. The C_2 conformation is computed to be 1.3 kcal mol⁻¹ less stable than the D_{2h} conformation, and both conformations are minima in their potential energy surfaces. Both conformations have a long, multicenter C–C bond between its two [TCNE]⁺ fragments and the interaction energy (E_{int}) is dominated by the electrostatic component (E_{el}). However, due to their different geometries, the nature of the intradimer bond in the C_2 and D_{2h} conformers differs, being 2e⁻/6c and 2e⁻/4c in a MO description for the C_2 and D_{2h} conformer has a 6e⁻/4c bond, whereas for the C_2 conformer has a 10e⁻/6c bond, and both VB descriptions are equivalent to their respective MO description.

Besides the repulsive (radical anion)⁻...(radical anion)⁻ interactions, the π -[TCNE]₂²⁻ conformational preference is expected to be strongly affected by the size and shape of the adjacent cations. These are accounted for by E_{el} and E_{er} while smaller cations have a larger E_{el} (i.e., alkali cations possess significantly stronger electrostatic interactions than bulkier alkylammonium cations). Furthermore, cations with different shapes will lead to anisotropies in E_{el} and E_{er} that may lead to new cation- π -

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 $[TCNE]_2^{2-}$ structural arrangements that minimize void space. Thus, cations larger than Cs⁺ but smaller than $[NMe_4]^+$, especially with different shapes and hydrogen bonding, may lead to new structural conformations and new bonding features for π - $[TCNE]_2^{2-}$ and their likely associated long bonds.

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- [24] [NMe₄][TCNE] was synthesized by means of the following reaction. TCNE (1,117 mg; 8.727 mmol) dissolved in MeCN (6 mL) was added dropwise to an [NMe₄]CN (0.874 g; 8.460 mmol) slurry in MeCN (ca. 22 mL) in a Schlenk flask with an airtight syringe, and the solution immediately turned dark. The solution was placed under vacuum for about 5 min to remove any remaining cyanogen from the solution. The solution was transferred back to the dry-box and concentrated in vacuo to near dryness. A minimal amount MeCN was added to dissolve any remaining solids and the solution was filtered through dry Celite to remove any unreacted [NMe₄]CN. Crystallization of the product was achieved via Et₂O vapor diffusion, and the product was filtered and washed with minimal (ca. 2 to 3 mL) fresh MeCN. The final product was dried under vacuum with minimal heating for about 30 min .Yield 646 mg (37%).
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