Hexacyanotriquinarenemethane Dianion

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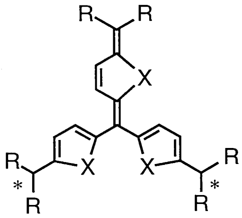
Hexacyanotriquinarenemethane dianion is obtained as a stable, highly teterapolar substance in one step by the reaction of 4-lithiophenyldicyanomethyllithium with ethyl chloroformate. The acidity of its conjugate acid was determined to be pK_a1 = *ca.* 2.5 and pK_a2 = 3.0.

Trimethylenemethanes (TMM) and their di-ionic species have attracted considerable attention from both theoretical and physicochemical point of view.[1] Di-ions of TMM tend to take a tetrapolar structure (tripodal charge separation) to minimize electronic repulsion.[2,3] We have recently reported the synthesis of triquinarenemethane (TQM) di-ions,[4,5] **1** and **2**, which are novel members of TMM family extended by insertion of aromatic rings. These di-ions are featured by the enhanced tetrapolar property owing to aromatizing tendency of the quinoid forms. In this context hexacyanotriquinarenemethane (HCTQM) dianion $\mathbf{3}^{2-}$ is an attractive molecule from the viewpoints of not only its own structure and properties but also the comparison of its features with hexacyanotrimethylenemethane dianion $\mathbf{4}^{2-}$ and hexacyano-[3]radialene dianion $\mathbf{5}^{2-}$.[6,7] We here report the synthesis and properties of HCTQM dianion $\mathbf{3}^{2-}$.



1: X = S, R = Ph or *p*-Tol
(* = + or -)
2: X = CH=CH, R = Ph or *p*-Tol
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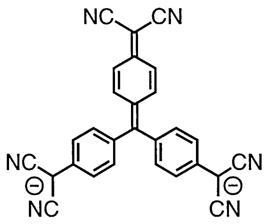
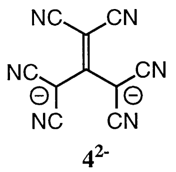
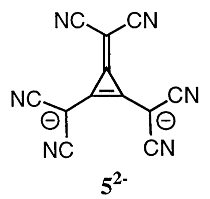


$\mathbf{3}^{2-}$



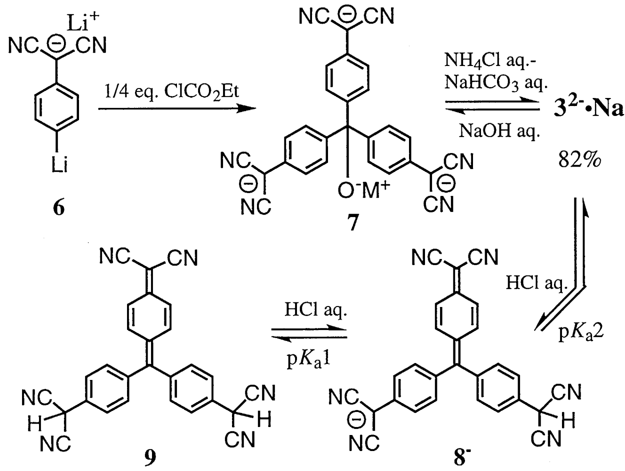
$\mathbf{4}^{2-}$



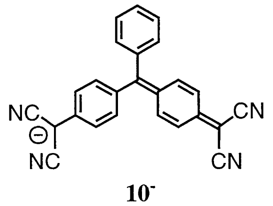
$\mathbf{5}^{2-}$

In the accompanying paper,[8] we reported the synthesis of 7,7-dicyano-*p*-quinodimethane derivatives using new dilithium compound **6** as the key synthon. Dianion **6** was found to be also applicable to the synthesis of $\mathbf{3}^{2-}$. Reaction of **6** with ethyl chloroformate (1/4 eqiuv.) at -78 ℃ followed by addition of aqueous ammonium chloride and then sodium hydrogen carbonate yielded the disodium salt of $\mathbf{3}^{2-}$ (Scheme 1). The salt is water-soluble, but extractable with ethyl acetate from aqueous solution; therefore, washing of the crude aqueous solution of $\mathbf{3}^{2-}$ with ether or benzene followed by extraction with ethyl acetate afforded almost pure salt of $\mathbf{3}^{2-}$ as chocolate colored solid in 82% yield. Notable is easy dehydration of the intermediate trianionic *tert*-alcohol **7** to $\mathbf{3}^{2-}$ even under the weakly alkaline condition, indicating good thermodynamic stability of the dianion. Dilute aqueous solution of $\mathbf{3}^{2-}$ is cyan blue (λ_{max} 726 nm) in color and is slowly bleached over several weeks at room temperature. Treatment of $\mathbf{3}^{2-}$ with dilute hydrogen chloride yielded conjugate acid **9** quantitatively.

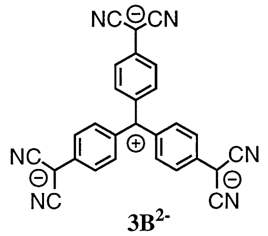
Reaction of **6** with methyl benzoate (1/3 equiv.) in place of ethyl chloroformate under similar conditions gave monoanion $\mathbf{10}^{-}$ in 74% yield, demonstrating its good synthetic applicability.



Scheme 1



$\mathbf{10}^{-}$



$\mathbf{3B}^{2-}$

^{1}H and ^{13}C NMR spectra of HCTQM dianion $\mathbf{3}^{2-}$ are simple, showing C_3 symmetry of the molecule (Table 1). The most remarkable feature is a very large difference of ^{13}C chemical shifts between the central quarternary carbon (Cα: δ 174.62) and the outer dicyanomethylene carbons (Cβ: δ 42.42). While the chemical shift of Cα is comparable to that of bis(2-thienyl)phenylmethyl cation (δ 176.0)[9] to indicate the presence of considerable positive charge on Cα, that of Cβ lies between the corresponding carbon of $\mathbf{5}^{2-}$ (δ 24.8) and 7,7-dicyano-8,8-bis(4-dimethylaminophenyl)quinodimethane **11** (δ 55.13).[8] The chemical shift difference of $\mathbf{3}^{2-}$, Δδ (Cα - Cβ) = 132.2 ppm, is 1.15 times larger than that of **11** (Δδ 115.4) indicative of remarkably large resonance contribution of the tetrapolar structure $\mathbf{3B}^{2-}$.[10] The IR frequencies of nitrile stretching (2183 and 2155sh cm^{-1}) are comparable to those of anion radical salts of TCNQ.[11]

The UV-vis spectra of $\mathbf{3}^{2-}$ shows negative solvent effect in consonant with the highly tetrapolar property at the ground state

Table 1. Selected physical and spectroscopic data of 3^{2-}, **9** and 10^{-}

$3^{2-}\bullet 2Na^+$: chocolate colored plates, mp > 300 °C; ^{1}H-NMR (400 MHz, CD_3OD) δ = 7.04 (AA'BB', J = 8.8, 1.6 Hz, 6H) 7.19 (AA'BB', J = 8.8, 1.6 Hz, 6H); ^{13}C-NMR (101 MHz, CD_3OD) δ = 42.42 (Cβ), 121.16, 124.49, 131.64, 139.30, 153.51, 174.62 (Cα).

9: red plates, mp 221-222 °C; IR (KBr) ν = 2211 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} (log ε) = 469 nm (4.40); ^{13}C-NMR (67.9 MHz, CD_3Cl) δ = 27.89, 74.94, 111.14, 113.75, 125.59, 127.80, 128.75, 128.84, 132.42, 133.55, 136.07, 141.24, 154.58.

$10^{-}\bullet Na^+$: violet plates; IR (KBr) ν = 2192, 2155 cm^{-1}; UV-vis (EtOH) λ_{max} (log ε) = 496 (4.20), 788 nm (4.79); ^{1}H-NMR (400 MHz, CD_3OD) δ = 7.10-7.52 (m, 13H); ^{13}C-NMR (101 MHz, CD_3OD) δ = 48.22 (Cβ), 115.58, 124.49, 128.60, 131.15, 132.11, 134.88, 139.91, 142.62, 159.88, 163.21 (Cα).

(λ_{max} = 726 nm/H_2O; 738 nm/MeOH; 761 nm/EtOAc, and 767 nm/CH_2Cl_2). In contrast to the large difference between pK_a1 and pK_a2 of the conjugate acid of 4^{2-},[6] pK_a1 and pK_a2 of **9** were found to be very close to each other. In aqueous buffered solutions (HCl-NaOAc), the visible absorptions of monoanion 8^- were not observed separately due to the overlap with the absorptions of 3^{2-} over pH range of 0.9-6.9, although the absorption maxima between 700 and 800 nm are slightly shifted toward longer wavelength at the lower pHs (Figure 1). The visible absorptions of 8^- are expected to be similar to those of 10^- (λ_{max} = 786 nm in the same buffered solution). When a dichloromethane solution of **9** was titrated, however, with pyridine, the absorption maximum of 8^- was observed at 813 nm separated from 763 nm of 3^{2-}. From these results, pK_a1 and pK_a2 of **9** are estimated to be about 2.5 and 3.0, respectively. Thus, **9** is a stronger acid than phenylmalononitrile (pK_a = 5.3[12]) by about 2.5 pK units, but far weaker acid than the conjugate acid of 4^{2-} whose acidity was reported to be comparable to sulfuric acid. The reason for the marked weakening in the acidity of the first hydrogen of **9** may be that while delocalizarion of the negative charge in 8^- should benefit delocalization energy as the case in protonated monoanion 4^-, it should cause at the same time bond alternation in the benzene rings to result in decrease of their aromatic resonance energy.

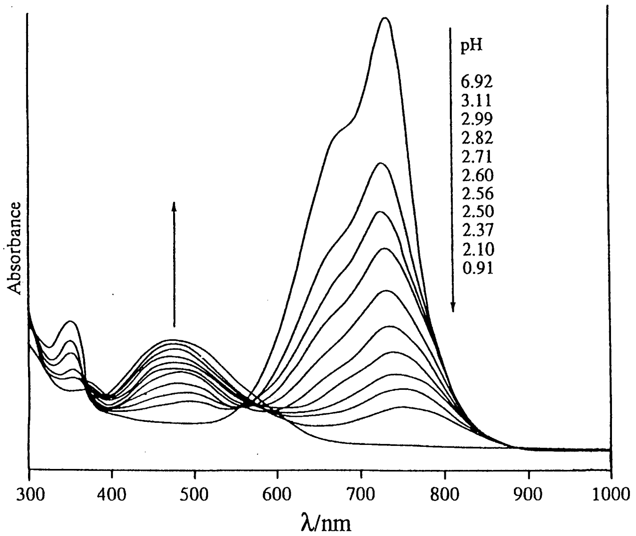


Figure 1. UV-vis spectral change of 3^{2-} at various pH in HCl-NaOAc buffer solutions.

In agreement with the highly tetrapolar property shown by the NMR spectra, 3^{2-} undergoes addition of hydroxide ion at Cα back to colorless trianion **7** (M = H)[13] in aqueous NaOH, and 3^{2-} is regenerated upon dilution to weakly basic (Scheme 1).

The cyclic voltammetry of 3^{2-} exhibits two reduction waves and one oxidation wave between -2.5 and 1.0 V (vs. Ag/AgCl) with the oxidation wave being about twice of the reduction waves in the integrated area.[14] The first reduction (-0.83 V) is reversible, but the second reduction (-1.71 V: peak potential) and the oxidation (+0.45 V: peak potential) are irreversible to suggest the formation of fairly stable trianion radical 3^{3-} and reactive tetraaion 3^{4-} and diradical $3^{2\bullet}$, respectively.

Further studies on 3^{2-} and related compounds are in progress.

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References and Notes

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4 IUPAC name for the parent diradical of $3^{2\bullet}$ is [7,7-bis(4-methylphenyl)-1,4-dimethylene-2,5-cyclohexadiene]diyl for which we here use the trivial name "triquinarenemethane (TQM)" for simplicity and similarity to "trimethylenemethane". There can be other family members such as tri-*ortho*-quinarenemethane and trithienoquinarenemethane. The name "quinarene" has been used for the cyclic cross-conjugated molecules having an inserted *p*-quinonoid ring.[15]

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10 According to the ^{13}C shift dependence on the π charge (167 ppm/π electron), the $\Delta\delta$ value observed corresponding to π charge differnce of 0.79. Coupled with the π charge density of phenyldicyanomethyl anion from AM-1 calculation,[16] the following π charge densities are estimated for 3^{2-}: +0.51 for Cα, -0.28 for Cβ, -0.16 for the CN, and -0.24 for the *p*-phenylene part.

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13 NMR data of **7**: ^{1}H NMR (270 MHz/D_2O-NaOH) δ = 6.52 (AA'BB', J = 8.6, 2.0 Hz), 6.62 (AA'BB', J = 8.6, 2.0 Hz); ^{13}C NMR (67.9 MHz/D_2O-NaOH) δ = 26.20, (ca. 83), 118.18, 118.36, 130.31, 136.17, 138.25).

14 Measured in dimethylformamide at 25 °C using n-$Bu_4N^+ClO_4^-$ as an electrolyte and ferrocene (E_{ox} = +0.52 V) as a reference compound.

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