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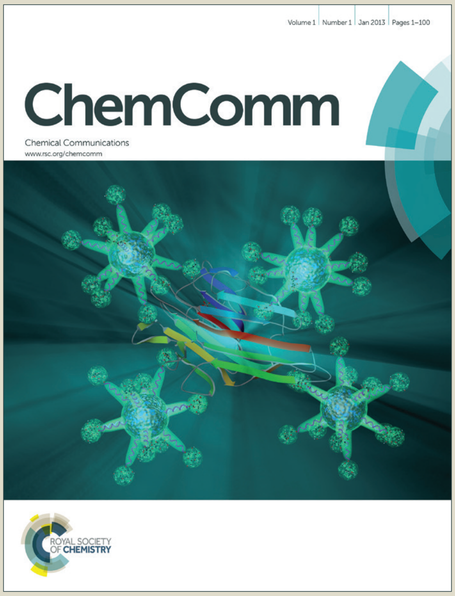

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A Thermal Expansion Investigation on the Melting Point Anomaly in Trihalomesitylenes

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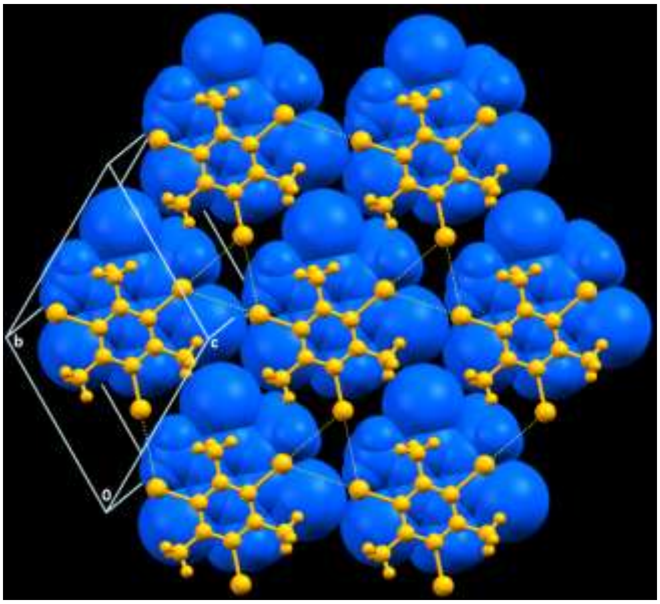
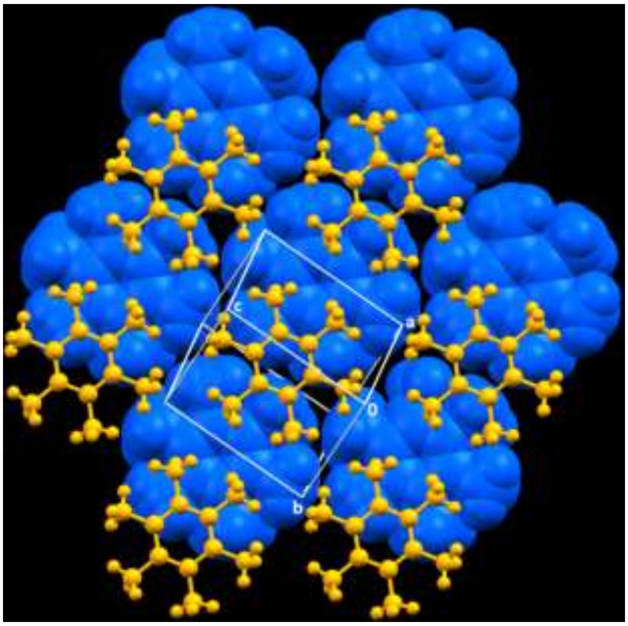
Generally the order of melting points of halogenated compounds is found to be I>Br>Cl whereas, in the series of trihalomesitylenes the order follows as Br>I≈Cl. This melting point anomaly has been explained in terms of their thermal expansion behaviours. The order of thermal expansion in this series is found to be Br<I≈Cl.

Molecular chlorine is a gas, bromine is a liquid, whereas iodine is a solid at STP. In general, the melting points of the iodo compounds are found to be higher than that of the corresponding bromo or chloro compounds.[1] Melting point is a complex phenomenon. It depends upon intermolecular interactions, molecular weight etc. Stronger interactions and higher molecular weight generally cause higher melting point in a system. There are two distinct types of interhalogen interactions known in the literature, type I (cis and trans) and type II.[2] It is known that the relative strength of the interhalogen interactions follows the order as I···I>Br···Br>Cl···Cl which is also the order of their atomic weights and polarizabilities. These interactions have been studied by theoretical calculation, statistical analysis, charge density analysis etc.[3] It is also known that modulations in stronger interaction caused by a thermal stimuli is relatively less compared to that in weaker interactions.[4] Hence, one would expect that the melting point order in the trihalomesitylenes to be followed as trichloromesitylene (TCM) < tribromomesitylene (TBM) < triiodomesitylene (TIM). Interestingly, the melting point of TCM (MP = 205 °C) and TIM (MP = 206 °C) are comparable, whereas TBM (MP = 226 °C) possesses highest melting point among these three trihalomesitylenes.[5] It has been shown that the elements with higher melting points generally show smaller thermal expansion[6] and we have shown this inverse relationship in a series of organic diacid compounds[7] as well as in a series of halogenated organic compounds[3b]. Therefore, this melting point anomaly, in the family of trihalomesitylenes, led us to study the thermal expansion properties of this series of compounds.

The crystal structure of TCM was first reported by Carrie and coworkers in 1995 and then Bosh et al. reported the crystal structures of TBM and TIM in 2002.[2b] Desiraju et al. have further studied the latter two structures to study the mechanical properties in their solid-states in 2006.[8] The structures are quite simple – forming two-dimensional layered structures mediated via interhalogen interactions, there is no other strongly interacting functional group in the systems and all the three halogenated structures are isostructural (Fig. 1). The halogen atoms form halogen trimer synthons via type II interhalogen interactions. One more interesting fact is that the corresponding methylated compound, hexamethylbenzene (HMB, MP = 166 °C)[5a], also possesses similar crystal structure.[9] The similarity of the trihalomesitylenes and HMB structures suggests that the packing is driven by steric factors, symmetry as well as halogen-halogen interactions. All the four crystal structures are solved in $P\bar{1}$ space group and there is only one molecule in the asymmetric unit of the trihalomesitylenes, whereas only a half molecule is found in the asymmetric unit of the HMB crystal structure.



(a)



(b)

Fig. 1 Crystal packing diagrams of (a) TIM and (b) HMB. Bottom layers (blue) are shown in space fill model and the top layers (orange) are shown in ball and stick model.

We have performed variable temperature single crystal X-ray diffraction (VTSXRD) studies on these four systems in the 118-262 K temperature range with an interval of 36 K (Table S1). When the change in unit cell volume (ΔV_{uc})/no. of molecules in the unit cell (Z) (i.e. ($V_T - V_{118}$)/Z) is plotted against temperature (T), the rate of expansion with increasing temperature is found to be highest in the HMB system in this series of structures. This rate of expansion in TIM is found to be similar to TCM, whereas TBM shows the minimum expansion among these four systems (Fig. 2). This observation supports the inverse relationship between thermal expansion and melting point of the materials for all the four compounds studied here. These systems show moderate thermal expansion coefficients along all the three principal axes (Table S2).

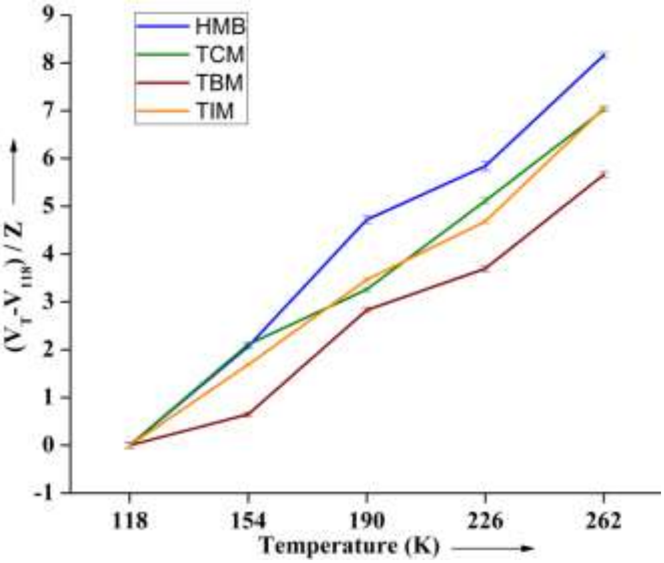


Fig. 2 Plot of the change in unit cell volume/Z vs. temperature.

We also have compared thermal expansion in area as well as along the interplanar distance among these isostructural systems. Though, the change in interplanar distances ($IP_T - IP_{118}$) follows the order HMB>TCM>TBM>TIM, where TCM is marginally smaller than HMB and TIM is marginally smaller than TBM (Fig. 3), interestingly the change in area (A_T-A_{118}) with temperature clearly indicates that the order of expansion of the 2D sheets is HMB>TCM≈TIM>TBM (Fig. 4). This observation is in contrary to the general expectation that the strongly interacting iodo trimer synthons would cause smaller expansion in heavier TIM than that of bromo and chloro trimer synthons in the crystal structure of relatively lighter TBM and TCM respectively. Therefore, we were interested to analyze the variation in halogen···halogen distances with temperature (Table S3).

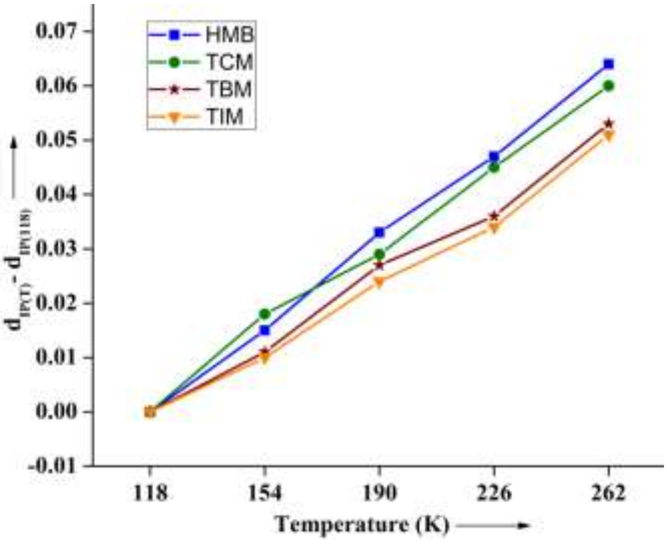


Fig. 3 Plot of change in interplanar distance vs. temperature.

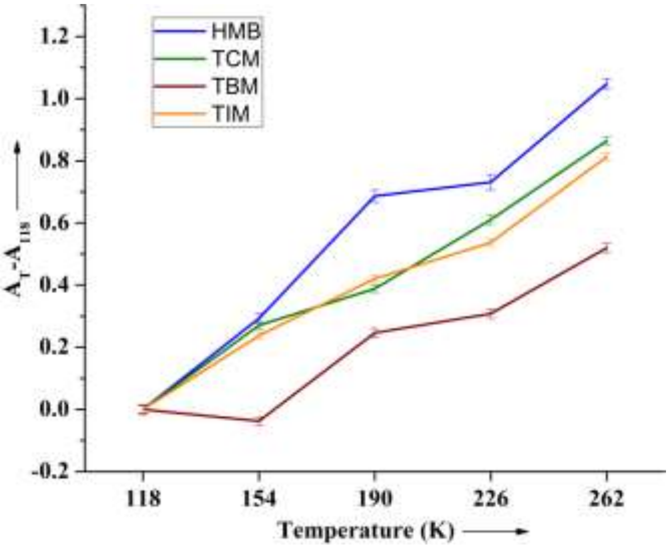


Fig. 4 Plot of the change in area vs. temperature.

Recently, we have shown that the effect of temperature change on the variation in interhalogen interaction distances follows the order I···I < Br···Br < Cl···Cl in two sets of isostructural halogenated systems.[3b] Interestingly, in the present family of structures the order is found to be as Br···Br < I···I < Cl···Cl (Fig. 5). As a result, the change in area in TBM is smaller than that in TIM crystal structure. It is known that the order of interhalogen interaction strength is I···I > Br···Br > Cl···Cl and stronger interactions are less affected by temperature change compared to the weaker interactions. Therefore, this observation could not be explained in terms of interhalogen interaction strength alone. Comparison of packing coefficients (Table S4, calculated using PLATON program[10]) of the structures suggests that the TBM molecules are more efficiently packed (packing coefficient 72.5% at 118 K) compared to the TIM molecules (packing coefficient 70.1% at 118 K) in their respective crystal structures. This is rather expected, because the size of a bromo group (25.7 $Å^3$) is comparable to the size of a methyl group (26.0 $Å^3$), but an iodo group (32.0 $Å^3$) is much larger than a methyl group.[1h] As the molecules are assembled via weak interhalogen and van der Waals interactions, better packing in TBM renders more stability to the system compared to TIM.

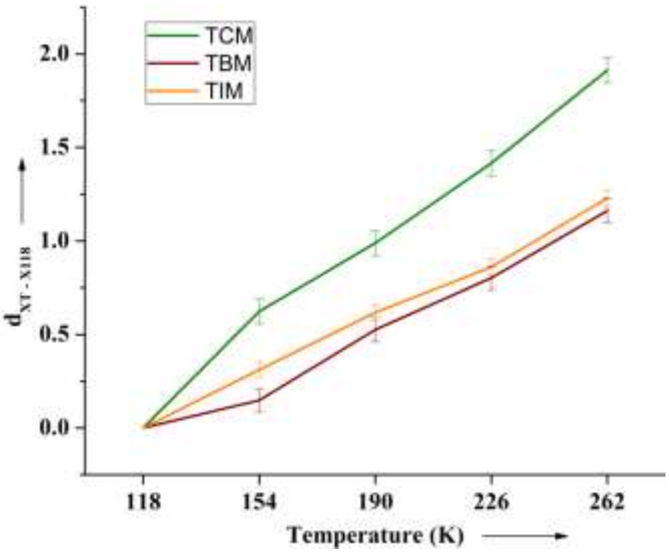


Fig. 5 Plot of the change in average interhalogen interaction distance vs. temperature.

Conclusions

In summary, we have studied thermal expansion properties of the three isostructural trihalomesitylene compounds along with their methyl analogue. The isostructurality across the systems helped us to perform relative thermal expansion studies in these crystals, as the thermal expansion in a material highly depends upon its crystal structure[11]. The volumetric thermal expansions in the systems are able to explain the melting point anomaly in the series. The order in melting point is $MP_{HMB}<MP_{TCM}\approx MP_{TIM}<MP_{TBM}$ and the order in thermal expansion is $\Delta V_{HMB}>\Delta V_{TCM}\approx\Delta V_{TIM}>\Delta V_{TBM}$ in the temperature range 118-262 K. Larger thermal expansion in TIM compared to that in TBM causes lower melting point in TIM than expected. The larger thermal expansion in volume of the TIM system is originated from larger expansion in area of the 2D layer which is also evident from the faster change in halogen···halogen interaction distances with temperature.

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Notes and references

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Crystallization: Single crystals of HMB, TBM and TIM were produced from ethyl acetate, whereas TCM single crystals were produced from dichloromethane solution at room temperature using slow evaporation of solvent method.

Variable temperature single crystal X-Ray diffraction: Five data sets were collected in each system at an interval of 36 K by gradually heating the crystals from 118 K to 262 K. Temperature was controlled by an Oxford Cryojet HT instrument. X-ray crystal data were collected on Xcalibur Eos, Agilent Technologies Ltd. with Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption correction using spherical harmonics, implemented inn SCALE3 ABSPACK scaling algorithm were applied.[12] Structure solution and refinement were performed with SHELXS-97[13a] and XL[13b] respectively in Olex 2.1-2 package[14]. All the non-hydrogen atoms have been refined anisotropically. In all the structures carbon bonded hydrogen atoms have been placed at calculated positions using riding model.

Electronic Supplementary Information (ESI) available: ORTEP plots, crystallographic data table, thermal expansion coefficients along the principal axes, halogen bond interaction geometry, packing coefficients at different temperatures and crystallographic data in cif format for the structures with CCDC 1057989-1058008 are all available in the supporting information for the article. See DOI: 10.1039/c000000x/

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