Evolution of intermolecular contacts with temperature and pressure in bromoethane and iodoethane

Podsiadło M¹, Bujak M², Olejniczak A¹

¹Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland
²Faculty of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland
marcinp@amu.edu.pl

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At ambient conditions two liquids, bromoethane, C₂H₅Br (MBE, m.p. 154.6 K) and iodoethane, C₂H₅I (MIE, m.p. 162.1 K), have been crystallized under both isobaric and isochoric conditions using in situ low-temperature and high-pressure techniques. The single-crystal X-ray diffraction studies were supported by compressibility and differential scanning calorimetry measurements. The results of our studies[1] demonstrate clear similarities and only slight differences in the behaviour of MBE and MIE. Both MBE and MIE show monoclinic isostructural phases that are stable down to 100 K/0.1 MPa and up to ca. 295 K/3.7 GPa with no symmetry or phase change. Decreasing temperature and increasing pressure mainly affect the intermolecular distances. As a result the shorter and new noncovalent interactions are introduced, in particular, with compression of the crystals. The Hirshfeld surface analysis of intermolecular contacts clearly shows the nature of occurrence and hierarchy of interactions pointing the role played by Br/I⋯Br/I contacts. The preferences for the formation of intermolecular contacts in MIE are more pronounced, and do not require such extreme conditions, than in case of MBE. It is notable that the attractive Br/I⋯Br/I and Br/I⋯H contacts could be basically classified as type I interactions. The Hirshfeld analysis also indicates that both MBE and MIE molecules in their crystals, upon cooling or compression, are brought closer with each other without main changes in their mutual orientations. This observation, besides the contribution associated with understanding of the noncovalent interactions and their role on the fundamental processes of crystallization, opens the way to engineer the stable molecular systems that, remaining their structural properties, could be safely cooled or squeezed in the relatively wide range of temperature and pressure. These facts along with the specific response of the crystals to the external forces could be utilized in the design of new materials.

References

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