Formation of different framework structured dimeric diaions formed from the reduction of 2,4,6-tricyano-1,3,5-triazine and 1,3,5-tricyanobenzene†

Rico E. Del Sesto, Atta M. Arif and Joel S. Miller*

Department of Chemistry, University of Utah, 315 S. 1400 E. RM 2124, Salt Lake City, Utah, 84112-0850, USA. E-mail: jsmillar@chemistry.utah.edu

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Reduction of 2,4,6-tricyano-1,3,5-triazine (1) and 1,3,5-tricyanobenzene (2) leads to dianionic dimers with long, ~1.57 Å, central C–C bonds. In contrast to 1, which dimerizes at the nitrile substituted carbon, 2 has a different motif as it dimerizes at the hydrogen substituted carbon.

Polynitrile substituted organic molecules are strong electron acceptors that have enabled the development of molecule-based conductors† and magnets.2 For the latter, reduced radical-anion cations can coordinate to metal centers to build covalently bonded extended structures in 1-, 2-, and 3-D.2 New, reduced polynitrile acceptors may lead to new structure types and new properties. The 2,4,6-tricyano-1,3,5-triazine (1) and 1,3,5-tricyanobenzene (2) polynitriles have not received much attention. Their D_{3h} symmetry presents the opportunity for some sp² character. The two rings are twisted 67° about the C–N–C bond it is in excellent agreement with 1.57 Å for C39–N2, 1.467 Å for C39–N1, 1.348 Å for C37–N1, 1.350 Å for C38–N1, and 1.289 Å for C38–N2. The longer bond lengths to C39/C40 and shorter bonds to N3/N5 indicate that the anionic charge is localized on the outer half of the ring. However, the rings maintain their planarity, and the bond bond angles around central C’s (C39 and C40) range from 106 to 118.5° indicating that they still maintain some sp² character. The two rings are twisted 67° about the C39–C40 bond, as defined by the C45–C39–C40–C64 torsion angle.

The τ_{CN} absorptions in 1 are at 2302w, 2276m, 2255s cm⁻¹, but occur only as a very weak peak at ~2245 cm⁻¹ in 1²⁻. The ring C=O aromatic stretch occurs at ~1520 cm⁻¹ for 1 that increases to ~1590 cm⁻¹ upon reduction and dimerization. The minimal change in the τ_{CN} frequency and 70 cm⁻¹ shift in the τ_{CN} also indicate that the anionic charge is localized within the ring.

EPR studies of [{Cr(mes)}⁺²]₂⁺ show only an absorption at g = 1.990, characteristic of bis(aryl)chromium(Ⅰ) cations, e.g. g = 1.9859 for [{Cr(C_6H_5)_2}⁺]. The temperature dependence of the magnetic susceptibility, χ, shows typical Curie-Weiss behavior, χ ∝ (T − θ)⁻¹, with an effective

† Dedicated to Michael Hanack on the occasion of the 70th birthday.


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moment of 2.40 μB between 20 and 300 K, and a θ value of –8 K. This is consistent with two independent S = 1/2 spins arising from the two CrII centers per formula unit, with a g-value of 1.990, which would have the expected room temperature effective moment of 2.43 μB.

The previously reported electrochemical reduction of 1,3,5-triazine results in this same dimerization producing the C–C σ-dimer, [C6H4N3]+·H, which could be isolated after proton abstraction from an aqueous solution, and characterized by NMR.

Similar irreversible electrochemical behavior was reported for $^2$ but an irreversible reduction at –1.35 V vs. SCE in MeCN, and an anodic irreversible oxidation at ~0.03 V. It was speculated that $^2$ was reduced to the dianion, $^2$–, which then reacts with a second $^2$ to form $^2$–, which would be isomorphous with the previously discussed $^2$–.

However, reduction of $^2$ with CoIIICp*2[CP*4]− (pentamethylcyclopentadienide), $[\text{CoIIICp}^*2]^+\text{[CP}^*4\text{]}^-$ produced the o-dimer of $^2$, involving the unsubstituted ring carbons, $[\text{C}1\text{aH}_3\text{N}_3]^+\cdot\text{[C}1\text{aH}_3\text{N}_3\text{]}^-$ (Fig. 2), with the central C50–C53σ distance at 1.56 Å, comparable to $^2$. The C50 carbons are sp3 hybridized with all bond angles averaging 109.4°. Bond lengths within the benzene rings are C50–C51 1.509(4), C51–C52 1.362 Å, C52–C53 1.424(4), C53–C54 1.405 Å, C54–C55 1.364 Å, and C55–C50 1.523 Å.

Dimerization of $^1$ occurs at the substituted ring-C rather than at the ring-N, most likely due to formation of the more energetically stable C–C σ-bond (ca. 200 kJ mol−1) with respect to a N–N bond. However, $^2$ dimerizes at the unsubstituted ring, analogous to the radical cation of tris(dimethylamino)benzene, which also forms dimers at the unsubstituted carbon. Studies of the reaction of the $^2$–, via photoinduced electron transfer (in situ production of $^2$–), with benzyl11 and alkyl12 neutral radicals yielded major products of the benzyl/alkyl substituted 1 at the unsubstituted carbon as well. In both cases, the reactivity of $^2$– at the unsubstituted carbon was attributed to the spin density being highest at those carbons, hence dimerization of the radical anion at these carbons as well. This behavior is similar to that of the 1,3,5-tripyrroldino benzene, which also dimerizes upon reduction at the unsubstituted carbon.13

The [{CoIIICp*2}]+·$^2$– is EPR silent at room temperature, and is diamagnetic at 20 and 300 K consistent with $S = 0$ CoIII and $S = 0$ dimerized organic radicals. Analogous to the $^2$– and $^2$–, similar types of o-dimers have been reported for TCNE14 and TCNQ15 radical anions. In both cases, the o-bond can undergo hemolytic cleavage by thermolysis yielding the original individual radical anions.14–16

The isolated electron transfer complexes suggest that the formation of a stable radical anion of $^1$– and $^2$– is not favorable, as they undergo dimerization to produce the closed-shell dimers, $^1$2 and $^2$2, respectively. Although $^1$ is not isolated, these results suggest that some type of molecular rearrangement or reaction, possibly through an intermediate similar to the isolated $^2$–, is responsible for the unexpected EPR signal seen in the reduction of 1 by Carrington and coworkers.3

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Notes and references

1 [Cr(mes)2]+·$^1$– was prepared from the reduction of Cr(mes)2 and $^{18}$O, $^{18}$O (Nujol)/cm−2 2720, 159ys, 1327w, 1150w, 1127w, 910w, 514d.
2 Crystal data for [{Cr(mes)2}]+·$^2$–: MeCN:CoIIICp*2N3, M = 938.042, triclinic, space group P1, a = 13.2998(4), b = 13.3685(3), c = 15.7869(4), β = 65.20(16)°, γ = 79.8899(17)°, V = 76.2468(16) Å3, Z = 2, $\rho_{\text{calc}} = 1.263$ Mg m−3, absorption coefficient 0.488 mm−1, F(000) = 980, reflections collected 16356, independent reflections 10914 [R(int) = 0.0331], GOF = 1.018, R = 0.0505, wR2 = 0.1129. CCDC 163649.
3 [{CoIIICp*2}]+·$^2$– was prepared from the reduction of CoIIICp*2 with $^{18}$O, $^{18}$O (Nujol)/cm−2 2168, 2160s, 1582s, 1499s, 1359m, 1310m, 1103m, 1023m, 877m, 632w.
4 Crystal data for [{CoIIICp*2}]+·$^2$–: MeCN:CoIIICp*2N3, M = 1006.13 triclinic, space group P1, a = 12.4960(3), b = 12.5636(4), c = 16.2297(4), α = 76.7828(14)°, β = 67.4601(12)°, γ = 70.5232(12)°, V = 2467.55(11) Å3, Z = 2, $\rho_{\text{calc}} = 1.248$ Mg m−3, absorption coefficient 0.664 mm−1, F(000) = 1064, reflections collected 18947, independent reflections 12130 [R(int) = 0.0344], GOF = 1.020, R = 0.0505, wR2 = 0.1008. In the unit cell there are two halves of [C6H4N3]+ of the 2 dimers asymmetrically oriented within the cell. In this case, C50 and C51 are in the unit cell, and C50 and C411 are visualized by expansion of the asymmetric unit (Fig. 2). CCDC 163650.
5 See http://www.mltp.org/supdata/acc/b1/b108297f.pdf for crystallographic data in CIF or other electronic format.