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An Incommensurately Modulated Small-Molecule Crystal Structure

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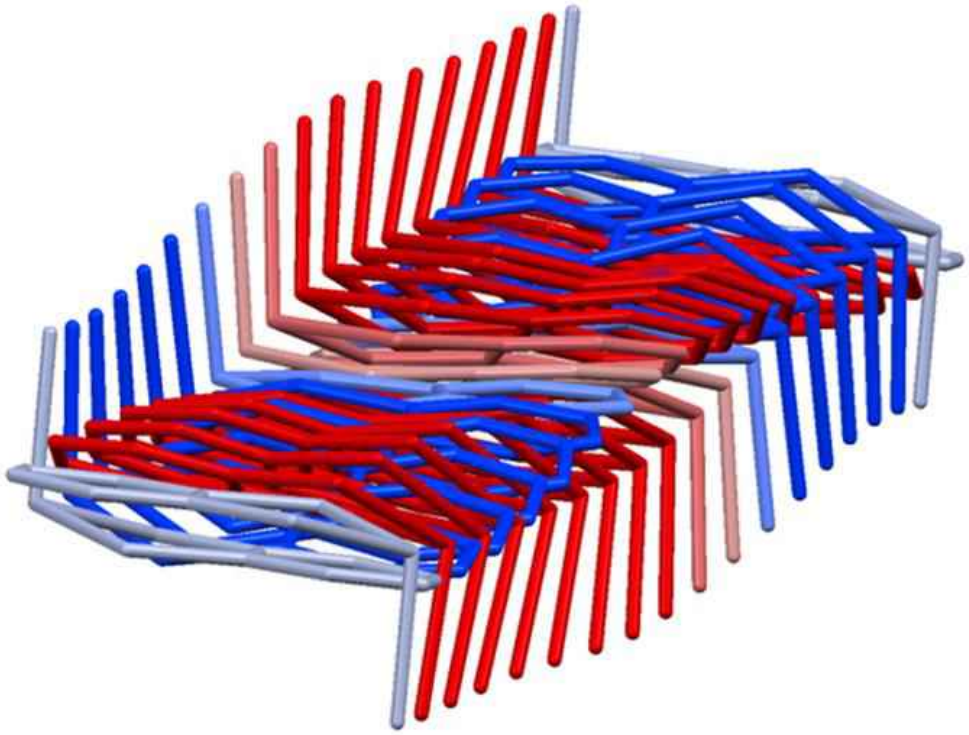
The first diffraction patterns measured for crystals of 2-chloro-benzo-1,3,2-dithiarsole (C6H4S2AsCl) showed an exceptionally large triclinic cell. After routine data collection the structure could be solved without difficulty; 17 independent molecules were found. A successful conventional refinement of the 170 independent non-H atoms was possible if restraints were applied (similar bond lengths and angles for all molecules; rigid-bond restraints; three sets of 8 anisotropic displacement parameters for the S and C atoms). At convergence R, wR2 were 0.042, 0.107 for 859 variables, nearly 4K restraints and more than 24K unique reflections of which 8774 have I>2σ(I). All displacement ellipsoids were positive definite. The display program Mercury revealed that the molecules form ribbons with a core of closely spaced As and Cl atoms. Because the ribbon is obviously modulated, and because Z' = 17 is both very large and prime, the possibility of an incommensurate structure had to be considered. A new integration of the original frames using EVAL14 gave a modulation vector with components 5.012(2)/17, -3.187(2)/17, 8.016(3)/17; the modulation is clearly incommensurate in the b* direction. Refinement with JANA2006 (811 variables, 11,119 unique reflections, no restraints) gave R, wR2 values 0.045, 0.116. The overall packing is determined by the stacking of the aromatic rings and probably by the segregation of interacting As and Cl atoms. A conventional refinement of a disordered, average (Z' = 1) structure revealed two basic orientations of the C6S2 plane that must be correlated in several directions if impossibly short intermolecular contacts are to be avoided. Along the modulation vector q the orientation of the C6S2 plane varies smoothly, but q is not a direction in which the molecules are in contact. The reasons for the unusual modulation will be discussed, as will the signs that a modulated, high-Z' molecular crystal structure is actually incommensurate.



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