

## Poster Presentation

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### *Nitrile-Halogen Interactions in Some Bridge-Flipped Isomeric Benzylideneanilines*

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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.

[1] W. Ojala, J. Smieja, J. Spude et al., *Acta Cryst. Sect. B: Struct. Sci.*, 2007, 63, 485-496, [2] W. Ojala, K. Lystad, T. Deal et al., *Cryst. Growth Des.*, 2009, 9, 964-970, [3] W. Ojala, T. Arola, A. Brigino et al., *Acta Cryst. Sect. C: Cryst. Struct. Commun.*, 2012, 68, o270-o278

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