Supramolecular Effects to Explain a Nonstatistical Disorder

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The parent unsubstituted indigo compound is planar with an aromatic system delocalized over the entire molecule, while a series of *N*-monoacylindigo and *N*,*N*'-diacylindigo compounds, for which the change of the short H···O distances directly correlates with the changing acidity of the relevant C–H group and the corresponding changing basicity of the corresponding C=O group, was used twenty-five years ago to convincingly demonstrate the existance of intramolecular C–H···O hydrogen bonding interactions [1]. This work reports analysis of another compound in the same series, *N*,*N*'-di(methoxyacetyl)indigo. While the two halves of the di(methoxyacetyl) derivative would seem to be chemically equivalent, they unlike other symmetric indigos, are not structurally equivalent. Furthermore, one methoxy group is ordered in the crystal structure and the other is disordered with occupancy factors of 0.6:0.4. Both the nonequivalence and the nonstatistical disorder can be understood on the basis of supramolecular analysis of the intra- and inter-molecular noncovalent interactions of the highly distorted indigo molecule.

The current structure contains the intramolecular C−H···O hydrogen bonds that induce both twisting of the ring systems and doming of the ring systems relative to the central bond, as noted for other *N*-acyl substituted indigo structures [1] (d[C···O] = 3.044 and 3.071 Å for the two halves). Both acyl oxygen atoms participate in stronger intramolecular C−H···O hydrogen bonds to phenylene hydrogen atoms (d[C···O] = 2.812 and 2.882 Å, respectively). These four interactions are essentially identical in both disorder Parts A and B, as well as in the previously described *N*-acyl substituted indigo structures, and determine the twisting/doming of the indigo ring system. Addition of the ether oxygen atoms (methoxy groups) distinguishes the current structure from the previous structures. There can be only one intramolecular C−H···O hydrogen bond interaction between the two methoxyacetyl groups extending above the central C−C bond. When the C−H···O (d[C···O] = 3.322 Å) bond forms, it reorients the corresponding atoms towards opposite sides of the molecule making formation of a second intramolecular C−H···O hydrogen bond in the same region of space impossible, and creating the conditions for the chemically equivalent groups to be structurally nonequivalent. Finally, to understand the disorder, another intramolecular hydrogen bond (d[C···O] = 3.208 Å) forms, fixing the ordered methoxy group in place. The reorientation caused by this bond makes it impossible for the corresponding bond to form to the second methoxy-methyl group, which leaves the remaining ether oxygen in a larger space than its volume. The major occupancy position corresponds to the weakest of the intramolecular C−H···O bonds (d[C···O] = 3.322 Å). An intermolecular C−H···O (d[C···O] = 3.296 Å) hydrogen bond however, favors the minor occupancy position, as it orients the methyl hydrogen atoms such that there are two intermolecular hydrogen bonds for the minor orientation, but only one intermolecular hydrogen bond for the major orientation.

[1] Smith, B. D.; Haller, K. J.; Shang, M. *J. Org. Chem.* **1993** 6905-6907.

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