

*Compressed interactions and properties of methyl-amine polymorphs*Andrzej Katrusiak¹, Marcin Podsiadlo¹, Anna Olejniczak¹¹Faculty Of Chemistry, Adam Mickiewicz University, Poznan, Poland

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A series of simplest aliphatic amines, methylamine (MA), dimethylamine (DMA) and trimethylamine (TMA), has been studied at high pressure by single-crystal X-ray diffraction. The revealed structure-property relations include the melting temperature and pressure correlating with intermolecular interactions and molecular symmetries. All these compounds, as well as analogous ammonia NH₃, are gaseous at ambient conditions and represent an important class of compounds widely used in organic chemistry and in industry. The structures of NH₃, MA and TMA have been previously determined at ambient pressure and low temperature. Liquid MA freezes at 179.7 K and the crystal structure of its phase I has been determined at 123 K; it is orthorhombic, of space group Pcab, with Z=8 and Z'=1 [1]. DMA at ambient pressure freezes at 181.0 K, however its structure has not been reported yet. TMA has the lowest melting point, of 156.1 K, and its crystal structures at 143 K and 118 K has been reported as trigonal phase I, of space group P, with Z=2 and Z'=0.333 [2,3]. Presently we have found five new polymorphs of methylamines: one of MA (phase II, space group Fdd2), two of DMA (phase I, space group C2/c and phase II, P21/c) and two of TMA (phase II of space group P21/n and phase III, P21/m). We have found that the freezing pressure of NH₃ and TMA are similar and much lower than those of MA and DMA. This unexpected result has been explained by intermolecular interactions in these crystal structures. Phase diagrams of the methylamines have been outlined up to 6 GPa.

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