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Pseudo-Oxocarbons. Synthesis of 2,1,3-Bis-, and 1, 2, 3-Tris (Dicyanomethylene) Croconate Salts. New Bond-Delocalized Dianions, "Croconate Violet" and "Croconate Blue"*

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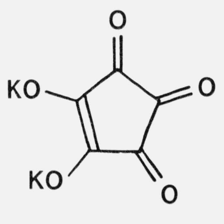
Synthesis and characterization of new bond-delocalized dianions, e.g., 2, 1,3-bis-, 1, 2, 3-tris (dicyanomethylene) croconate salts have been described. The dianions reported represent a new class of aromatic, nonbenzenoid compounds, named pseudo-oxocarbons. A study of their physical, analytical and chemical properties offer a new direction in the chemistry of oxocarbons.

Key words: Acid; aromatic; bond-delocalized; croconic; dianion; malononitrile; nonbenzenoid; oxocarbon; salt; synthesis

1. Introduction

The bright yellow dipotassium croconate **1** and croconic acid (**1**, K = H, 4,5-dihydroxy-4-cyclopentene-1,2,3-trione) were first isolated by Gmelin [1][1] in 1825, from the black, explosive, side-reaction product (e.g. $K_6C_6O_6$ + KOC≡COK), by the reaction of carbon with potassium hydroxide, in a pioneer, industrial attempt to manufacture potassium. Although the chemistry of croconic acid was subsequently studied by many workers [2], the chemistry and the unique molecular properties of the croconic salts (e.g. **2**, dipotassium salt) were first seriously investigated when a symmetrical, delocalized structure for the dianion **2** was proposed by Yamada et al. [3] in 1958. A few years later [4], the dianion **2** and the related deltate [5], squarate, rhodizonate, and tetrahydroxyquinone anions were recognized by West et al. [2,4] as members of a new class of aromatic oxocarbons $[C_nO_n]^{m-}$. Complete vibrational and normal-coordinate analysis showed that the croconate dianion **2** has indeed a planar, delocalized structure with D_{5h} symmetry [6,7].



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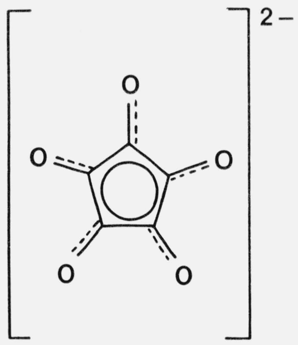

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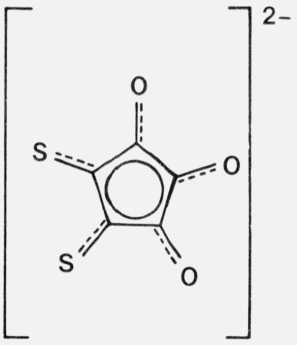

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Studies pertinent to the aromatic, oxocarbon dianions in which the original carbonyl oxygen atoms in $[C_nO_n]^{m-}$ are either partially or completely replaced have been made; these included the nitrogen [8], sulfur [9,10], selenium [11],

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*Part X in a series: Oxo- and pseudo-oxocarbons. For previous parts, see ref. [20, 21].

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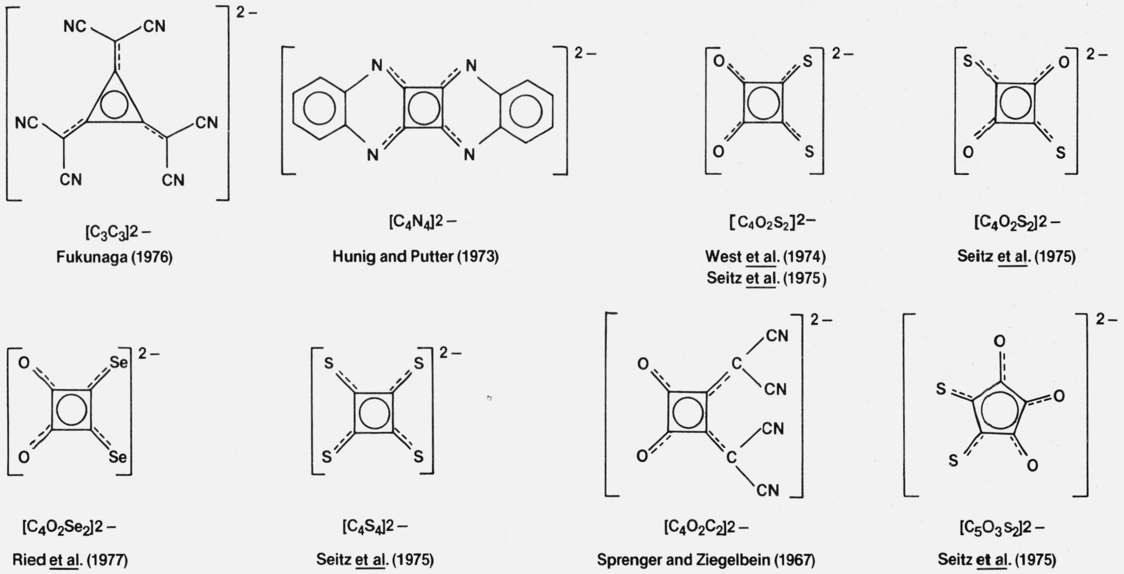
[1] Figures in brackets indicate literature references at the end of this paper.



$[C_3C_3]2-$
Fukunaga (1976)

$[C_4N_4]2-$
Hunig and Putter (1973)

$[C_4O_2S_2]2-$
West et al. (1974)
Seitz et al. (1975)

$[C_4O_2S_2]2-$
Seitz et al. (1975)

$[C_4O_2Se_2]2-$
Ried et al. (1977)

$[C_4S_4]2-$
Seitz et al. (1975)

$[C_4O_2C_2]2-$
Sprenger and Ziegelbein (1967)

$[C_5O_3S_2]2-$
Seitz et al. (1975)

FIGURE 1. *Some aromatic pseudo-oxocarbon dianions.*

and dicyanomethylene [12,12a,13] analogs of the squarate mono- [12a] and dianion [12,13], a sulfur analog of the croconate, e.g. the dianion **3** [14], and the tris(dicyanomethylene)-cyclopropane dianions [15] (fig. 1).

2. Reaction of cyclic triones and oxocarbons with malononitrile

2.1. Reaction of cyclic triones

The reactions of *vic*-polyketones can be characterized as the chemistry of highly activated carbonyl groups. In acyclic polycarbonyl compounds, the reactivity is due to the destabilization of polyketones, as a result of flexibility of the adjacent dipolar carbonyl groups. Cyclic triketones, however, in which the unfavorable dipolar interaction between adjacent carbonyl groups is maximal and the carbonyl groups are eclipsed (*S-cis*-conformation) are more reactive in regard to the formation of hydrates, aldols, half-acetals, and other addition compounds, as compared to the open-chain triones [S-*trans* (staggered) conformation] [16–18]. Schönberg and Singer [18] studied the uncatalyzed reaction of a variety of cyclic triketones, e.g., 1,2,3,-indantrione and ninhydrin (1,2,3-indantrione monohydrate) with enolizable β-diketones and other active methylene compounds (e.g. $NC-CH_2-COOC_2H_5$), and found that they all react at the more polarized, central carbonyl group to give aldols in good yield. The authors [18] also confirmed the report [19] that the uncatalyzed reaction of malononitrile with indanetrione in benzene yields an aldol product, e.g., 2-(dicyanomethylene)-1,3-indandione. As observed in this laboratory [20], direct fusion of ninhydrin with an excess of malononitrile (1–2 min at 100–110 °C), followed by methanol treatment of the cold reaction mixture, produced 2-(dicyanomethylene)-1,3-indandione in over 85 percent yield. Surprisingly, the yield of the above aldol product was almost quantitative, following brief refluxing (5–10 min) of indanetrione (or ninhydrin) with malononitrile in aqueous solution.

2.2. Reaction of oxocarbons

In contrast to ninhydrin (or similar cyclic 1,2,3-triones), croconic acid (also a cyclic 1,2,3-trione) on treatment with malononitrile (and other active methylene compounds) yielded a different aldol product. Conversely, a complex reaction was anticipated and observed following treatment of the cyclic polyketo compounds, including three-, four-, five-, and six-membered oxocarbons and their conjugate acids, with malononitrile (or mono-substituted malononitrile). The polymeric products (or a malononitrile trimer), for example, were isolated on treatment of the six-membered oxocarbons or their acids with the reagent. However, a recent report [20a] described the reaction between tetrahydroxy-p-benzoquinone (THQ) and malononitrile, to give a benzo-difuran derivative.

The review by West and Niu [2] and the survey by Rubin [16] discussed only briefly the reaction of oxocarbons [2] or vicinal polyketones [16] with malononitrile; the literature survey showed only three reports on this topic. On treatment of dibutyl squarate with malononitrile in the presence of sodium butoxide in butanol, Sprenger and Ziegenbein [12] obtained a deep-yellow, disodium salt of 1,2-

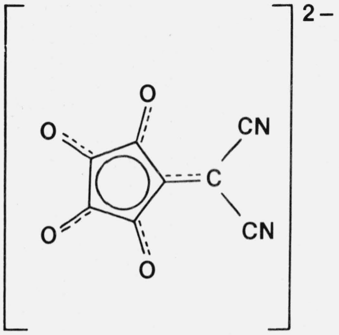
bis(dicyanomethylene)-3-cyclobutene-3,4-dione, a new analog of the squarate dianion (fig. 1). Recently, on treatment of the "activated" bis(dimethylamide) of squaric acid with malononitrile in the presence of triethylamine in dichloromethane, Seitz et al. [12a] isolated in 65 percent yield a red triethylammonium salt of (2,4-dicyanomethylene)-3-(dimethylamino)-1-oxo-3-cyclobutene; the bond-delocalized salt is a new example of the aromatic pseudo-oxocarbon of the squarate monoanion $[C_4C_2ON]^-$. Fukunaga [15] used an indirect method to synthesize a 1,2,3-tris(dicyanomethylene) deltate salt. Thus, in the presence of six equivalents of sodium hydride, hexacyanotrimethylenecyclopropanediide (fig. 1) was obtained in almost quantitative yield by the reaction of tetrachlorocyclopropene with three equivalents of malononitrile in 1,2-dimethoxyethane; the product was isolated as the bis(tetrabutylammonium) salt [15].

A recent preliminary communication [20,21] described the preparation, and some of the properties, of the croconate dianion analogs in which one, two or three of the carbonyl oxygen atoms in **2** are replaced by the dicyanomethylene group, e.g., the dianions **4**, **5**, and **6**; this paper is an extension of the preliminary study.

Thus, the dianions **4**, **5**, and **6** and the dianions reported [8–15] (fig. 1) may be regarded as members of a new class of aromatic, nonbenzenoid, pseudo-oxocarbons with the general formula $[C_nO_mX_{n-m}]^{r-}$ where X= =C− ,N,P,S,Se, etc. A new symbolism (put in brackets) to represent pseudo-oxocarbons is shown for dianions **4**, **5** and **6** and for compounds in figure 1. A shorthand symbolism to show the position of substitution on the ring could also be used. For example, for the dianion **5** $[C_5C(1,3)O_3]^{2-}$, the dianion **6** $[C_5C(1,2,3)O_2]^{2-}$; also for **5** $[C_5X(1,3)O_3]^{2-}$ and **6** $[C_5X(1,2,3)O_2]^{2-}$, X = C(CN)$_2$, or examples from figure 1 $[C_4O_2S(1,2)]^{2-}$; $[C_4O_2S(1,3)]^{2-}$; $[C_4C(1,2)O_2]^{2-}$; $[C_5O_3S(4,5)]^{2-}$ or hypotetical $[C_5NO(1,3)S(4,5)]^{2-}$ or $[C_6O(2,3,5,6)S(1,4)]^{2-}$.

2.3 New Preparation of 1,2-Bis (dicyanomethylene)-3-cyclobutene-3,4-dione

On treatment of dibutyl squarate with malononitrile in the presence of sodium butoxide in butanol, Sprenger and Ziegenbein [12] obtained a deep-yellow disodium salt of 1,2-bis (dicyanomethylene)-3-cyclobutene-3,4-dione (fig. 1); $\lambda_{max}^{H_2O}$ 380 (ε 34000), 265 (ε 12000), 226 nm (ε 15400). Using somewhat different reaction conditions we obtained a salt of apparently the same compound absorbing, however, at the longer wavelength and of considerable higher intensity.



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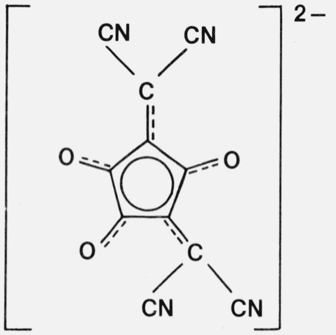
$[C_5O_4C_1]^{2-}$



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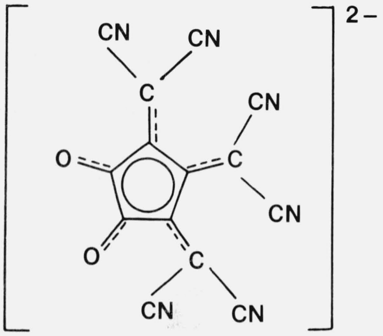
$[C_5O_3C_2]^{2-}$



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$[C_5O_2C_3]^{2-}$

2.3.1 Preparation of 1, 2-bis (dicyanomethylene) squarate

Squaric acid (4-dihydroxy-3-cyclobutene-1,2-dione)[2] (3.5g) and malononitrile (5.2g) are dissolved in butanol (125 mL) and heated under reflux. A potassium methoxide solution (4.2 g of potassium methoxide in 10 mL methanol) is added dropwise (15 min) and the whole is stirred for a further 45 min under reflux. The crystals formed are removed by filtration. After being washed with methanol and ether the product is dried in vacuo; yield of the yellow to yellow-orange, crystalline powder is 6.5 g. The crude product (lg) is extracted with boiling water (10 mL) and filtered on a layer of decolorizing carbon (to remove impurity absorbing at 482 nm). The dipotassium salt of 1,2-bis(dicyanomethylene)-3-cyclobutene-3,4-dione crystallizes as the monohydrate. $\lambda_{max}^{H_2O}$ 423 (ε 111000), 308 nm (ε 4800).

ν_{max}^{KBr} 2480w (C–H), 2285w, 2170s (C≡N), 1770w (C=O), 1645sh, 1600s (C=O+C=C), 1505s [(C=C(CN)$_2$], 1410s (anion), 1300m, 1160vw, 950w, 780w, 690w, 680w.

Calcd. for $C_{10}N_4O_2K \cdot H_2O$: C, 39.46; H, 0.66; N, 18.40, K, 25.69. Found: C, 39.49; H, 0.70; N, 18.15; K, 25.39.

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[2] Certain trade names and compant products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

Concentration and cooling (ice bath) of the filtrate, gave a light-yellow crystalline product (∼150 mg); the IR spectrum of this salt showed much stronger absorption in the carbonyl region (1755–1770 cm^{-1}).

$\lambda_{max}^{H_2O}$ 422 (ε 23300), 383 (ε 23800), 344(sh) (ε 14900), 258nm (ε 14400).

ν_{max}^{KBr} 2170s (C≡N), 1755s (C=O), 1660s (C=O+C=C), 1525s [(C=C(CN)$_2$], 1420s (dianion), 1235m, 1120m, 855 m. The electronic spectrum of the crude mixture (6.5 g batch, 114 mM) showed bands at 482 (sh) (ε 1800), 423 (ε 19500), 382 (ε 8000), 341 (ε 24400), 312 nm (ε 11000). Both salts (orange and yellow) are under further study.

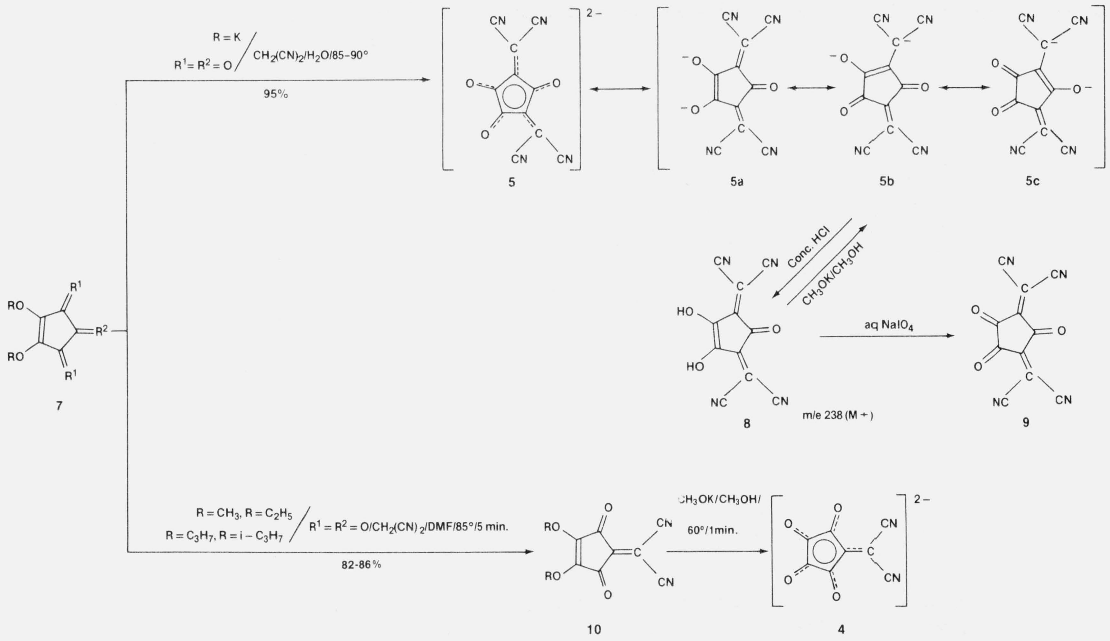
3. Reaction of croconates with malononitrile

3.1 1,3-bis(dicyanomethylene) croconate salts. Croconate violet. Cyclic voltammetry

Treatment of dipotassium croconate (**7**, R=K, R^1=R^2=O) (also **1** and **2**, dipotassium salt), or other alkali croconates (**7**, R=Li, Na, Rb, Cs, NH_4; R^1=R^2=O) [22] with a 1 to 2 molar excess of malononitrile in aqueous solution at 85–90 °C yields the dipotassium salt of 1,3-bis-(dicyanomethylene)-2-oxo-4-cyclopentene-4,5-diol, e.g., the salt of **5**, e.g. **7** [R=K, R^1=C(CN)$_2$, R^2=O] (95% yield). Recrystallization from hot water gives the salt of **5** as deep-blue, metallic needles; it crystallizes as the dihydrate.

The dipotassium salt of **5** is a dye[3] named "croconate violet" because of its intense violet color in solution; $\lambda_{max}(H_2O)$ 533 nm (ε 100000). The infrared spectrum of the dipotassium salt of **5** is relatively simple, consistent with a relatively symmetrical structure for the dianion of the salt. The almost planar, symmetrical structure for the dianion **5** was confirmed by the X-ray crystal structure of its dipotassium salt; the dianion **5** has a bond-delocalized structure with D_{5h} symmetry of the ring. Moreover, the strong bands observed at 1620, 1580 and 1520 cm^{-1} [C=O + C=C + C=C (CN)$_2$] may indicate possible contributions from the resonance forms (**5a**↔**5c**). The strong band observed at 1430 cm^{-1} may be ascribed to the skeletal vibration of the dianion [15]. The highly absorbing salt of **5** gave indeed the Raman spectrum. (fig. 2A). The observed Raman bands in the carbonyl region at 1672, 1610, 1597, 1554 cm^{-1} [C=O +C=C+C=C(CN)$_2$], at 1494 [C(CN)$_2$], and at 1473 cm^{-1} (dianion vibration) support the contributions from the resonances forms **5a**↔**5c**. In the ^{13}C NMR spectrum [9:1 H_2O–D_2O+T_1 relaxation reagent,[4] external Me_4Si], the ring of the salt of 5 contains three nonequivalent carbon atoms and shows three ^{13}C resonances for the ring carbon atoms, e.g., peaks at δ 181.4 (C=O, C-2) 172.0 (C=C, C-4 + C-5), and 147.8 [C=C(CN)$_2$]; also at δ 120.51 (C≡N), 119.5 (C≡N), and 51.4 [C=**C**(CN)$_2$][5] which support the symmetrical structure of the dianion.

The solid ^{13}C NMR spectrum of the salt **5** showed some interesting results; the observed ^{13}C resonances were at δ 182 (C=O, C-2 + C-4 + C-5), 148 [C=C(CN)$_2$] (C-1 + C-3); also two broad cyano bands (apparently arising from



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[3] Aqueous or alcoholic solutions of the salt of 5 or of the acid 8 impart adherent stains to the skin; consequently, all operations require the use of protective gloves.

[4] The T_1 relaxation reagent [gadolinium trichloride ($GdCl_3$) (0.05*M*) + tetrasodium (ethylenediamine) tetraacetate (EDTA) (0.05*M*] was needed to lower the relaxation, as evidenced by a broadening of peaks in the ^{13}C NMR spectra of this and similar compounds in this series.

[5] The unusual, high-field, ^{13}C chemical-shift at 51.4 p.p.m., assigned to the exocyclic, olefinic carbon atoms in the salt of 5, can be explained as due to the shielding effect by the triplet bond of the cyano group, e.g. [C=*C*(C≡N)$_2$↔C=*C*(C=N)$_2$]. This is observed for a series of similar and model compounds, and the study will be published separately.

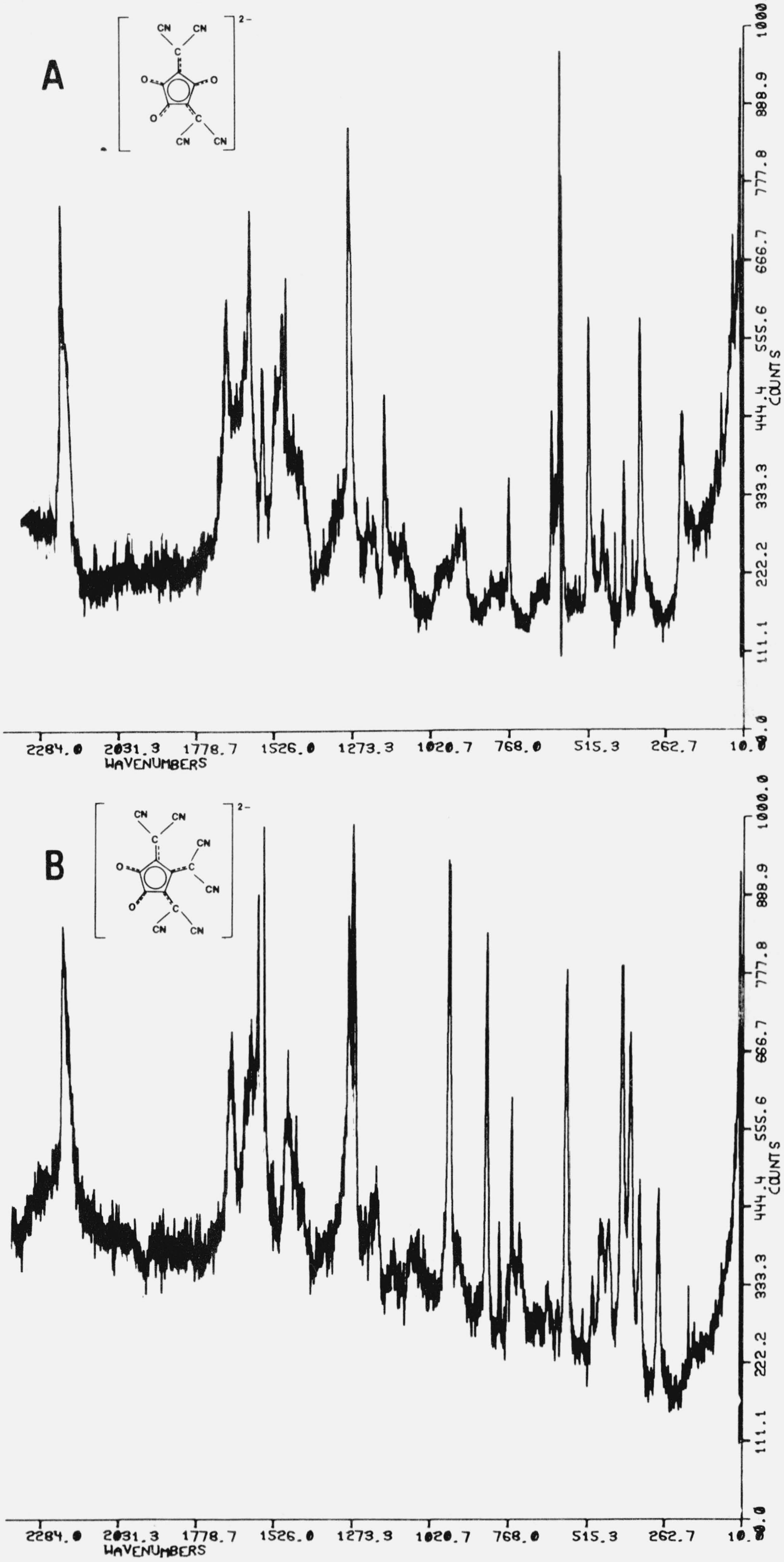

FIGURE 2. *The laser Raman spectra (1.5mW power, λ 514.5nm, solid) of dipotassium salt of* **5** *(croconate violet, (A)) and the dipotassium salt of* **6** *(croconate blue, (B)).*

two nonequivalent cyano groups) at δ 140 (C≡N) and δ 80 (C≡N) [with a median value of δ 110, compared to δ 120 (C≡N) observed for a solution]; also at δ 54 $C{=}C(CN)_2$). The spectrum also showed a series of spinning sidebands, e.g., at δ 322, 280, 230, 40 and 0. The assignments of the bands were based on the integrated band intensities. (fig. 3) Cyclic voltammetry of the salt of **5** (in water) (0.1M sodium perchlorate as the supporting electrolyte, and a glassy carbon electrode) revealed a reversible oxidation potential (at a scan rate of 50 mV.s^{-1} and a current sensitivity of 5 μA/fs) at +0.52 V *vs.* SCE as the reference electrode, as compared to the less easily oxidized dilithium croconate ($E_{1/2}$ = +0.59 V, also reversible). The salt of **5** (and its conjugate acid **8**) apparently undergoes two-electron reduction and shows two irreversible, peak potentials at −0.88 and −1.33 V. (a dropping-mercury electrode). The two-electron reduction probably involves a dicyanomethylene group and a keto group, e.g. $C{=}C(CN)_2 + C{=}O \rightarrow HO\text{-}C{=}C\text{-}CH(CN)_2$. The redox reaction is pH dependent; the reduction step, for example, proceeds faster in alkaline media, in agreement with stepwise hydrolysis (0.1-0.2M aqueous potassium hydroxide) of the salt of **5** to give, *via* intermediate dianion **4**, the croconate dianion **2** (e.g., disappearance from the visible spectrum of a band at 534 nm and appearance first of a band at 444 nm, followed by a band of the final product at 363 nm); the conversion is about ten times faster at 70 °C. As shown by thin-layer chromatography, the electrochemical reduction product of the salt of **5** showed similarities to a product obtained by controlled reduction of the salt with sodium borohydride. The cyclic voltammogram of the salt of **5** bears some resemblance to that of dilithium croconate, having reduction peaks at −0.48 and −1.33 V (reduction to dihydrocroconate), dimethyl croconate (**7**, R=,R^1=R^{2}O) at +0.59 V (reversible oxidation), −0.51 and −1.30 V (irreversible reduction), and croconic acid (**7**, R=H, R^1=R^2=O) at +0.58, −0.49 and −0.98 V (measured in 1:1*N,N*-dimethylformamide—water and a glassy carbon electrode vs. SCE).

Detailed, cyclic voltammetry and polarography of the salts of **4**, **5** and **6**, under various experimental conditions, in regard to the number of electrons transferred in the redox process, the degree of reversibility of the process, and the character of the limiting currents will be reported elsewhere.

The x-ray analysis was particularly helpful in determination of the 1, 3-positions for the dicyanomethylene groups in the dipotassium salt of **5** (see also fig. 4A and the next paper in this journal); the salt is a semiconductor with an electrical conductivity 2 × 10^{-6} Ω^{-1} cm^{-1}, single crystal, 300K) [23]; the value is comparable with that of tetracyanoquinodimethane potassium salt (TCNQ$^-$K$^+$).

When the reaction of croconic acid with malononitrile was conducted in warm aqueous *N,N*-dimethylformamide

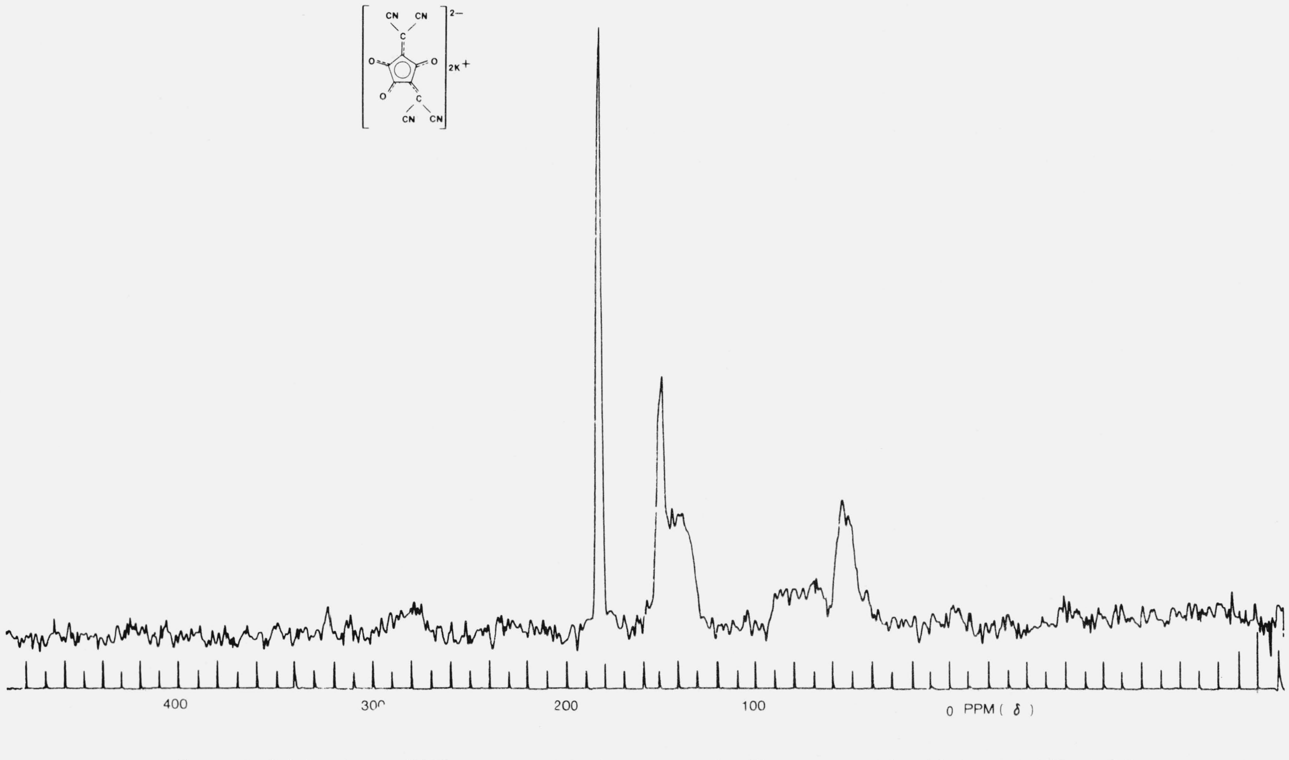

FIGURE 3. *Solid carbon-13 NMR spectrum of the dipotassium salt of* **5** *(croconate violet, dihydrate, 14MHz, 28 °C).*

the product was a very intensely violet dye [$\lambda_{max}(H_2O)$ 532 nm (ε 97000)][6]; the dye was readily converted into the dipotassium salt of **5** on treatment with potassium methoxide in warm methanol. Similar formation of an anion-dye of type **5** was observed when the reaction was performed in the presence of pyridine or triethylamine.

The solution chemistry of salts of **5** in strongly acid media is most interesting. For example, when the dipotassium salt of **5** is dissolved in sulfuric acid (or in perchloric, phosphoric, or hydrocloric acids) (50 mM, 2M to 12M) the original violet color of the solution (533 nm) gradually changes via orange (532 sh, 456 sh, 450 nm) to bright yellow (458, 389 nm); the rate of a change is generally faster in concentrated acids. Neutralization of the yellow solution regenerates the pink color due to the dianion **5**, indicating that the color is at least partially due to protonation (e.g., formation of the oxonium salt or conjugate acid) and possible hydrolysis of the dicyanomethylene groups.

3.2 Preparation of croconate violet (5, dipotassium salt)

A mixture of dipotassium croconate [22] (1 g of anhydrous, or an equivalent of the trihydrate), malononitrile (3g), and water (15 mL) is heated at 85–90 °C for 1 h. The product crystallizes from the deep-violet solution on cooling; however; it is preferable to concentrate the reaction mixture (nitrogen flush, 85 °C) to 3 to 5 mL and cool. The product is then isolated by trituration of the solid with methanol; yield 1.4 g (97%). Recrystallization from hot water gives **5** (dipotassium salt) as deep-blue, metallic needles; **5** crystallizes as the dihydrate. The salt loses water of crystallization beginning at 137 °C and decomposes at 425 °C. $\lambda_{max}^{H_2O}$ 533 (ε 100000), 444 (ε 13800), 354 (ε 3600), 312 (ε 6200), 280 (ε 8400), 253 (ε 19500), 237 (ε 16000), 226 nm (ε 11200)[7].

ν_{max}^{KBr} (cm^{-1}) 3560m, 3500w, 3460m (C–H), 2195s ($C\equiv N$), 1680s ($C=O$), 1620s, 1580s, 1520s [with overtones at 1640w, 1630w, 1590w, 1560w, to give a sixtet, $C=O + C=C + C=C(CN)_2$], 1445s (dianion), 1160w, 1080w, 820w, 760m.

3.3 Preparation of monopyridinium croconic salts

Generally, in non-aqueous aprotic solvents, a proton-transfer reaction between amines (B) and phenols, e.g. polyhydric phenols (AH), leads to the formation of ion-pairs, e.g., $B + AH \rightleftarrows B^+HA^-$, in a molecular-complex product. On treatment with amines, in non-aqueous aprotic solvents, a series of oxocarbon acids (e.g. benzenehexol, tetrahydroxyquinone, and rhodizonic, croconic, but rarely squaric acid), also undergo a proton-transfer reaction, to yield molecular complexes that are under study. The literature contains no report on the preparation of the monoanion of croconic acid, although its existence in solution has been postulated [3]. The UV and visible spectra of the monoanion croconate (e.g. monopyridinium salt of croconic acid) show considerably less intense bands, e.g., $\lambda_{max}^{H_2O}$ 362 (ε 32000) and 335 nm (sh) (ε 23000), as compared to the dianion croconate [dilithium croconate, $\lambda_{max}^{H_2O}$ 363 (ε 45000) and 336 nm (sh) (ε 32000)] or croconic acid [$\lambda_{max}^{H_2O}$ 362 (ε 54500) and 335 nm (sh) (ε 39000)]; however, the bands are more intense than in those given by dihydrocroconic acid [$\lambda_{max}^{H_2O}$ 282 (288) nm (ε 17000)] or in the dianion dihydrocroconate [dipotassium salt, $\lambda_{max}^{H_2O}$ 322 (ε 6600) and 276 nm (sh) (ε 3000)]. The preparation of a new monopyridinium salt of croconic acid, an ion-pair molecular complex, is described next. The salt can be used in the preparation of analogs of Croconate Violet.

3.3.1. Preparation of monopyridinium croconate

To a solution of croconic acid (trihydrate, 0.22 g) [22] in warm 1,4-dioxane was added pyridine (0.3 mL) with stirring. The anhydrous product (yield 0.2 g) crystallized on cooling. Recrystallization from methanol–ether gave the monopyridinium croconic salt as deep-yellow microcrystals, m.p. 218–221 °C (dec). $\lambda_{max}^{H_2O}$ 362 (ε 32000), 335 (sh) (ε 23000), 261 (sh) (ε 4000), 254.3 (ε 6100), and 248 nm (ε 5500); ν_{max}^{Nujol} 3440w (OH), 1750m, 1710m ($C=O$), 1630 ($C=O+C=C$), 1650w, 1220w, 1160w, 1130w, 1070m, 760m, and 680m. The mass spectrum showed a typical ion-pair (or charge-transfer) molecular-complex pattern: *m/e* 79 ($M^{+\cdot}$) (pyridine), *m/e* 142 ($M^{+\cdot}$) (cronconic acid). Calc. for $C_{10}H_7NO_5$:C, 54.33; H, 3.19; N, 6.33. Found: C, 54.18; H, 3.21; N, 6.52.

3.3.2 Preparation of dihydrocroconic acid (2,4,5-trihydroxy-4-cyclopentene-1,3-dione)

To a solution of sodium croconate (trihydrate, 5 g) [22] in 0.75M aqueous sodium hydroxide (150 mL) was gradually introduced sodium borohydride (2g); the mixture was stirred for 2 hours and kept for an additional 16–18 hours at room temperature. The still yellowish solution was carefully acidified with glacial acetic acid (12 mL) and the suspension was filtered through a layer of Celite–carbon. The clear filtrate was evaporated at 40–45 °C to a syrup; to remove boric acid, the syrup was successively evaporated with methanol (4 × 100 mL), to give the salt as a white solid (yield 4.2–4.5 g; the crude disodium dihydrocroconate contains 5 to 8 percent of sodium acetate). The crude salt was de-ionized with Amberlite 120 (H^+) resin (125 mL). The resin was washed with water (750 mL) and, on addition of glacial acetic acid

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[6] The other bands of the bis(*N,N*-dimethylformamide) salt of 5 (dihydrate) were at 593(sh) (ε 5500), 495(sh) (ε 33000), 444 (ε 14000), 418(sh) (ε 12000), 356 (ε 5500), 311 (ε 8400), 281(sh) (ε 11000), 253 (ε 20500) and 236 nm (ε 18600).

[7] The once-recrystallized sample of the dipotassium salt of 5 showed a high degree of purity; UV λ_{max} 533 (ε 89500), 444 (ε 13000), 354 (ε 3400), 312 (ε 6000), 280 (ε 8200), 253 (ε 19000), 237 (ε 15800), 226 nm (ε 11000).

(50 mL), the eluate was evaporated at 40–50 °C apparently to dryness. The solid was treated with warm methanol, the suspension was filtered through a layer of Celite and acid-washed carbon, and the filtrate concentrated to 15–20 mL; cooling in a refrigerator gave small, colorless needles of dihydrocroconic acid; yield 1.0 g. An analytically pure sample was prepared by recrystallization from methanol–acetone; the acid crystallizes as the dihydrate, and melts at 120–121 °C (effervescence). $\lambda_{max}^{H_2O}$ 282 (288) (ε 17000); ν_{max}^{Nujol} 3600w, 3200w, (OH), 1730sh, 1700s ($C=O$), 1610s ($C=O+C=C$), 1270m, 1240w, 1190w, 1140w, 1080s, 935s, 835w, 800w, and 675w; ^{13}C NMR (Me_2SO-d_6, Me_4Si) δ 179.5 ($C=O$), 177.7 ($C=O$), 133.8 ($C=C$), 132.0 ($C=C$), 73.1 (HC-OH), 66.9 (HC-OH); the spectrum indicates on a possible existence of an equilibrium mixture; the reaction is under study. The mass spectrum did not show the molecular-ion peak: *m/e* 110(M-2OH), *m/e* (110-CO), *m/e* 54 (82-CO). Calc. for $C_5H_8O_7$: C, 33.34; H, 4.47. Found: C, 33.09; H, 4.40.

Cyclic voltammetry of dihydrocroconic acid (concentration 25.1 mM, 0.1 $NaClO_4$, 1:1 H_2O-DMF, mercury electrode, at a scan rate of 50 $mV.s^{-1}$) shows an irreversible reduction potential at −1.63V, as compared to croconic acid reduction peaks at −1.36, −1.50, and −1.63V (also irreversible).

The acid formed a triacetate, m.p. 170–172 °C λ_{max}^{MeOH} 279 nm (ε 18000). The acid was converted into the dipotassium salt on titration with potassium methoxide in methanol $\lambda_{max}^{H_2O}$ 322 (ε 6600) and 276 nm (sh) (ε 3000). ν_{max}^{Nujol} 3380w (OH), 1730w ($C=O$), 1670w, 1650m ($C=O+C=C$) 1525m, 1240w, 1135m, 1060s, 1000m, 930s, 830w, 750w, 660w.

An aqueous solution of the acid (or a salt) was warmed with aqueous cupric acetate; the red precipitate of cuprous oxide was filtered off; the warm filtrate was acidified with acetic acid and mixed with aqueous barium chloride, to give golden crystals of barium croconate (not observed in the original solution that was not treated with an oxidizing reagent; manganese dioxide can also be used as the oxidant).

4. Croconic acid violet

Brief warming (3–5 min, 85 °C) of the dipotassium salt of **5** with concentrated hydrochloric acid yielded orange crystals of a new, crystalline oxocyanocarbon acid **8** [(1,3-dicyanomethylene-2-oxo-4-cyclopentene-4,5-diol], [m.p. 260–270 °C dec., *m/e* 238 (M^+), ^1H NMR (Me_2SO-d_{-6}) δ 9.53 (S, 1H)[8], ^{13}C-NMR (9:1 H_2O-D_2O+T_1 relaxation reagent,[4] external Me_4Si) δ180.8 ($C=O$) 171.0 ($C=C$), 147.0 [$C=C(CN)_2$], 114.2 ($C\equiv N$), 112.7 ($C\equiv N$), and 51.4 [$C-C(CN)_2$][5] termed "croconic acid violet" that is a high intensity dye: UV (H_2O) λ_{max} 533 (ε 78500), 444 (ε 10500), 354 (ε 2800), 312 (ε 4800), 281 (ε 6700), 253 (ε 15000), 237 (ε 1200), and 226 sh, nm (ε 9800)[9].

Note that aqueous solutions of either the salt of **5** or the acid **8** absorb in the same region of the visible spectrum; moreover, their high and nearly identical molar extinction coefficients (ε 100000 vs. 78500) are indicative of the complete ionization of the latter in aqueous solution. Cyclic voltammetry of the acid 8 showed the irreversible reduction potentials at −0.88 V and −1.33 V, values identical with those of its salt, e.g., the dipotassium salt of **5**. The acid **8** is one of the strongest oxocyanocarbon acids thus far discovered, with $pK_2=0.07\pm0.02$ [24]; the pK_1 is difficult to be measured because of an irreversible protonation of the monoanion in solution of strong acids (HCl). The high acidity-constant of the oxocyano-carbon acid **8** is considered to be due to the considerable delocalization of π-electrons in the substantially planar ring of its dianion **5**, as is also observed for the oxocarbon acids and their anions [2]. The partial infrared spectrum (KBr) of acid **8** shows bands at 2220m ($C\equiv N$), 1780s, 1728s ($C=O$), 1670s, 1618s, 1580s and 1520m cm^{-1} [$C=O$ + $C=C$ + $C=C(CN)_2$],[10] pointing to existence of tautomeric forms in the solid **8**. The acid **8** was reconverted into the dipotassium salt of **5** by careful neutralization (CH_3OK–CH_3OH or aqueous K_2CO_3 at 60–70 °C for 5–15 min), and this procedure is the best way found thus far for preparing the other alkali salts of type **5** (Li, Na, Rb, Cs); the lithium salt, extremely soluble in water, was recrystallized from methanol-ether. The acid is a potential electron-acceptor. Oxidation of **8** with bromine or nitric acid in water or acetic acid yielded polymeric products; treatment of **8** with aqueous sodium periodate, followed by extraction with ethyl acetate gave an orange product ($\lambda_{max}^{CH_3OH}$ 430–440 nm) believed to have structure **9**. However, acid **8** was oxidized to a colorless deliquescent product on treatment with 30 percent aqueous hydrogen peroxide.

4.1 Formation of butyl ester of 8

Formation of butyl ester of **8** in 1-butanol (68.5 mM) was evident from its UV spectrum: λ_{max}^{BuOH} 572 (sh) (ε 18500), 542 (ε 24000), 439 (ε 20200), 418(sh) (ε 13300), 305 (ε 7000) and 245 nm (ε 14500). Increase in intensity of the band 541 nm (ε 40000) was observed on addition of one drop of water to the original solution of **8**: $\lambda_{max}^{BuOH+H_2O}$ 584(sh) (ε 10000), 541 (ε 40000), 440 (ε 15500), 312 (ε 6100) and 248 nm (ε 14000) (partial ester hydrolysis to give **8**).

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[8] As compared to other oxocarbon acids [^1H NMR in (Me_2SO-d_{-6})], the proton shifts (due to the association or complexation) were: tetrahydroxyquinone δ 4.08, benzenehexol (hexahydroxybenzene) 4.68, rhodizonic acid 4.85, croconic acid 6.49,and squaric acid 7.68.

[9] The once-recrystallized sample of 8 showed a high degree of purity: UV $\lambda_{max}^{H_2O}$ (ε 77400), 444 (ε 10500), 354 (ε 2800), 312 (ε 5000), 281 (ε 7000), 253 (ε 15300), 237 (ε 12600), 226 nm(sh) (9800); λ_{max}^{MeOH} 534 (ε 71200), 438 (ε 15800), 356 (ε 2800), 314 (ε 6300), 281 (ε 8400) and 248 nm (ε 19500); note that the band at 237 nm given in water disappeared in methanol. Decrease in intensity of the band 534 nm (ε 71200) in methanol may be due to interaction of the strong oxocyanocarbon acid 8 with a solvent, e.g., esterification reaction.

[10] Other bands were at 1475m, 1410m, 1350m, 1200m, 1115m, 1085s, 1000m, 825w, 800w, 790w, 700m and 660w.

5. 2-(Dicyanomethylene) croconate salts

5.1 2-(Dicyanomethylene) alkyl croconates

Treatment of dimethyl, diethyl, or dipropyl croconate (**7**, $R=CH_3$, $R^1=R^2=O$ [25]; $R=C_2H_5$, $R^1=R^2=O$ [25]; $R=C_3H_7$ or $R=i\text{-}C_3H_7$, $R^1=R^2=O$) in *N,N*-dimethylformamide with malononitrile produces golden plates of 2-(dicyanomethylene) alkyl croconates, e.g. **10** ($R=CH_3$; C_2H_5; C_3H_7; i-C_3H_7) in 82–86 percent yield. These are efficient electron-acceptors; with polycyclic, aromatic hydrocarbons (e.g. pyrene, benz[a]pyrene, or anthracene), they form deep-colored, charge-transfer complexes. For example, the crystal structure of the 1:1 red complex [pyrene—**10** ($R=C_2H_5$)] has recently been determined [26]; a novelty of the structure, surprisingly, lies in its crystal unit-cell that comprises two pyrene molecules differing in symmetry. With tetrathiafulvalene (TTF) as the donor, 2-(dicyanomethylene)alkyl croconates **10** ($R=CH_3$;C_2H_5;C_3H_7), however, form charge-transfer salts that are semiconductors [20]. Chemically, 2-(dicyanomethylene) alkyl croconates react readily with aniline in warm alcohol to give deep-red dyes of structure similar to that described for the product of reaction of 2-(dicyanomethylene)-1,3-indandione with the reagent [27].

5.2 Preparation of 2-(dicyanomethylene)-4,5-dimethoxy-4-cyclopentene-1,3-dione (10, $R=CH_3$)

To a warm solution of dimethyl croconate (**7**, $R=CH_3$, $R^1=R^2=O$) (0.2 g) in warm *N,N*-dimethylformamide (10 mL) is added malononitrile (1 g), and the mixture is stirred at 60–70 °C for 3 minutes. The resulting, deep-red solution is then carefully diluted with water (or aqueous methanol) to incipient crystallization. The crude product (0.22 g, 86%) is recrystallized from aqueous methanol (or a little butyl acetate), to give (**10**, $R=CH_3$) as lustrous, golden plates, m.p. 183–184 °C. Mass spectrum: *m/e* 213 (M^{+}); UV (CH_3OH) λ_{max} 430 (sh) (ε 5400), 406 (ε 6400), 320 (ε 4100), 258 mm (ε 11400); IR (KBr) ν_{max} 2220m (C≡N); 1742w (C=O); 1690s, 1655s C=O+C=C); 1560s cm $^{-1}$ [$C=C(CN)_2$]. Other bands were at 3020w, 2960m, 2850w (C-H), 1480s, 1430s, 1350s, 1315m, 1240m, 1215m, 1190m, 1150m, 1130s, 1080m, 965s, 930m, 830m, and 780m; ^{1}H NMR ($Me_2SO\text{-}d_{-6}$) δ 4.40. Similarly, starting with diethyl croconate (**7**, $R=C_2H_5$, $R^1=R^2=O$), the diethoxy derivative (**10**, $R=C_2H_5$) was prepared in 85 percent yield; m.p. 124–125 °C (aqueous methanol); *m/e* 246 (M^{+}); UV $\lambda_{max}^{CH_2Cl_2}$ 430 (sh) (ε 10000), 412 (ε 11500), 330 (ε 8000), 260 nm (ε 12400) ν_{max}^{KBr} cm^{-1}, **10** ($R=C_2H_5$): 2970m (C–H), 2220w (C≡N), 1680s (C=O), 1640m (C=O+C=C), 1560s [$C=C(CN)_2$], 1480m, 1420s, 1380s, 1360w, 1345s, 1330s, 1235m, 1185w, 1165w, 1145m, 1140m, 1100w, 1090w, 985s, 890w, 870w, 845w and 790m. ^{1}H NMR ($DMSO\text{-}d_6$) δ 1.48 (t, J=7 Hz); 4.95 (q, J=7 Hz); ^{13}C NMR ($Me_2SO\text{-}d_6$) δ 179.0 (C=O, C-1+C-3), 174.9 (C=C, C-4+C-5), 152.1 [$C=C(CN)_2$], 116.5 (C≡N), and 53.8 [$C=\mathbf{C}(CN)_2$]; also a triplet with slight splittings at 63.1, 56.9, and 50.7 (CH_2) and a quartet at δ 27.00, 21.4, 15.9, and 10.4 (CH_3).

Similarly, the corresponding 4,5-dipropyl derivatives of **10** were prepared; $R=C_3H_7$, m.p. 114–115 °C, *m/e* 274 (M^+) (85% yield); UV $\lambda_{max}^{CH_2Cl_2}$ 434 (sh) (ε 11500), 416 (ε 13600) 330 (ε 9300), 260 nm (ε 13500); $R=i\text{-}C_3H_7$, m.p. 145–146 °C, *m/e* 274 (M^+) (82% yield); UV $\lambda_{max}^{CH_2Cl_2}$ 440 (sh) (ε 5300), 414 (ε 6700), 326 (ε 5200), 256 nm (ε 9400); ν_{max}^{KBr} **10** ($R=i\text{-}C_3H_7$):2995m, 2935w, 2840w (C–H), 2200m (C≡N), 1665 (C=O), 1630 (C=O+C=C), 1565s, 1515 [$C=C(CN)_2$], 1405s, 1380m, 1330w, 1310s, 1240m, 1180m, 1150s, 1130m, 1090s, 1070w, 900w, 890m, 850m, 830m, 785w, 775w and 750s.

5.3 2-(Dicyanomethylene)-4,5dihydroxy-4-cyclopentene-1,3-dione (4, dipotassium salt)

Careful, alkaline hydrolysis of **10** ($R=CH_3$, C_2H_5, C_3H_7 or $i\text{-}C_3H_7$) caused a substantial change in color, to give the new, violet dianion 4, to which a bond-delocalized structure is assigned. The infrared spectrum (KBr) of the dipotassium salt of **4** showed bands at 1715 sh, 1660s (C=O), 1620s, 1585s, and 1570 sh [$C=O+C=C+C=C(CN)_2$][11], indicating possible contributions from the resonance forms, analogous to 5a↔5c. However, the fully symmetrical (D_{5h}) structure proposed for the croconic ring of the dianion **4** still awaits confirmation by x-ray diffraction study.

5.4 Preparation of the dipotassium salt of 4

To a warm solution of 2-(dicyanomethylene)-4,5-dimethoxy-4-cyclopentene-1,3-dione (**10**, $R=CH_3$) (50 mg in 1 mL of methanol) was added in *one portion* potassium methoxide (15 mg); after mixing, the red solution was quickly evaporated to dryness at 60 °C with a stream of nitrogen. The crude product was extracted with warm chloroform (3×3 mL) and the solid recrystallized from water (slow concentration at room temperature), to give cherry-red crystals of the dipotassium salt of **4** (yield 30 mg). The salt crystallizes as the dihydrate; UV $\lambda_{max}^{H_2O}$ 533 (ε 70000), 444 (ε 12000), 356 (sh) (ε 3200), 312 (ε 5200), 280 (sh) (ε 6600), 253 (ε 14000), 235 (sh) (ε 12000); ^{13}C NMR (9:1 $H_2O\text{-}D_2O$, T_1 relaxation reagent,[4] external Me_4Si) δ 180.4 (C=O), 173.5 (C=C), 150.6 [$C=C(CN)_2$], 117.0 (C≡N), and 52.6 [$C=\mathbf{C}(CN)_2$].

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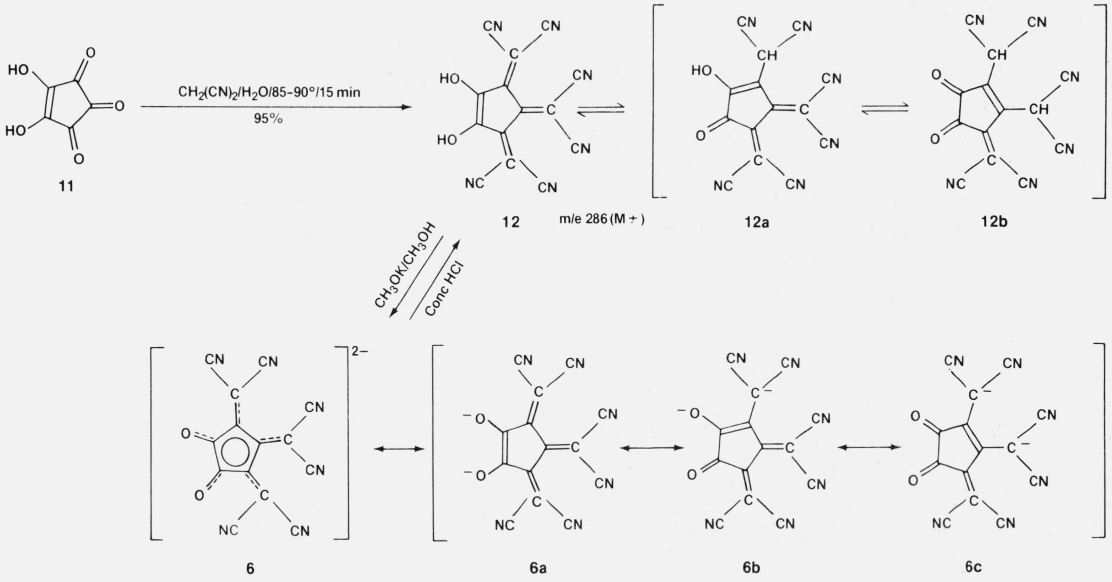
[11] Other bands were at 2860s, 2820w, 2720w (C–H), 2180s, 2100m (C≡N), 1430s (dianion), 1380m, 1350m, 1300m, 1180m, 1075s, 970w, 905m, 770m, 760m and 665w.

5.5 2-(Dicyanomethylene)-4,5-dihydroxy-4-cyclopentene-1,3-dione 10 (R = H)

Careful heating of the dipotassium (or disodium) salt of **4** with 10M hydrochloric acid (3–5 min at 75–80 °C) yielded orange crystals of the new oxocyanocarbon **10** (R = H) [2-(dicyanomethylene)-4,5-dihydroxy-4-cyclopentene-1,3-dione] [m.p. 210–220 °C dec., *m/e* 190 ($M^{\dagger}$)]; UV $\lambda_{max}^{H_2O}$ 533 nm (ε 62000), 444 nm (ε 11500), IR ν_{max}^{KBr} (cm^{-1}) 2210w, 2190m (C≡N), 1760m, 1710s (C = O), 1635s, and 1570s [C = O + C = C + C = C(CN)$_2$]; isolation and purification of the labile acid **10** (R = H) were difficult.

6. 1,2,3-Tris (dicyanomethylene) croconate salts. Croconic acid blue

Unlike the reaction of the croconic salts (e.g., their dianions) with malononitrile (to give croconate violet of type **5**), the direct interaction of croconic acid **11** (also **1**, K = H, **7**, R = H, $R^1 = R^2 = O$) with malononitrile in warm water gives a new oxocyanocarbon acid **12** [1,2,3-tris(dicyanomethylene)-4-cyclopentene-4,5-diol], that is also a new solvatochromic dye. When a mixture of croconic acid and malononitrile in water was briefly heated at 85–90 °C, shining, purple plates of the product began to crystallize after 10 minutes of reaction. The compound isolated (in over 90% yield), termed "croconic acid blue," 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 alcohol) is red [UV (CH_3COCH_3) 475–480 nm], but in water, it is deep blue [(H_2O) 597–600 nm][12]. The infrared spectrum (KBr) of **12** shows strong bands at 1755s, 1700sh (C = O), 1650s, 1590s, and 1520s [C = O + C = C + C = C(CN)$_2$], indicating possible existence in the crystalline material of the tautomers **12a**$\rightleftharpoons$**12b**.[13] The acid **12** is a strong oxocyanocarbon acid (pK_2 ~1) [24]; it is stronger than croconic acid, but weaker than croconic acid violet **8**. Oxidation of **12** with sodium periodate or hydrogen peroxide gave a syrupy product, not yet characterized. The acid **12** in water at room temperature (sensitive toward UV irradiation) hydrolyzes slowly (95% in 85 days) to yield the more thermodynamically stable, croconic acid violet **8** λ_{max} (H_2O 534nm); in warm (95 °C) 10M hydrochloric acid, the acid **12** hydrolyzes completely in a few minutes to produce croconic acid violet **8**. However, excessive heating of **12** in water causes apparent polymerization, to give as product deep-green, lustrous plates [$\lambda_{max}^{H_2O}$ 590–595 sh, 535, 510, and 490 nm]; it showed no molecular-ion peak in its mass spectrum, and the elemental analysis of which was close to that of the starting material plus three molecules of water per molecule (found: C, 49.77; H, 2.54; N, 23.23). The compound may be identified by its poorly resolved infrared spectrum (KBr): 2200s (C≡N), 1750sh, 1730sh, (C O), 1660w (C = O + C = C), 1400w, 1230sh, 1170w, 1075w, 1000sh, and 760w.



Hence, the behavior of malononitrile towards croconates has a two-fold character: it can produce either 1,3-bis(dicyanomethylene) salts of type **5** with croconic salts or 1,2,3,-

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[12] The visible absorption band (at 475–480 nm) is extremely sensitive to a trace of water; the maximum shifts easily to longer wavelength (600 nm) on simple dilution, unless strictly anhydrous solvent is used.

[13] Other bands (KBr or mull) were at 3620w, 3530w, 3290w (OH), 3140m C-H), 1450m, 1430s, 1360m, 1330w, 1130w, 1090m, 990w, 930w, 825m, and 760m.

tris(dicyanomethylene) acid **12** with croconic acid. The reaction of the reagent with croconic acid esters to yield 2-(dicyanomethylene) alkyl croconates (e.g., **10**, R = alkyl) is an additional example characteristic for this enolic, cyclic 1,2,3,-trione.

6.1 Preparation of croconic acid blue (12)

A mixture of croconic acid [22] (500 mg), malononitrile (1.2 g), and water (10 mL) is heated at 85–90 °C for 15 minutes 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%); the product is 97 percent pure (TLC). Analytically pure **12** is prepared as follows: a sample (100 mg) in water (20 mL) is boiled under reflux (2–3 min) and rapidly filtered; the purple filtrate is then concentrated at 25–30 °C to give the acid **12** as deep-purple plates, yield: 60 mg. The acid **12** is quite soluble in methanol or acetone, moderately soluble in water, and difficulty soluble in ether or chloroform. Calc. for $C_{14}H_2N_6O_2$. 1.5 H_2O; C, 53.68; H, 1.61, N, 26.83. Found: C, 53.92; H, 1.59; N, 26.80. The acid **12** melts at 228–230 °C (dec.), *m/e* 286 ($M^{\dot{+}}$), UV $\lambda_{max}^{H_2O}$ 600 (ε 55000), 520 sh (ε 16000), 400 sh (ε 12000), 378 (ε 11000), 318 (ε 12000), 278 (ε 11500), 232 nm (ε 9600); $\lambda_{max}^{CH_3OH}$ 606 (ε 55800), 515 (ε 16000), 406 (ε 14200), 380 sh (ε 12300), 321 (ε 12000), 281.5 (ε 11000), 269 (ε 11200), 245.5 sh (ε 11200), 232.5 nm sh (ε 9700). λ_{max}^{BuOH} 608 (ε 31500), 504 (24400), 474(sh) (ε 18000), 412 (11200), 322 (ε 13000), 266 nm (ε 15400) (partial esterification of **12**).

^1H NMR ($Me_2SO\text{-}d_{-6}$ δ 10.30 (S, IH), ^{13}C NMR (9:1 $H_2O-D_2O + T_1$ relaxation reagent, external Me_4Si) δ 177.1 (C = C, C-4 + C-5), 148.0 [**C** = C(CN)$_2$, C-1 + C-3], 140.3 [**C** = C(CN)$_2$, C-2], 119.4 (C≡N, C-1 + C-3), 118.2 (C≡N, C-2),[14] 51.3 [C = **C**(CN)$_2$, C-1 + C-3], and 52.3 ppm [C = **C**(CN)$_2$, C-2].

6.2 Croconate blue (salts of 6)

Acid **12** was readily converted into the green-blue dipotassium salt of [1,2,3,-tris(dicyanomethylene)-4-cyclopentene-4, 5-diol], e.g. **6**, on careful titration with potassium methoxide in methanol. Similarly bis(tetramethylammonium)[15] or pyridinium salts of **6** were prepared.

The dipotassium salt of **6** is a dye,[2] named "croconate blue" because of its intense blue color in solution. The electronic spectrum of the dianion **6** in aqueous solution shows peaks at 599 (ε 54600), 538sh (ε 32000), 398 (ε 12000), 378 (ε 13000), 314 (ε 18000), 285 (ε 16000) and 234 nm (ε 14000).

Note that the salt of **6** and the acid **12** absorb in the same region, with the same intensity in the visible spectrum (ε 54600 vs. ε 55000). The infrared spectrum (KBr) of the dipotassium salt of **6** shows strong bands at 1670s (C = O), 1620s, and 1570m cm^{-1} [C = O + C = C + C = C(CN)$_2$][16] indicating possible contributions from the resonance forms **6a**↔**6c**. The Raman spectrum of the salt of **6** (fig. 2B) shows bands at 1654, 1596, 1572, 1551 cm^{-1} (C = O + C = C + C(CN)$_2$) and at 1472 cm^{-1} (dianion vibration) also indicating possible contributions from the resonance forms **6a**↔**6c.**

The ^{13}C NMR spectrum of **6** (9:1 $H_2O\text{-}D_2O + T_1$ relaxation reagent,[4] external Me_4Si) exhibited peaks at 178.0 (C = C, C-4 + C-5), 147.3 [**C** = C(CN)$_2$, C-1 + C-3], 139.1 [**C** = C(CN)$_2$, C-2], 120.2 (C≡N, C-1 + C-3), 118.6 (C≡N, C-2)[17], 52.2 [C = **C**(CN)$_2$, C-1 + C-3], and 53.3 [C = **C**(CN)$_2$, C-2]; the spectrum resembled that of the acid **12**, which supports the symmetrical structure of the dianion **6** and the dianion **12**, formed by ionization. Cyclic voltammetry and DC polarography of the dipotassium salt of **6** may indicate stepwise reduction by a two-electron, transfer mechanism as shown by three irreversible, peak potentials at −0.69, −0.93, and −1.15V. An almost indentical reduction process was observed for the acid **8**, with the irreversible potentials at −0.69, −0.94, and −1.18 V. The two-electron electrochemical-reduction apparently involves two neighboring dicyanomethylene groups, e.g., $2C = C(CN)_2 \rightarrow (NC)_2CH\text{-}C = C\text{-}CH(CN)_2$, to give a product having a substituted-fulvalene structure. Electrochemistry of the dipotassium salt of **6** (or acid **12**) revealed the first reduction wave at −0.69 V vs. SCE. This value indicates that **6** (or **12**) is much easier to reduce than the dipotassium salt of **5** ($E_{1/2}$ −0.88V vs. SCE). A further study of the electrochemistry of salts of **5** and of **6**, or of acids **8** or **12**, is in progress, including isolation and identification of the redox products. The high acidity of the oxocyanocarbon acid **12** is typical of the symmetrical, bond-delocalized structure of its dianion **6** (as also observed for the dianions **4** and **5** and their conjugate acids). However, a stereomodel of the crowded dianion **6** (the Van der Waals contacts between two neighboring nitrogen atoms is less than 3 A°), indicates that, in order to relieve steric hindrance of the 1, 2,3-tris(dicyanomethylene) groups, a staggered conformation of all cyano groups in **6** will be required (fig. 4B); the calculated twist of the dicyanomethylene group about C-2 and the deviation from the plane of the ring is about 30°.[17] Partial evidence for the *trans* (staggered) conformation of the cyano groups in the dianion **6** (and the acid **12**) is given by their ^{13}C NMR spectra.[18]

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[14] The peak was split into six poorly resolved peaks at 119.0, 118.7, 117.9, 117.5, 115.3 and 112.7 ppm, which may reflect some different conformations of the cyano group.

[15] The bis(tetramethylammonium) salt of 6 showed the following electronic spectrum, $\lambda_{max}^{H_2O}$599 (ε 65000), 512 (sh) (ε 18000), 398 (ε 14000), 378 (ε 14000), 316 (ε 14500), and 282 nm (ε 14000).

[16] Other bands were at 2190s (C≡N), 1465s (skeletal vibration of the dianion), 1265w, 1080w, 830w, 790w, 760w, and 720w.

[17] The planarity of the dianion **6** still awaits confirmation by x-ray crystal structure; indeed, it is very difficult to prepare a sample suitable for x-ray diffraction analysis; the bis(tetramethylammonium) salt of **6** may be the next choice.

[18] 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.

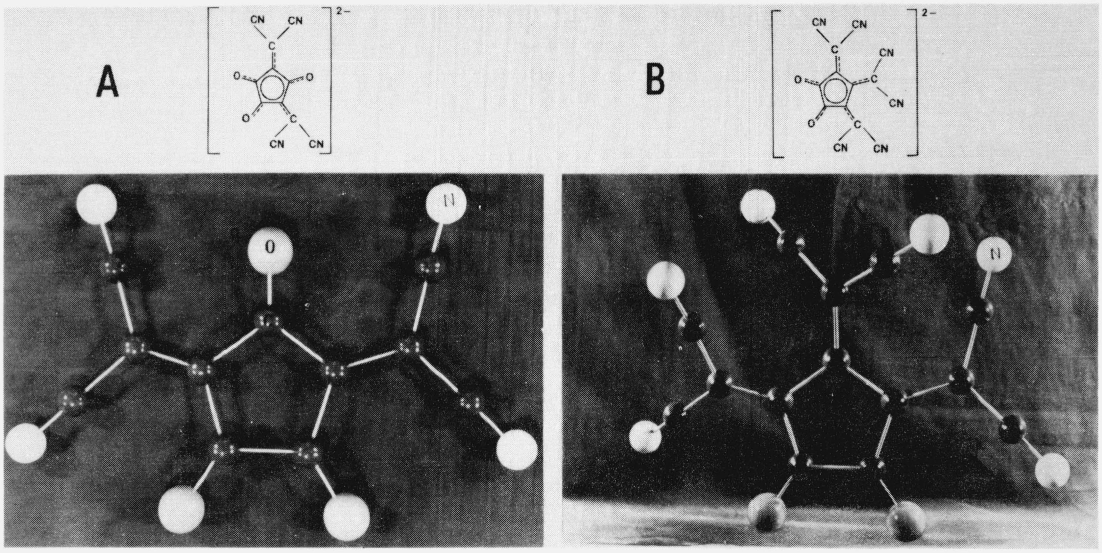

FIGURE 4. *A stereomodel of the dianion* **5** *(A) and the dianion* **6** *(B); note the twist of the dicyanomethylene group about C-2 in the dianion* **6**.

6.3 Facile, alkaline hydrolysis of the croconate blue salts

Diminution in symmetry in the dianion **6** is probably associated with instability of its salts in aqueous, alkaline media. The bis(tetramethylammonium) or dipotassium salt of **6** in ∼0.1 *M* aqueous potassium hydroxide soloution (pH 13.2) almost instantaneously (2 to 3 sec, on the spectrophotometer scale) split off the 2-(dicyanomethylene) group to yield the croconate violet dianion **5** (a prompt hypsochromic shift from 600 to 534 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 **4** (band at 444 nm, a change from B to C in ∼4 h), and then, the yellow croconate dianion **2** (bands at 362 and 333 (sh) nm), a change from C to D in ∼40h, as the final product.

6.4 Preparation of croconate blue (6, dipotassium salt)

The acid **12** (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 shining, green-blue crystals of the dipotassium salt of **6**, yield: 220 mg. The product crystallizes as the trihydrate. Calc. 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. Similarly, the bis(tetramethylammonium) salt of **6** was obtained as lustrous, green-blue rosettes: it crystallizes as the dihydrate. Calc. for $C_{22}H_{24}N_8O_2 \cdot 2\ H_2O$: C, 55.98; H, 5.54; N, 23.42. Found: C, 56.12; H, 5.88; N, 23.68. The dipotassium salt of **6** loses one molecule of water of crystallization per molecule on storage at room temperature. 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.

7. Stable free-radicals on autoxidation of oxocarbon acids and their salts

Freshly prepared, colorless benzenehexol [28], kept *in vacuo* in the dark (or under argon in a refrigerator) remains relatively free from colored impurities for an extended period of time. However, when a freshly prepared sample of benzenehexol is exposed to air and light for as little as 8 hours, it acquires a pink coloration, and the e.s.r. spectrum shows the presence of a paramagnetic impurity (table 1). The nature of the impurity is as yet unknown; usually, autoxidation of phenols (or polyhydroxy aromatics) involves a semiquinone type of free radical. A broad, one-line, e.s.r. spectrum (ΔH 11.51G and large g values, table 1) observed for the stable radical of benzenehexol may indicate further reaction of the initial semiquinone intermediate with oxygen, to give a peroxo type of species. The usual concentration of a paramagnetic impurity in benzenehexol is ∼0.1 percent after 12 hours of exposure, reaching 1–1.5 percent in 6 weeks and 2–2.5 percent after 1 year of storage at room temperature [the values were verified with a standard dipicrylhydrazyl (DPPH) solution]. The crude benzenehexol can be purified by recrystallization (strong HCl + $SnCl_2$)

TABLE 1. *ESR Measurements of Paramagnetic Species on Autoxidation of Some Oxocarbons and Their Acids*

Compound	g Value	Linewidth ΔH, Gauss	State	Temperature K	Intensity of Peak
Benzenehexol	2.0378	11.51	Solid	300	medium
	2.0383	8.93	Solid	77	medium
	2.0377	11.05	Aqueous solution[a]	77	medium
Tetrahydroxyquinone (THQ)	2.0413	8.22	Solid	77	very weak
Na THQ	2.0381	6.60	Solid	77	strong, symmetrical, one-line
	2.0380	10.3	Aqueous solution[a]	77	weak
Rhodizonic Acid	2.0395	9.4	Solid	77	very weak
NH_4 Rhodizonate	2.0386	7.05	Solid	77	medium to strong
Na Croconate	2.0400	15.30	Solid	77	very weak
Ag Croconate	2.0425	16.45	Solid[b]	77	weak

[a] Polycrystalline at 77K.

[b] Little or no paramagnetic species were observed in croconic acid, triquinoyl, leuconic acid, or squaric acid. Dismutation and degradation reactions were not sought.

[28]. The minute proportions of paramagnetic species were observed in crude pentahydroxybenzene, in 1,2,3,4- or 1,2,3,5-, but not in 1,2,4,5-tetrahydroxybenzene; also in 1,2,3- or 1,2,4-, but not in 1,3,5-trihydroxybenzene; also in 1,2-benzenediol.

In the oxocarbon series, autoxidation is especially pronounced for the alkali salts of tetrahydroxyquinone. The disodium salt of tetrahydroxyquinone (NaTHQ) autoxides slowly at room temperature to yield the more thermodynamically stable disodium rhodizonate (Na rhodizonate), with migration of a sodium atom; the rate of conversion is ~50 percent in 3 months, and >95 percent in 6 months. As expected, autoxidation of NaTHQ in aqueous solution is considerably faster. The rate of autoxidation of NaTHQ is faster at higher temperatures, to give >98 percent conversion into Na rhodizonate, on heating at 170 ° for 24 hours, and this procedure has been used synthetically [22]. There is not doubt that autoxidation of NaTHQ to Na rhodizonate is a free-radical process, and this was supported by monitoring of the oxidation rate in the e.s.r. cavity; also by the visible (in 2.5*M* HCl) or infrared spectroscopy (mulls).

Frequently, the presence of a minute paramagnetic impurity cannot be observed by e.s.r. at room temperature; low-temperature e.s.r. (liquid nitrogen) is recommended for verification. Table 1, for example, shows that a trace of a paramagnetic impurity in benzenehexol was observed in the solid at room temperature and at 77K; the same impurity can be extracted with water, and showed the same e.s.r. parameters. In the synthesis of oxocarbons for magnetic or electrical studies, it is necessary to use pure reagents and solvents; it is also essential that the paramagnetic purity of a product should be checked by low-temperature (77K), e.s.r. spectroscopy.

8. Summary

Either partial or complete replacement of the original, carbonyl oxygen atoms in three-, four-, five-, or six- membered oxocarbon anions $[C_nO_n]^{m-}$ by a hetero-atom, a nonmetal, or a metal, e.g., with the C=O equivalent, π-isoelectronic groups C=C, C=N, C=P, C=S, C=Se, etc., may yield a series of unusual oxocarbon analogs, named pseudo-oxocarbons. Many of these new oxocarbons may be of considerable interest to the theoretical chemist in regard to their molecular symmetry, the planarity of their anions, and their novel, nonbenzenoid aromaticity.

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