

Poster Presentations

[MS10-P16] What happens to symmetry and pseudo-symmetry of molecular crystals on cooling? Andrei S. Batsanov,

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According to crystallographers' lore, if a polymorphic transformation occurs on cooling of a molecular crystal, it normally involves lowering of the crystal symmetry and hence an increase of the number of symmetrically independent molecules (Z'). However, the kinetic and thermodynamic explanations are not unequivocal [1] and the experimental evidence has never been reviewed systematically. In this work, a CSD [2] survey revealed substantially higher occurrence of $Z' > 1$ for low-temperature than for room-temperature studies: 14.0% vs 10.9% for organic and 8.3% vs 5.3% for organometallic compounds, with a nearly 2:1 difference for $Z' \geq 3$. The occurrence of different space groups is also significantly skewed towards lower symmetry at lower temperature. A survey of over 1,000 compounds for which both room- and low-temperature polymorphs have been fully characterised, reveals comparable probabilities of Z' increasing through an increase of the lattice translations (i.e. structure modulation) and through disappearance of a symmetry element within a constant lattice. The increase of symmetry and/or decrease of Z' on cooling is rare but not unknown. A number of experimental case-studies are presented, involving single-crystal to single-crystal phase transitions. Thus, imido complexes $\text{PhNTaCl}_3(\text{DME})$ and 2,6- $\text{}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NWCl}_3(\text{PMe}_3)_2$ undergo phase transitions at 212.5 and 185 K, respectively, with the retention of the space groups ($P2_1/c$ and $P2_12_12_1$) and trebling of one cell parameter. Thereby Z' increases from 1 to 3. 2,5-trans-diphenyl-1,3-dioxane-2-carboxylic acid methyl ester, $\text{C}_{18}\text{H}_{18}\text{O}_4$, converts around 250 K from space group $I2/a$ to $P2_1/c$ with a simultaneous doubling of the b parameter,

thus rising Z' from 1 to 4. Most remarkably, two compounds with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Bpin) groups undergo transitions with an increase of symmetry on cooling. The unstable monoclinic form of 2,4- $\text{Me}_2\text{C}_6\text{H}_2(\text{Bpin})_2$ -1,5 converts from space group $P2_1$ to $P2_1/c$ at 114 K ($Z' 2 \rightarrow 1$), while the triclinic form of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Bpin})_2$ ($P 1$, $Z'=2$) below 200 K converts irreversibly to monoclinic lattice with a double unit cell volume ($P2_1/n$, $Z'=2$). These unusual phase transitions can be attributed to conformational flexibility of the Bpin group, low packing density defects of the parent structures and high concentration of defects in them. Remarkably, both compounds have denser polymorphs which show no phase changes between 293 and 100 K, viz. triclinic $\text{Me}_2\text{C}_6\text{H}_2(\text{Bpin})_2$ ($P 1$, $Z'=1$) and monoclinic $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Bpin})_2$ ($P2_1$, $Z'=3$).

It can be concluded that a substantial share of reported structures with $Z' > 1$ may be the result of overlooked phase transitions during flash-cooling. Why do these transitions result in modulation rather than lowering of the space-group symmetry? Is this an intrinsic effect of lattice-controlled rearrangement, or an artefact of a biased dataset? Obviously, a single crystal is more likely to survive modulation than the loss of a symmetry element, which often yields an unworkable twin. One way to resolve this dilemma is to grow crystals (from solution) below the temperature of modulation, which is the subject of further study.

[1] Steed, J.W. (2003) *CrystEngComm* **5**, 169-179.

[2] Cambridge Structural Database, version 5.34 (November 2012).

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