5-Ethoxy-1,2-benzoquinone 2-Oxime

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Abstract

The structure of the title compound, $C_8H_9NO_3$, has been determined in order to compare the molecular structures of uncomplexed and complexed 5-alkoxy-1,2-benzoquinone 2-oxime, and those of 5-alkoxy- and 5-alkylamino-1,2-benzoquinone 2-oxime. The title compound has a stronger quinoid character than the 5-methoxy derivative complexed to cobalt(III) and shows less charge delocalization than the 5-alkylamino derivative.

Comment

Benzoquinone monooximic molecules have attracted much attention because of the varied and unusual properties of their metal complexes (Charalambous, Fogg, Gaganatsou & Hendrick, 1993; Barjesteh, Charalambous & Pathirana, 1993; Carugo, Djinović, Rizzi & Bisi Castellani, 1991). A major drawback in using these complexes, for example, in metal extraction processes, organic synthesis or medicinal chemistry, is their generally low solubility in most solvents. Recently, this problem has been solved by using 1,2-benzoquinone 2-oximes with alkylamino or alkoxy substituents in position 5. Soluble complexes of 5-ethylamino-1,2-benzoquinone 2-oxime with potassium and calcium have been synthesized and their structures determined (Charalambous, Rees, Thomas, Carugo & Bisi Castellani, 1995; Charalambous & Carugo, 1996). The soluble complex tris(5-methoxy-1,2-benzoquinone 2-oximato)cobalt(III), having both *fac* and *mer* stereochemistry, has been isolated and characterized, and the crystal structure of the *fac* isomer has been reported (Charalambous, Raghvani, Carugo & Bisi Castellani, 1996; Sardone, Bisi Castellani, Carugo & Charalambous, 1994). Of the uncomplexed 5-alkylamino-1,2-benzoquinone 2-oximes, the 5-ethyl, 5-pentyl and 5-hexyl derivatives have been structurally characterized (Charalambous, Rees, Thomas, Carugo & Bisi Castellani, 1995; Charalambous, Thomas, Carugo & Bisi Castellani, 1996*a,b*). Unfortunately, the known structures of neutral uncomplexed 5-alkoxy-1,2-benzoquinone 2-oximes are poorly refined (Crowder, Morley & Taylor, 1959; Romers,

1964; van Oijen & Romers, 1966). Therefore, this precludes the possibility of deducing the effects of complexation on the molecular structure of the 5-alkoxy ligands and a comparison of the molecular structures of the 5-alkylamino and 5-alkoxy derivatives. For this reason, we report here the crystal structure of 5-ethoxy-1,2-benzoquinone 2-oxime, (I).

(I)   (II)
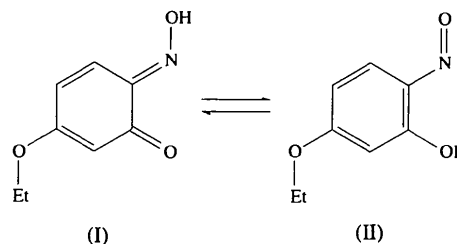
The title molecule (Fig. 1) is clearly quinoidal (I) and not phenolic (II), as shown by both the alternation of long and short bonds within the six-membered ring and the position (experimental) of the acidic H atom. If this compound is compared to the 5-methoxy-1,2-benzoquinone 2-oximato ligand in the cobalt(III) complex (Charalambous, Raghvani, Carugo & Bisi Castellani, 1996), it appears that the neutral uncomplexed ligand has a stronger quinoidal character than the deprotonated complexed one. Such a feature is also common to unsubstituted 1,2-benzoquinone 2-oximes and has been explained in terms of charge delocalization within the chelate ring (Carugo, Djinović, Rizzi & Bisi Castellani, 1991).
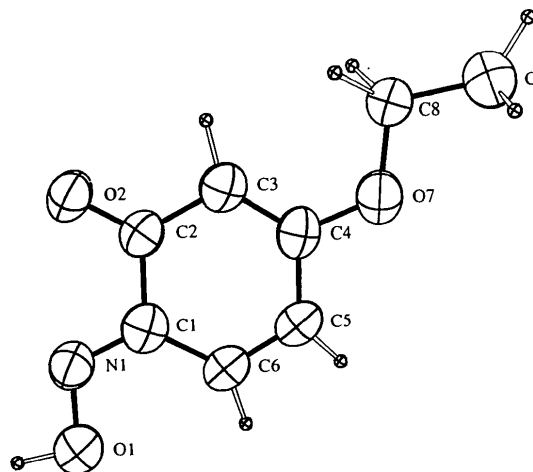

Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids.

The crystal packing is stabilized by van der Waals interactions (weak stacking interactions between six-membered rings translated in the **a** direction may be present), but the most remarkable intermolecular interaction is a hydrogen bond (Fig. 2), which forms strands parallel to **b** [O1—H1O 0.98 (5), H1O···O2[i] 1.64 (5),

O1$\cdots$O2^i 2.602 (5) Å, O1—H1O$\cdots$O2^i 164 (5)°; symmetry code: (i) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$].
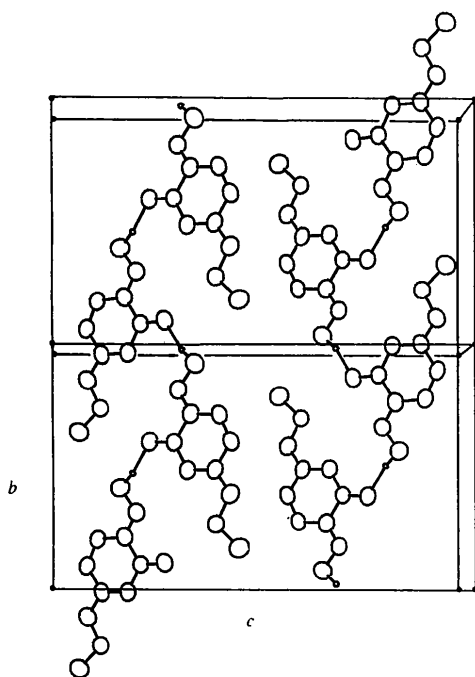
Fig. 2. Packing diagram viewed down the a axis. Note the strands parallel to the b axis.

Monoclinic
$P2_1/n$
$a = 3.979\,(1)$ Å
$b = 10.800\,(2)$ Å
$c = 18.713\,(5)$ Å
$\beta = 90.71\,(3)°$
$V = 804.0\,(4)$ Å^3
$Z = 4$
$D_x = 1.381$ Mg m^{-3}

Cell parameters from 25
  reflections
$\theta = 30$–$35°$
$\mu = 0.858$ mm^{-1}
$T = 293$ K
Needle
0.30 × 0.08 × 0.05 mm
Yellow

Data collection

Enraf–Nonius CAD-4
  diffractometer
$\omega/2\theta$ scans
Absorption correction:
  none
2109 measured reflections
1557 independent reflections
760 observed reflections
  $[I > 2\sigma(I)]$

$R_{int} = 0.015$
$\theta_{max} = 70°$
$h = 0 \rightarrow 4$
$k = -2 \rightarrow 13$
$l = -22 \rightarrow 22$
3 standard reflections
  frequency: 60 min
  intensity decay: 0.5%

Refinement

Refinement on F
$R = 0.066$
$wR = 0.057$
$S = 0.981$
760 reflections
113 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.03$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Atomic scattering factors
  from *International Tables*
  for X-ray Crystallography
  (1974, Vol. IV)

No charge delocalization within the O7—C4—C3—C2—O2 moiety appears either in the present structure or that of the tris(5-methoxy-1,2-benzoquinone 2-oximato)cobalt(III) complex. In fact, although the C3—C4 bond is slightly longer than C5—C6, the C3—C4 bond distance is much shorter than that of C2—C3. This seems to be the major difference between the 5-alkoxy- and 5-alkylamino-1,2-benzoquinone 2-oximes. The latter, in fact, generally displays statistically equivalent C2—C3 and C3—C4 bond distances, with a corresponding lengthening of the C2—O2 bond and a shortening of C4—N7, indicating a partial charge separation between atoms N7 (positive) and O2 (negative) (the labels O7 and N7 are permuted in the 5-alkoxo and 5-alkylamino structures).

Experimental

The title compound was prepared by reaction of 3-ethoxyphenol in aqueous ethanol with sodium nitrite and hydrochloric acid. The resultant orange solid was chromatographed with toluene to give orange solid 5-ethoxy-1,2-benzoquinone 2-oxime, which was recrystallized from toulene.

Crystal data

$C_8H_9NO_3$
$M_r = 167.16$

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.485 (1)	0.4210 (3)	0.1627 (2)	6.37 (8)
O2	0.2673 (9)	0.1075 (3)	0.2683 (2)	5.20 (7)
O7	0.7843 (8)	−0.1180 (3)	0.0822 (2)	4.95 (7)
N1	0.406 (1)	0.3179 (4)	0.2010 (2)	4.44 (9)
C1	0.518 (1)	0.2172 (4)	0.1728 (2)	4.1 (1)
C2	0.422 (1)	0.1009 (4)	0.2109 (2)	3.9 (1)
C3	0.521 (1)	−0.0147 (4)	0.1803 (2)	4.1 (1)
C4	0.684 (1)	−0.0156 (4)	0.1168 (2)	3.9 (1)
C5	0.778 (1)	0.0965 (4)	0.0806 (2)	4.4 (1)
C6	0.699 (1)	0.2082 (4)	0.1069 (2)	4.2 (1)
C8	0.715 (1)	−0.2376 (4)	0.1144 (2)	4.5 (1)
C9	0.818 (1)	−0.3354 (5)	0.0617 (3)	5.5 (1)

Table 2. *Selected geometric parameters* (Å, °)

O1—N1	1.363 (5)	C1—C6	1.440 (7)
O2—C2	1.247 (5)	C2—C3	1.430 (6)
O7—C4	1.345 (5)	C3—C4	1.361 (6)
O7—C8	1.453 (6)	C4—C5	1.440 (7)
N1—C1	1.291 (6)	C5—C6	1.341 (7)
C1—C2	1.496 (6)	C8—C9	1.505 (7)
C4—O7—C8	118.2 (3)	C2—C3—C4	119.5 (4)
O1—N1—C1	112.9 (4)	O7—C4—C3	125.1 (4)
N1—C1—C2	114.9 (4)	O7—C4—C5	112.6 (4)
N1—C1—C6	125.9 (4)	C3—C4—C5	122.3 (4)
C2—C1—C6	119.0 (4)	C4—C5—C6	121.3 (4)
O2—C2—C1	119.6 (4)	C1—C6—C5	119.8 (4)
O2—C2—C3	122.4 (4)	O7—C8—C9	107.3 (4)
C1—C2—C3	118.0 (4)		

All non-H atoms were refined anisotropically by full-matrix least-squares methods. All H atoms were experimentally positioned, with only the oxime H atom refined isotropically. All other H atoms were not refined, but their displacement parameters were kept proportional ($\times 1.3$) to those of their neighbouring non-H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1985). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN* (Fair, 1990). Software used to prepare material for publication: *SDP*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: NA1176). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Polymerizable Methacrylate Carbohydrate Derivatives: 1,2:3,4-Di-O-isopropylidene-6-O-methacryloyl-α-D-galactopyranose and 1,2:5,6-Di-O-isopropylidene-3-O-methacryloyl-α-D-glucofuranose

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Abstract

The title structures, both $C_{16}H_{24}O_7$, have been determined to investigate the possibility of using these carbohydrate-containing monomers or related compounds for solid-state polymerization. The orientation of the methacrylate groups in the galactose derivative is suitable for solid-state reaction but the distance between the potentially reacting vinyl C atoms is too great, 5.065(5) Å, for a facile reaction. The glucose derivative is disordered, with one of the isopropylidene rings assuming two different envelope conformations in the crystal. In the glucose derivative there are no approaches of the appropriate vinyl group atoms closer than 6.439(3) Å.

Comment

Solution free-radical polymerization of carbohydrate methacrylate derivatives leads to products consisting of a poly(methyl methacrylate) backbone with pendant carbohydrate groups. This type of polymer has been known for some time, interesting examples being the work of Black, Dewar & Rutherford (1963) and Iwakura, Imai & Yagi (1968). It has recently been recognized that such carbohydrate-containing polymers have attractive properties for use as biomaterials (Wang *et al.*, 1992). Since polymer tacticity and its control are very important for the practical application of polymeric biomaterials, we are investigating the possibility of solid-state polymerization of carbohydrate methacrylate derivatives. As a first step toward this goal, we have determined the crystal structures of the title compounds because they are