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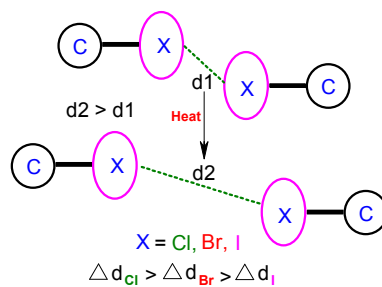
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TOC



The order of thermal expansion of the interhalogen interactions is $\text{I}\cdots\text{I} < \text{Br}\cdots\text{Br} < \text{Cl}\cdots\text{Cl}$, indicating that the order of interhalogen interaction strength is $\text{I}\cdots\text{I} > \text{Br}\cdots\text{Br} > \text{Cl}\cdots\text{Cl}$.

The Effect of Temperature on Interhalogen Interactions in a Series of Isostructural Organic Systems

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The thermal expansion behaviors of two sets, the guest-free forms and the ethyl acetate solvates, of interhalogen interaction mediated isostructural networks of 2,4,6-triethyl-1,3,5-tris(4-halophenoxy)methylbenzene (halo = Cl, Br and I) have been studied. In both of the series, the order of increase in interhalogen distances with increasing temperature is I...I < Br...Br < Cl...Cl which is actually the reverse order of interhalogen interaction strength.

Recently halogen bonds have attracted lots of interest in the area of structural chemistry and materials science.¹ Two special issues in *Cryst. Growth Des.* and *CrystEngComm* have been dedicated to the halogen bonding.² O/N...X-C types of strong halogen bonds have been described as parallel to the conventional, well studied hydrogen bonds.³ The energy, propensity etc. of these strong interactions have been studied by theoretical calculation, competition experiment, statistical analysis, thermal expansion etc.⁴ Although, there are lots of reports and studies on the O/N...X-C types of halogen bonds, interhalogen interactions, specially involving organic halogens,^{5,6} have not drawn much attention. This lack of interest on interhalogen interactions could be due to the weak nature of these interactions. There are two distinct types of interhalogen interaction geometries, based on the two C-X...X angles (θ_1 and θ_2) in a C-X...X-C contact, known in the literature, type I ($\theta_1 \approx \theta_2$), and II ($\theta_1 \approx 180^\circ$ and $\theta_2 \approx 90^\circ$).⁷ Guru Row et al. have further categorized the type I interactions into two types, *cis* and *trans*.⁸ It is known that the stronger interactions are less affected by the temperature change compared to the weaker interactions.⁹ Therefore, we were interested to study the effect of temperature on different types of interhalogen interactions. The interhalogen interactions have been studied previously by theoretical calculation, statistical analysis, charge density analysis etc.¹⁰⁻¹² To the best of our knowledge, this is the first report where thermal expansion has been used as a tool to analyze comparative strength of the interhalogen interactions. As the thermal expansion of a material highly depends upon its crystal packing,¹³ it is important to perform this study within an isostructural environment to nullify the structural influence as much as possible. We have chosen 2,4,6-triethyl-1,3,5-tris(4-halophenoxy)methylbenzene (halo = Cl, Br and I) as a system

because they form two sets of isostructural lattices,⁶ the guest-free forms and the ethyl acetate solvates and in all these structures the interhalogen interactions play an important role.

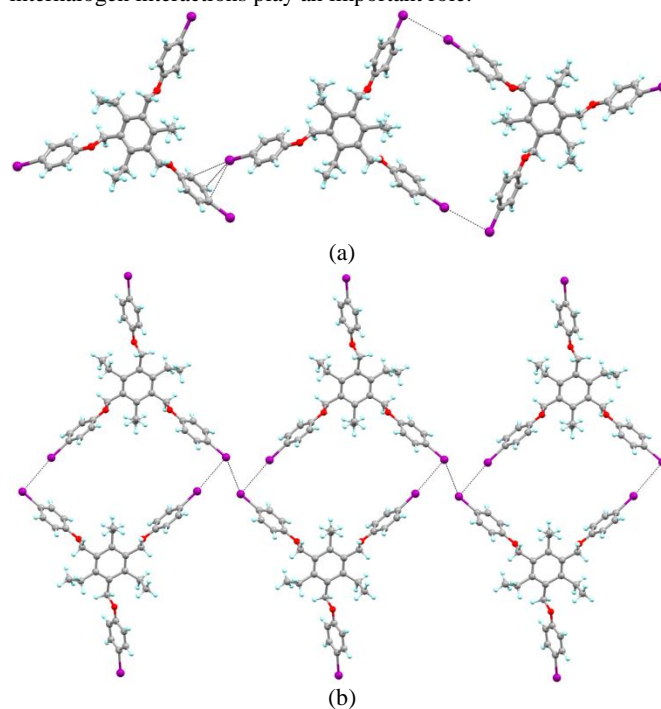


Fig. 1. Interhalogen interactions in (a) I-gf and (b) I-ea.

The guest-free form of the iodo derivative (I-gf) of the compound is solved in a monoclinic space group $P2_1/n$ with two ordered molecules in the asymmetric unit at 118 K. One of the three phenoxy groups is oriented above the plane of the central aromatic ring, whereas the other two phenoxy groups are oriented down the ring in these two molecules in the asymmetric unit. At room temperature, there is only one molecule in the asymmetric unit which is partially disordered. The bromo (Br-gf) and the chloro (Cl-gf) analogues are

solved in the $P2_1/c$ space group with two molecules in the asymmetric units at 118 K. In the asymmetric units of Br-gf and Cl-gf, all the three phenoxy groups in one molecule are directed down the plane of the middle ring, whereas in the other molecule, the arrangement of the phenoxy groups is similar to the I-gf molecule. At 262 and 298 K, there is only one disordered molecule in the asymmetric unit of the Br-gf crystal structures, whereas in the case of Cl-gf crystal, there are three molecules in the asymmetric unit at 226, 262 and 298 K. Two of the three molecules are partially disordered in Cl-gf. Although, at higher temperatures three systems have different Z' values, at lower temperature they are converged to the same structure ($Z'=2$) after phase transition. Fortunately, after the phase transition the gross packing patterns remain same which has allowed us to compare the structures across the different phases. In spite of different molecular conformations, interestingly all the three systems, I-gf, Br-gf, and Cl-gf, are isostructural. Interhalogen interactions play an important role in all these crystal structures. Two of the three halogens of a molecule are involved in a type-II interhalogen interaction, whereas the third one is involved in a halogen $\cdots\pi$ bond to form a one-dimensional (1-D) molecular tape (Fig. 1a).

All the three ethyl acetate solvates of iodo (I-ea), bromo (Br-ea) and chloro (Cl-ea) compounds are solved in the $P\bar{1}$ space group with one molecule, each of the host and the guest in the asymmetric unit. The guest molecules are highly disordered and could not be modeled from the difference electron density Fourier map. Squeeze program¹⁴ of PLATON has been used to deal with the residual electron density due to the disordered guest molecules and the host:guest ratios have been confirmed by thermal gravimetric analysis (Fig. S1). The conformations of the phenoxy groups in these three structures are similar to that in the I-gf form. All the three sets of solvates are isostructural. Similar to the guest-free form, two of the three halogens are involved in a type II interhalogen interaction, whereas the third one is involved in a halogen $\cdots\pi$ interaction. But the halogen pair, involved in type II interhalogen interaction, further interacts with another pair via type I interhalogen interaction to produce a “Z” shaped halogen tetramer synthon (Fig. 1b).

We have performed variable temperature single crystal X-ray diffraction (VT SXRD) analysis on these two sets of isostructural systems to study mainly the change in the interhalogen interaction distances with temperature. Diffraction quality single crystals suitable for single crystals X-ray analysis of each of the three guest-free systems and the three solvates were chosen, and six data sets for each system were collected within the range of 298 – 118 K by gradual cooling of the crystals at an interval of 36 K (Fig. S2). Analysis of the crystal structures, collected at different temperatures, shows that the average I \cdots I distances increased rather slowly with increasing temperature, whereas the effect of temperature difference is found to be maximum on the average Cl \cdots Cl distances among these three kinds of interhalogen interactions (Fig. 2a). This observation is not only true in the case of three isostructural guest-free systems, but also for the three isostructural ethyl acetate solvates (Fig. 2b). It also has been noticed that this order of expansion in the interhalogen interaction distances is not merely a consequence of the overall thermal expansion of the crystal lattices. We have compared the volumetric thermal expansion of the systems within each series of isostructural solids. Analysis of the volumetric thermal expansion suggests that among the guest-free systems, expansion of the Cl-gf form is maximum (3.4%), which is followed by Br-gf (3.1%) and then I-gf (2.8%) between the temperature range 118–298 K (Fig. 3a). But this trend of volume expansion is not observed in the case of the three isostructural solvates, where the expansion in volume for

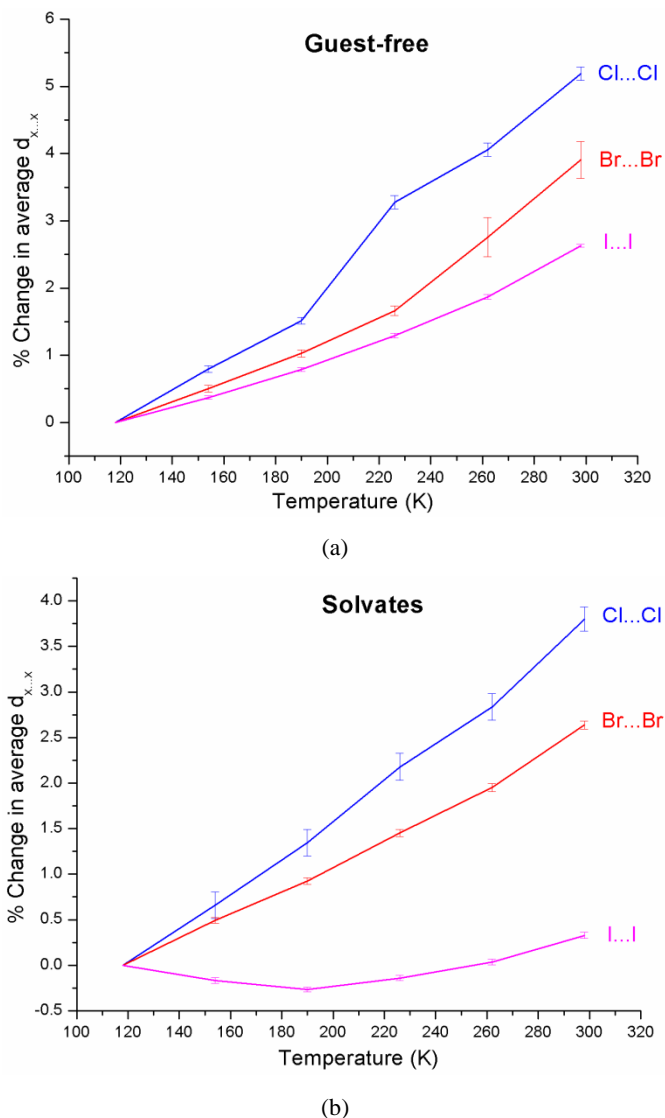


Fig. 2. % Change in halogen \cdots halogen distances with temperature in the (a) guest-free systems and (b) solvates.

these three systems are very close to each other within this temperature range (Fig. 3b). The volume expansions in Cl-ea, Br-ea and I-ea are 4.4%, 4.2% and 4.4% respectively. It is interesting to note that the volume expansions of the solvates are 1–1.5% more compared to that of their corresponding guest-free forms. Therefore, the guest molecules are capable of influencing and increasing the thermal expansion of the host lattice. The change in interhalogen interactions and volume suggests that the thermal expansion of the interhalogen distances are controlled by the relative strengths of the interhalogen interactions and the strongest I \cdots I interaction is affected least whereas the weakest Cl \cdots Cl interaction is affected most by the temperature change in these interhalogen interaction mediated isostructural series of crystal structures. It is interesting to note here that the order of melting point of these three compounds is I-gf (217–219 °C) > Br-gf (201–203 °C) > Cl-gf (176–178 °C),⁶ which is just reverse to the order of their volumetric thermal expansion properties. This trend of thermal expansion and melting point relationship is generally observed among the elements¹⁵ and previously we have shown the presence of this trend also in the case

of an odd-even diacid series¹⁶. We also have analyzed the change in C–X bond lengths and thermal vibration of the halogens, involved in interhalogen interactions, with respect to temperature. There is no clear cut trend in these two sets of parameters. Among the guest-free systems, the % change in average atomic thermal vibration of the Cl and I are comparable but it is comparatively higher for the Br group, whereas in the case of solvates, the change in Cl and Br groups are very much similar, but it is comparatively less for the I group within this temperature range (Fig. S3). On the other hand, the variations in C–X bond lengths with temperature are much smaller compared to X···X distances in all the six systems reported here and hence, that do not alter the overall trend observed for the order of change in X···X distances with temperature in this study (Fig. S4).

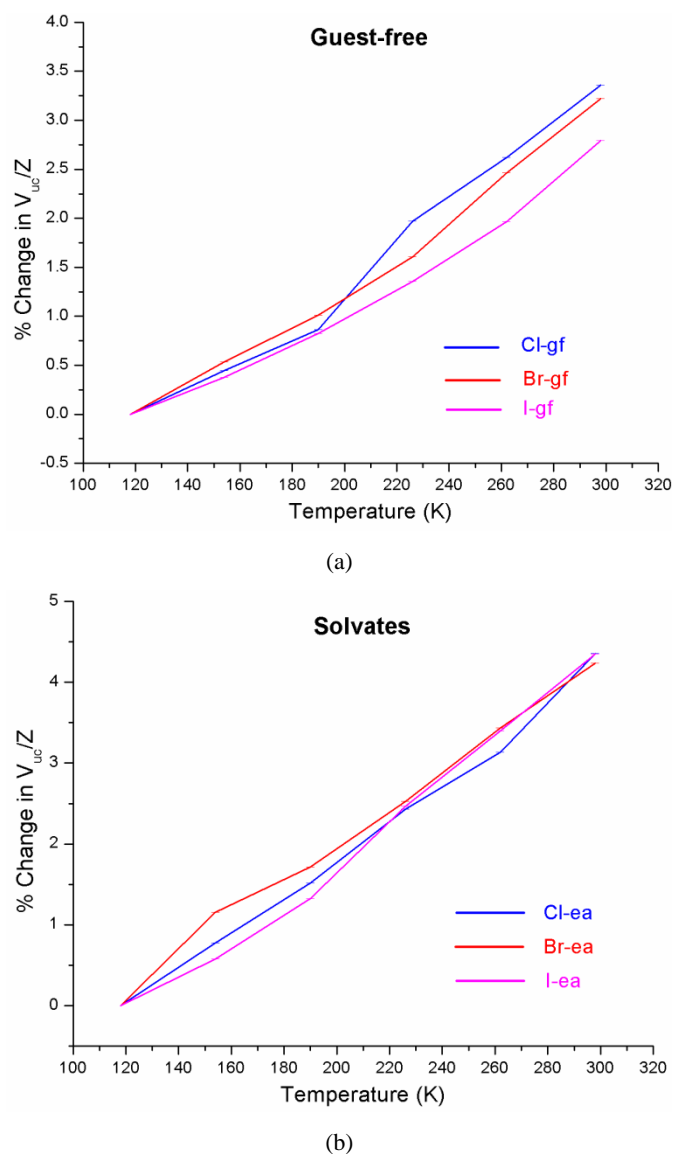


Fig. 3. % Change in unit cell volume (V_{uc}) / number of host molecules per unit cell (Z) with temperature in the (a) guest-free systems and (b) solvates.

There are few important studies on the interhalogen interactions reported in the literature. Based on the interaction distances between halogens in N-methyl-3,5-dibromopyridinium bromide/iodide crystal structures, Resnati et al. reported that I⁻ is a better halogen bond

acceptor than Br⁻ in X···Br–C interactions.¹⁷ On the other hand, Brammer et al. have studied a series of crystal structures containing M–X···X'–C (M is metal, X and X' are halogens) halogen bonds and shown that the angles around X and X' are respectively bent and linear and thus X is a halogen bond acceptor and X' is a halogen bond donor. They have systematically varied X and X' and analyzed the distances between these two groups in this series of crystal structures. Based on the interhalogen distances they have concluded that the order of halogen bond acceptor (X) capacity is Cl > Br > I, but the halogen bond donor (X') capacity is just in a reverse order.¹⁸ Price et al. have shown attractive nature of the C–Cl···Cl–C interaction via theoretical calculations.¹¹ Statistical study by Desiraju and Parthasarathy suggests that the relative strength of the interhalogen interactions follows the order as I···I > Br···Br > Cl···Cl > F···F. They conducted the study in 1989 on halo-hydrocarbon crystal structures, available in CSD version 3.1.¹² We have performed a quick database search to check the propensity of interhalogen interactions between two identical halogen atoms in the present database (CSD version 5.34, update November 2012)¹⁹ which also gives a similar picture reported by Desiraju and Parthasarathy. The criteria of our search was, only C, H and Cl/Br/I atoms are present, 3D coordinates available, not disordered, no error, not polymeric, no powder, no ions, only organic, X···X distances are within the sum of van der Waals radii + 0.2 Å. The occurrence of I···I (63%) interactions is found to be more than that of Br···Br (58%) interactions and they are followed by weaker Cl···Cl (53%) interactions. Thus, the statistical survey also supports the thermal expansion result reported in this present study.

In summary, we have analysed the effect of temperature on two sets of isostructural crystal structures which are assembled via interhalogen interactions. In both of the series, the order of increase in interhalogen distances with increasing temperature is I···I < Br···Br < Cl···Cl which is actually the reverse order of interhalogen interaction strength. The result of this VTSXRD analysis on the relative strength of interhalogen interactions is consistent with the result obtained by Desiraju and Parthasarathy via statistical analysis. The order of volumetric thermal expansion of the guest-free forms is found to be reverse to the order of their melting points. The volumetric thermal expansions of all the three solvates are higher than that of corresponding guest-free forms, indicates the influence of guest molecules on the thermal expansion of the host network.

Experimental Section

X-ray crystallography. X-ray crystal data were collected on Xcalibur Eos Oxford Diffraction Ltd. with Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Temperature was controlled with an Oxford Cryojet HT instrument. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm were applied.²⁰ Structure solution and refinement were performed with SHELXS²¹ and SHELXL²² respectively using Olex2-1.1 software package²³. Hydrogen atoms attached to the carbon atoms were placed in the calculated positions using riding model. SQUEEZE routine of PLATON was used to treat the residual electron density due to the highly disordered guest molecules. Three carbon atoms of the central ring and one ethyl group in each of the two molecules are disordered over two sites in Cl-gf structures at 226, 262 and 298 K. Four carbon atoms of the central ring, two ethyl groups, one 4-bromophenoxymethylene group and another methylene group are disordered over two positions in the Br-gf structures at 262 and 298 K. Three carbon atoms of the central ring, one ethyl group, one 4-halophenoxymethylene group and one CH₂O group are disordered over two positions in

the I-gf structures at 298 K and in all the ethyl acetate solvates of the three compounds. Treatment of the disordered atoms has been given in the Supporting Information (Fig. S2).

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Notes and references

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Electronic Supplementary Information (ESI) available: TG plot, ORTEP diagrams, plots for the % change in average Ueq values and in C–X bond lengths of those involved in interhalogen interactions with temperature, crystallographic data, interhalogen interaction geometry data, Vuc/Z data, average Ueq values and C–X bond lengths for the halogens involved in interhalogen interaction, statistical analysis on interhalogen interactions; and crystallographic data in CIF format for the structures with CCDC 962405-962440. See DOI: 10.1039/c000000x/

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