

SUPPLEMENTARY MATERIAL

Experimental details

Table S-1. Crystallization results

Table S-2. o-TBD/HMB unit cells

Table S-3. m-TBD/HMB unit cells

Table S-4. p-TBD/HMB unit cells

Figure S-1. ORTEP drawings for ORTHO

Figure S-2. ORTEP drawings for PARA-I

Figure S-3. ORTEP drawings for PARA-II

Figure S-4. ORTEP drawings for PARA-III

Figure S-5. ORTEP drawings for PARA-IV

Figure S-6. ORTEP drawings for META-I

Figure S-7. ORTEP drawings for META-II

Figure S-8. Photograph of PARA-III to PARA-II transformation

Figure S-9. Possible ordered layers in META-I

Figure S-10. Pi overlap in ORTHO

Figure S-11. Pi overlap in PARA-I

Figure S-12. Pi overlap in PARA-II

Figure S-13. Pi overlap in PARA-III

Figure S-14. Pi overlap in PARA-IV

Figure S-15. Pi overlap in META-I

Figure S-16. Pi overlap in META-II

CIF-1. ORTHO

CIF-2. PARA-I

CIF-3. PARA-II

CIF-4. PARA-III

CIF-5. PARA-IV

CIF-6. META-I

CIF-7. META-II

X-ray - specific Supplemental

In META-I the intensity statistics suggested a centric structure. Oscillation photographs around all three axes both at room temperature and low temperature confirmed that the unit cell was correct; they showed no apparent disorder streaks. With $Z = 1$ in $P\bar{1}$, however, the TDB molecule would lie on a center of symmetry and therefore must be disordered. To deal with the disorder Cl and CN were put at each position of the ring with the occupancies constrained to total one at each position. It was found that within experimental error only four of the six ring positions contained CN groups. For the initial refinement a TDB molecule, constrained to have idealized bond lengths, and angles, was allowed to be disordered across a center of symmetry but was not required to have the ring center coincide with the symmetry center. The anisotropic displacement parameters for pairs of atoms *para* to each other including the *para* Cl and CN were constrained to be the same. With these restraints the refinement converged smoothly. The constraints were then removed and the final refinement carried out. An attempt to use one of the two orientations of the TDB as a starting point for solution and refinement in $P1$ did not lead to any reasonable conclusion.

Statistics for META-I suggested that the space group was $P\bar{1}$ and not $P1$, but this still required two TDB and two HMB in the asymmetric unit. Inspection of the diffraction pattern suggested that the crystal might be twinned. A unit cell determination was made on a new crystal using longer scan times than usual; 81 of the 82 peaks found could be indexed with the cell reported in Table 1. Further, the program DIRAX (Duisenberg, 1992) was used to look for possible twin components in this set of reflections; none could be found. Direct methods gave several more-or-less plausible solutions that did not refine well, but eventually the solution was found that is reported here, with two TDB in general positions, one HMB in a general position and two HMB on inversion centers. The two TDB molecules are related by a pseudo center of symmetry, and all three HMB molecules are related by pseudo translations. In addition

each of the TDB molecules proved to be disordered between two positions that were related by additional pseudo centers. This large amount of non-crystallographic symmetry, which had led to difficulty in getting the trial structure, also led to difficulty in the initial refinement. The model used had both restraints and constraints. In the three HMB molecules chemically equivalent bond lengths were restrained to be the same with an s.u. of 0.001 Å but the anisotropic displacement parameters on the crystallographically independent carbon atoms were allowed to vary freely. In the TDB molecules the bond lengths and angles were allowed to vary freely in the major components of the disorder but were constrained in the minor components to be identical to those in the major components. In addition the anisotropic displacement parameters were constrained to be identical for atoms in the major and minor components that were closer than 1 Å to each other and also to be identical for atoms related by the pseudo center of symmetry. With these restrictions the refinement converged to physically reasonable results. At this point the constraints on the bond lengths in the HMB were removed and the final refinement carried out. As mentioned earlier, five different data sets were collected on four different crystals. All gave similar results. If complete order was assumed, the final R values were about 0.15. If the disorder was included as described above, the final R values were between 0.07 and 0.08. If the disorder parameters in the two TDB molecules were refined independently, the occupancies were 0.80 to 0.85 and differed by up to 15 s.u.'s. However, the occupancies between the two data sets measured on the same crystal also differed by about the same amount. This suggested that the s.u.'s for the occupancies were unrealistically low and that the occupancies for the two independent molecules were probably equal; they were made equal in the final refinement. The occupancy for the major component for the structure reported in Table 1 0.8152 with a calculated s.u. of 0.0010; a more realistic description would be 0.82 with an uncertainty of 0.02. The final difference maps all were similar with peaks about 1 e/Å³ near the nitrile carbon atoms in the TDB molecules. This suggests that there is additional disorder, which was

looked for, but no reasonable model could be found. Also, it should be noted that the META-I and II structures are very closely related as is described in the *Discussion* section. However, this close relationship was not recognized until both structures had been independently solved.

The crystal of PARA-IV, mentioned earlier, was mounted and a unit cell determined at room temperature. When the cell was recognized as belonging to a new polymorph, the crystal was cooled with the intention of collecting a low-temperature data set. At low temperature a unit cell could not be determined. Visual inspection of the crystal showed that the cooling process had induced a transformation and the crystal, which had been a well-shaped needle, was changed to three connected segments, presumably twins, each bent at an approximately 60° angle to the adjacent segment, but with each segment still transparent. The crystal was moved so that, as far as possible, only the end segment was in the X-ray beam, and a new cell determined. Very surprisingly, the new cell at -99°C was the same as the room temperature cell, except for the contraction to be expected from the cooling. A data set was collected, to be on the safe side, with the intention of replacing it with data from a single crystal later. As described above, no additional sample was found and the structure was solved from the data set from the twinned crystal. The structure had four crystallographically independent molecules, two of each kind, all located on centers of symmetry. The chemically similar pairs were constrained to have similar geometries in the early stages of the refinement, but in the final refinement were unconstrained. It was clear from a comparison of the final F_O and F_C values that some of the observed intensities were affected by the twinning, but it was not clear what the twin law was, and no corrections were made.