Molecular Recognition *via* C–H···O Hydrogen Bonding. Crystal Structure of the 1 : 1 Complex 4-Nitrobenzoic Acid–4-(*N*,*N*-Dimethylamino)benzoic Acid

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Mutual recognition of the nitro and dimethylamino substituent groups is possible in organic crystals through the formation of a cyclic C–H···O hydrogen bonded dimer with an approximate stabilising energy of -2.45 kcal mol^{-1} (1 cal = 4.184 J).

The deliberate design of highly specific solid-state structures is of considerable significance in organic chemistry today because these supramolecular entities have important implications in the development of new optical, magnetic and electronic systems.[1] For effective molecular recognition and crystal engineering, there must be a successful juxtapositioning of molecules using various non-bonded interactions of different strengths, directionalities and distance dependence properties.[2]

The overwhelming majority of recent publications on molecular recognition are concerned with hydrogen bonding of the conventional type, that is the so-called 'strong' O–H···O and N–H···O hydrogen bonds.[3–5] Typical receptors include aminopyridines and pyrimidines, pyridones and carboxylic acids. In this communication too, we have dealt with carboxylic acids and more particularly with the 1 : 1 molecular complex **1** formed by 4-nitrobenzoic acid **2** and 4-(*N*,*N*-dimethylamino)benzoic acid, **3**. Yet within the crystal structure of **1**, the molecular arrays are constructed with not only O–H···O hydrogen bonds (as might have been expected) but also, and quite specifically, with much weaker C–H···O hydrogen bonds.[6]

Hydrogen bonded dimers formed by 4-aminobenzoic acid with substituted nitrobenzoic acids have been studied previously by experimental[7] and computational[8] methods. In addition to O–H···O hydrogen bonding of the carboxy groups, there is a network of N–H···O hydrogen bonds involving amino and nitro groups. Although it has been stated that 'H

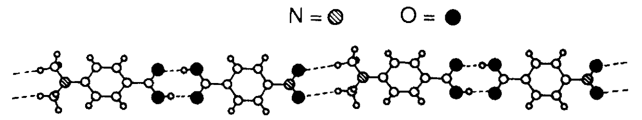
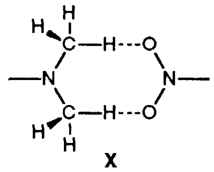


Fig. 1 The O–H···O and C–H···O hydrogen bonds (----) in the linear chain motif of **2** and **3** molecules in the crystal structure of **1**. Only one of the two sets of disordered positions of the carboxy groups is shown.

bonding between the nitro and amino groups is precluded by methylation of the amino groups',[8] such a statement is only true to a first approximation when C–H···O bonds are not considered. The present work was prompted by this statement as it is well known that a methyl group can be an effective C–H···O bond donor.[9]

Orange–yellow crystals of complex **1** (m.p. 235 °C) were obtained readily from acids **2** (m.p. 238 °C) and **3** (m.p. 243 °C) either from a mixed solution in methanol or by grinding in the solid state. The X-ray spectra of the powder of both of the materials obtained are identical. A view of the crystal structure† of **1** is shown in Fig. 1. Acid molecules are linked by O–H···O hydrogen bonds of 2.606(3) and 2.632(3) Å to form dimers and both carboxy groups are completely disordered. More interestingly, these dimers are themselves organised using two C–H···O bonds involving nitro and dimethylamino groups [C···O 3.658(4), 3.725(4) Å; H···O 2.71(3), 2.71(3) Å; C–H···O 164(2), 172(2)°]. We have shown earlier that all C···O distances of up to 3.80 Å or even up to 4.00 Å may have to be considered as acceptable C–H···O bonds.[6,10] The linear, acentric motif shown in Fig. 1 is characterised by O–H···O and C–H···O dimer rings. It is pertinent to note that the H atoms of the two methyl groups were located cleanly with difference-Fourier syntheses and refined independently. These methyl groups are ordered and the six C–H bond lengths so obtained (0.94–1.03 Å) are acceptable; the low *R*-factor and positional e.s.d.s allow one to make confident statements regarding the position of the H atoms and therefore, regarding the effectiveness of the C–H···O interactions in the structure. It is especially worth noting that the conformations of the two methyl groups are such that the two C–H···O angles within the C–H···O dimer ring are very close to 180°. The relevant H atoms lie only 0.11(3) and 0.16(3) Å from the mean C–H···O dimer ring plane (atoms N,O,O,N,C,C) that is itself planar to within ±0.034(3) Å.

The significance of these C–H···O and O–H···O interactions in complex **1** was evaluated by semi-empirical computational methods using the AM1 approximation.[11] This method has previously been used to model the energies of O–H···O hydrogen bonds in related carboxylic acid complexes.[8] The geometry in the crystal structure of **1** was the starting point for these calculations. The O–H···O and C–H···O energies were evaluated by optimising the O–H···O and C–H···O dimers, respectively, and subtracting the energies of the individually optimised monomers **2** and **3**. The hydrogen bonding energy for the O–H···O dimer was found to be −6.7 kcal mol^{-1} (1 cal = 4.184 J), which agrees with values obtained in similar calculations but not with the empirical Lippincott–Schroeder energy (−13.5 kcal mol^{-1}). The hydrogen bonding energy for the C–H···O dimer was found to be −2.45 kcal mol^{-1}. The O–H···O geometry and energy are poorly calculated in SCF methods because of the overestimation of H···H repulsions in the dimer ring[8] and neglect of electron correlation effects,[12,13] but there are no similar sources of error in the calculation of the C–H···O bond energies. The hydrogen bonds in the optimized structures are as follows: O–H···O dimer O···O 3.04 Å, 3.10 Å, H···O 2.07 Å, 2.12 Å, O–H···O 174.6°, 175.0°; C–H···O dimer C···O 3.49 Å, 3.45 Å, H···O 2.42 Å, 2.33 Å, C–H···O 157.0°, 174.7°.



X

The presence of the ring **X** is not an isolated curiosity in the structure of complex **1** but is a recurring pattern in other structures also. As such, the mutual recognition of these two electronically distinctive functional groups might be effective for supramolecular architecture. Retrieval from the 1990 version of the Cambridge Structural Database[14] (82 129 entries) yielded 79 crystal structures that contained both nitro and dimethylamino groups (*R*-factor <0.10 and no metal atom present). Of these, 28 structures contained a C–H···O dimer ring with the same topological connectivity as is displayed in complex **1** and had C···O distances of less than 3.80 Å. Out of these, the C–H···O dimer ring is planar (angle between the NO_2 and NC_2 planes of less than 12°) in 12 structures. Good examples of this planar **X** motif can be found in (*E*,*E*)-butane-2,3-dione bis(4′-nitrophenylhydrazone)-*N*,*N*-dimethylformamide solvate (BOWSOV), *trans*-*N*,*N*-dimethyl-2-nitroethenamine (MNETAM) and *N*-*p*-nitrobenzylidine-*p*-dimethylaminoaniline (NBZMAA).

This work shows that it is important for structural chemists to consider both strong and weak hydrogen bonds, when attempting to understand and control the geometry of supramolecules.

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† *Crystal data* for complex **1**: Mo-Kα radiation, monoclinic, $P2_1/c$, $Z = 4$, $a = 15.181(3)$, $b = 7.126(1)$, $c = 14.258(3)$ Å, $\beta = 93.81(2)°$, 1438 observed (3σ) reflections out of 2139 collected with $2 < 2\theta < 50°$, SHELX76, $R = 0.038$, $R_w = 0.038$, C,N,O anisotropic, H isotropic. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.