## How close can Halogen Atoms get in a Crystal – Triphenylmethylbromide

<u>Céline Besnard</u><sup>a</sup>, Fabrice Camus<sup>a</sup>, Mogens Christensen<sup>b</sup>, Marc Fleurant<sup>a</sup>, Andy Fitch<sup>c</sup>, Phil Pattison<sup>a,d</sup>, Marc Schiltz<sup>a</sup>, <sup>a</sup>Laboratory of Crystallography, EPFL, Lausanne, Switzerland. <sup>b</sup>University of Aarhus, Denmark. <sup>c</sup>ESRF Grenoble, France. <sup>d</sup>Swiss-Norwegian BL, ESRF, Grenoble, France. E-mail: celine.besnard@epfl.ch

The crystal structure of triphenylmethylbromide (TPMB) displays unusually close halogen…halogen contacts between neighbouring molecules. The shortest Br…Br distance is 3.203 Å at room temperature, which is about 0.5 Å smaller than the sum of the van-der-Waals radii [1]. An investigation of the crystal structure of TPMB as a function of temperature was performed, to check if the lattice contraction would allow a further compression of the Br…Br contacts.

We found that a reversible phase transition occurs at about 160K, where the single crystal splits up into different domains. The soformed twinned crystal recovers back to a single domain on passing through the phase transition back to the high temperature form.

Analysis of the twinned data allowed us to solve the structure of the low temperature phase which turns out to be isomorphic to one of the three known polymorphs of triphenylmethylchlorid (TPMC) [2]. Inspection of the low and high temperature structures reveals the mechanism of the phase transition: upon lowering the temperature, the Br...Br distances decrease down to a limiting value at 160K. Beyond that point, the molecules undergo a rearrangement whereby the C–Br bonds are tilted away from the 3 fold-axis, thus leading to a lowering of the crystal symmetry from P –3 to P –1.

[1] Dunand A., Gerdil R., Acta Cryst., 1984, B40, 59. [2] Kahr B., Carter R.L., Mol. Cryst. Liq. Cryst., 1992, 219, 79.

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