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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.040
 wR factor = 0.117
Data-to-parameter ratio = 9.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

4,5-Dimethoxycyclopent-4-ene-1,2,3-trione

The title compound (alternative name dimethyl croconate), $\text{C}_7\text{H}_6\text{O}_5$, is the first example of a croconate ether. The molecule is essentially planar and exhibits a local symmetry (C_{2v}) that is different from that shown by the croconate dianion (C_{5h}), indicating that the geometry of these compounds is very sensitive to the electric charge state.

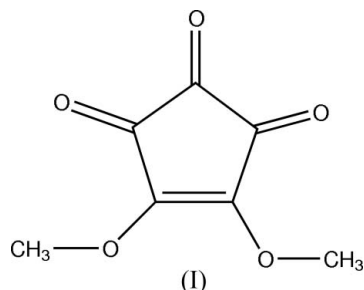
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Comment

Dipotassium croconate and croconic acid were synthesized by Gmelin (1825). In spite of their early discovery, croconate compounds have been investigated and synthesized to a limited extent because of the difficulty of obtaining them in large quantities (Seitz & Imming, 1992). The reported crystal structures of croconate derivatives can be sorted into three groups, *viz.* croconic acid and its salts, coordination compounds, and other croconate derivatives where the O atoms are replaced by organic groups containing N or S atoms. To our knowledge, the structure of the title compound, (I), is the first reported example of a croconate ether.



In the title molecule, the five-membered C-atom ring, the O atoms and one methyl C atom (C1) share the same plane, the other methyl C atom (C2) being displaced by merely 0.20 (1) Å. In some sense, the molecule resembles a planar tortoise. The $\text{C}6=\text{O}4$ bond (the 'head'), and the $\text{C}7=\text{O}5$ and $\text{C}5=\text{O}3$ bonds (the 'forelegs'), show typical $Csp^2=O$ double-bond character, while the $\text{C}3-\text{O}1$ and $\text{C}4-\text{O}2$ bonds (the 'hind legs'), display Csp^2-O single-bond character (Table 1). The carbon-carbon bonds in the body of the tortoise can also be divided into three groups, *viz.* the $\text{C}6-\text{C}7$ and $\text{C}6-\text{C}5$ 'shoulder' bonds [mean value 1.506 (5) Å], the $\text{C}7-\text{C}3$ and $\text{C}5-\text{C}4$ side bonds [mean value 1.453 (5) Å], and the $\text{C}3=\text{C}4$ bottom bond [1.373 (5) Å]. As a result, the molecule possesses C_{2v} symmetry, with C-C and C-O bonds in the ranges 1.373 (5)–1.509 (5) and 1.202 (4)–1.319 (4) Å, respectively. The molecular geometry is very similar to that reported for croconic acid (Braga *et al.*, 2001), but remarkably different from that observed in the croconate dianion, in which the

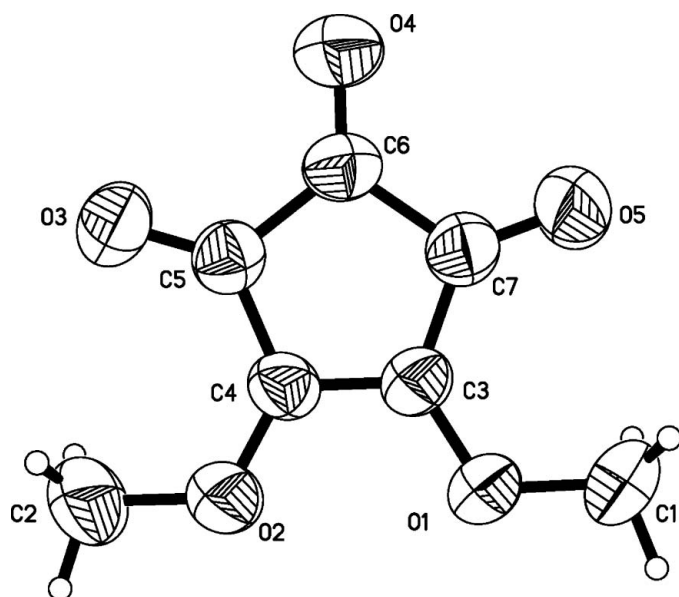


Figure 1
Molecular structure, with displacement ellipsoids at the 30% probability level.

differences between the five C—C bonds are very small and the five C—O bonds are almost identical. In $\text{Rb}_2\text{C}_5\text{O}_5$, for example, the C—C and C—O bond lengths fall in the ranges 1.458 (7)–1.47 (1) and 1.24 (1)–1.244 (8) Å, respectively (Braga *et al.*, 2002). Similarly, in $\text{Cs}_2\text{C}_5\text{O}_5$, the corresponding ranges are 1.448 (7)–1.46 (1) and 1.226 (8)–1.261 (9) Å (Braga *et al.*, 2002). It can be concluded that the croconate dianion has a local symmetry close to C_{5h} and enjoys more π conjugation in comparison with the structure of the croconate ring in the neutral title molecule.

Interestingly, the bond-length pattern of the croconate ligand in coordination compounds is intermediate between the neutral croconate molecule and the dianion in its salts. In $[\text{Fe}_2(\text{bpym})_2(\text{C}_5\text{O}_5)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (bippy = 2,2'-bipyrimidine), the bond lengths [C—C = 1.449 (3)–1.484 (3) Å and C—O = 1.236 (3)–1.265 (3) Å] are comparable to those of the dianion (Sletten *et al.*, 1998). In $[\text{Cu}(\text{bipym})(\text{C}_5\text{O}_5)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ [C—C = 1.429 (2)–1.499 (2) Å and C—O = 1.224 (2)–1.279 (2) Å] and $[\text{Cu}_2(\text{bipym})(\text{C}_5\text{O}_5)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ [C—C = 1.425 (3)–1.500 (3) Å and C—O = 1.220 (2)–1.273 (2) Å] (Castro *et al.*, 1994), the geometry of the croconate ligand approximates to that of the title molecule; thus some charge-transfer should occur from the anionic ligand to the metal. Therefore the bond-length pattern within the croconate ligand in a metal complex may serve as a useful indication of the charge transfer.

Experimental

The title compound was prepared according to the literature method (Williams, 1976). Dipotassium croconate (5 g) was dissolved in water (300 ml) and treated with silver nitrate in the absence of light. Disilver croconate (7.5 g) was obtained and dried at 323–333 K for

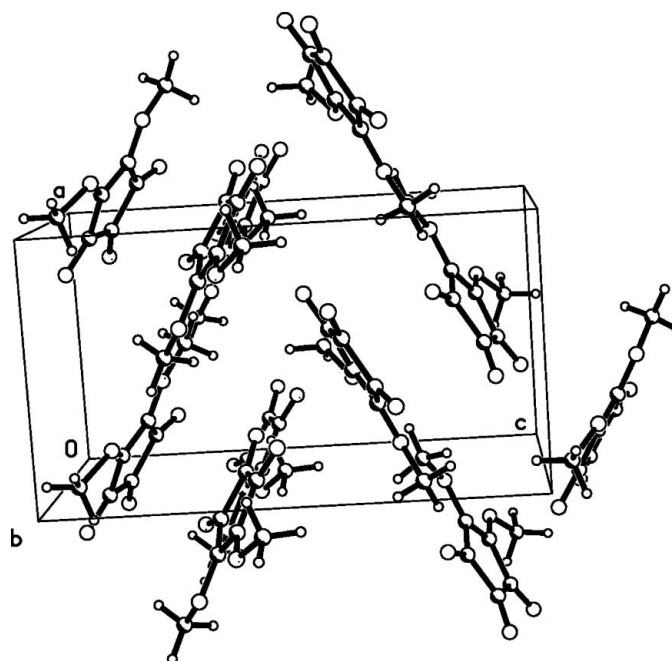


Figure 2
Packing diagram of the title compound.

several hours. The anhydrous disilver croconate was then placed in a Soxhlet extractor fitted on a flask containing methyl iodide (7 ml) and anhydrous benzene (200 ml, treated with Na wire). The mixture was heated under reflux for 4 h. The orange reaction solution was concentrated to 30 ml and cooled. The precipitated yellow crystals were collected and recrystallized from anhydrous benzene.

Crystal data

$\text{C}_7\text{H}_6\text{O}_5$
 $M_r = 170.12$
Orthorhombic, $P2_12_12_1$
 $a = 7.181$ (5) Å
 $b = 8.069$ (5) Å
 $c = 13.015$ (5) Å
 $V = 754.1$ (8) Å³
 $Z = 4$
 $D_x = 1.498$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 38 reflections
 $\theta = 5.3$ – 12.5°
 $\mu = 0.13$ mm⁻¹
 $T = 293$ (2) K
Prism, yellow
 $0.38 \times 0.28 \times 0.22$ mm

Data collection

Bruker *P4* diffractometer
 ω scans
Absorption correction: ψ scan
(*XSCANS*; Siemens, 1996)
 $T_{\min} = 0.880$, $T_{\max} = 0.971$
2052 measured reflections
1026 independent reflections
512 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -16 \rightarrow 16$
97 standard reflections
every 3 reflections
intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.117$
 $S = 0.94$
1026 reflections
110 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.13$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.14$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.149 (14)

Table 1

Selected geometric parameters (Å, °).

O1–C3	1.319 (4)	C3–C4	1.373 (5)
O1–C1	1.448 (5)	C3–C7	1.452 (5)
O2–C4	1.315 (4)	C4–C5	1.454 (5)
O2–C2	1.445 (5)	O4–C6	1.202 (4)
O5–C7	1.222 (5)	C5–C6	1.502 (5)
O3–C5	1.219 (4)	C6–C7	1.509 (5)
C3–O1–C1	120.0 (3)	O3–C5–C6	125.4 (3)
C4–O2–C2	120.0 (3)	C4–C5–C6	105.2 (3)
O1–C3–C4	120.4 (3)	O4–C6–C5	126.7 (4)
O1–C3–C7	128.5 (3)	O4–C6–C7	126.1 (4)
C4–C3–C7	111.1 (3)	C5–C6–C7	107.2 (3)
O2–C4–C3	120.0 (3)	O5–C7–C3	129.8 (4)
O2–C4–C5	128.8 (4)	O5–C7–C6	124.9 (4)
C3–C4–C5	111.2 (3)	C3–C7–C6	105.2 (3)
O3–C5–C4	129.3 (4)		

All H atoms were positioned geometrically and allowed to ride on their attached atoms, with C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Friedel pairs were merged before the final refinement because of the absence of significant anomalous scattering effects.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve

structure: SIR92 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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