

Molecular Packing Preferences of “Bridge-Flipped” Isomeric Molecules

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Molecules we have designated “bridge-flipped isomers” differ only in the orientation of a bridge of atoms connecting two major parts of the molecule, as among benzylideneanilines (Ar-CH=N-Ar' vs. Ar-N=CH-Ar') and among arylhydrazones (Ar-CH=N-NH-Ar' vs. Ar-NH-N=CH-Ar'). The common occurrence of disordered benzylideneaniline crystal structures having multiple orientations of the bridge raises the question of whether this disorder could be created artificially by means of co-crystallization of bridge-flipped isomers. Because co-crystallization would be facilitated by isostructuralism of the two components, we are examining solid-state structural features that would cause bridge-flipped isomers to assume similar molecular packing arrangements. These include (1) hydrogen bonding that might enforce similar packing arrangements; (2) Lewis acid-Lewis base interactions that might encourage similar packing arrangements; and (3) molecular planarity in benzylideneanilines that would minimize the effect of conformational differences on packing arrangements. Obstacles to isostructuralism have been found to include differences in molecular position of key H-bonding groups, differences in conformation enforced by intramolecular H-bonding, and competing intermolecular interactions (e.g. halogen-nitrile vs. halogen-halogen vs. nitrile-hydrogen). Although our studies have not resulted in the preparation of isostructural isomers to date, they have provided insight into the packing preferences of these compounds.

Keywords: intermolecular interactions and packing in small-molecule crystals, disordered molecular crystals, cocrystals