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Salts of maleic and fumaric acids with oxine: the role of isomeric acids in hydrogen-bonding patterns

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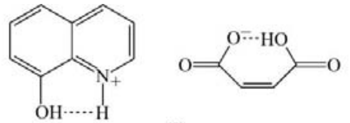
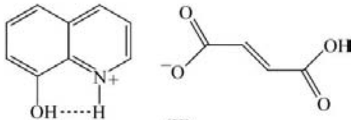
Both maleic and fumaric acid readily form adducts or complexes with other organic molecules. The 1:1 adduct formed by quinolin-8-ol (oxine) with maleic and fumaric acid are salts, namely 8-hydroxyquinolinium hydrogen maleate, $C_9H_8NO^+\cdot C_4H_3O_4^-$, (I), and 8-hydroxyquinolinium hydrogen fumarate, $C_9H_8NO^+\cdot C_4H_3O_4^-$, (II). The cations and anions of both salts are linked by ionic $N^+—H\cdots O^-$ hydrogen bonds. The maleate salt crystallizes in the space group $P2_12_12_1$, while the fumarate salt crystallizes in $P\bar{1}$. The maleic and fumaric acids in their complex forms exist as semimaleate and semifumarate ions (mono-ionized state), respectively. Classical N—H···O and O—H···O hydrogen bonds, together with short C—H···O contacts, generate an extensive hydrogen-bonding network. The crystal structures of the maleate and fumarate salts of oxine have been elucidated to study the importance of noncovalent interactions in the aggregation and interaction patterns of biological molecules. The structures of the salts of the *Z* and *E* isomers of butenedioic acid (maleic and fumaric acid, respectively) with quinolin-8-ol are compared.

Comment

Oxine (quinolin-8-ol, 8-HQ), a monoprotic bidentate chelating agent, and its derivatives are widely used as analytical reagents and potential anti-amoebic agents (Bambury, 1979). The complexes and the heterocycle itself exhibit antiseptic, disinfectant and pesticide properties (Phillips, 1956). Its solution in ethanol is used as a liquid bandage. 8-HQ was also once of interest as an anticancer drug (Shen *et al.*, 1999). In this paper, we present the maleic and fumaric acid complexes of 8-HQ, *viz.* (I) and (II), respectively.

Maleic acid, the *Z* isomer of butenedioic acid, has been used as a simple building block in supramolecular architectures in two and three dimensions (Bowes *et al.*, 2003; Jin *et al.*, 2003). The maleic acid anion can exist in the fully deprotonated form, or as hydrogen maleate with one of the carboxyl groups protonated (Lah & Leban, 2003). Several singly dissociated maleate salts are reported in the Cambridge Structural Database (Version 5.29; Allen, 2002). Fumaric acid, the *E* isomer of butenedioic acid, is of interest since it is known to form supramolecular assemblies with N-aromatic compounds (Batchelor *et al.*, 2000). It tends to form infinite chains arranged in a nearly coplanar manner *via* pairs of strong O—H···O hydrogen bonds. This organic dicarboxylic acid crystallizes in two polymorphic forms; one is monoclinic, space group $P2_1/c$ (Brown, 1966), and the other triclinic, space group $P\bar{1}$ (Bednowitz & Post, 1966). In both crystal structures, the acid molecules are linked by carboxyl $R_2^2(8)$ (Bernstein *et al.*, 1995) hydrogen-bond pairs, forming one-dimensional supramolecular tapes. An extensive network of hydrogen bonds is observed in the majority of the crystal structures of salts of fumaric acid (Shan *et al.*, 2003; Alagar, Krishnakumar *et al.*, 2003; Videnova-Adrabińska, 1996; Smith *et al.*, 1997; Li *et al.*, 2007; Büyükgüngör *et al.*, 2004). The title compounds, (I) and (II), are the salts of oxine with the *cis* and *trans* dicarboxylic acids maleic and fumaric acid, the *Z* and *E* isomers of butenedioic acid, respectively. They have been studied to explore their hydrogen-bonding patterns.


(I)


(II)

The structures of compounds (I) and (II) are shown in Figs. 1 and 2, respectively. The asymmetric unit of (I) consists of a 1:1 complex of a semimaleate anion and the hydroxyquinolinium cation. Compound (II) consists of a 1:1 complex of a semifumarate anion and the hydroxyquinolinium cation. The 8-HQ molecules in both compounds are protonated at atom N1. Proton transfer observed between the 8-HQ N atom and the carboxyl groups of both (I) and (II) is confirmed by the increase in the internal angles at N1, which are 122.1 (3) and 122.71 (12)° in (I) and (II), respectively, compared with 119° observed in neutral 8-HQ (Roychowdhury *et al.*, 1978).

The C8—O8 bond lengths in the 8-HQ cations in (I) and (II) are 1.338 (4) and 1.3434 (17) Å, respectively. These distances are shorter than the bond lengths observed in the neutral 8-HQ molecule (1.39 Å). Furthermore, the exocyclic angles, C7—C8—O8 and C9—C8—O8, in the cation of (I) are 126.0 (3) and 116.0 (3)°, respectively, and those in the cation of (II) are 126.08 (12) and 115.76 (11)°, respectively. These angles are significantly different from those observed in neutral 8-HQ (118.2 and 120.3°). This difference in the bond lengths and angles may be attributed to the presence of weak intramolecular N—H···O hydrogen bonds. Similar hydrogen bonds, represented by a graph-set motif of *S*(5), have been observed and cause analogous bond-angle distortions in the

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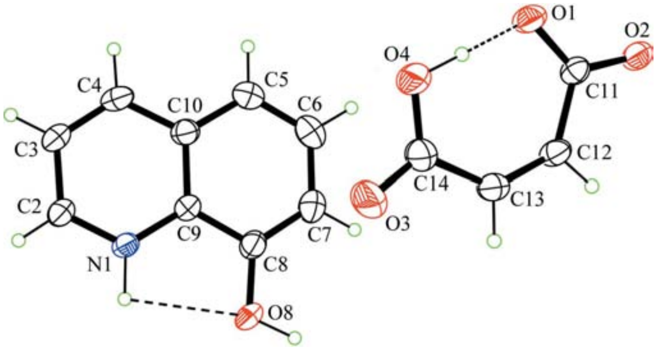

Figure 1
The structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate intramolecular hydrogen bonds.

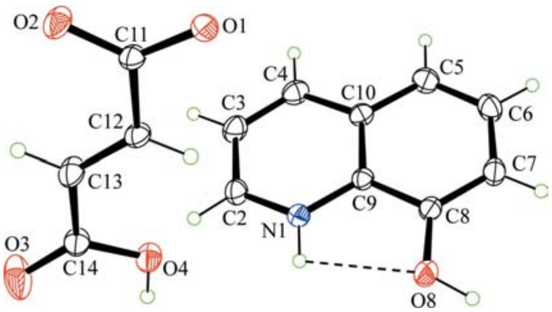

Figure 2
The structure of compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the intramolecular hydrogen bond.

structures of many 8-hydroxyquinolinium and related cation compounds (Balasubramanian & Muthiah, 1996; Balasubramanian & Thomas Muthiah, 1996; Jebamony & Thomas Muthiah, 1998; Banerjee *et al.*, 1984; Smith *et al.*, 2004). The O1—C11 and O4—C14 bonds of the semimaleate anion are longer than O2—C11 and O3—C14, showing differences between the C—O and C═O bond types of the carboxyl group (Borthwick, 1980). Similarly, the O1—C11 and O4—C14 bonds of the semifumarate anion are longer than the O2—C11 and O3—C14 bonds.

The 8-HQ cations in both (I) and (II) are essentially planar. The dihedral angles between the fused rings are 0.77 and 2.23°, respectively, and the total puckering amplitudes (Cremer & Pople, 1975) *Q* are 0.026 (4) and 0.059 Å, respectively. The semimaleate and semifumarate anions are almost planar. The angles between the planes of the two halves of the semimaleate anion in (I) and those of the semifumarate anion in (II) (O1/O2/C11/C12 and O3/O4/C13/C14) are 1.58 and 14.83°, respectively. The semimaleate anion is planar with a *cis* conformation about the central C═C bond [C11—C12—C13—C14 = −0.2 (8)°], while the semifumarate anion is planar with a *trans* conformation about the central C═C bond [C11—C12—C13—C14 = 179.94 (14)°]. Both the cations and anions of (I) and (II) are individually planar, but with dihedral angles of 10.92 (11) and 73.17 (3)°, respectively.

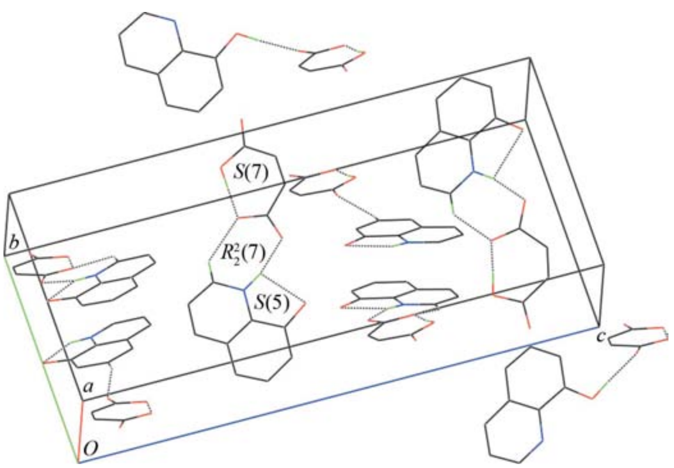

Figure 3
Part of the crystal structure of (I), showing the formation of $R_2^2(7)$, *S*(7) and *S*(5) hydrogen-bonded motifs. For the sake of clarity, only H atoms involved in hydrogen bonding are shown. Dashed lines represent hydrogen bonds.

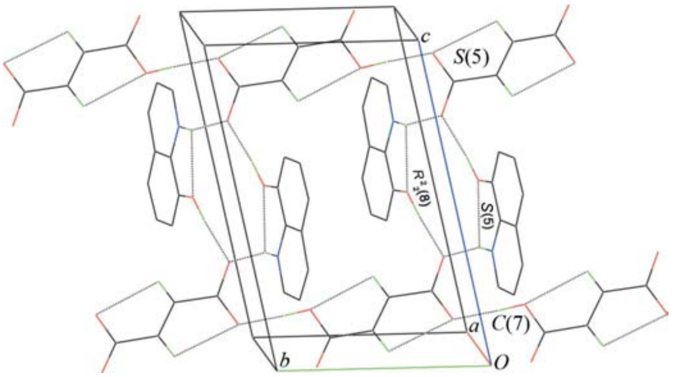

Figure 4
Part of the crystal structure of (II), showing the formation of rings propagating perpendicular to the *ac* plane. For the sake of clarity, only H atoms involved in hydrogen bonding are shown. Dashed lines represent hydrogen bonds.

The crystal packings of compounds (I) and (II) are stabilized by an extensive network of hydrogen bonds, which are summarized in Tables 1 and 2. Parts of the crystal structures of (I) and (II), depicting the hydrogen-bonding interactions and the formation of hydrogen-bonded motifs, are shown in Figs. 3 and 4, respectively. In both compounds, a strong intermolecular $N^+—H\cdots O^-$ hydrogen bond exists between the deprotonated carboxylate group of the anion and the hydroxyquinolinium N atom of the cation. An intramolecular hydrogen bond between atoms O1 and O4 in the semimaleate ion of (I) is found to be asymmetric, as in the crystal structures of maleic acid itself (James & Williams, 1974) and several maleate salts of various amino acids (Alagar, Krishnakumar *et al.*, 2001, Alagar *et al.*, 2002; Alagar, Subha Nandhini *et al.*, 2003; Rajagopal *et al.*, 2001, 2002). However, in the crystal structures of the complexes of maleic acid with DL- and L-arginine (Ravishankar *et al.*, 1998), L-hystidine and L-lysine

(Pratap *et al.*, 2000), and L-phenylalaninium (Alagar, Krishnakumar & Natarajan, 2001), this intramolecular hydrogen bond is symmetric and generates an $S(7)$ motif. C—H···O intramolecular interactions generate an $S(5)$ motif in the semifumarate anion in molecule (II).

Intermolecular hydrogen-bonding interactions between the semimaleate anions in (I) are not observed. The hydroxyquinolinium cation is connected to the anion by N1—H1···O2^{i} and C2—H2···O1^{i} interactions to form a ring motif described by a graph-set motif of $R_2^2(7)$ [symmetry code: (i) $x-1$, $y+1$, z]. In (II), however, intermolecular hydrogen-bonding interactions between the semifumarate anions, as well with the cations, are observed. The anions are linked by chains propagating parallel to the [010] direction *via* O4—H4*A*···O2 hydrogen bonds and can be described by a graph-set motif of $C(7)$. Hydroxyquinolinium cations form infinite stacks propagating parallel to the [010] direction, the distance between adjacent molecules within a stack being 7.44 Å. A pair of cations and a pair of anions are linked through O—H···O and N—H···O hydrogen bonds to form a ring motif, represented by a graph-set motif of $R_2^2(8)$. The cations and anions in (I) aggregate through hydrogen bonds to form an extensive three-dimensional network, while in (II), they aggregate through hydrogen bonds to form a two-dimensional network.

Experimental

Equimolar quantities of maleic acid and 8-HQ were dissolved in water. The solution was stirred well and set aside to crystallize. Yellow needle-shaped crystals of (I) suitable for X-ray diffraction analysis were obtained from the resulting solution after a week of slow evaporation. In a similar manner, equimolar quantities of fumaric acid and 8-HQ were dissolved in water. The solution was stirred well and set aside to crystallize. Yellow crystals of (II) suitable for X-ray diffraction analysis were obtained from the resulting solution after a week of slow evaporation.

Compound (I)

Crystal data

$C_9H_8NO^+\cdot C_4H_3O_4^-$
$M_r = 261.23$
Orthorhombic, $P2_12_12_1$
$a = 5.3777$ (3) Å
$b = 10.0563$ (7) Å
$c = 22.4243$ (12) Å
$V = 1212.70$ (13) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 273$ K
0.40 × 0.30 × 0.22 mm

Data collection

Bruker Kappa-APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\rm min} = 0.957$, $T_{\rm max} = 0.976$
7633 measured reflections
1764 independent reflections
1291 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.134$
$S = 1.16$
1764 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	1.00	1.73	2.714 (4)	167
N1—H1···O8	1.00	2.37	2.666 (3)	96
O4—H4*A*···O1	1.03	1.40	2.427 (4)	174
O8—H8···O2^{ii}	0.94	1.70	2.643 (3)	177
C2—H2···O1^{i}	0.93	2.31	3.058 (5)	137
C6—H6···O3^{iii}	0.93	2.43	3.324 (6)	160

Symmetry codes: (i) $x-1, y+1, z$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$; (iii) $x+1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.89	1.92	2.7711 (15)	159
N1—H1···O8	0.89	2.33	2.6673 (14)	102
O4—H4*A*···O2^{i}	0.94	1.60	2.5327 (13)	177
O8—H8···O1^{ii}	0.92	1.70	2.6151 (14)	175
C2—H2···O2^{iii}	0.93	2.49	3.2042 (17)	133
C12—H12···O4	0.93	2.45	2.7657 (15)	100
C13—H13···O2	0.93	2.49	2.7988 (16)	100

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z$.

Compound (II)

Crystal data

$C_9H_8NO^+\cdot C_4H_3O_4^-$
$M_r = 261.23$
Triclinic, $P\overline{1}$
$a = 7.3282$ (3) Å
$b = 7.4363$ (3) Å
$c = 11.5680$ (5) Å
$\alpha = 79.349$ (2)°
$\beta = 74.994$ (2)°
$\gamma = 89.337$ (2)°
$V = 597.97$ (4) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 273$ K
0.30 × 0.20 × 0.16 mm

Data collection

Bruker Kappa-APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\rm min} = 0.967$, $T_{\rm max} = 0.982$
15682 measured reflections
4437 independent reflections
3049 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.152$
$S = 1.07$
4437 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

For compound (I), which crystallizes in the space group $P2_12_12_1$, the Friedel equivalents were merged prior to the final refinement cycles and the absolute structure was assigned arbitrarily. O- and N-bound H atoms were located in difference Fourier maps and held fixed, with O—H = 0.94 and 1.03 Å in (I), and 0.92 and 0.94 Å in (II), N—H = 1.00 Å in (I) and 0.89 Å in (II), and with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$ and $1.2U_{\rm eq}({\rm N})$. C-bound H atoms in both compounds were included in calculated positions and treated as riding atoms, with C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

For both compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT-Plus* (Bruker, 2004); data reduction: *XPREP* in *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for*

Windows (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3028). Services for accessing these data are described at the back of the journal.

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