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Unique homo and hetero carboxylic acid dimer-mediated supramolecular assembly: rational analysis of the crystal structure of 3,5-dinitrobenzoic acid and 4-(*N*-methylamino)benzoic acid

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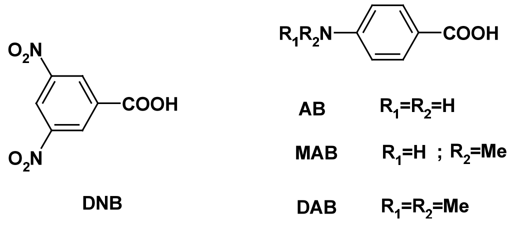
Abstract—3,5-Dinitrobenzoic acid and 4-(*N*-methylamino)benzoic acid form co-crystals comprising homo and hetero carboxylic dimers that can be rationalized through acceptor–donor interactions between -NO_2 and -$NH(CH_3)$ groups. © 2002 Elsevier Science Ltd. All rights reserved.

"Crystal engineering,[1a] design of solid state structures, particularly of organic solids, is one of the current frontier research areas,[2–4] not only just for the simplicity associated with the 'synthesis' of the materials through noncovalent bonds but also for the simplicity of the mechanisms of assembly."[1] Several reports of the systematic study of the formation of the complexes have been recently reported.[2–9] One of the distinct synthetic strategies for supramolecular networks is the retrosynthetic approach: identifying the building block in the form of supramolecular synthons or couplings.[3a] In addition, the concept of reorganization of supramolecular couplings,[10] or synthons[3] or molecular motifs[11] existing within the reactant structures explains the formation of a specific type of complex alone over the other choices as seen in the molecular complex between 3,5-dinitrobenzoic acid and 1,4-diiodobenzene.[2c]



Among the noncovalent bonds, hydrogen bond mediated assemblies have been well studied.[4] Among the various organic functional groups, the carboxylic acid group is well known to form cyclic hydrogen-bonded dimers, and in supramolecular assemblies this cyclic motif can appear as either homo or hetero depending upon the molecules involved in the recognition pattern, with the former type being the major. Noteworthy examples are the molecular complexes of 3,5-dinitrobenzoic acid (DNB) with 4-aminobenzoic acid (AB) and with *N*,*N*′-dimethylaminobenzoic acid (DAB). While, DNB and AB form a hetero dimer complex,[12] DNB and DAB form homo dimers[13] as shown in Scheme 1. However, formation of both homo and hetero dimers within a supramolecular assembly was hitherto unknown.

Since AB and DAB lie on the opposite sides forming hetero and homo cyclic carboxyl dimers with DNB, natural instinct suggests that 4-(*N*-methylamino)benzoic acid, MAB, which lies between AB and DAB in the series AB→DAB, could form both types of dimers.

Indeed, that is the case and it will be discussed in this communication emphasizing the salient features of the homo and hetero complex along with a strategic approach as to how such supramolecular complexes could be generated using a knowledge of packing arrangements of molecules in the crystal structures of reactant compounds.

Co-crystallization of DNB and MAB from methanol yielded single crystals of good quality suitable for characterization by X-ray diffraction methods.[14] Crystal structure analysis revealed that DNB and MAB form a 1:2 complex (Fig. 1a), consisting of both hetero and

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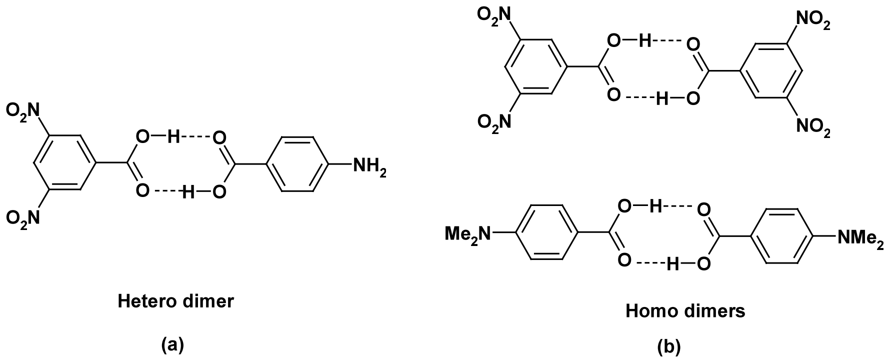


Hetero dimer
(a)

Homo dimers
(b)

Scheme 1. Homo and hetero dimers of AB, DAB and DNB.

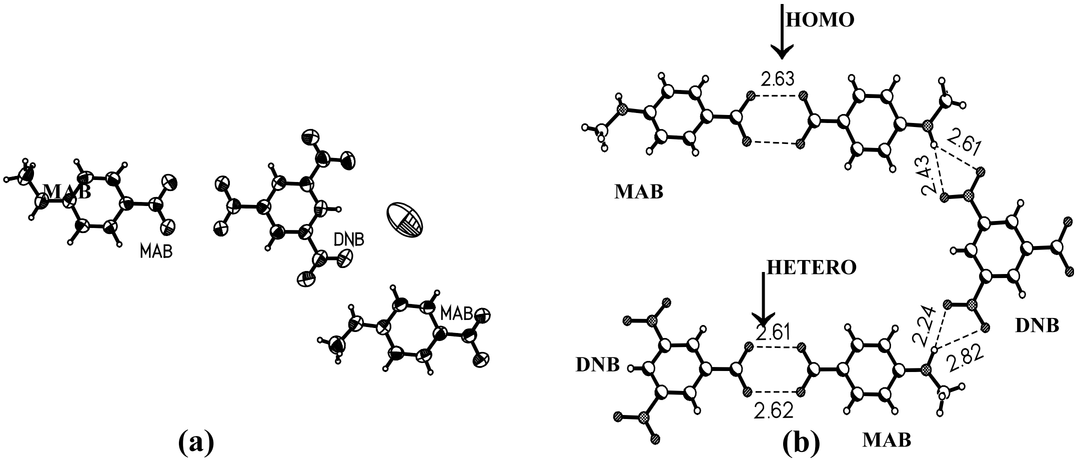


Figure 1. (a) Asymmetric unit showing 1:2 ratio of DNB and MAB. (b) Two-dimensional arrangement of homo and hetero dimers of DNB and MAB.

homo dimers. The 1:2 ratio is always maintained in the crystal lattice, irrespective of the composition of the reactants in the solution.

In the two dimensional arrangement, shown in Fig. 1b, each DNB molecule is connected to two symmetry independent MAB molecules forming bifurcated N–H···O hydrogen bonds between -NO_2 and -NH groups. The corresponding hydrogen bond distances (H···O, 2.24, 2.82 Å; 2.43, 2.61 Å) are in agreement with similar distances found in the complex of DNB:DAB. Further, each of the two molecules of MAB, in turn, interacts with one MAB and one DNB molecule, thereby forming homo and hetero carboxylic dimers. While the hetero dimer is an unsymmetrical cyclic coupling with O···O distances of 2.61 and 2.62 Å, the homo dimer is a symmetrical cyclic coupling with an O···O distance of 2.63 Å.

In the three-dimensional structure (shown in Fig. 2), this assembly is further arranged in such a manner that homo and hetero dimers form distinctly different types of pattern. While, hetero dimers form a continuous helical pattern, the homo dimers are sandwiched between the double helices in a linear fashion. Interestingly, this arrangement leads to the creation of small voids, which are filled by water molecules (the lone atoms in the Fig. 2).

Although, as expected, the DNB and MAB complex has homo and hetero carboxylic dimers, it is interesting to note a unique feature that homo dimers are formed between MAB molecules only; there are no DNB dimers. This is rather surprising as DNB dimers are indeed more stable than MAB dimers by 3 kcal/mole energy, based on the semi-empirical calculations performed, following Dannenburg's approach.[15] This

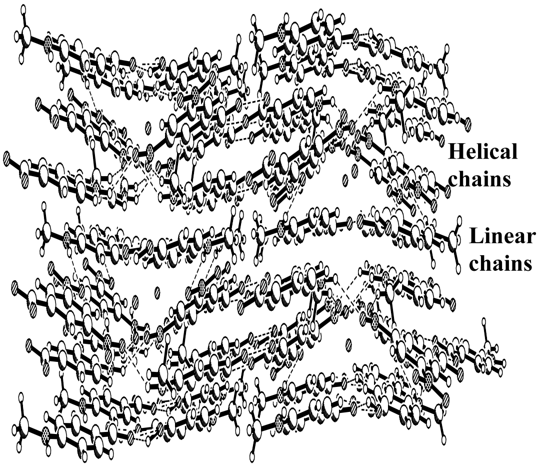
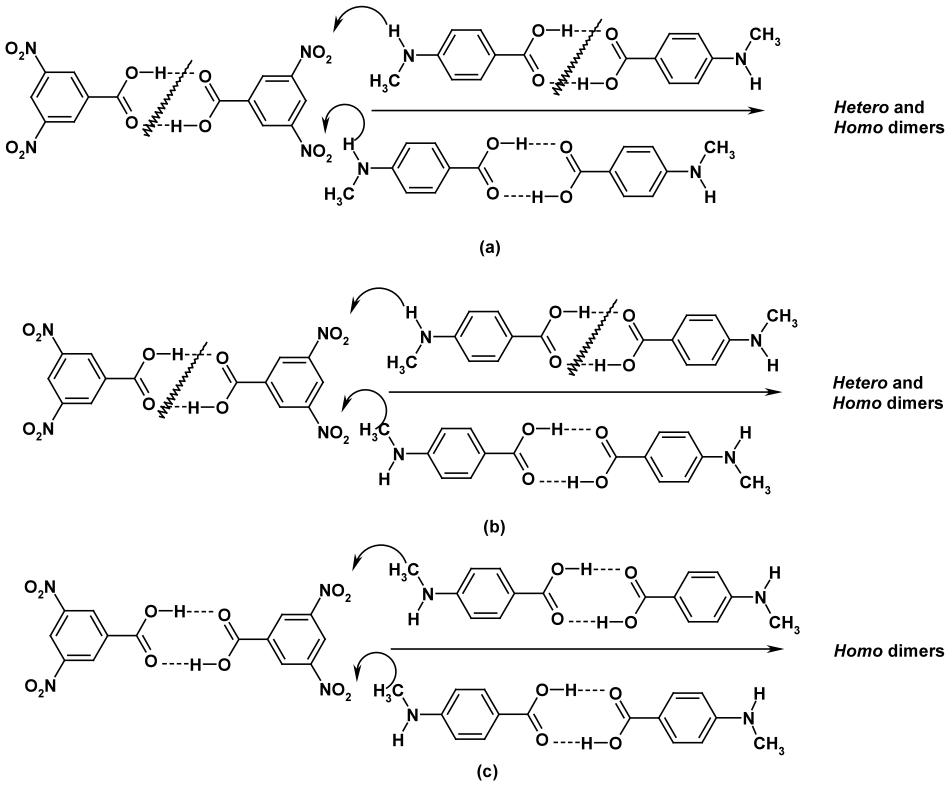


Figure 2. Three-dimensional arrangement of homo and hetero dimers in the crystal structure of DNB and MAB.



Scheme 2. Three possible ways of interaction between DNB and MAB. Arrows show the interaction between the potential functional groups leading to the breaking of hydrogen bonded couplings (represented by hazy lines across the hydrogen bonded dimers).

prompted us to formulate a plausible explanation to account for the formation of the unusual homo and hetero dimer complexes observed in this study.

Possible reaction paths are shown in Scheme 2. Since a carboxyl group, in general, forms an eight-membered cyclic network, it is appropriate to consider acids as dimers, at least, in the solid state.[16] In such a situation, formation of homo and/or hetero dimer complexes between two different acids would require breaking of the -COOH dimers. At ambient conditions, this is possible, only if additional forces destabilize the dimeric unit, as carboxylic dimers are the robust entities among the known noncovalent motifs.[1a] Hence, it appears that reaction between the acids would be initiated with interaction between other functional groups, forming weak noncovalent bonds in the reactant structures, which may perturb the stronger hydrogen bond moieties appropriately.[17]

As a result, interaction of DNB with either MAB or AB or DAB could be established through acceptor–donor recognition of NO_2 and NRR′ groups. In such a recognition, dimers of DNB and MAB could interact in three possible ways (see Scheme 2), depending upon whether -NH or -N(CH_3) groups are involved in the recognition process.

It is evident from Scheme 2 that in the process (a), the interaction between the acceptor and donor moieties occurred through the formation of strong N–H···O hydrogen bonds, which are comparable to O–H···O hydrogen bonds in strength and other properties. However, in the processes (b) and (c), the interaction is established by C–H···O hydrogen bonds, which are weaker than O–H···O hydrogen bonds. Hence comparing all the three possibilities, it can be concluded that process (a) is more favourable than (b) and (c) as the stronger cyclic motif between -COOH could not be perturbed by weak hydrogen bonds, which is an important step for the formation of homo and/or hetero complex formation.

In conclusion, a unique homo and hetero supramolecular assembly has been reported. In addition, it has been shown that acceptor–donor moieties forming weak noncovalent bonds in the parent crystal structures would reorganize prior to the other groups involved in the formation of stronger noncovalent bonds and play a crucial role in the formation of a specific supramolecular architecture.

Acknowledgements

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14. Crystal data for the complex of DNB and MAB: $C_{23}H_{22}N_4O_{10}$, monoclinic, space group, $C2/c$, $a=15.293(2)$, $b=10.841(1)$, $c=29.615(4)$ Å, $\beta=90.36(1)°$, $V=4909.8(1)$ Å^3, $Z=8$, $D_{\text{calcd}}=1.392$ Mg m^{-3}, μ (Mo Kα) = 0.95 mm^{-1}, $2\theta_{\text{max}}=50°$; of 2525 observed reflections, 2271 were unique ($I>3\sigma(I)$) and were used in the final refinement, which converged to $R_1=0.059$, $wR_2=0.188$. Reflection data were collected on a Enraf-Nonius, CAD4 diffractometer (Mo Kα, $\lambda=0.71069$) at $T=300$ K. SHELXTL-PLUS suite of programs were used for the structure solution as well as for the full-matrix least-squares refinements on F^2.
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16. It may appear not to be true in solution wherein dimer→monomer transformation is possibly a reversible process and at any given time monomers of different acids could form a hetero dimer. However, it has been noted that in general molecular complexes (including the complex in this study) which are generated from solution growth, can also be synthesized, with identical features, directly in the solid state as well, wherein existence of monomers is ruled out, by grinding the components in a mortar and pestle. Hence, conclusions drawn from solid state studies could be extended to solution growth experiments also.
17. Somewhat like substitution reactions in covalent synthesis of organic compounds.