Interplay of strong and weak hydrogen bonding in molecular complexes of some 4,4′-disubstituted biphenyls with urea, thiourea and water

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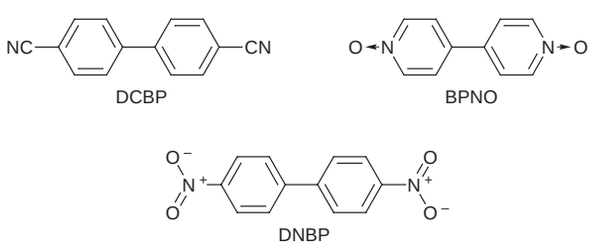
The crystal chemistry and engineering of a new family of host–guest complexes is described. 4,4′-Dicyanobiphenyl (DCBP) forms a 1:1 complex, 1 with urea wherein the DCBP host forms large hexagonal channels *via* C–H···N hydrogen bonds and the urea guest molecules are arranged in N–H···O ribbons which fit completely within the host channels. By analogy, 4,4′-bipyridine *N*,*N*′-dioxide (BPNO) was selected as a molecule that can form a corresponding C-H···O based channel. BPNO forms complexes with urea (2), thiourea (3) and water (4). Structures 2 and 3 provide some points of comparison with the structure of 1 but are not fully equivalent to it. In structure 4, the smaller guest water is able to fit neatly within the smaller hexagonal channel of BPNO and in this sense, the degree of structural predictability is satisfactory. To obtain another structure similar to that of 1, 4,4′-dinitrobiphenyl (DNBP) was identified as an alternative host compound. This choice was justified by the structure of its 1:1 complex, 5 with urea. In all cases, the guest molecules interact with each other *via* strong hydrogen bonds and form an essential template for the weak hydrogen bonded assembly of the host network structure but the latter is still of some significance. One finds consequently, in complexes 1-5, a constructive interplay of strong and weak hydrogen bonds.

Introduction

Hydrogen bonds play a central role in crystal engineering because of their strength, directionality and flexibility.[1] Strong hydrogen bonds such as O–H···O and N–H···O are well-known in this context, but weak interactions such as C–H···O and C–H···N have also attracted considerable interest because of their frequent occurrence in organic crystal structures.[2] There is an advantage in jointly employing strong and weak hydrogen bonds in crystal design strategies because the number of functional groups that are capable of forming weak interactions is much larger,[3] so a much wider range of molecules with diverse functionalities can be employed.

The crystal structures of molecular complexes offer opportunities for study of the interplay of strong and weak hydrogen bonds.[3] This work was initiated by the observation that 4,4′-dicyanobiphenyl (DCBP) and urea form a 1:1 complex **1**, the structure of which is quite different from other known complexes of urea.[4] This prompted the question as to whether it would be possible to engineer other structures that would be similar to that of **1**. In this paper, the crystal structures of the molecular complexes of some 4,4′-disubstituted biphenyls (DCBP; 4,4′-bipyridine *N*,*N*′-dioxide, BPNO; 4,4′-dinitrobiphenyl, DNBP) with urea, thiourea and water are discussed. The molecular components in these complexes (**2**–**5**) have been successively arrived at using retrosynthetic arguments based on topological equivalences of the important supramolecular synthons in the preceding structures.[5] In general, these arguments have been developed in an attempt to identify robust and simple structural elements in abstruse hydrogen bonded arrangements wherein the strong and weak hydrogen bonds could mutually interfere to a substantial extent.[5] It may be noted that of the two components in the complexes, the molecular structure of the substituted biphenyl is the far more invariant. Therefore, and somewhat subjectively, the networks generated with the biphenyl moiety are considered to be the host frameworks and the smaller co-crystallised molecules are taken to be the guests.



1 DCBP•urea (1:1)
2 BPNO•urea (1:1)
3 BPNO•thiourea (1:1)
4 BPNO•water (1:2)
5 DNBP•urea (1:1)

Experimental

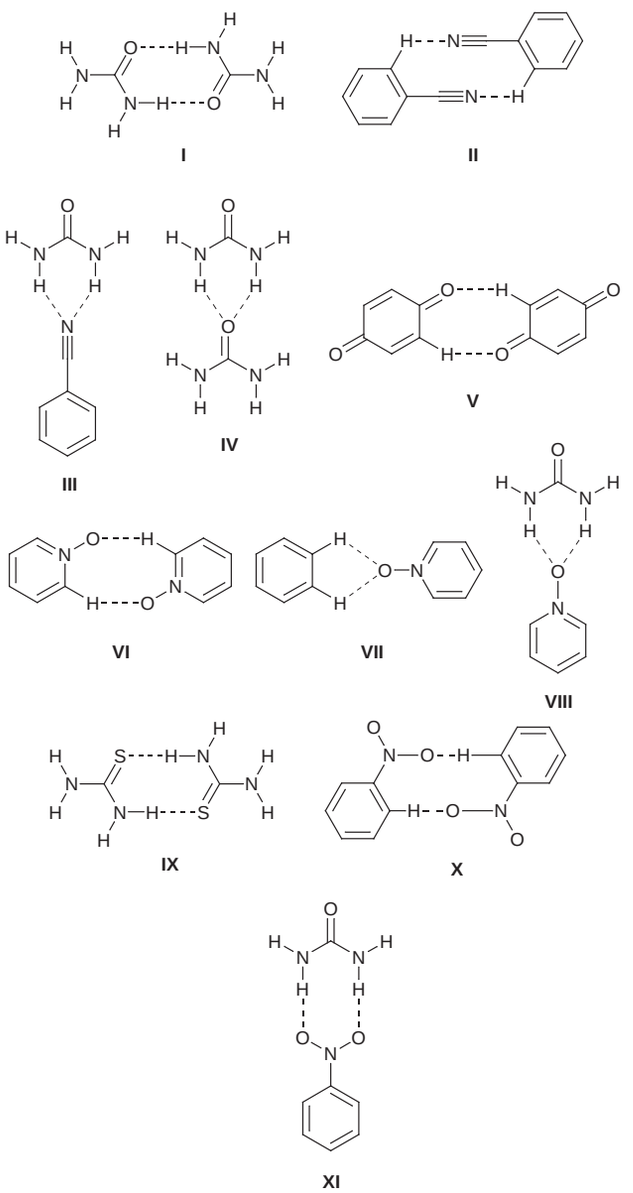
X-Ray crystallography

Diffraction quality crystals of complexes **1**, **2**, **3**, **4** and **5** were prepared by crystallising the two components in a 1:1 molar ratio from appropriate solvents (Table 1). Single crystals of hydrate **4** were obtained by crystallising BPNO from aqueous EtOH. The structure solutions were carried out with SHELXS-86 and the refinements with SHELXL-93, both being built-in versions in the Siemens SHELXTL Plus (PC Version) package.[6] In the final cycles of full-matrix refinements (on F for **1** and **2**, on F^2 for **3**–**5**) all non-H atoms were treated anisotropically while the H-atoms were fixed and allowed to refine as riding atoms. Other details of the X-ray data collection, structure

solution and refinement are given in the supplementary information.†

Cambridge Structural Database (CSD) analysis

Screens −28, −55, 153, 85, 35 and 88 were set to eliminate organometallic entries, structures without coordinates, entries with unmatched chemical and crystallographic connectivities, entries with disorder and *R*-factor greater than 0.10 in the CSD (Version 5.14, October 1997, 175 093 entries).[7] Duplicate structures of lower precision were removed in all the searches. Synthon **I** (shown in Scheme 1 with other synthons observed in



Scheme 1

structures **1**–**5**) was found to occur 20 times in 12 urea complexes (2.50 < N···O < 3.80 Å; 120 < N–H···O < 180°). Synthon **II** was found to occur 96 times in 73 cyanobenzenes having an *ortho* H-atom (2.50 < C···N < 3.80 Å; 120 < C–H···N < 180°) with the mean C···N distance being 3.529 Å and the mean angle θ being 147.8°.

† Full lists of bond lengths and bond angles, atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme, see 'Instructions for Authors' *J. Chem. Soc., Perkin Trans.* 2, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/132.

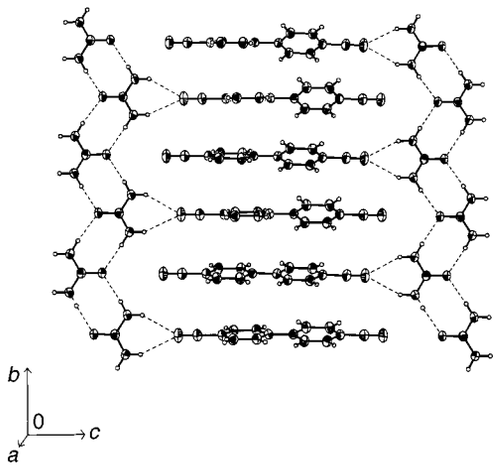


Fig. 1 Structure of complex **1**. The urea ribbon along [010] forms bifurcated N–H···N hydrogen bonds to DCBP molecules. The thermal ellipsoids of the non H-atoms are drawn at the 35% probability level. All hydrogen bonds are represented by dashed lines in this and subsequent figures.

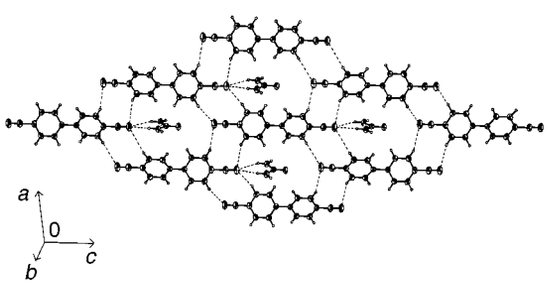


Fig. 2 Hexagonal C–H···N layer of DCBP molecules in complex **1**. The stacked layers are slightly staggered and generate channels, each of which accommodates a urea ribbon.

Results and discussion

4,4′-Dicyanobiphenyl:urea 1 : 1 complex, 1

The urea molecules form a linear ribbon that is constituted with dimer synthons **I** arranged in a zig-zag manner with *syn* N–H···O hydrogen bonds (Fig. 1, Table 2). Each ribbon is nearly planar and is enclosed in a hexagonal channel composed of DCBP molecules (Fig. 2). The rather open framework of DCBP molecules does not collapse because the channels are filled by the urea ribbons. The zig-zag networking of C–H···N hydrogen bonds between DCBP molecules, mediated by synthon **II**, (geometrical details of hydrogen bonds in this and other synthons are found in Table 2) is topologically similar to that of the N–H···O bonds in the urea ribbons. The *anti* H-atoms of each urea ribbon form bifurcated N–H···N≡C hydrogen bonds with the DCBP layers *via* synthon **III** leading to the three-dimensional supramolecular structure. Dipole-dipole interactions between adjacent C≡N groups could provide additional stabilisation to the host framework.[8] The binding of urea to the host framework is also stabilised by weak C–H···O and C–H···N hydrogen bonds, involving the H-atoms *ortho* to the central C–C bond of the biphenyl moiety and O- and N-atoms of the urea molecules (C–H···O; C···O, 3.552, 3.770 Å; H···O, 2.493, 2.926 Å; θ = 165.4, 134.9° and C–H···N; 3.946, 3.844; 2.876, 2.832 Å; 169.1, 155.5°; all hydrogen bond distances reported in this paper are normalised to standard neutron lengths, 1.083, 1.009 and 0.983 Å for C–H, N–H and O–H distances respectively).

The hydrogen bonding between the cyano groups and the *anti*-H atoms of urea in complex **1** differs from other channel inclusion compounds of urea with longer chain dinitriles.[4] In the latter cases, urea molecules are arranged in a head-to-tail

Table 1 Crystallographic data for the compounds in this study

	1	2	3	4	5
Empirical formula	$C_{14}H_8N_2\cdot CH_4N_2O$	$C_{10}H_8N_2O_2\cdot CH_4N_2O$	$C_{10}H_8N_2O_2\cdot CH_4N_2S$	$C_{10}H_8N_2O_2\cdot (H_2O)_2$	$C_{12}H_8N_2O_4\cdot CH_4N_2O$
Formula wt.	264.3	248.2	264.3	224.22	304.27
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$(#14)	$P2_12_12_1$(#19)	$C2/c$(#15)	$C2/m$(#12)	$P2_12_12_1$(#19)
a/Å	9.142(1)	7.162(2)	18.197(2)	14.811(1)	7.289(1)
b/Å	7.235 (2)	10.221(2)	6.826(2)	8.474(1)	9.216(2)
c/Å	20.867(2)	15.255(3)	20.100(3)	4.264(1)	20.135(4)
α/°	90	90	90	90	90
β/°	95.96(1)	90	104.21(1)	101.86(1)	90
γ/°	90	90	90	90	90
Z	4	4	8	2	4
V/Å^3	1372.7(4)	1118.8(6)	2420.4(7)	523.69(6)	1352.6(4)
D_{calc}/Mg m^{-3}	1.279	1.474	1.451	1.422	1.494
R_1	0.0572	0.0420	0.0549	0.0482	0.0671
wR_2	0.0647	0.0524	0.0576	0.1196	0.1490
Goof	1.41	1.24	1.20	1.04	1.14
N-total[a]	4301	1165	2777	2581	4533
N-unique[b]	3148	1165	2124	497	2500
(R_{int})	(0.0332)	(0.00)	(0.0338)	(0.0463)	(0.0267)
N-observed[c]	1490	941	1242	496	2495
Variables	181	164	163	44	200
Crystal shape	needle	needle	needle	prism	prism
Solvent	EtOH	MeOH	DMF	EtOH	$MeNO_2$
Diffractometer	Siemens P4	Rigaku AFC7R	Siemens P4	Siemens Smart CCD	Rigaku RAXIS IIc

[a] N-total is the total number of reflections collected. [b] N-unique is the unique data. [c] N-observed is the number of observed reflections with $I > 2\sigma(I)$.

Table 2 Geometrical parameters of the various synthons in this study[a]

		Distances and angles		
Synthon	Compound	D/Å	d/Å	θ/°
I	**1**	2.920(3)	1.92	171
		2.953(3)	1.95	172
	2	2.919(4)	1.94	164
		2.914(4)	1.94	163
	5	2.916(4)	1.91	176
		2.925(4)	1.92	175
II	**1**	3.759(5)	2.77	151
		3.888(5)	3.00	140
		3.802(5)	2.79	155
		3.779(5)	2.81	148
III	**1**	3.292(4)	2.38	150
		3.280(4)	2.37	150
VI	**3**	3.306(6)	2.24	167
		3.524(7)	2.46	169
		3.427(5)	2.34	179
	4	3.477(3)	2.40	171
VII	**2**	3.409(4)	2.57	133
		3.630(4)	3.07	113
		3.154(4)	2.37	128
		3.357(4)	2.84	110
VIII	**2**	2.957(4)	2.02	153
		3.050(4)	2.16	146
IX	**3**	3.456(4)	2.45	178
X	**5**	3.558(4)	2.84	124
		3.570(4)	2.55	156
		3.424(4)	2.83	115
		3.652(4)	2.60	163[b]
		3.918(4)	2.91	155[b]
		3.478(4)	2.47	155[b]
		3.318(4)	2.74	113
XI	**5**	3.276(3)	2.36	150
		3.261(3)	2.34	151

[a] All H-atoms are normalised to the standard neutron lengths. The terms D, d and θ are as usually defined (see ref. 3). [b] C–H···O hydrogen bond bifurcated at H-atom.

fashion to form a linear chain mediated by synthon **IV**.[9] In any event, the recognition between the two components in complex **1** is delicately matched. This is inferred by the fact that DCBP is the only one among ten or so aromatic nitriles that was even found to form a molecular complex with urea in co-crystallisation experiments.

Synthon **I** is also found in some other molecular complexes of urea.‡ In the inclusion compounds with tetraalkylammonium halides, the halide ion acts as a spacer unit that interconnects the urea ribbons.[10] The extended ribbon variation of **I** is present in LUTDUR, CRWNUR and TOZHOF, as in **1**. The C–H···N hydrogen bonds in **1** are considerably longer when compared with other occurrences of synthon **II** in say, 1,4-dicyanobenzene and 1,2,4,5-tetracyanobenzene. The much weaker C–H···N interaction in **1** may be attributed to the fact that it co-exists with the stronger N–H···N≡C hydrogen bonds of synthon **III**. Interestingly, the geometrical parameters of C–H···N hydrogen bonds in **1** closely match those in the complex of 1,3,5,7-tetrabromoadamantane with hexamethylenetetramine (C–H···N; D, 3.747, d, 2.783 Å, θ, 148.1°), wherein the C–H···N hydrogen bonds are solely responsible for the formation of the solid complex.[11] Attempts were made to assess the significance of C–H···N hydrogen bonding in related structures by growing single crystals of pure **1** and also its complexes with thiourea and selenourea. However, these experiments were unsuccessful.[12]

4,4′-Bipyridine *N*,*N*′-dioxide:urea 1:1 complex, 2

Consider the C–H···N dimer synthon **II** in complex **1**. It is known that **II** is equivalent to the well-known C–H···O dimer synthon **V**, as is seen by the relationship between the crystal structures of 1,4-dicyanobenzene and 1,4-benzoquinone. Such a relationship was extended to the C–H···O synthon **VI** and retrosynthetic considerations led to an identification of 4,4′-bipyridine *N*,*N*′-dioxide, BPNO as a material for molecular complexation. Accordingly, BPNO was co-crystallised with urea to give complex **2**. Contrary to our expectation, however, **2** is not isostructural to **1**. While the urea ribbon constituted with synthon **I** is retained in **2** (Fig. 3), the BPNO molecules are arranged in a skewed fashion with C–H···O synthons **VII**

‡ Refcodes: CRWNUR, DUXZAX, JELSEY, LEMHIU, LUTDUR, SLCADC, TIPWIY, TONGOS, TOZHOF, UROXAL, URPRBN and VEJXAJ.

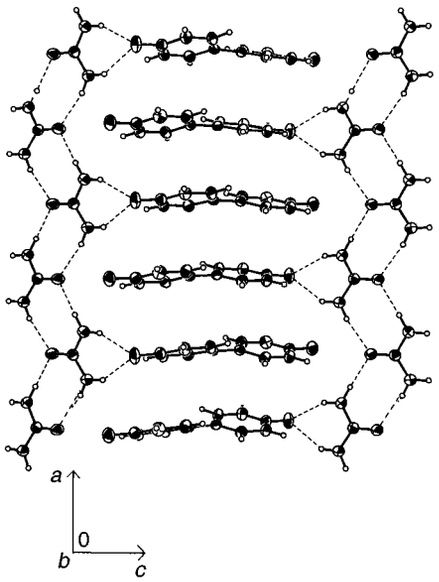


Fig. 3 Structure of complex **2** to show the urea ribbon. Notice the bifurcated N–H···O hydrogen bonds to the BPNO molecule.

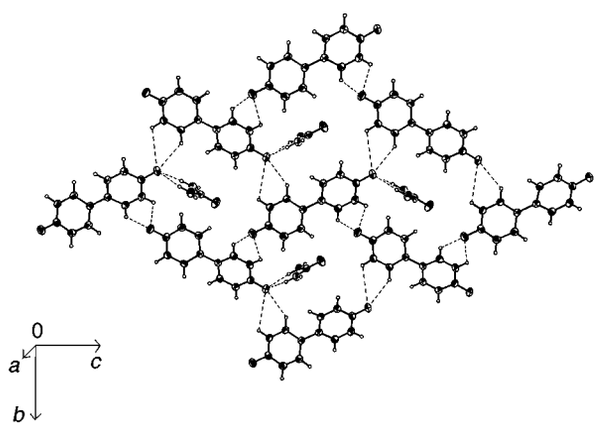


Fig. 4 Skewed arrangement of BPNO molecules in the crystal structure of complex **2**

(Fig. 4) and unlike the arrangement of DCBP molecules in **1**. Stacking of the BPNO molecules along [100] leads to the formation of channels that are occupied by the urea ribbon. The ribbons are N–H···O hydrogen bonded to the channels with synthon **VIII** making use of *anti* N–H atoms along with stabilisation from C–H···O and C–H···N hydrogen bonds as in **1** (C–H···O: *D*, 3.559, 3.543; *d*, 2.735, 2.520 Å; θ, 132.8, 157.0° and C–H···N: *D*, 3.583, 3.678, 3.882, 3.853; *d*, 2.689, 2.606, 2.800, 2.919 Å; θ, 139.5, 170.3, 177.1, 144.6°). The O-atoms of the host therefore accept four hydrogen bonds, two strong N–H···O bonds and two weak C–H···O bonds. Since the structure of **2** was felt to have diverged too much from that of **1** another lead, namely complex **3**, was investigated.

4,4′-Bipyridine *N*,*N*′-dioxide:thiourea 1:1 complex, 3

In order to explore this series of structures further, the 1:1 complex **3**, of BPNO and thiourea was prepared. In **3**, the thiourea molecules form discrete centrosymmetric N–H···S dimers (synthon **IX**). These dimers do not extend to an infinite ribbon as in **1** and **2** but are connected to BPNO molecules at three stacking levels along [010] with N–H···O hydrogen bonds labelled i, j and k in Fig. 5 (N–H···O; *D*, 2.955, 2.802, 2.927; *d*, 1.967, 1.924, 1.951 Å; θ, 165.9, 143.8, 161.9°). A view down (40$\bar{2}$) is of interest (Fig. 6). The BPNO molecules form a bilayer structure that contains elements of the hexagonal network that

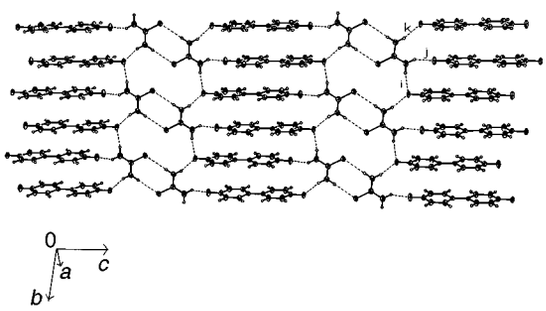


Fig. 5 Thiourea dimers and their coordination with BPNO molecules in the crystal structure of complex **3**

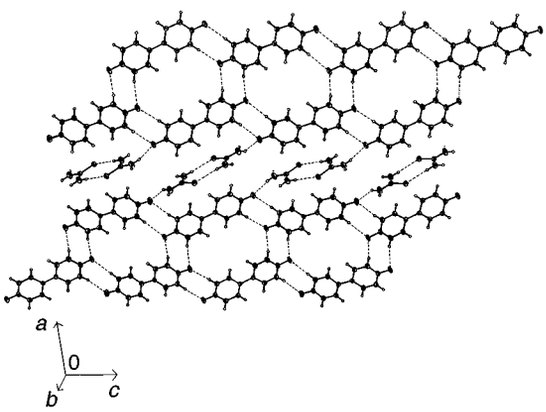


Fig. 6 Bilayer hexagonal loop structure formed by BPNO molecules in complex **3** with interleaving thiourea

was anticipated, though not observed, for complex **2**. The thiourea dimers are too wide to fit into the hexagonal channels and remain outside, being connected to them through N–H···O hydrogen bonds. Additionally, the step-like arrangement of the BPNO bilayers is shown in Fig. 7. As observed in complexes **1** and **2**, C–H···S and C–H···N hydrogen bonds provide additional stabilisation to the coordination of thiourea and the host framework (C–H···S; *D*, 3.670, 3.607; *d*, 2.770, 2.801 Å; θ, 140.6, 131.2° and C–H···N; *D*, 3.758, 3.715; *d*, 2.732, 2.720 Å; θ, 157.8, 152.7°). If complex **1** is the starting point of this crystal engineering exercise, **2** and **3** pose dilemmas for different reasons. In **2**, the urea guest ribbon structure is retained intact but the BPNO host does not yield the expected hexagonal network. In **3**, on the other hand, the network is obtained (in a finite bilayer pattern) but the thiourea guest component no longer forms the infinite ribbon, as seen in **1** (and **2**). Indeed it is now even situated outside the hexagonal channel. In a sense therefore, both urea and thiourea molecules are too large to be accommodated in a hexagonal C–H···O based network of BPNO molecules and it was felt that only a very small guest molecule might be included within the network.

4,4′-Bipyridine *N*,*N*′-dioxide:water 1:2 complex, 4

The dihydrate **4** was obtained by crystallising BPNO from aqueous EtOH. Fig. 8 shows that the desired hexagonal network of BPNO molecules, constituted with synthon **VI**, has been obtained. The molecular layers are found in the (402) planes. The guest water molecules form linear hydrogen bonded zig-zag chains with O···O separations of 2.503 and 2.605 Å. The chains are situated wholly within the host channels, as anticipated (Fig. 9). The O-atom is disordered restricting appropriate assignment of the H-atom positions. The water molecules are attached to the BPNO host network with additional O-H···O hydrogen bonds (*D*, 2.683; *d*, 1.702 Å; θ, 175.1°), and stabilised by C–H···O hydrogen bonds (*D*, 3.619, 3.668; *d*, 2.652, 2.673 Å; θ, 148.4, 152.8°).

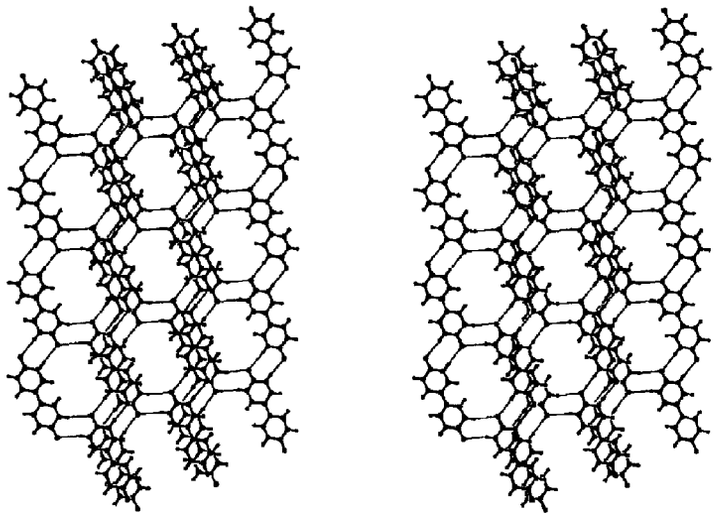


Fig. 7 Stereoview of the stepped stacking of BPNO bilayers in complex **3**. The thiourea molecules are omitted for clarity.

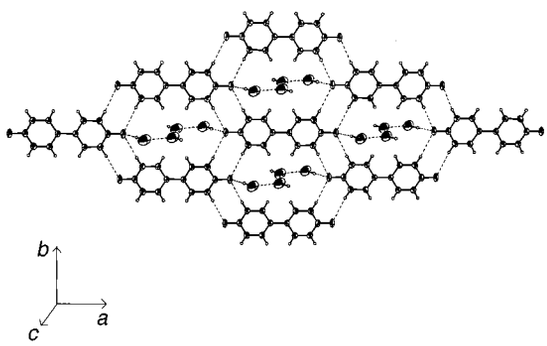


Fig. 8 C–H···O layer in complex **4** with water molecules in the hexagonal cavities. Only one of the H-atoms of the water molecule is shown for clarity. Notice that $Z' = 0.25$ for this crystal structure.

4,4′-Dinitrobiphenyl:urea 1:1 complex, 5. Rationale for crystal engineering

Starting with complex **1** (DCBP–urea), we have attempted to obtain similar crystal structures in related molecular complexes. Noting the topological similarity between synthons **II** and **VI**, the structural chemistry of BPNO was explored in its complexes with urea, thiourea and water. Structures **2** and **3** provide some points of comparison with the structure of **1** but are not fully equivalent to it. In structure **4**, the smaller guest water is able to fit neatly within the smaller hexagonal channel of BPNO and in this sense, the degree of structural predictability is satisfactory. The next logical step was to try and obtain a structure similar to that of **1** but with urea or thiourea as the guest. For this purpose a channel larger than that in BPNO is required and it was felt that 4,4′-dinitrobiphenyl, DNBP would form such a channel. Such a framework would be mediated by C–H···O synthon **X**. Our expectations were fully borne out in the structure of the 1:1 complex **5**, of DNBP with urea. This structure is very similar to that of **1**. The infinite urea ribbon is retained and linked to the DNBP molecules with N–H···O hydrogen bonded synthons **XI** (Fig. 10). The close similarity between the attachment of urea to DNBP, DCBP and BPNO in **5**, **1** and **2** may also be noted. The hexagonal arrangement of the host molecules is shown in Fig. 11 from which it may be seen that the urea ribbons are completely enclosed within the hexagonal channels as seen in complex **1**. As in complexes **1**–**4**, weak C–H···O hydrogen bonds provide additional stability for the coordination of urea to the host framework (C–H···O 3.835, 3.967; 2.807, 2.897 Å; 158.3, 169.6°). At this stage, the CSD was examined for other complexes of DNBP and interestingly, a 3:1 molecular complex with 4-biphenylol similar to **5**, was found.[13]

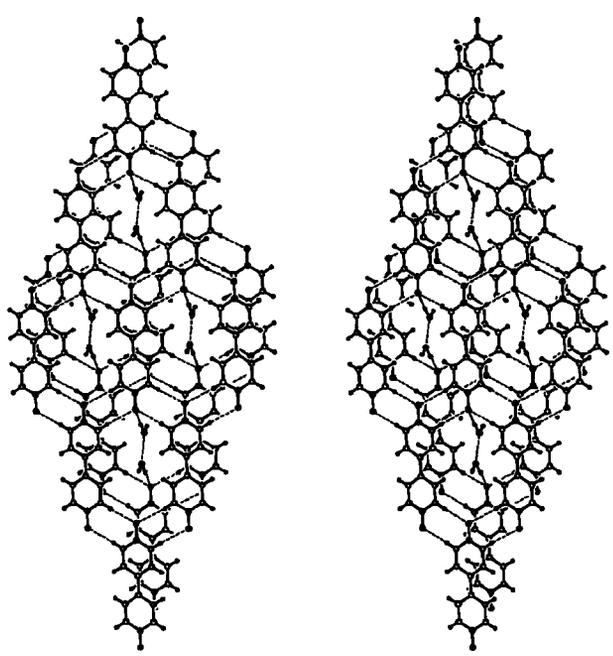


Fig. 9 Stereoview showing coordination between water molecules and the BPNO host in complex **4**

Comparison of structures 1–5

Analysis of the crystal structures of complexes **1**–**5** shows that they are closely related. In all cases, two types of molecular components are present: (1) the guests, urea, thiourea and water with strong hydrogen bonding functionalities; (2) the hosts, DCBP, BPNO and DNBP with weak and strong hydrogen bonding functionalities (C–H, N-O, C≡N). Three categories of hydrogen bonds are found in these complexes: (1) the guest···guest interactions are strong hydrogen bonds in the urea ribbon in complexes **1**, **2** and **5**, and in the thiourea dimers in **3**; (2) the host···host weak hydrogen bonds include those in the hexagonal layers in complexes **1**, **4** and **5**, in the layered orthogonal arrangement of BPNO molecules in complex **2** and in the bilayers in complex **3**; (3) strong and weak hydrogen bonds of the guest···host type are found in all five complexes.

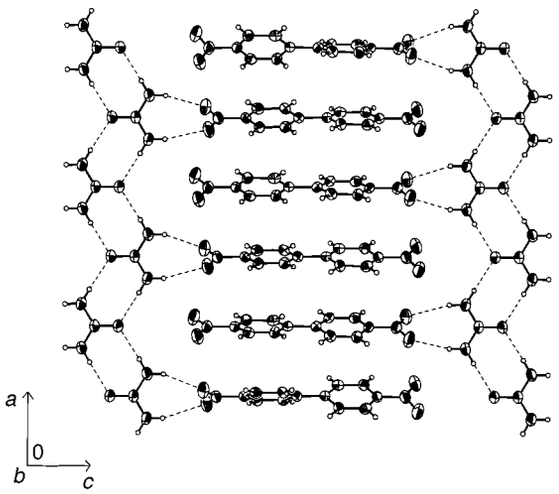


Fig. 10 Structure of complex **5**. The urea ribbon along [100] is shown. Note its coordination with DNBP molecules. Compare this with Fig. 1.

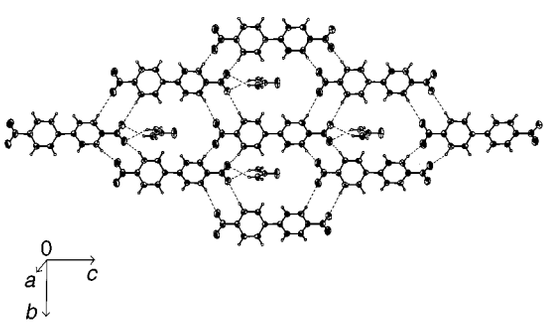


Fig. 11 Hexagonal C–H···O layer of DNBP molecules in complex **5**. Compare this with Fig. 2.

The geometry of the various synthons observed in all these crystal structures is summarised in Table 2. The dihedral angles between the phenyl rings of the host compounds, the C=O···N–C torsion angles between urea and its neighbours in complexes **1**, **2** and **5** and the π···π stacking details in all the crystal structures are listed in Table 3. In all cases, the guest with strong hydrogen bonds acts as an essential template for the formation of the host network structure with the (sometimes weak) C–H···O/N hydrogen bonds. Consequently, it might be said that there is a constructive interplay of strong and weak hydrogen bonds in these structures.

In **1**, the hexagonal host channel has enough space to accommodate the urea ribbon. The nearest distance between the N-atoms of the channel is 8.66 Å and the mean distance between the C-atoms in the interior is 6.90 Å. Perhaps the urea molecule is just too large to adopt a similar structure when co-crystallised with BPNO and a different packing with a more comfortable channel size is observed in **2**. The nearest distance between the N-atoms here is 8.16 Å and the mean distance between the C-atoms in the interior is 6.74 Å but the shape of the channel, in section, is different. In **3**, the thiourea molecule, which is even bigger than urea, cannot fit in the arrangements of either **1** or **2**, and prefers a different packing. In **4**, the molecular arrangement is simpler since the water molecule is smaller than urea or thiourea and can easily occupy the channels formed by the BPNO. In **5**, the DNBP molecules are arranged with an expectedly larger hexagonal channel and this accommodates the urea ribbon. The mean distance between the O-atoms is 9.11 Å and the mean internal distance between the C-atoms is 6.99 Å. The size of the hexagonal channels demarcated by C–H···O or C–H···N hydrogen bonds depends on whether the acceptor group is cyano, *N*-oxide or nitro. To ascertain if

Table 3 Some geometrical parameters for compounds **1**–**5**

Structure	φ^a/°	τ^b/°	π···π[c]/Å
1	31.9	3.1, 6.7	3.736, 3.794
2	26.4	8.3, 12.4	3.700, 3.823
3	1.8		3.657, 3.849
4	0		3.901
5	38.4	−2.2, −2.8	3.671, 3.692

[a] φ is the dihedral angle between the rings of the biphenyl moiety. [b] τ is the angle made by the mean planes of the urea molecule and the nearest hydrogen bonded urea molecule. [c] π···π is the distance between ring centroids of stacked host molecules.

the hexagonal channel of the DNBP framework is large enough to accommodate thiourea, DNBP was co-crystallised with thiourea. A 1 : 1 complex was obtained but the crystal structure could not be solved.

Single component crystals are useful for the identification of supramolecular synthons whereas multi-component crystals are useful in assessing the robustness of these synthons. The molecular complexes described in this paper have preorganised strong and weak hydrogen bonding molecular functionalities that generate robust synthons. Specifically, we note that: (1) urea forms an uncommon ribbon structure in complexes **1**, **2** and **5** through synthon **I** instead of the usual ribbon synthon **IV**; (2) thiourea forms a dimeric synthon **IX** which is topologically similar to synthon **I** but this does not extend to the ribbon structure; (3) water is O-H···O hydrogen bonded to the BPNO host in hydrate **4**; (4) synthons **VI** and **X** constituted with C–H···O hydrogen bonds are similar to synthon **II** in that they lead to a layer arrangement of host molecules. The similarities between the structures described here and the logical progression from complex **1** to, successively **2**, **3**, **4**, and finally **5** shows that other members of this new family of molecular complexes may also be deliberately engineered.

Conclusions

A major current concern in crystal engineering is that similarity in molecular structures in a set of compounds does not necessarily lead to a similarity in crystal structures. Any crystal structure consists of a large number of supramolecular synthons that are the result of the hierarchical preferences of the various molecular functionalities. Of this large number, a few synthons are more important in that they are robust. The identification of these more significant synthons and the search for their topological equivalents is therefore the basis of workable strategies of crystal engineering, if what is needed are other structures similar to the reference structure. This more practical approach is recommended because the *ab initio* prediction of crystal structures is not a procedure that is generally possible today. These concerns are felt more acutely in the present family of structures where there is considerable interference between the various kinds of hydrogen bonds. While the host···host C–H···O and C–H···N bonds are sometimes very weak, they must contribute in some measure to overall crystal stabilisation because the guest···guest patterns are uncommon in the absence of these particular hosts. All this reinforces the idea that strong and weak hydrogen bonds must be considered jointly in the analysis and design of crystal structures.

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