

Molecular Packing Properties of Some Symmetrically Substituted Diaryl Furoxans

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Benzonitrile oxides can form three different dimers in solution depending on the reaction conditions: the 1,2,5-oxadiazole-2-oxide or furoxan; the 1,4,2,5-dioxadiazine; or the 1,2,4-oxadiazole-4-oxide. As part of our study of the solid-state chemistry of benzonitrile oxides, we have determined the crystal structures of six furoxans: *bis*(3-bromophenyl)furoxan (**I**), *bis*(3-chlorophenyl)furoxan (**II**), *bis*(4-chlorophenyl)furoxan (**III**), *bis*(2,3-dichlorophenyl)furoxan (**IV**), *bis*(3-nitrophenyl)furoxan (**V**), and *bis*(4-methylphenyl)furoxan (**VI**). We have found **I** and **II** to be isomorphous and both **III** and **VI** to occur in both monoclinic and orthorhombic forms (as reported by previous workers in the case of **III**; conformational polymorphs in both cases). No single intermolecular interaction or packing motif appears to be shared by all of these structures, although ring stacking interactions are observed in some of them, and certain similarities in packing permitted by the size and shape similarity between chloro and methyl substituents are observed between orthorhombic **III** and monoclinic **VI**. The eight structures exhibit a range of disorder from essentially ordered to 50:50 disordered at the furoxan ring, the exocyclic oxygen atom being located adjacent to either nitrogen atom in the disordered structures. In only one structure, monoclinic **III** (space group *C2/c*), is the molecule disordered about a crystallographic symmetry element, a twofold axis. Although furoxan structures have been reported in which the ring lies in a crystallographic mirror plane, no structures have been reported in which the ring is disordered about a perpendicular mirror plane. In contrast, the sterically similar heterocyclic rings of certain maleic and succinic anhydride derivatives are reported to lie perpendicular to crystallographic mirror planes, but we have found no examples of structures in which the anhydride ring lies in these planes.