Intramolecular Geometry and Intermolecular Interactions of the CNO Group of Crystalline Benzonitrile Oxides: A Comparison with Phenyl Cyanates, Phenyl Isocyanates, and Phenyl Azides

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Benzonitrile oxides dimerize readily unless they bear a bulky substituent at one or both of the ring positions *ortho* to the CNO group. It is perhaps this high reactivity that has resulted in the description of few benzonitrile oxides in the crystallographic literature. As part of a study of the solid-state chemistry of benzonitrile oxides, we have determined by single-crystal X-ray diffraction the crystal structures of four halogenated derivatives: 2,6-dichlorobenzonitrile oxide (I); 2,3-dichlorobenzonitrile oxide (II); 3-bromobenzonitrile oxide (III), and 4-chlorobenzonitrile oxide (IV). With respect to dimerization capability, the substitution patterns represented by these molecules range from maximally hindered (the 2,6-dichloro compound I) to maximally unhindered (the 4-chloro compound IV). The geometry of the nitrile oxide group is found to be strongly dependent on the substitution pattern. The CNO moiety in previously published structures, all of which bear at least one *ortho* substituent, is consistently nonlinear, with both the C-C≡N and the C≡N-O bond angles deviating from strict linearity and the C-C≡N angle showing the larger of the two deviations. In our I-IV series the C-C≡N angle ranges from 171.5(2)° in III, comparable to the greatest deviations from linearity reported previously, to 179.5(2)° in maximally unhindered IV, to our knowledge the most linear geometry for this group yet reported. We have found no single molecular packing motif to be common to all reported benzonitrile oxides, although motifs in some of them are also observed among the phenyl cyanates, the phenyl isocyanates, and the phenyl azides described in the Cambridge Structural Database.