

Supplementary Information

Antioxidant and anticancer activities of supramolecularly controlled magnetostructural halo-oximes of lawsone

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This file replaces the previously published ESI file which contained incorrect CCDC deposition numbers.

Results and discussion

Crystal structure and supramolecular self-assembly

Table 1: Crystallographic data for halo-lawsone oximes

Compound	Chloro (1)	Bromo (2)	Iodo (3)
Empirical formula	C ₁₀ H ₆ ClNO ₃ ·0.5H ₂ O	C ₁₀ H ₆ BrNO ₃ ·0.63H ₂ O	C ₁₀ H ₆ INO ₃ ·2H ₂ O
Formula weight	232.63	278.07	351.09
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	20.874(13)	21.092(6)	15.892(3)
<i>b</i> (Å)	20.426(12)	20.588(6)	4.5575(9)
<i>c</i> (Å)	4.638(3)	4.6388(13)	18.335(4)
β (°)	90	90	110.667(3)
Volume (Å ³)	1978(2)	2014.3(10)	1242.5(4)
Z	8	8	4
D _{calc} (g cm ⁻³)	1.562	1.834	1.877
μ (mm ⁻¹)	0.376	4.073	2.586
F(000)	952	1096	680
Crystal size (mm ³)	0.51 x 0.04 x 0.03	0.56 x 0.08 x 0.06	0.34 x 0.12 x 0.06
Ab. correction	Multi-scan	Multi-scan	Multi-scan
T _{min}	0.8312	0.2088	0.4734
T _{max}	0.9888	0.7921	0.8603
<i>h</i> , <i>k</i> , <i>l</i> (min, max)	(-24, 24), (-24, 23), (-5, 5)	(-19, 25), (-24, 17), (-5, 4)	(-13, 18), (-5, 5), (-21, 21)
Reflns collected	13938	9724	5759
Unique reflns	3496	3437	2180
Observed reflns	2773	2925	2008
R _{int}	0.0878	0.0389	0.0231
No. of parameters	289	290	178
No. of restraints	4	15	8
GoF on F ²	1.160	1.050	1.048
R _{obs}	0.0808	0.0425	0.0258
wR ₂ obs	0.1479	0.0962	0.0645
R _{all}	0.1048	0.0543	0.0280
wR ₂ all	0.1580	0.1019	0.0660
Δρ _{max} , Δρ _{min} (e.Å ⁻³)	0.354 and -0.271	0.614 and -0.340	0.556 and -0.264
CCDC deposition no	737076	737077	737078

The oxygen O4 in **1** and O5 in **2** of the water molecule accepts H-atom (H1A) from the oxime moiety and donates its H-atom to the carbonyl oxygen O3A of the next molecule A. The two adjacent molecules of A, which are bridged through water molecule, have almost perpendicular orientation in **1** as well as in **2** and same is the case with water molecule in **1**. Another chain formed by molecule A and oxygen O4 runs parallel to the earlier chains in **2**. In case of **1**, the oxime group (N1B-O1B-H1B) donates its H-atom (H1B) to the water oxygen O4 and carbonyl oxygen O3B makes bifurcated O-H...O hydrogen bond by accepting two H-atoms, H2A and H4B from molecule A and water molecule, respectively. The $\pi\cdots\pi$ stacking between the two dissimilar rings resulted in the shifting of successive molecules along layer with the development of stepping in stacking of molecules. The adjacent layers of molecules A and B run in antiparallel fashion along the *c*-axis linked via longer but linear halogen bonding contact between the Cl1B atom and carbonyl oxygen O3A (Cl1B...O3A = 3.332 Å, \angle C3B-Cl1B...O3A = 156.2°) and weak C-H...Cl interactions involving C5A-H5A of molecule A and Cl1B of molecule B, thus forming bilayers. The neighbouring bilayers diagonal to the *ab*-plane are bridged through water molecule.

The geometries of the $\pi\cdots\pi$ interaction in both the molecules of **1** are comparable with the inter-centroid distances being Cg...Cg = 3.588 Å (symmetry code: *x*, *y*, -1+*z*) and 3.495 Å (symmetry code: *x*, *y*, 1+*z*) for molecules A and B, respectively. The two rings make a dihedral angle of 1.23° (molecule A) and 1.66° (molecule B) and the corresponding perpendicular distances from the centroid of one ring to the plane of other and vice versa are 3.385 and 3.408 Å for molecule A and 3.435 and 3.438 Å for molecule B.

The geometries of the $\pi\cdots\pi$ interaction in both the molecules of **2** are comparable with the inter-centroid distances being Cg...Cg = 3.512 Å (symmetry code: *x*, *y*, 1+*z*) and 3.617 Å (symmetry code: *x*, *y*, -1+*z*) for molecule A and B, respectively. The two rings make a dihedral angle of 1.39° (molecule A) and 1.22° (molecule B) and the corresponding perpendicular distances from the centroid of one ring to the plane of other are 3.457 and 3.458 Å for molecule A and 3.397 and 3.423 Å for molecule B. The $\pi\cdots\pi$ stacking between the two dissimilar rings resulted in the shifting of successive molecules along layer with the development of stepping in stacking of molecules. The adjacent stacked layers of molecules A and B along the *c*-axis are stitched via halogen bonding contact involving Br1A and carbonyl oxygen O3B and weak C-H...Br contact between C5B-H5B of molecule B and Br1A of molecule A thus forming bilayers (Fig. 1).

The hydroxyl groups O1B-H1B and O2B-H2B donate their respective protons to the oxygen (O4 and O5) of the water molecules and carbonyl oxygen O3A. The C5B-H5B of the phenyl ring also makes almost linear C-H...Br contact with the bromine Br1A of molecule A. In turn, the atoms O2B, O3B and Br1A accept protons from the C5A-H5A, O5 and C8A-H8A to form C5A-H5A...O2B, O5...O3B and C8A-H8A...Br1B contacts.

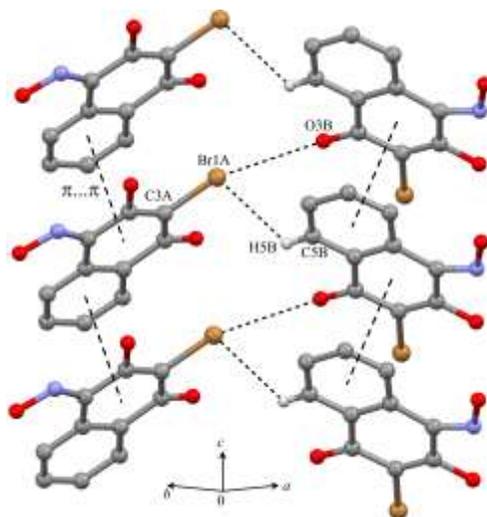


Fig. 1. Linking of molecules along the *c*-axis *via* halogen bonding and aromatic $\pi\cdots\pi$ stacking interactions in **2**.

In case of **3** the geometry of the $\pi\cdots\pi$ interaction is somewhat weak with the inter-centroid distances being $Cg\cdots Cg = 4.136(2)$ Å (symmetry code: $x, -1+y, z$). The two rings make a dihedral angle of 2.53° and the corresponding perpendicular distances from the centroid of one ring to the plane of other and vice versa are 3.554 and 3.595 Å. The hydroxyl group (O1-H1A) of the oxime moiety of the host molecules also donates its H-atom to oxygen O5 the other water molecule; in turn the water molecules O5 donates its H-atom (H5B) to the carbonyl oxygen O3 and accepts hydrogen atom H4B from the water molecule O4.

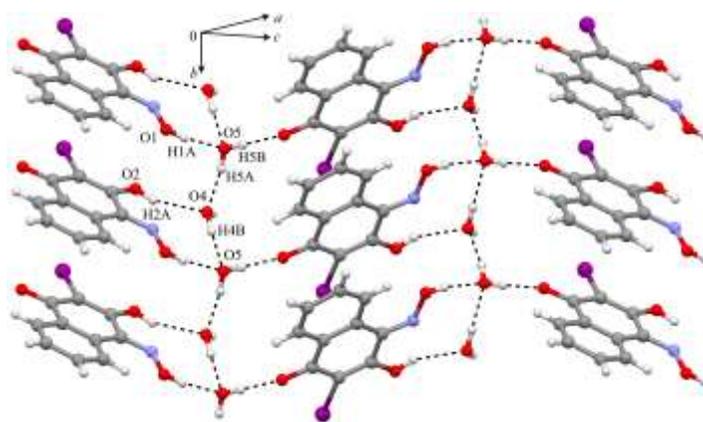


Fig. 2. Molecular packing viewed diagonal to *ac*-plane showing organization of the stacked layers of the host molecules through water molecules via O-H...O interactions in **3**.

Molecular packing in other direction revealed the stacking of host molecules to form layered arrangement. These stack layers are bridged through water molecules *via* O-H...O interactions; both the water molecules are arranged in the channel across the crystallographic 2_1 -screw axis connected together *via* O-H...O interactions and also stitching the stacked layers of host molecules (Fig. 2).

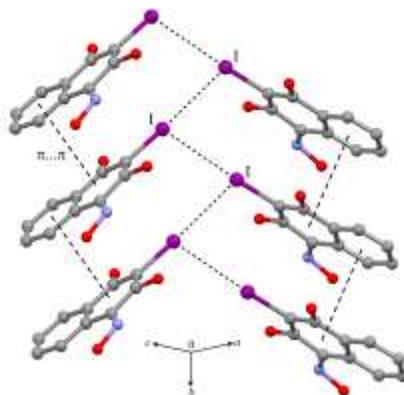


Fig. 3. Linking of molecules in **3** along the *c*-axis *via* short I...I contact and aromatic π ... π stacking interactions.

Table 2(a). Geometrical parameters for intermolecular O-H...O interactions in **1**, Cl-LwOx [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...Cl(1A)#1	0.82(5)	2.87(7)	3.464(6)	130(7)
C(8B)-H(8B)...Cl(1A)#2	0.93	2.83	3.607(7)	141.6
C(5B)-H(5B)...O(2A)#3	0.93	2.54	3.125(8)	121.5
C(5A)-H(5A)...Cl(1B)	0.93	2.91	3.564(7)	128.9
O(4)-H(9)...O(3A)#1	0.82(5)	2.15(6)	2.861(8)	144(9)
O(4)-H(4B)...O(3B)#4	0.84(6)	2.25(5)	2.926(8)	138(7)
O(1B)-H(1B)...O(4)#5	0.82	2.06	2.794(8)	149.0
O(2B)-H(2B)...O(1A)#5	0.82	2.34	3.051(7)	144.9
O(1A)-H(1A)...O(4)	0.82	2.10	2.754(8)	136.5
O(2A)-H(2A)...O(3B)#4	0.82	2.26	2.945(6)	140.7

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y+1/2,z+1/2 #2 x-1/2,-y+1/2,z #3 -x+3/2,y-1/2,z+1/2 #4 -x+3/2,y+1/2,z-1/2 #5 -x+1,-y+1,z+1/2

Table 2(b). Geometrical parameters for intermolecular O-H...O interactions in **2**, Br-LwOx [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1B)-H(1B)...O(5)	0.85	2.05	2.71(2)	134.9
O(1B)-H(1B)...O(4)#1	0.85	2.07	2.818(8)	145.7
O(1A)-H(1A)...O(5)#2	0.82	1.76	2.487(19)	147.0
O(1A)-H(1A)...O(4)#2	0.82	2.16	2.879(9)	146.2
O(2B)-H(2B)...O(3A)#3	0.82	2.25	2.910(5)	138.1
O(2A)-H(2A)...O(1B)#4	0.82	2.33	3.021(6)	142.8

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z-1 #2 -x+1,-y+1,z-1/2 #3 -x+3/2,y-1/2,z-1/2 #4 -x+1,-y+1,z+1/2

Table 2(c). Geometrical parameters for intermolecular O-H...O interactions in **3** (I-LwOx) [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5B)...O(3)#1	0.800(19)	1.98(2)	2.775(4)	172(4)
O(5)-H(5A)...O(4)#2	0.810(18)	1.97(2)	2.764(4)	169(4)
O(4)-H(4B)...O(5)#3	0.824(19)	2.08(2)	2.883(4)	166(4)
O(4)-H(4A)...O(2)#4	0.812(19)	2.17(2)	2.949(4)	160(4)
O(1)-H(1A)...O(5)#4	0.810(19)	1.85(2)	2.648(3)	167(4)
O(2)-H(2A)...O(4)#5	0.792(18)	2.10(2)	2.815(4)	151(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 -x+1,-y+2,-z+1 #3 -x+1,-y+1,-z+1 #4 -x+3/2,y+1/2,-z+1/2 #5 x+1/2,-y+3/2,z-1/2

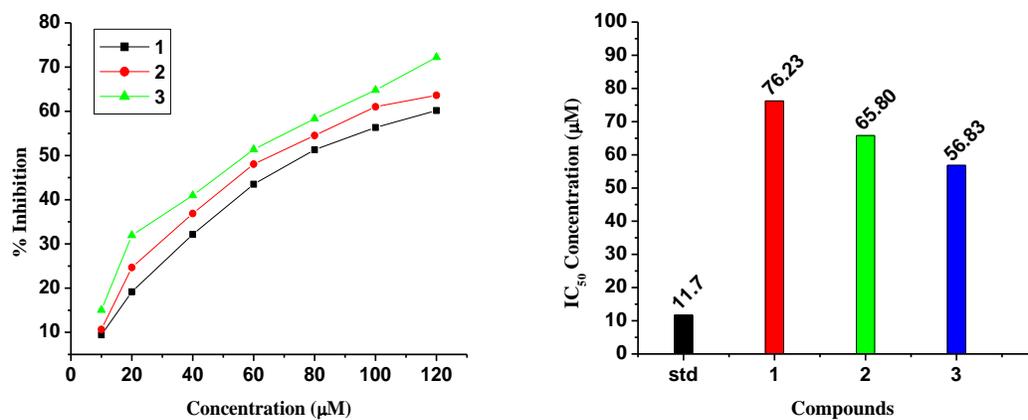


Fig. 4: DPPH chemical assay: (a) Scavenging of DPPH radical in terms of % Inhibition vs. conc. (µM) (b) IC₅₀ concentration (µM) vs. compounds (Std, 1, 2 and 3).