

## Concomitant Polymorphs Exhibiting Differences in the Halogen Bonding Contacts

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The 'halogen bonding' interactions are receiving increasing attention due to their potential applications in crystal engineering and host-guest chemistry.<sup>1</sup> The C-halogen...O bonding is comparable in energy with the conventional H-bonding interactions.<sup>2</sup> Tri-*O*-*p*-halo-benzoyl-*myo*-inositol 1,3,5-orthoformates (halo = chloro (**1**), bromo (**2**)) produced concomitant polymorphs when crystallized from a number of solvents. Crystals (of **2** from chloroform) of Form I (Triclinic, P-1) were large octahedral blocks whereas Form II (Monoclinic, C2/c) were long, thin whiskers. Although common interactions such as Br...Br and C-H...O exist in both the forms, notable differences were seen in the halogen bonding contacts. Form I makes C-Br...O=C whereas Form II shows C-Br...O-C (orthoformate bridge) contacts. The Br...O distances are less than the sum of their van der Waals radii (3.173 Å in Form I & 3.027 Å in Form II) with better linearity in Form I (C-Br...O 173.8°) than in Form II (163.4°). To examine the propensity of the C-halogen...O contacts with differently hybridized O atoms, a brief survey of CCDC carried out showed better directionality of halogen bonds involving carbonyl oxygen than ether O atoms.

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