Poster Presentation

MS43.P28

Nitrile-Halogen Interactions in Some Bridge-Flipped Isomeric Benzylideneanilines

W. Ojala¹, K. Lystad¹, J. Smieja¹, J. Fermanich¹, C. Ojala²

¹University of St. Thomas, Department of Chemistry, St. Paul, Minnesota USA, ²Normandale Community College, Department of Chemistry, Bloomington, Minnesota USA

We designate as “bridge-flipped isomers” those pairs of molecules that differ only in the orientation of a bridge of atoms linking two major molecular fragments: in benzylideneanilines, Ar-CH=N-Ar’ vs. Ar-N=CH-Ar’; in phenylhydrazones, Ar-NH-N=CH-Ar’ vs. Ar-CH=N-NH-Ar’ (Ar = aryl). We use them as a context in which to evaluate the roles of molecular conformation, hydrogen bonding, space-filling requirements, and supramolecular synthons in establishing crystalline isomorphism or non-isomorphism. To examine nitrile-halogen and halogen-halogen interactions in solid isomeric benzylideneanilines, we have determined the structures of 2-cyanobenzylidene-2’-iodoaniline (I), 2-iodobenzylidene-2’-cyanoaniline (II), 2-cyanobenzylidene-2’-bromoaniline (III), 2-cyanobenzylidene-2’-chloroaniline (IV), and 2-chlorobenzylidene-2’-cyanoaniline (V) by single-crystal X-ray diffraction. I/II and IV/V are bridge-flipped isomeric pairs. I, III, and IV are isomorphous; the I/II and IV/V pairs are not. In I, III, and IV, translationally related molecules are linked into chains by C≡N⋯X contacts; no close X⋯X contacts occur. Although C≡N⋯X contacts between translationally related molecules define chains in II similar to those in I, III, and IV, and although II likewise lacks close X⋯X contacts, the molecular packing arrangements differ (monoclinic for I, III, and IV vs. triclinic for II). V in contrast assumes an orthorhombic structure from which the C≡N⋯X interaction is absent and which is isomorphous with 2-chlorobenzylidene-2’-chloroaniline (VI), the nitrile group of V exchanged for the aniline-side chlorine of VI, that chlorine atom in VI not involved in a close intermolecular Cl⋯Cl contact. Although neither C≡N⋯X nor X⋯X contacts result in isomorphous bridge-flipped isomers in the cases of I/II and IV/V, the C≡N⋯X contacts apparently play a major structure-defining role and supersede any potential X⋯X contacts in I-IV.


Keywords: bridge-flipped isomers, Lewis acid-base interactions, isomorphism