Concomitant Dimorphs of tri-*O*-[*p*-halobenzoyl]-*myo*-inositol 1,3,5-orthoformates with different halogen bonding contacts: first order crystal-to-crystal thermal phase transition of Kinetic form to the thermodynamic form

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Supplementary Material (ESI)

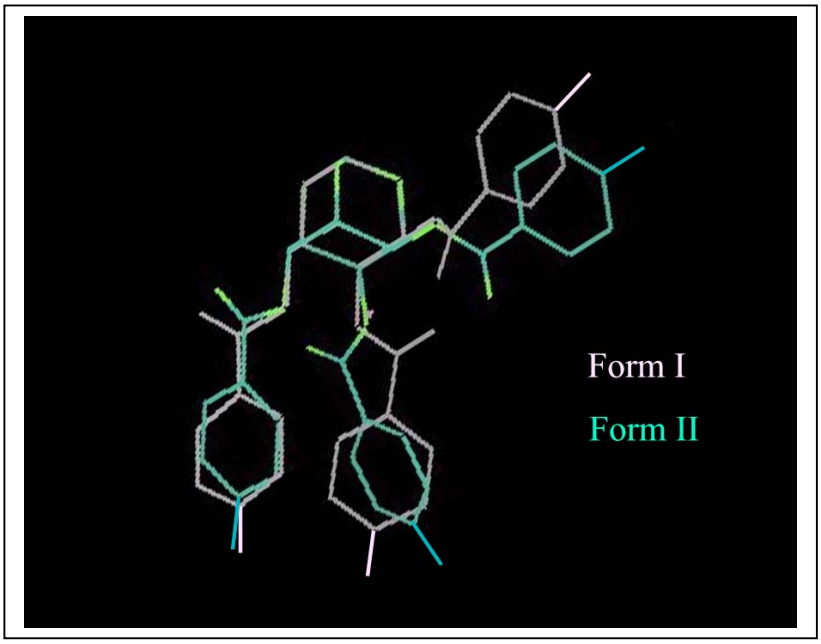


Fig. 1 Overlap of molecules in Form I and II crystals. The equatorial benzoate group shows the maximum conformational difference, changes are also seen in the orientation of axial benzoates.

Other Intermolecular Interactions: Form I

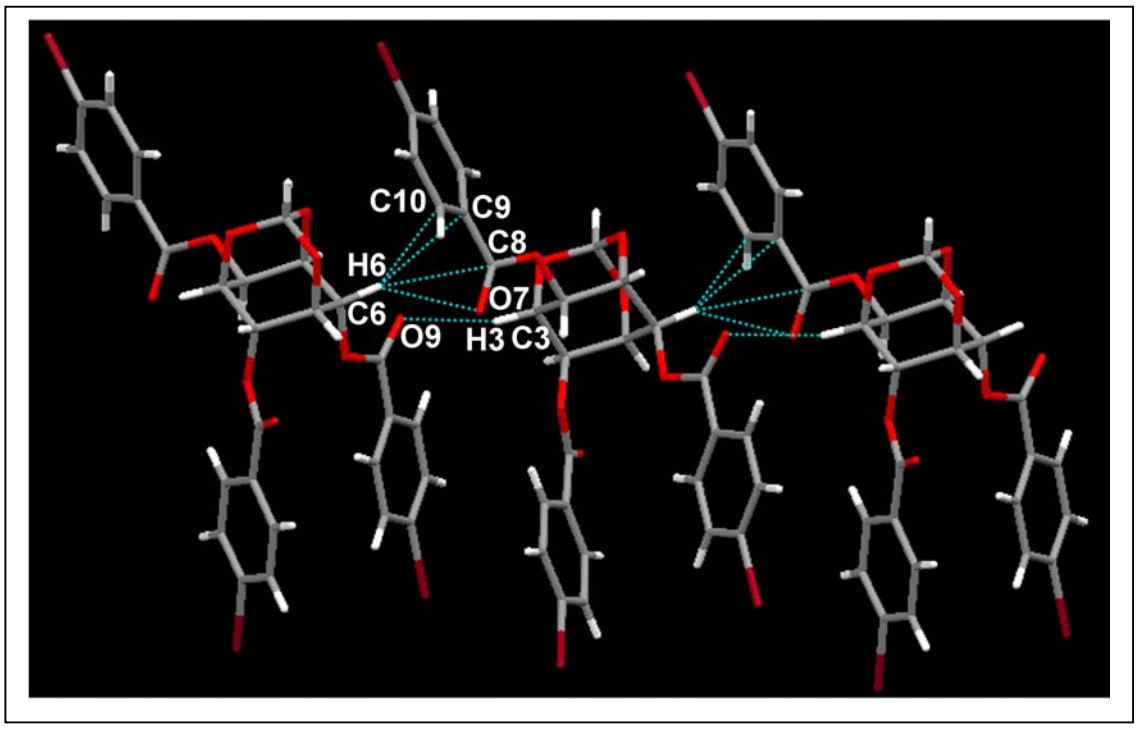


Fig. 2 A view of molecular packing showing C-H…π and C-H…O (C3-H3…O9 and C6-H6…O7) intermolecular interactions along c-axis in Form I of **1**. The geometrical parameters are given in Table

Other Intermolecular Interactions: Form I

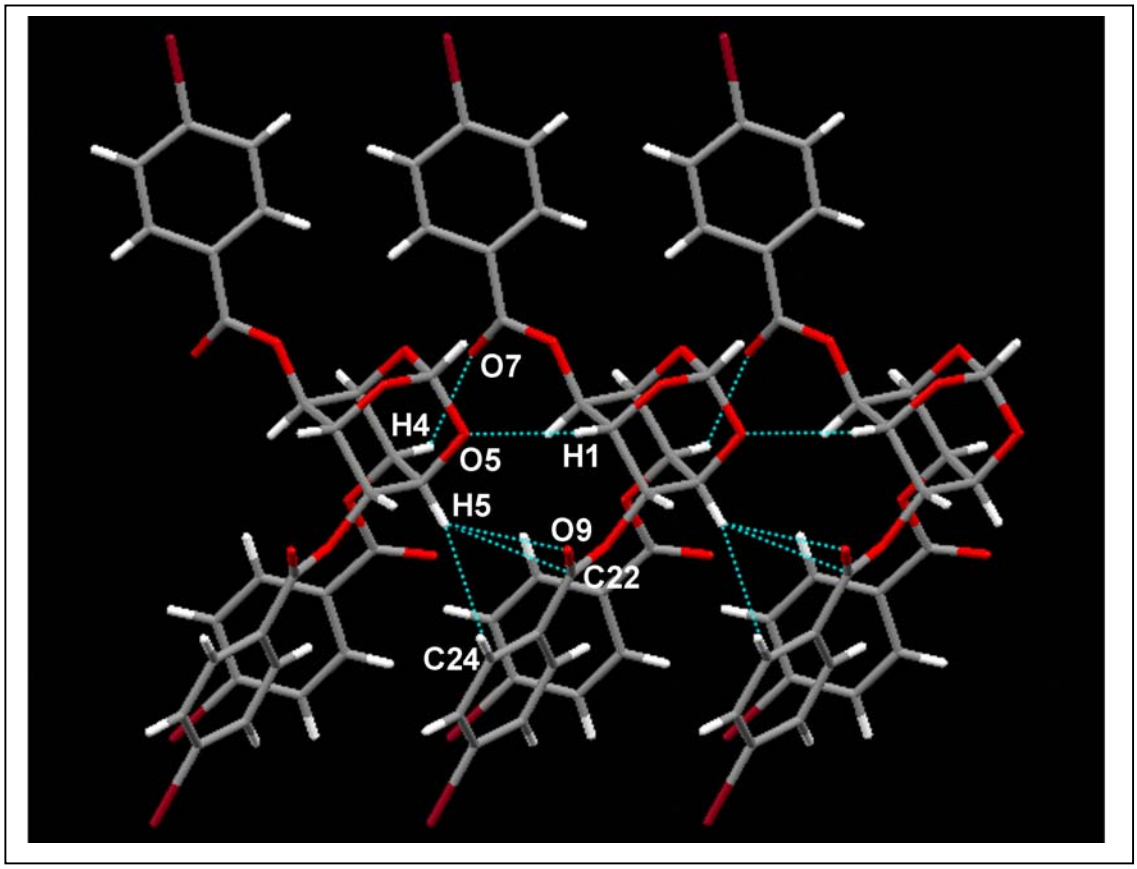


Fig. 3 A view of molecular packing showing C-H…π as well as C-H…O intermolecular interactions (C1-H1…O5 and C5-H5…O9, C4-H4…O7) along b-axis in Form I of **1**.

Other Intermolecular Interactions: Form I

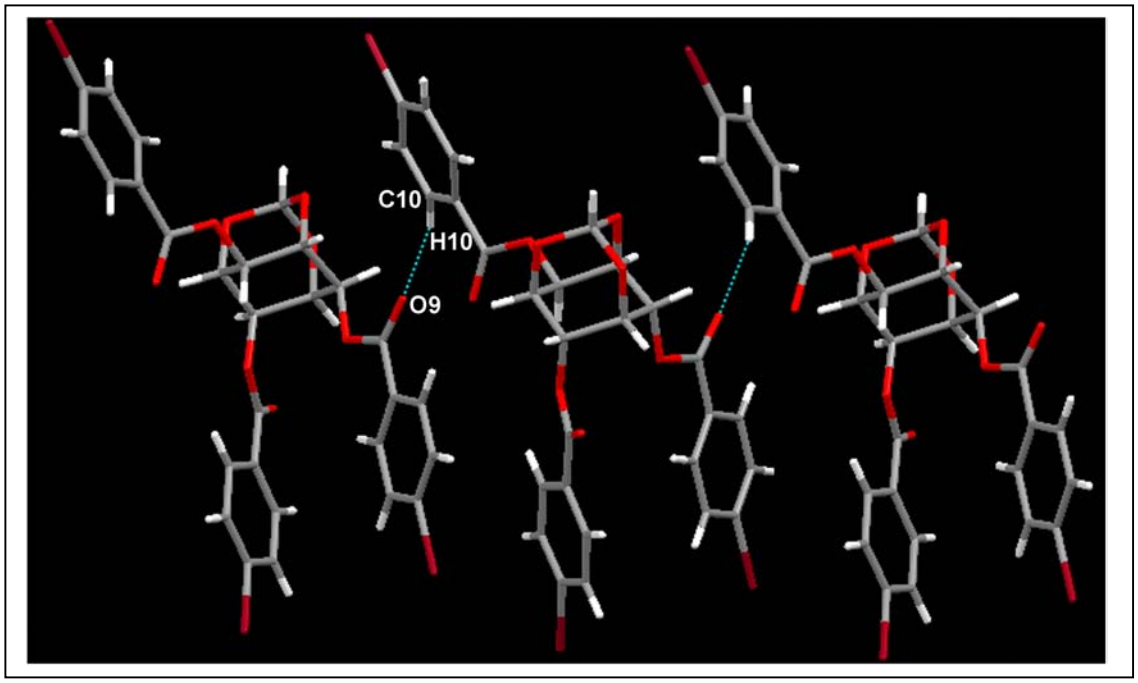


Fig. 3 A view of molecular packing showing C10-H10…O9 interaction along c-axis in Form I of **1**.

Other Intermolecular Interactions: Form II

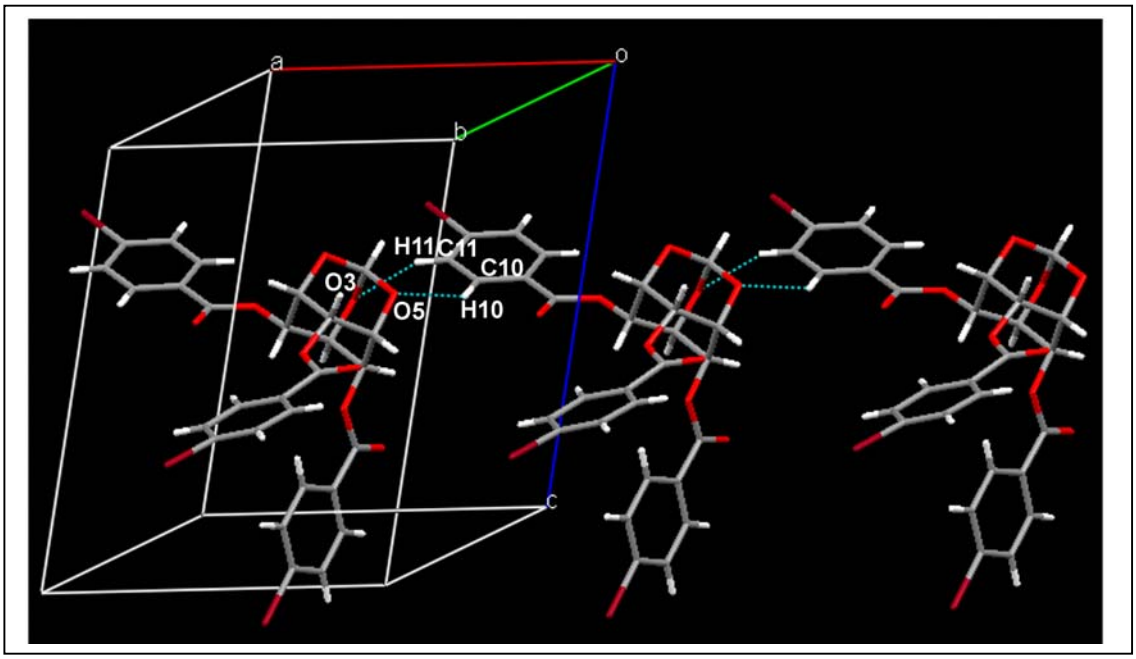


Fig. 4 A view of molecular packing showing C-H…O (C11-H11…O3 and C10-H10…O5) interactions between the unit translated molecules of Form II of **1** along a-axis. Geometrical parameters are given in Table.

Other Intermolecular Interactions: Form II

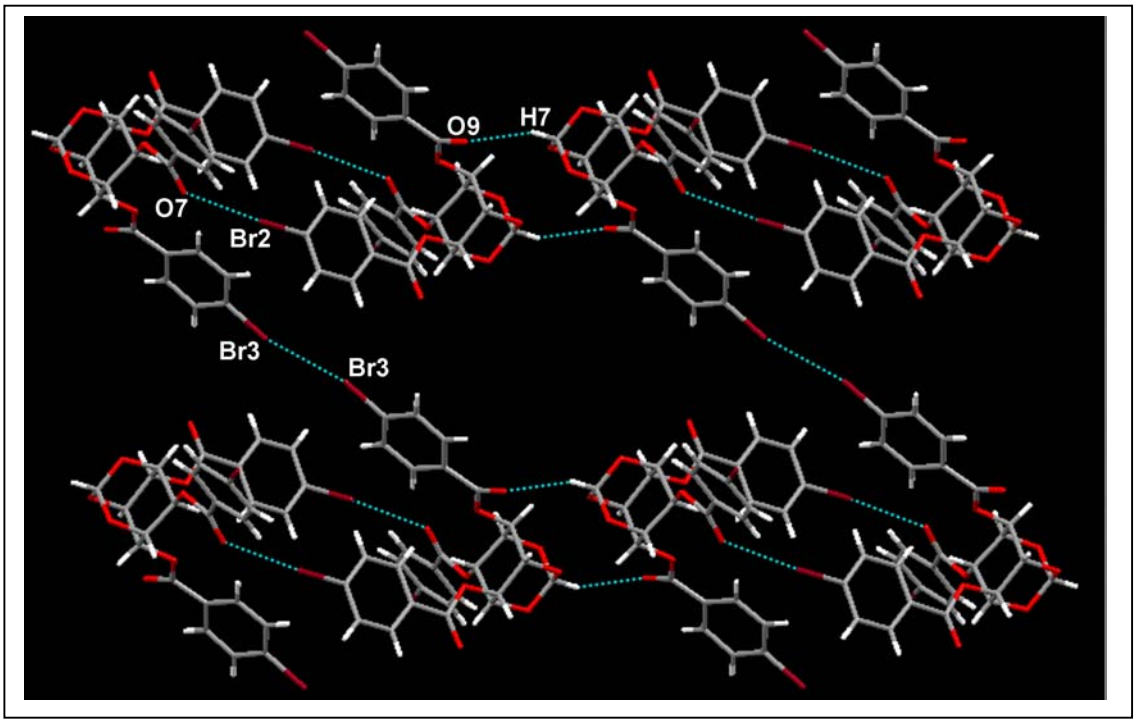


Fig. 5 A view of molecular packing showing the halogen bonded dimers linked by C7-H7…O9 interaction along c-axis and by short Br3…Br3 contacts (3.444(4) Å) along a-axis in Form II of **1.**

Other Intermolecular Interactions: Form II

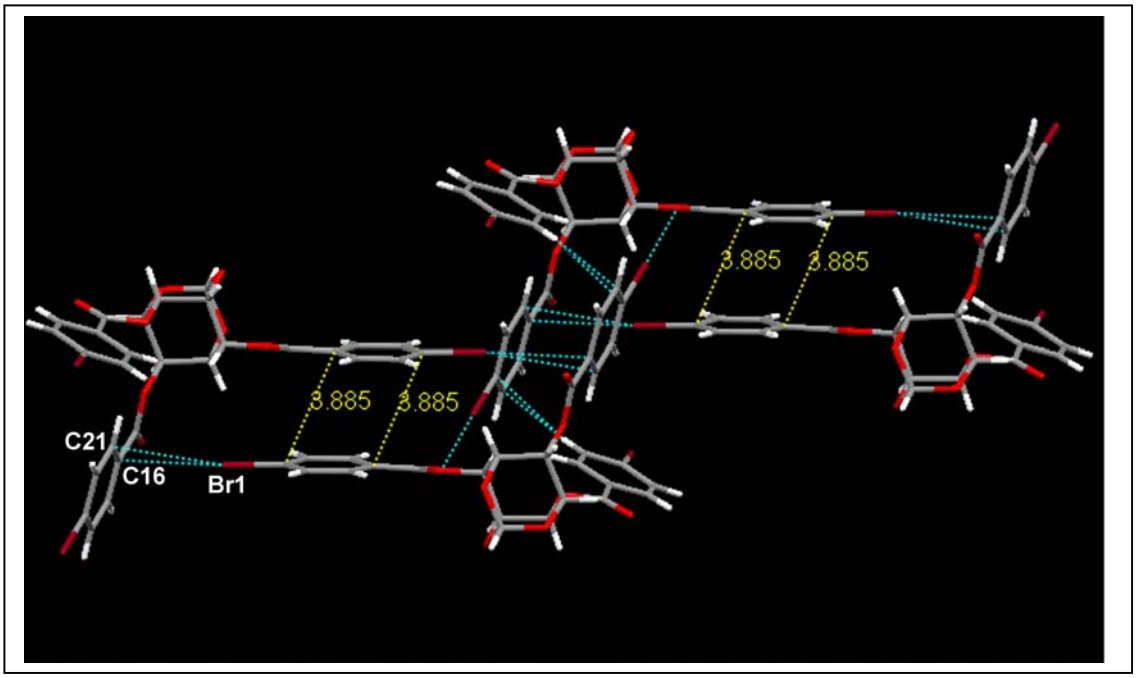


Fig. 6 A view of molecular packing showing phenyl…phenyl (π…π) contacts between the centrosymmetric pairs of molecules, marked are also C-Br…π contacts in Form II of **1** diagonal to bc plane.

A view of packing indicating possible pathway of transformation

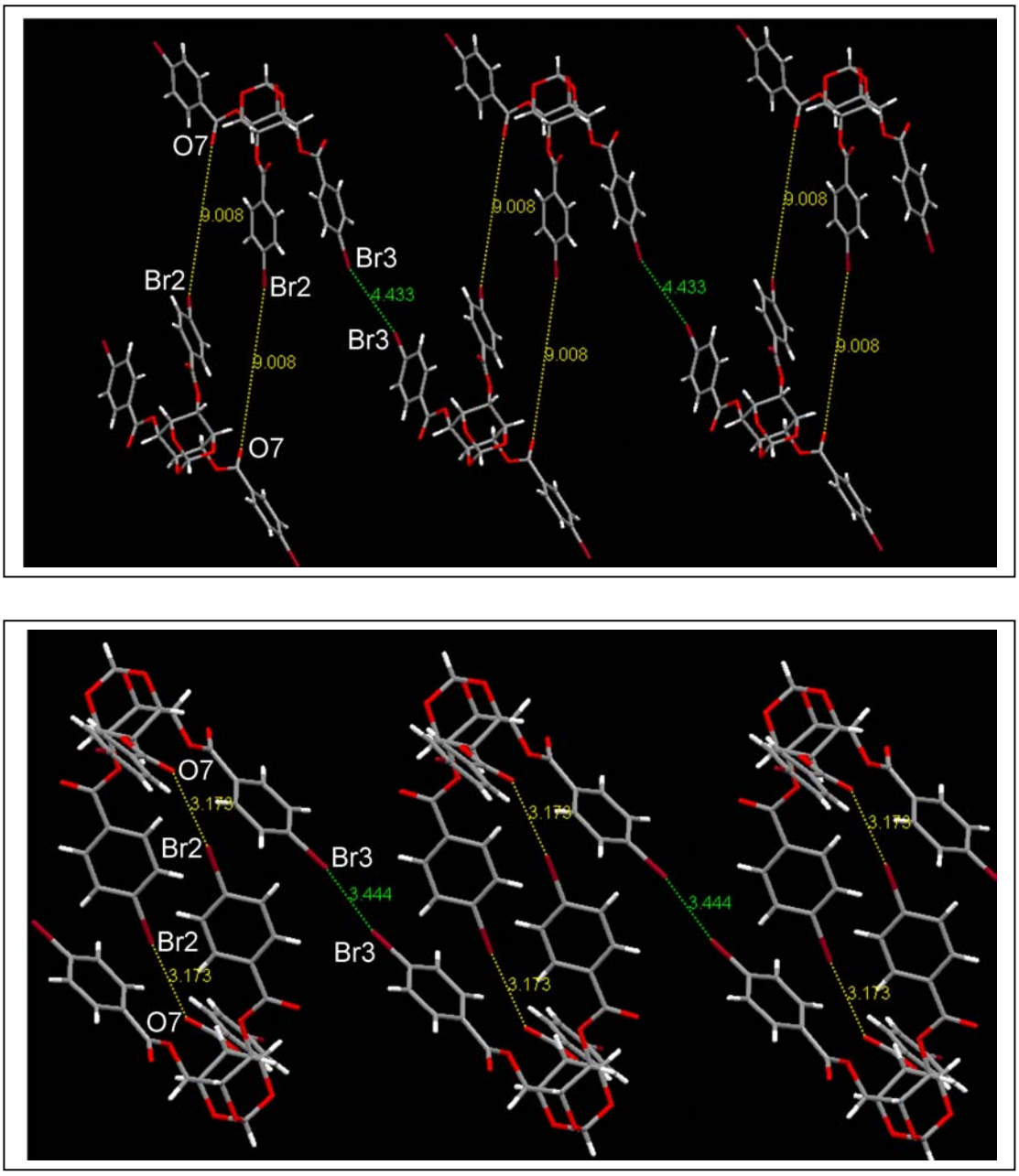


Fig. 7 A similar view of the molecules linked via Br3…Br3 conctacts in (A) Form I and (B) Form II. Upon heating the crystals of Form I, a 'closing in' of Br2….O7 contacts is thought to give rise to halogen bonded dimers as in Form II.

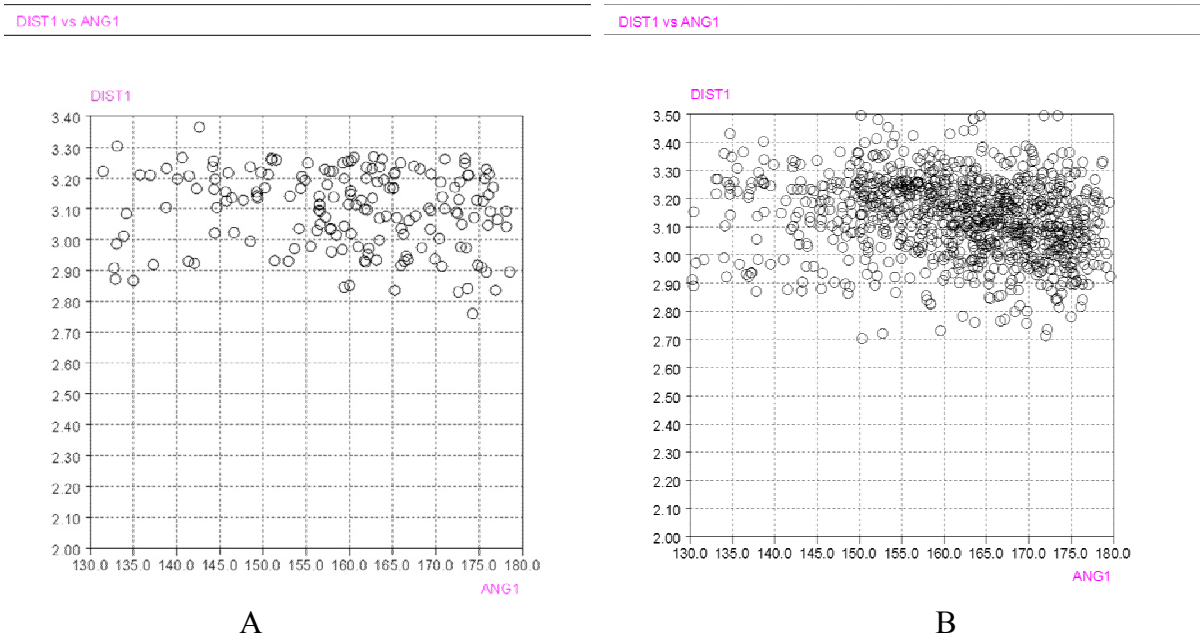
Table 1. Intermolecular C-H…O / C-H…halogen Interactions:

	D-H…A	H…A (Å)	D…A (Å)	D-H…A (°)
Form I of **1**	C(1)-H(1)...O(5)#1	2.38	3.248(6)	146.7
	C(3)-H(3)...O(9)#6	2.39	3.339(6)	163.7
	C(4)-H(4)...O(7)#4	2.48	3.278(6)	138.0
	C(5)-H(5)...O(9)#4	2.76	3.413(6)	124.4
	C(6)-H(6)...O(7)#5	2.53	3.370(6)	143.8
	C(10)-H(10)...O(9)#3	2.55	3.450(6)	163.3
	C(21)-H(21)...O(8)#1	2.88	3.318(6)	110.3
	C(24)-H(24)...O(7)#2	2.73	3.646(6)	167.5
Form II of **1**	C(5)-H(5)...Br(2)#9	3.03	3.715(4)	128.4
	C(6)-H(6)...O(5)#7	2.77	3.495(4)	131.1
	C(7)-H(7)...O(9)#7	2.71	3.373(5)	125.2
	C(10)-H(10)...O(5)#8	2.82	3.610(4)	144.1
	C(11)-H(11)...O(3)#8	2.60	3.374(5)	140.9
	C(13)-H(13)...O(8)#10	2.78	3.445(5)	129.8
	C(13)-H(13)...Br(2)#11	3.12	3.720(4)	123.8
	C(14)-H(14)...O(8)#10	2.95	3.533(5)	122.2
	C(18)-H(18)...O(9)#9	2.55	3.351(5)	144.5
	C(27)-H(27)...Br(2)#12	3.10	3.745(5)	128.4
	C(28)-H(28)...Br(2)#12	3.12	3.761(4)	127.5
Form II of **2**	C(1)-H(1)...O(7)#16	2.75	3.483(3)	132.4
	C(3)-H(3)...O(3)#17	2.71	3.560(3)	144.8
	C(5)-H(5)...Cl(2)#14	3.20	3.958(3)	135.8
	C(6)-H(6)...O(5)#18	2.46	3.256(3)	138.6
	C(7)-H(7)...O(9)#18	2.66	3.363(3)	129.0
	C(10)-H(10)...O(5)#13	2.83	3.525(3)	132.8
	C(11)-H(11)...O(3)#13	2.57	3.432(3)	153.4
	C(13)-H(13)...O(8)#17	2.77	3.381(4)	124.0
	C(13)-H(13)...Cl(2)#15	3.12	3.598(3)	113.6
	C(14)-H(14)...O(8)#17	2.77	3.384(4)	124.5
	C(18)-H(18)...O(9)#14	2.43	3.240(4)	144.8
	C(27)-H(27)...O(1)#16	2.64	3.360(4)	134.9

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z #2 x,-y,z+1/2 #3 x,-y,z-1/2 #4 x,y+1,z #5 x,-y+1,z+1/2 #6 x,-y+1,z-1/2 #7 -x+1,-y,-z+1 #8 x+1,y,z #9 -x+1,-y,-z+2 #10 -x+1,-y+1,-z+1 #11 x,y+1,z-1 #12 -x+2,-y,-z+2 #13 x-1,y,z #14 -x+1,-y+2,-z+1 #15 x,y-1,z+1 #16 -x,-y+2,-z+2 #17 -x+1,-y+1,-z+2 #18 -x+1,-y+2,-z+2

The CSD Survey on Different Types of Halogen Bonding

CSD search was carried out with CSD v5.26 (November, 2004), constrains applied were R < 0.075, distances ≤ sum of van der waals radii and angles in the range 130-180º. The search included halogen atoms X (X=F, Cl, Br, I) and differently hybridized oxygen atoms (carbonyl and ether). Combined as well as separate search was performed for organic and organometallic compounds. Combined search resulted in 1045 hits for the halogen bonding between X atom and carbonyl oxygen atom and 411 between X atom and ether oxygen atom. Separate CSD search gave 893 hits for the organic compounds and 152 hits for the organometallic compounds for halogen bonding involving carbonyl oxygen and 344 hits for organic compounds and 67 hits for organometallic compounds for halogen bonding involving ether oxygen respectively.



A B

Fig. 8 Scatter plots of distance X…O (Å) vs angle C-X…O (º) for (A) Organometallic and (B) Organic compounds for C-X…O=C, X = F, Cl, Br, I.

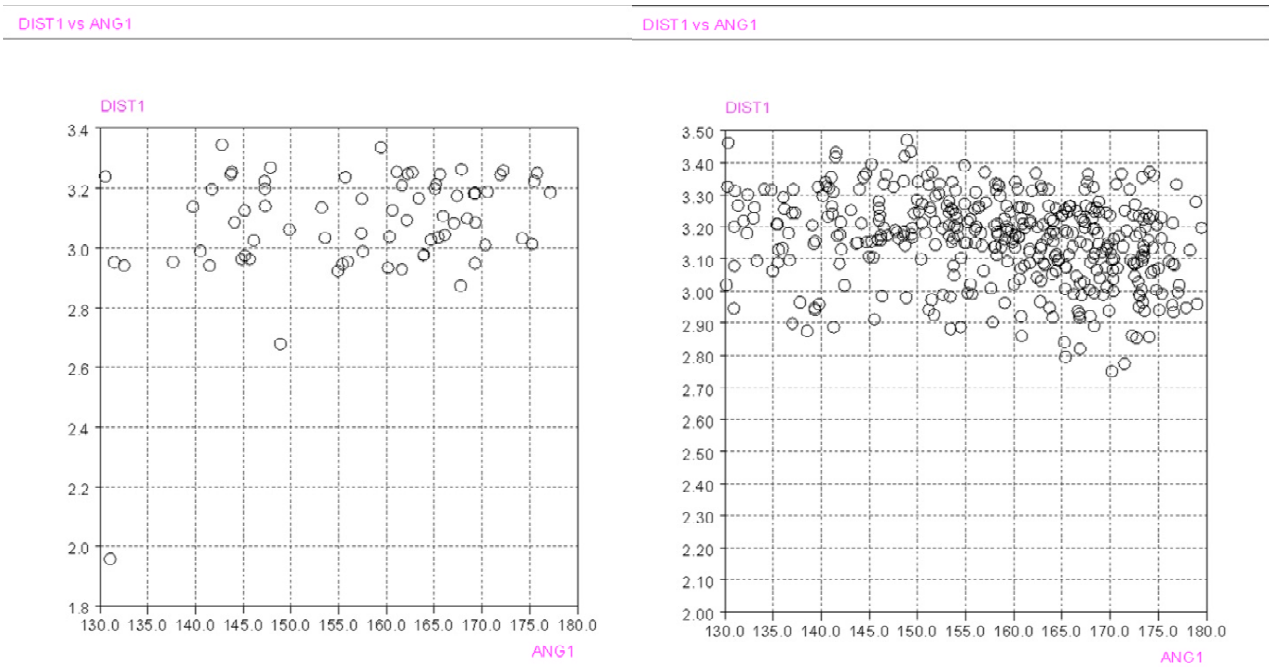


Fig. 9 Scatter plots of distance X…O (Å) vs angle C-X…O (º) for (A) Organometallic and (B) Organic compounds for C-X…O-C, X = F, Cl, Br, I.

Table 2. Distribution of hits in CSD for various categories

		Organic Compounds	Organometallic Compounds
For Carbonyl Oxygen Atom (C-X…O=C)	X = F	42	14
	X = Cl	429	115
	X = Br	312	17
	X = I	114	6
For Ether Oxygen Atom (C-X…O-C)	X = F	22	14
	X = Cl	174	44
	X = Br	111	7
	X = I	38	2