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A Novel 2:1 Supramolecular Assembly of 3,5-Dinitrobenzoic acid and 1,4-Diiodobenzene

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Abstract: 3,5-Dinitrobenzoic acid, **1**, forms a 2:1 molecular complex with 1,4-diiodobenzene, **2**, through the formation of iodo-nitro interactions utilising one of its nitro groups, rather than forming a 1:1 molecular complex using both the nitro groups. The result suggests the importance of the hydrogen bond interactions present in the crystal of the parent molecule (**1**) in directing the interaction with other donor molecules (**2**).

Coupling of molecules through non-covalent interactions has emerged as a powerful tool for the synthesis of complex molecules with desired structural motifs.[1-4] Numerous examples that have appeared in the literature demonstrate the application of non-covalent bonds in the synthesis of new structures.[1] The formation of complexes or assemblies is considered to result from the recognition between the acceptor and donor moieties prevailing within the reactant molecules.[3] However, prediction of the nature of supramolecular assembly is still far from being a reality - for instance, occurrence of molecular complexes with arbitrary compositions.[2] Nevertheless, an analysis of the molecular packing of the reactant molecules and its immediate surroundings often throws light on the nature of interaction responsible for the formation of the supramolecular assembly. In this study we present the results of a careful investigation of the structure of a 2:1 complex of 3,5-dinitrobenzoic acid with 1,4-diiodobenzene, wherein the iodo-nitro interaction helps to bring in two molecules of the acid, each of which is hydrogen bonded to another acid molecule.

3,5-dinitrobenzoic acid, **1**, forms a 2:1 molecular complex with 1,4-diiodbenzene, **2**. Crystal structure determination of the complex[5] reveals that molecules of **1** and **2** recognise each other through the formation of a three centered iodo-nitro coupling consisting of two I...O interactions as shown in Fig. 1. The I...O distances of 3.50 and 3.87Å are within the acceptable limits described in the literature and conform to **Q** type contacts.[6] The carboxylic group of **1** joins the adjacent supramolecular assemblages through the formation of a

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centrosymmetric dimeric unit of O-H..O hydrogen bonds (H...O, 1.79Å). This arrangement ultimately leads to a helical type structure in the three dimensional network.

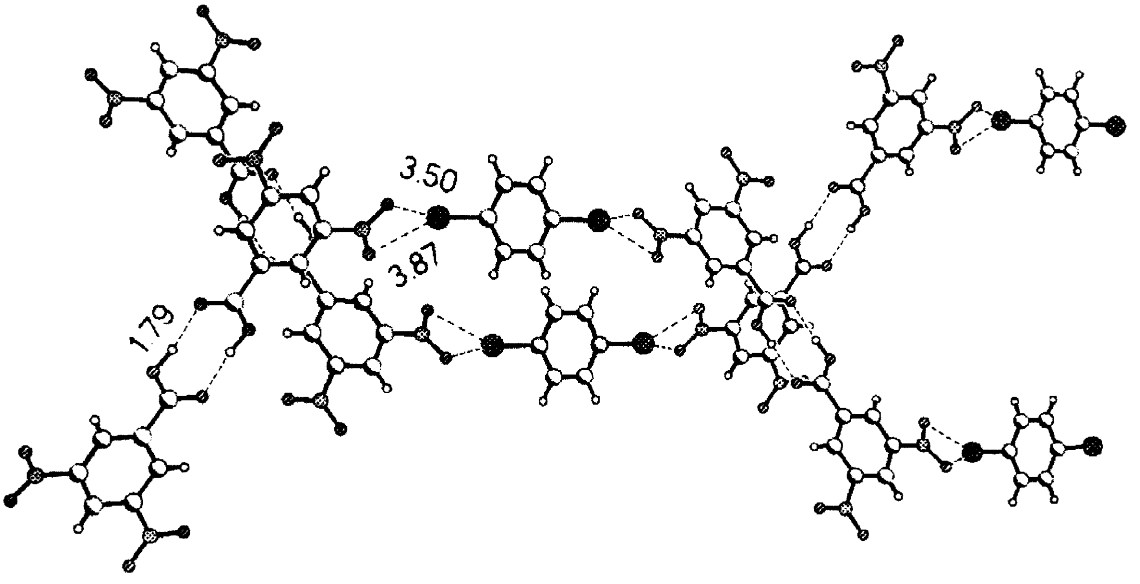
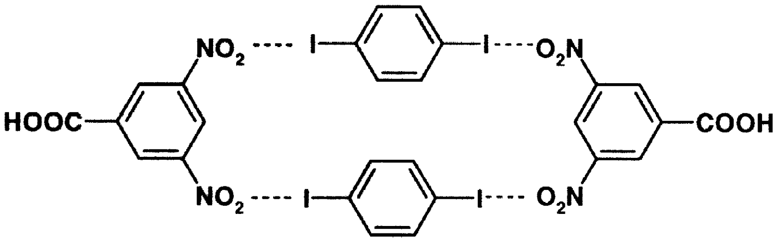
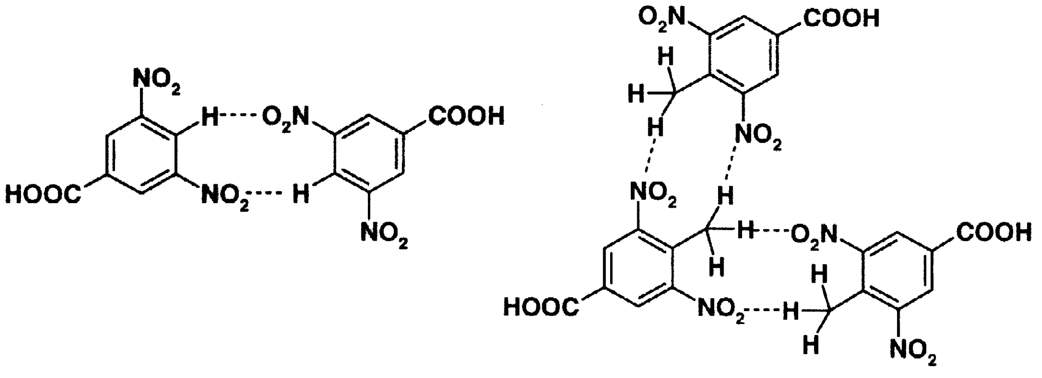


Figure 1: Packing arrangement of molecules of 3,5-dinitrobenzoic acid, **1** and 1,4-diiodobenzene, **2**, in the complex. The non-covalent bonds are represented in dashed lines. Unique intermolecular distances are only noted.



Scheme 1

In accordance with the previous reports of designing supramolecular assemblies using iodo-nitro interactions,[7] formation of a molecular complex between **1** and **2** is expected to be in the ratio of 1:1 as the acid **1** possess two nitro groups. Such a 1:1 complex between **1** and **2** is described by scheme 1. However, in the present case we obtain a 2:1 complex[8] (Fig. 1). In addition, we have found that 3,5-dinitro-4-methylbenzoic acid, **3**, which is analogous to **1** does not form any complex with **2**.



(a)

Scheme 2

(b)

Formation of a 2:1 complex (Fig. 1) between **1** and **2** could be rationalized on the basis of the following considerations. In the crystal structure of the acid **1**[9] one of the -NO_2 groups is involved in the formation of a centrosymmetric dimer through C-H...O hydrogen bonds as shown in scheme 2(a) while the other NO_2 group is essentially free. It would ,therefore, be natural for **1** to form only a 2:1 complex with **2** through the free nitro group. This effect is seen much more vividly in the structure of the acid[10] **3** where both the nitro groups are involved in the formation of centrosymmetric couplings with the adjacent molecules through C-H...O hydrogen bonds [scheme 2(b)], thereby preventing **3** from forming a complex with **2**. It seems therefore that the nature of hydrogen bonding or other interactions present in the crystal of the parent molecule (e.g. in **1** or **3**) may, in some cases, be used as a basis for rationalization of the nature of interaction with other donor/acceptor molecules.

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5) Crystal Data for complex of **1** and **2**: $2(C_7H_4N_2O_6)$: $(C_6H_4I_2)$, M=754.14, monoclinic, space group I2/a, a=9.647(1), b=8.978(1), c=28.263(2)Å, β=93.36(1)°, V=2443.7(3)$Å^3$, Z=4, ρ_{calcd}=2.050, $\mu(MoK_\alpha)$=2.646 mm^{-1}, F(000)=1448, λ=0.71073, Smart CCD area detector, Siemens, The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least squares on F^2 (SHELX-93; G. M. Sheldrick, Gottengen, 1993) to R_1=0.048 and wR_2=0.114. Residual density, min/max -0.898/1.023e.$Å^{-3}$.
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8) We exclusively obtain the 2:1 complex only even when we start with a 1:1 mixture of **1** and **2**. Furthermore, grinding **1** and **2** in a mortar and pestle also gives the complex of 2:1 composition.
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