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A novel additive organic supramolecular assembly: molecular complex of 3,5-dinitrobenzamide and 3,5-dinitrobenzonitrile

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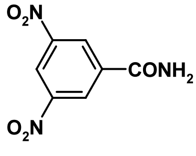
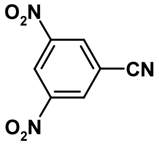
Abstract—Co-crystallization of 3,5-dinitrobenzamide and 3,5-dinitrobenzonitrile forms an additive assembly, in which simple addition of the hydrogen bonded networks that exist in the native crystal structures of the constituent compounds takes place. The additive nature is reflected in the unit cell dimensions of the assembly, with the *c*-axis in the assembly being nearly the same as the sum of the *c*-axes observed in the crystal structures of the constituents. © 2003 Elsevier Science Ltd. All rights reserved.

Crystal engineering[1] of organic supramolecular assemblies, through molecular recognition essentially involves two or more reactants, which can interact with each other by different types of intermolecular interactions (for example, hydrogen bonds), depending upon the nature of the organic functional groups present on the reactant molecules.[2–5] In this respect, a wide range of assemblies have been reported emphasizing the utilization of directional properties of a spectrum of hydrogen bonds (O-H···O, N–H···O, N–H···N, C–H···O, N–H···S, etc.) towards the synthesis of targeted assemblies.[6–10] In any case, the arrangement of the constituent molecules in the supramolecular assemblies is unique without any resemblance to their native crystal structures.

It is not surprising as the design strategy, even in the retrosynthetic approach,[5,6] is based on the interaction between the isolated molecules rather than the interaction between the ensembles of molecules, and also due to the fact that these assemblies are grown from solution, wherein molecular ensemble is not well understood. However, taking into account Dunitz's viewpoint[11] of crystal—*the supermolecule par excellence*, it might be possible to have interaction between the crystal lattices in an additive manner. In this communication, we report such a novel additive supramolecular assembly, observed in an aggregate of 3,5-dinitrobenzamide and 3,5-dinitrobenzonitrile.



DNBA



DNBN

In our endeavor to synthesize molecular complexes of amide compounds, utilizing the ability of *anti*-hydrogen atoms to form hydrogen bonds, we have chosen 3,5-dinitrobenzamide (**DNBA**) to co-crystallize with several substrates. In this connection, as the crystal structure of **DNBA** itself is unknown in the literature,[12] we have determined its crystal structure.

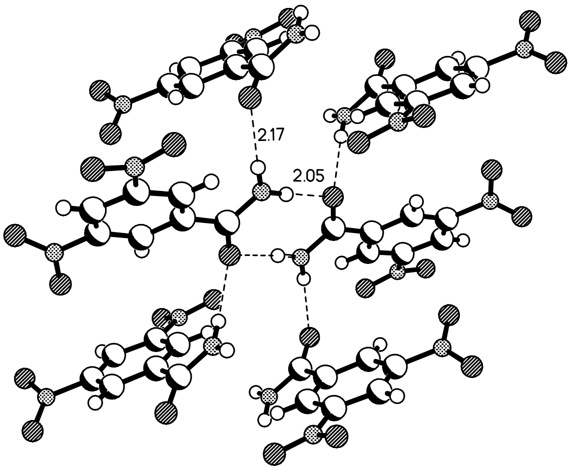


Figure 1. Arrangement of dinitrobenzamide (**DNBA**) molecules in its crystal lattice. Notice the arrangement of four molecules around the dimer unit.

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Table 1. Bond lengths and angles (°) of hydrogen bonds observed in the crystal structures of **DNBA**, **DNBN** and their adduct

Hydrogen bond		**DNBA**	**DNBN**	**DNBA:DNBN**
N–H···O	H···O	2.05, 2.17		1.99, 2.07, 2.08, 2.16
	N···O	2.91, 3.02		2.91, 3.00, 2.92, 3.00
	N-Ĥ···O	169, 172		172, 175, 171, 175
C-H···O	H···O	2.59, 2.82, 3.002.66		2.51, 2.58, 2.58, 2.59
	C···O	3.23, 3.57, 3.793.43		3.30, 3.48, 3.50, 3.36
	C–Ĥ···O	125, 138, 149	1.52	145, 158, 159, 148
C–H···N	H···N		2.55, 2.68	2.79
	C···N		3.44, 3.49	3.68
	C–Ĥ···N		166, 158	162

The crystal structure[13] of 3,5-dinitrobenzamide (**DNBA**), determined on the crystals obtained from a methanol solution, reveals that it does not form a 5.1 Å structure, which is a well known feature of simple amides[14] without any steric constraints.[15] Instead, **DNBA** molecules simply exist as dimers (Fig. 1), forming a well-known eight-membered cyclic ring through N–H···O hydrogen bonds (H···O, 2.05 Å) formed between the adjacent molecules related by inversion symmetry, utilizing *syn*-hydrogen atoms. However, the adjacent dimers are connected to each other by a single N–H···O hydrogen bond with an H···O distance of 2.17 Å (Table 1), utilizing the *anti*-hydrogen atom. As a result, each dimer is connected to four different amide dimers. As a result, the structure of **DNBA** is stabilized by the cyclic and acyclic hydrogen bonded networks. This is, indeed, a unique feature among the known amides, with a resemblance to imide compounds like cyanuric and trithiocyanuric acids, which also possess cyclic and acyclic hydrogen bonded networks.[8]

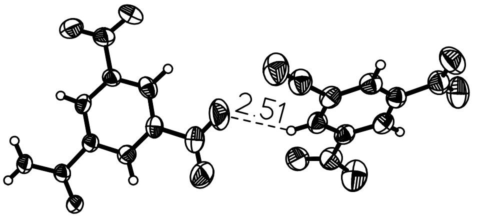


Figure 2. Molecular recognition pattern between **DNBA** and **DNBN** molecules in their complex.

Since the nature of supramolecular assemblies formed by those imides depends upon which type of network is being perturbed during the process of co-crystallization,[8d] we hoped that a similar situation would be encountered with **DNBA** as well, while forming supramolecular assemblies. Hence, we wished to synthesize a molecular complex between **DNBA** and 3,5-dinitrobenzonitrile (**DNBN**), presuming that complexation will occur between the –CN and –NH groups by forming N–H···N hydrogen bonds.

In contrast, and to our surprise, a 2:1 molecular complex[16] obtained from a methanol solution gave a supramolecular structure without the anticipated N–H···N hydrogen bond. Instead, the interaction was established between the constituents through a C–H···O hydrogen bond (H···O, 2.51 Å, Table 1) between a $-NO_2$ group and a phenyl hydrogen atom, as shown in Figure 2.[17]

However, the three-dimensional arrangement of the molecules in the crystal lattice is unique and quite fascinating. The packing analysis reveals that **DNBA**

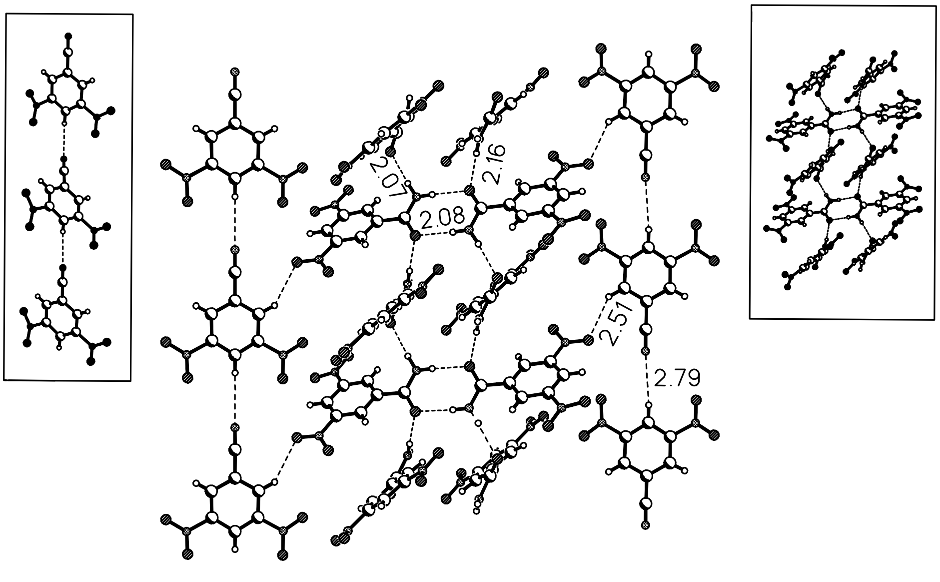


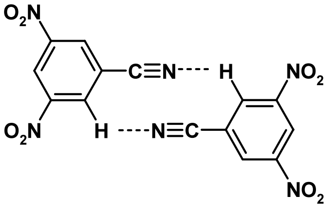
Figure 3. Arrangement of constituent molecules in the crystal lattice of the additive assembly of **DNBA** and **DNBN**. The insets correspond to the arrangement of **DNBN** (left) and **DNBA** (right) molecules in their native crystal structures.

and **DNBN** molecules are arranged in alternate columns in such a fashion that clusters of **DNBA** molecules are placed next to the chains of **DNBN** molecules and vice versa as shown in Figure 3.

While the **DNBN** molecules, in each chain, are held together by C–H···N hydrogen bonds (H···N, 2.79 Å, Table 1), in each cluster of **DNBA**, the molecules exist as dimers held together by a centrosymmetric cyclic N–H···O hydrogen bond with an H···O distance of 2.08 Å.[18] These dimers are, in turn, held together by single hydrogen bonds (H···O, 2.07 and 2.16 Å, Table 1). This kind of molecular packing has a close resemblance with the arrangement found in the native crystal structure of **DNBA**, which is shown as an inset on the right of Figure 3. This has prompted us to analyze the arrangement of **DNBN** molecules in the native crystal structure as well, in order to establish a correlation with the arrangement noted in the **DNBA**:**DNBN** complex.

A search of the Cambridge Structural Database (CSD)[12] retrieved seven crystal structures[19] corresponding to the molecular complexes of **DNBN** but no information on the parent crystal structure, except the unit cell dimensions (Refcode: DINFOV[20]). However, analysis of the molecular complexes has revealed an interesting feature that in a majority of these complexes, the **DNBN** molecules exist as dimers by forming cyclic C–H···N hydrogen bonds as shown in Scheme 1, unlike chains as noted in the present study. This has led us to determine the crystal structure of **DNBN**.

Crystal structure analysis[21] has revealed an intriguing feature of the packing of the molecules in the crystal lattice comprising both chains and dimers. The arrangement is shown in Figure 4. Primarily, the molecules constitute chains, held together by C–H···N hydrogen bonds (H···N, 2.55 Å, Table 1), as shown in Figure 4a (also as an inset on the left side in Fig. 3), similar to the chains noted in the molecular complex of **DNBA** and **DNBN** (present study). However, orientation of the chains is somewhat different (see Fig. 4b), with torsion angles of 17 and 1° between the adjacent molecules connected by C–H···N hydrogen bonds in the chains of pure **DNBN** and the complex of **DNBA** and **DNBN**, respectively. The adjacent chains are in turn, held together through cyclic C–H···N (H···N, 2.68 Å, Table 1) hydrogen bonds leading to the formation of dimers of **DNBN** molecules as noted in several molecular complexes of **DNBN** (Fig. 4c, compare with Scheme 1).



Scheme 1. A schematic representation of dimeric motifs observed in the crystal structures of co-crystals of 3,5-dinitrobenzonitrile.

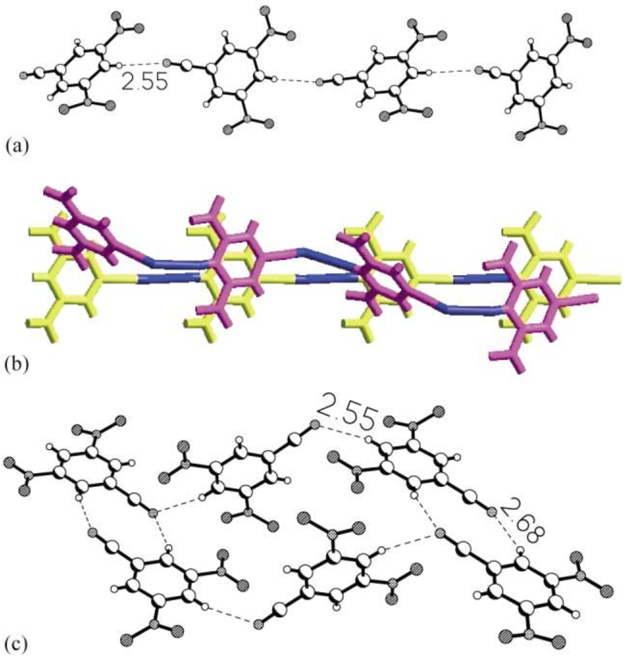


Figure 4. (a) Arrangement of molecules of **DNBN** in the form of chains held together by C–H···N hydrogen bonds. (b) Overlay diagram of chains of **DNBN** (pink) and **DNBA**:**DNBN** (yellow), the hydrogen bonds between the molecules are shown in blue. (c) Interaction between the adjacent chains forming dimers of **DNBN** through C–H···N interactions.

Thus, the complex of **DNBA** and **DNBN** can be regarded as an additive lattice of **DNBA** and **DNBN** lattices, as the arrangement of the molecules in the complex could be generated by, simply, placing the molecular networks from the parent crystal structures (insets in Fig. 3) next to each other. Taking advantage of this novel feature, we are exploring further the design of these types of structures in order to provide solutions for directed synthesis of supramolecular assemblies.

Acknowledgements

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References

1. (a) Desiraju, G. R. *Crystal Engineering*: *The Design of Organic Solids*; Elsevier: Amsterdam, 1989; (b) Desiraju, G. R. *Nature* **2001**, *412*, 397.
2. Lehn, J. M. *Supramolecular Chemistry*: *Concepts and Perspectives*; VCH: Weinheim, 1995.

3. (a) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383; (b) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gorden, D. M. *Acc. Chem. Res.* **1995**, *28*, 37.
4. *Comprehensive Supramolecular Chemistry*; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vogtel, F., Eds.; Elsevier: Oxford, 1996.
5. (a) Pedireddi, V. R.; Jones, W.; Chorlton, A. P.; Docherty, R. *Chem. Commun.* **1996**, 987; (b) Ranganathan, A.; Pedireddi, V. R. *Tetrahedron Lett.* **1998**, *39*, 1803; (c) Ranganathan, A.; Pedireddi, V. R.; Rao, C. N. R. *J. Am. Chem. Soc.* **1999**, *121*, 1752; (d) Pedireddi, V. R. *Cryst. Growth Des.* **2001**, *1*, 383; (e) Pedireddi, V. R.; PrakashaReddy, J. *Tetrahedron Lett.* **2002**, *43*, 4927.
6. (a) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311; (b) Thallapally, P. K.; Desiraju, G. R.; Bagieu-Beucher, M.; Masse, R.; Bourgogne, C.; Nicoud, J. *Chem. Commun.* **2002**, 1052; (c) Aitipamula, S.; Thallapally, P. K.; Thaimattam, R.; Jaskolski, M.; Desiraju, G. R. *Org. Lett.* **2002**, *4*, 921; (d) Vishweshwar, P.; Nangia, A.; Lynch, V. M.; Nangia, A.; Lam, C.; Mak, T. C. W. *Chem. Commun.* **2002**, 952.
7. Kolotuchin, S. V.; Fenlong, E. E.; Wilson, S. R.; Loweth, C. J.; Zimmermann, S. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2654.
8. (a) Pedireddi, V. R.; Belhekar, D. *Tetrahedron* **2002**, *58*, 2937; (b) Pedireddi, V. R.; Chatterjee, S.; Ranganathan, A.; Rao, C. N. R. *J. Am. Chem. Soc.* **1997**, *199*, 10867; (c) Pedireddi, V. R.; Ranganathan, A.; Ganesh, K. N. *Org. Lett.* **2002**, *3*, 99; (d) Ranganathan, A.; Pedireddi, V. R.; Sanjayan, G.; Ganesh, K. N.; Rao, C. N. R. *J. Mol. Struct.* **2000**, *522*, 87.
9. (a) Chang, Y. L.; West, M. A.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5991; (b) Aakeroy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, 397; (c) Aakeroy, C. B. *Acta Crystallogr.* **1997**, *B53*, 569.
10. (a) Ranganathan, D.; Lakshmi, C.; Karle, I. L. *J. Am. Chem. Soc.* **1999**, *121*, 6103; (b) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 988.
11. (a) Dunitz, J. D. *Pure Appl. Chem.* **1991**, *63*, 177; (b) *Structure Correlation*; Burgi, H. B.; Dunitz, J. D., Eds.; VCH: Weinheim, 1994; Vol. 2.
12. Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.
13. Crystal data for **DNBA**: $C_7H_5N_3O_5$, $M = 211.14$, orthorhombic, *Pbca* (No. 61), $a = 8.226(2)$ Å, $b = 8.897(2)$ Å, $c = 23.610(5)$ Å, $V = 1727.9(7)$ Å^3, $Z = 8$, $D_{\mathrm{cacld}} = 1.623$ g cm^{-3}, $F(000) = 864$, $\lambda(\text{Mo-K}\alpha) = 0.71073$, $T = 293$ K, reflections collected/unique 6751/1242 ($R_{\mathrm{int}} = 0.022$). Final GooF = 1.054, $R_1 = 0.036$, $wR_2 = 0.099$, 156 parameters, $\mu = 0.14$ mm^{-1}, R indices based on 1095 reflections with $I > 2\sigma(I)$ (refinement on F^2), absorption corrections applied, CCDC 183247.
14. (a) Leiserowitz, L.; Tuval, M. *Acta Crystallogr.* **1978**, *B34*, 1230; (b) Lewis, F. D.; Yang, J.; Stern, C. L. *J. Am. Chem. Soc.* **1996**, *118*, 12029; (c) Weinstein, S.; Leiserowitz, L.; Gil-Av, E. *J. Am. Chem. Soc.* **1980**, *102*, 2768; (d) Harkema, S.; Gaymans, R. J.; van Hummel, G. J.; Zylberlicht, D. *Acta Crystallogr.* **1979**, *B35*, 506; (e) Garcia-Tellado, F.; Geib, S. J.; Goswami, S.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 9265; (f) Brisson, J.; Gagne, J.; Brisse, F. *Can. J. Chem.* **1989**, *67*, 840; (g) Lewis, F. D.; Yang, J.-S. *J. Phys. Chem.* **1997**, *B101*, 1775.
15. Kuduva, S. S.; Blaser, D.; Boese, R.; Desiraju, G. R. *J. Org. Chem.* **2001**, *66*, 1621.
16. Crystal data for **DNBA** and **DNBN**: $2(C_7H_5N_3O_5){:}C_7H_3N_3O_4$, $M = 615.40$, monoclinic, $P2_1/c$ (No. 14), $a = 7.978(2)$ Å, $b = 8.962(2)$ Å, $c = 35.620(6)$ Å, $\beta = 93.30°$ (1), $V = 2542.6(10)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.608$ g cm^{-3}, $F(000) = 1256$, $\lambda(\text{Mo-K}\alpha) = 0.71073$, $T = 293$ K, reflections collected/unique 10704/3662 ($R_{\mathrm{int}} = 0.045$). Final GooF = 1.043, $R_1 = 0.046$, $wR_2 = 0.102$, 449 parameters, $\mu = 0.139$ mm^{-1}, R indices based on 2530 reflections with $I > 2\sigma(I)$ (refinement on F^2), absorption corrections applied, CCDC 188020.
17. A similar hydrogen bond is formed by the second **DNBA** molecule also, but the H···O distance is 2.58 Å.
18. The H···O distance in the dimer corresponding to the second **DNBA** molecule is 2.0 Å.
19. Refcodes: KIZVAQ, KOBFIQ, REDCIM, REDCOS, REDCUY, REDDAF, REDDEJ.
20. Colapietro, M.; Domenicano, A.; Marciante, C.; Portalone, G. *Eur. Cryst. Meeting* **1985**, *9*, 269.
21. Crystal data for **DNBN**: $C_7H_3N_3O_4$, $M = 193.12$, monoclinic, $P2_1/n$ (No. 14), $a = 5.803(1)$ Å, $b = 9.371(2)$ Å, $c = 15.026(3)$ Å, $\beta = 93.99°$ (3), $V = 815.1(3)$ Å^3, $Z = 4$, $D_{\mathrm{cacld}} = 1.574$ g cm^{-3}, $F(000) = 392$, $\lambda(\text{Mo-K}\alpha) = 0.71073$, $T = 293$ K, reflections collected/unique 3338/1169 ($R_{\mathrm{int}} = 0.018$). Final GooF = 1.218, $R_1 = 0.039$, $wR_2 = 0.109$, 149 parameters, $\mu = 0.133$ mm^{-1}, R indices based on 1046 reflections with $I > 2\sigma(I)$ (refinement on F^2), absorption corrections applied, CCDC 188019.