of the reactivity of the enamine 2 it completely decomposed on the GLC column and could not be measured directly. The free-energy difference between 1 and 2 at 91.6 °C, calculated from three runs containing three samples each, was 4.0 ± 0.1 kcal/mol.

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**Registry No.** 1, 694-55-3; 2, 57005-69-3.

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## Pseudooxocarbons. Synthesis of 1,2,3-Tris(dicyanomethylene)croconate Salts. A New Bond-Delocalized Dianion, Croconate Blue[1]

Alexander J. Fatiadi

*National Bureau of Standards, National Measurement Laboratory, Washington, DC 20234*

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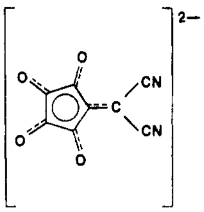
In a recent paper,[2,3] the synthesis and characterization of 2-(dicyanomethylene)- and 1,3-bis(dicyanomethylene)croconate salts, 1 and 2 (dipotassium salts), respectively, have been reported. The bond-delocalized dianions 1 and 2 are new additions to the aromatic oxocarbons[4] $(C_nO_n)^{m-}$. Here, the preparation and some of the properties of the croconate dianion analogue in which three of the carbonyl oxygen atoms are replaced by dicyanomethylene groups, e.g., the dianion 3 (dipotassium salt), are described.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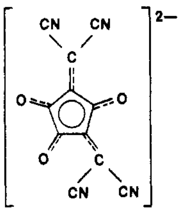
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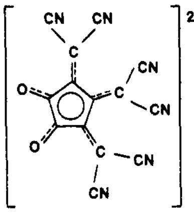
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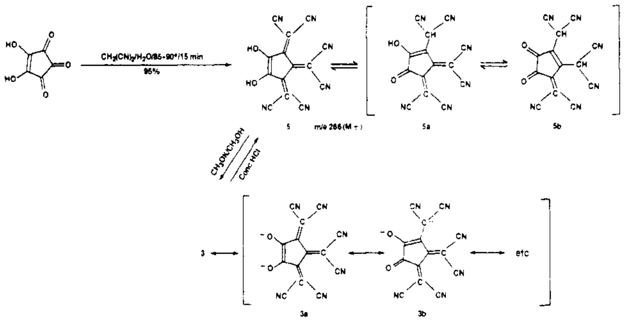
When a mixture of croconic acid (4) (4,5-dihydroxy-4-cyclopentene-1,2,3-trione) and malononitrile in water was briefly heated at 85–90 °C, a new oxocyanocarbon acid 5 was isolated in over 90 percent yield (Scheme I). It was termed "croconic acid blue" because of its intense blue color in water: UV ($H_2O$) 600 nm (ε 55000). The acid 5 is an intensely solvatochromic dye, the color of which is dependent on the polarity of the solvent; for example, its solution in anhydrous acetone (or ethyl alcohol) is red [UV ($Me_2CO$) 475–480 nm], but in water it is deep blue. The IR (KBr) of the acid 5 shows bands at 1755 (s), 1700 (sh, C═O), 1650 (s), 1590 (s), and 1520 cm$^{-1}$ [s, C═O, C═C, C═C(CN)$_2$], indicating the possible existence of tautomers with C–H structures 5a ⇄ 5b in the solid. The acid 5 is a strong oxocyanocarbon acid[5] (p$K_2 \approx 1$); it is stronger than croconic acid but weaker than croconic acid violet (the conjugate of 2). In water at room temperature, acid 5 hydrolyzes slowly (95% in 85 days) to yield the more thermodynamically stable croconic acid violet [UV ($H_2O$) 533 nm]. However, excessive heating of 5 in water causes apparent polymerization, to afford deep green, lustrous plates [UV ($H_2O$) 590–595 (sh), 535, 510, and 490 nm]; it showed no molecular-ion peak in its mass spectrum.

**Scheme I**



Acid 5 was readily converted into the green-blue dipotassium salt of 1,2,3-tris(dicyanomethylene)-4-cyclopentene-4,5-diol, e.g., 3, on careful titration with potassium methoxide in methanol. Similarly, bis(tetramethylammonium) or pyridinium[6] salts of 3 were prepared.

The dipotassium salt of 3 is a dye,[7] named "croconate blue" because of its intense, blue color in solution; the electronic spectrum of the dianion 3 in aqueous solution shows a band at 599 nm (ε 54600). It should be noted that the acid 5 and the salt of 3 absorb in the same region, with almost the same intensity in the visible spectrum (ε 54600 vs. 55000). The infrared spectrum of the dipotassium salt of 3 shows bands at 1670 (s, C═O), 1620 (s), and 1570 cm$^{-1}$ [m, C═O, C═C, C═C(CN)$_2$], indicating possible contributions from the resonance forms **3a** ↔ **3b** ↔ etc. Indeed, the highly absorbing salt gave a Raman spectrum ($\lambda_0$ 514.5 nm, Figure 1; see Experimental Section) showing a strong fluorescence at 900 cm$^{-1}$. The Raman spectrum of 3 (Figure 1) shows bands at 2208 (s, C≡N), 1654 (m, C═O), 1596 (m), 1572 (m), 1551 [s, C═O, C═C, C═C(CN)$_2$], and 1472 cm$^{-1}$ (m, dianion), also indicating possible contributions from the resonance forms **3a** ↔ **3b** ↔ etc. The $^{13}C$ NMR spectrum (Experimental Section) of 3 resembled that of the acid 5, which supports the symmetrical structure of the dianion 3 and the dianion 5 formed by ionization. Cyclic voltammetry of the salt (in water, 0.1 M sodium perchlorate as the supporting electrolyte, mercury electrode, concentration 240 mM, scan rate of 50 mV s$^{-1}$ vs. SCE) and DC polarography revealed a stepwise reduction by a two-electron-transfer mechanism, as shown by three irreversible peak potentials at −0.69, −0.93, and −1.15 V [e.g., $2C{=}C(CN)_2 \rightarrow (NC)_2CHC{=}CCH(CN)_2$]. The first reduction wave of the dipotassium salt of 3 at −0.69 V vs. SCE indicates that 3 is easier to reduce than the dipotassium salt of 2 ($E_{1/2}$ = −0.88 V vs. SCE) and more difficult than dilithium croconate ($E_{1/2}$ = −0.48 V vs. SCE).

The high acidity of the oxocyanocarbon acid 5 is typical of the symmetrical, bond-delocalized structure of its dianion 3 (as also observed for the dianions 1 and 2 and their conjugate acids). However, a stereomodel of the crowded dianion 3 (the van der Waals contacts between two neighboring nitrogen atoms are less than 3 Å) indicates that to relieve the steric hindrance of the 1,2,3-tris(dicyanomethylene) groups a staggered conformation of all of the cyano groups in 3 is required; the estimated twist

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[5] L. M. Schwartz, personal communication.

[6] All new compounds gave satisfactory elemental analyses.

[7] Aqueous or alcoholic solutions of 3 (acid or salt) impart adherent stains to the skin; consequently, all operations require the use of rubber or plastic gloves.

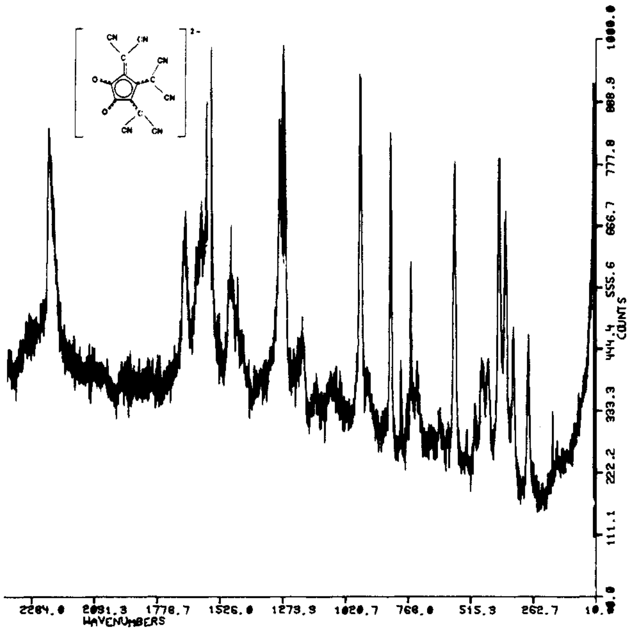

**Figure 1.** Laser Raman spectrum of the dipotassium salt of **3** ("croconate blue" dianion) ($\lambda_0$ 514.5 nm, 1.5-mW power, solid).

of the dicyanomethylene group about C-2 is[8] ~30°. Partial evidence for the trans (staggered) conformation of the cyano groups in the dianion **3** is given by its $^{13}C$ NMR spectrum.[9] Diminution in symmetry in the dianion **3** is probably associated with instability of its salts in aqueous, alkaline media. The bis(tetramethylammonium) or dipotassium salt of **3** in ~0.1 M aqueous potassium hydroxide (pH 13.2) almost instantaneously (2–3 s on the spectrophotometric scale) split off the 2-(dicyanomethylene) group to yield the croconate violet dianion **2** (with a prompt, hypsochromic shift from 600 to 533 nm). This rapid change is followed by much slower, stepwise hydrolysis of the remaining 1,3-bis(dicyanomethylene) groups to give, next, the orange dianion **1** (band at 444 nm in ~4 h) and then the yellow croconate dianion (bands at 362 and 333 (sh) nm in ~40 h) as the final product. The kinetics of the alkaline hydrolysis of the bis(tetramethylammonium) salt of **3** are first order with an apparent rate constant of $K_1 = 0.0136$ min$^{-1}$ (band 533–444 nm) and $K_2 = 0.001\,35$ min$^{-1}$ (band 440–362 nm). The dipotassium salt of **3** is a weak semiconductor having a compaction conductivity at room temperature of $1 \times 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$.

The dianions **1** and **2**,[2,3] the dianion described here, e.g., **3** $[C_5O_2[C(CN)_2]_3]^{2-}$, and the dianions reported[10–18] may be regarded as members of a new class of aromatic, nonbenzenoid pseudooxocarbons having the general formula $[C_nO_{n-m}X_m]^{r-}$, where X = =C, N, P, S, Se, etc.

## Experimental Section

$^1H$ NMR and $^{13}C$ NMR spectra were recorded with a Bruker HFX-11 spectrometer with tetramethylsilane as internal standard. The $T_1$ relaxation reagent [gadolinium trichloride ($GdCl_3$), 0.05 M] was needed in order to lower the relaxation rate, as evidenced by a broadening of peaks in the $^{13}C$ NMR spectra of compounds **3** and **5** and similar compounds in this series. IR spectra were obtained with a Perkin-Elmer 225 spectrometer, and UV spectra were obtained with a Cary 219 spectrophotometer.

**1,2,3-Tris(dicyanomethylene)-4-cyclopentene-4,5-diol (5).** A mixture of croconic acid (500 mg of anhydrous acid or an equivalent weight of the trihydrate),[19] malononitrile (1.2 g), and water (10 mL) is heated at 85–90 °C for 15 min and cooled. The product is isolated in two crops (concentration); the yield of the material thoroughly washed with water and dried in air is 700–750 mg (90–97%). Recrystallization from a little hot water gave the acid **5** as shiny, purple plates: mp 228–230 °C dec; UV ($H_2O$) $\lambda_{max}$ 600 nm ($\epsilon$ 55 000), 520 (sh, 16 000), 400 (sh, 12 000), 378 (sh, 11 000), 318 (12 000), 278 (11 500), 232 (9600); $^1H$ NMR ($CD_3SO$) $\delta$ 10.30 (s, 1 H); mass spectrum, m/e (relative intensity) 286 ($M^{+}\cdot$, 100), 258 (24), 230 (14), 203 (30), 176 (12). Anal. Calcd for $C_{14}H_2N_6O_2 \cdot 1.5H_2O$: C, 53.68; H, 1.61; N, 26.83. Found: C, 53.92; H, 1.59; N, 26.80.

**1,2,3-Tris(dicyanomethylene)-4-cyclopentene-4,5-diol Dipotassium Salt (3).** The acid **5** (200 mg in 10 mL of methanol) was neutralized with a slight excess of potassium methoxide in methanol (0.5 M, 2 mL); the isolated product (260 mg) was recrystallized from water (slow crystallization) to give shiny, green-blue crystals of the dipotassium salt of **3**, yield 220 mg. The product crystallizes as the trihydrate. The analytical sample gave the following data: UV ($H_2O$) $\lambda_{max}$ 599 nm ($\epsilon$ 54 600), 538 (sh, 32 000), 398 (12 000), 378 (13 000), 314 (18 000), 285 (16 000), 234 (14 000); Raman spectrum ($\lambda_0$ 514.5 nm, 3-mW power, solid), $\Delta\nu$ 280 (m), 342 (m), 401 (s), 458 (w), 578 (s), 730 (w), 789 (w), 833 (w), 900 cm$^{-1}$ (strong fluorescence); $^{13}C$ NMR (9:1 $H_2O$–$D_2O$ plus $T_1$ relaxation reagent, external $Me_4Si$) $\delta$ 178.0 (C=C, C-4 and C-5), 147.3 [C=C(CN$_2$), C-1 and C-3], 139.1 [C=C(CN)$_2$, C-2], 120.2 (C≡N, C-1 and C-3), 118.6 (C≡N, C-2),[9] 52.2 [C=**C**(CN)$_2$, C-1 and C-3], 53.3 [C=**C**(CN)$_2$, C-2]. Anal. Calcd for $C_{14}N_6O_2K_2 \cdot 3H_2O$: C, 40.38; H, 1.45; N, 20.18; K, 18.78. Found: C, 40.73; H, 1.43; N, 20.10; K, 18.59. The dipotassium salt of **3** loses one molecule of water of crystallization per molecule on storage at room temperature. Anal. Calcd for $C_{14}N_6O_2K_2 \cdot 2H_2O$: C, 42.19; H, 1.01; N, 21.09. Found: C, 42.24; H, 0.89; N, 21.27. Similarly, the bis(tetramethylammonium) salt of **3** was obtained as lustrous, green-blue rosettes; it crystallizes as the dihydrate. The electronic spectrum of the dianion **3** [bis(tetramethylammonium) salt] in aqueous solution shows peaks at 599 nm ($\epsilon$ 65 000), 512 (sh, 18 000), 398 (14 000), 378 (14 000), 316 (14 500), and 282 (14 000). Anal. Calcd for $C_{22}H_{24}N_8O_2 \cdot 2H_2O$: C, 55.98; H, 5.54; N, 23.42. Found: C, 56.12; H, 5.88; N, 23.68.

**Acknowledgment.** The author thanks Dr. L. M. Doane for the cyclic voltammetry, Dr. B. Coxon for the $^{13}C$ NMR spectrum, Dr. L. R. Hilpert for the mass spectra, Dr. John Blaha for the Raman spectrum, and F. J. Savluk for some spectral measurements.

**Registry No.** 3, dipotassium salt, 72893-87-9; 3, bis(tetramethylammonium) salt, 72905-23-8; 4, 488-86-8; 5, 72905-24-9; malononitrile, 109-77-3.

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(8) The planarity of the dianion 3 still awaits confirmation by X-ray crystal structure analysis.

(9) The broad peak was split into a poorly resolved sextet at 119.0, 119.6, 119.3, 118.7, 117.9, and 117.7 ppm, apparently due to the staggered conformation of the cyano groups.

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