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3D, 2D and 1D networks via N-H···O and N-H···N hydrogen bonding by the bis-amide analogues: Effect of chain lengths and odd-even spacers

GARGI MUKHERJEE and KUMAR BIRADHA*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India
e-mail: kbiradha@chem.iitkgp.ernet.in

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Abstract. The synthesis, crystal structures and hydrogen bonding networks of four members of the bis(pyridinecarboxamido)alkane and bis(pyridyl)alkanediamides series ($1 \leq n \leq 8$), where the amide moieties are separated by alkyl chain ($-(CH_2)_n-$) having even or odd number of $-(CH_2)$-groups are explored and correlated with the previously reported structures. The odd members (n= odd) of both the series are found to adopt three-dimensional networks in contrast to the 1D or 2D structures of the even members (n= even). This odd-even effect on the dimensionality of the networks however disappears with increase in chain length.

Keywords. Odd-even effect; amide-to-amide hydrogen bond; pyridine interferences; organic diamondoid.

1. Introduction

Various types of intermolecular interactions, in particular the hydrogen bonding interactions between the functional groups of the molecules, result in the formation of different types of networks.[1–3] The prediction of these supramolecular networks depends on the information that lies in the functional groups, which are present in the molecules, and the identification of the supramolecular synthons between those functional groups. The preference for one supramolecular synthon over the other depends on the combination of various factors such as energetic, steric and solvation of the functional groups. The formation of the final supramolecular array in a crystal is a result of the balance between all the intermolecular interactions and the geometry of the molecules. Recently, we have explored the crystal structures of two homologous series of bis(pyridinecarboxamido)alkane (amide) and bis(pyridyl)alkanediamides (reverse amide) (scheme 1).[4] Our previous studies revealed that both the series show the odd-even effect[5] on the nature of hydrogen bond and their network features. As the derivatives contain two amide moieties and two pyridine units, the molecules can be assembled through either N-H···O or N-H···N or both the interactions. The β-sheets[6] or (4,4) networks[7] formed by N-H···O or N-H···N hydrogen bond, are the two most common motifs displayed by the even members of the amide series. The amide molecules (**1** and **2**) are assembled mostly *via* amide-to-amide recognitions while pyridine interferences to amide-to-amide hydrogen bond is more prominent in case of reverse amide series (**3** and **4**), i.e., N-H···N interaction is preferred over N-H···O hydrogen bond. In contrast to the 1D or 2D structures of the even ones, 3D structures are more regular in case of odd ones. To confirm the trend, in this report we have synthesized four more derivatives of both the series including the higher ends and crystallized them. The crystal structures and preference for amide-to-amide hydrogen bonding is analyzed in comparison with the previously reported structures.

2. Experimental

2.1 *Materials*

All the reagents and solvents employed were commercially available and used as supplied without further purification. Triphenylphosphite and pyridine were obtained from Merck Co. Azeloyl chloride, nicotinamide, 3-pyridinecarboxylic acid and 4-pyridinecarboxylic acid were obtained from Aldrich Co. α,ω-diamino alkanes, 3-aminopyridine, 4-aminopyridine and formaldehyde solution were obtained from Spectrochem-India.

2.2 *Physical measurements*

^{1}H NMR (200 MHz) spectra were recorded on a Bruker-AC spectrometer at room temperature Elemental analyses were obtained with a Perkin Elmer

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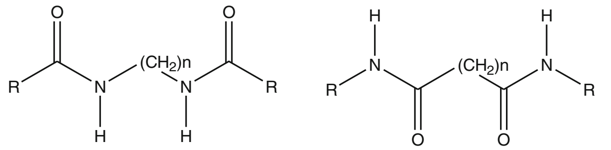

1: R= 3-pyridyl, **2**: R= 4-pyridyl **3**: R= 3-pyridyl, **4**: R= 4-pyridyl

(**a**) n = 1 (**b**) n = 3 (**c**) n = 5 (d) n= 7

(**e**) n = 2 (**f**) n = 4 (**g**) n= 8 (h) n = 8

Scheme 1. Schematic presentation of amide derivatives.

instrument, series II, CHNS/O analyzer 2400. Melting point measurement was carried out using Fisher Scientific instrument Cat. No. 12-144-1.

The single crystal data was collected on Bruker APEX-2 CCD X-ray diffractometer that uses graphite monochromated MoKα radiation (λ = 0.71073 Å) by hemisphere method. The structures are solved by direct methods and refined by least square methods on F^2 using SHELX-97.[9] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model.

2.3 *Synthetic procedures*

2.3a *Procedure for synthesis of **1a***: Nicotinamide suspended in 35% neutralized formaldehyde solution was refluxed for an hour at 100°C, cooled and recrystallized from acetone to yield N-hydroxymethylnicotinamide. This solid was heated at 200°C to yield **1a**. The product was recrystallized from hot water. Diffractable quality crystals were obtained from DMF.

1a, Yield = 73%, M.p 235–240 °C. Anal. Calcd for $C_{13}H_{12}N_4O_2$: C, 60.93%; H, 4.72%; N, 21.86%; Found: C, 61.65%; H, 4.33%; N, 21.98%.

2.3b *Procedure for synthesis of **2c** and **2d***: The derivatives **2c** and **2d** were synthesized by the following procedure. To a solution of 4-pyridinecarboxylic acid (4 g, 1 mmol) in pyridine (40 mL) was added corresponding α, ω-diaminoalkane (2 mmol). The solution was stirred for 15 min and triphenyl phosphite (9 mL, 2 mmol) was added slowly. The mixture was refluxed for 4 h at 100 °C in an oil bath. A brown solution resulted, which after volume reduction yielded a brown oil. This was taken up in chloroform (10 mL), washed three times with water, four times with saturated sodium bicarbonate solution, and then again three times with water. The resulting chloroform solution was dried over sodium sulfate and concentrated. 30 mL of ice-cold diethyl ether was added dropwise to the concentrated light brown. The mixture was stirred in an ice bath for 1 h. The white solid obtained was dried and recrystallized. **2c** and **2d** were crystallized from (1:1) mixture of methanol-toluene and methanol-DMSO solutions, respectively.

2c, Yield = 40%, M.p 120–124 °C. Anal. Calcd for $C_{17}H_{24}N_4O_2$: C, 58.61%; H, 6.94%; N, 16.08%; Found: C, 58.56%; H, 6.89%; N, 15.88%.

Table 1. Crystallographic parameters for **1a**, **2c**, **2d** and **3d**.

Molecules	**1a**	**2c**	**2d**	**3d**
Formula	$C_{13}H_{12}N_4O_2$	$C_{17}H_{24}N_4O_4$	$C_{19}H_{24}N_4O_2$	$C_{38}H_{48}N_8O_4$
Mol.Wt.	256.27	348.40	340.42	680.84
T (K)	293(2)	296(2)	293(2)	293(2)
System	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space Group	*Fdd*2	*C*2/*c*	$P2_1/c$	*P*-1
a(Å)	20.679(7)	17.7550(12)	4.8639(5)	4.715(4)
b(Å)	28.501(10)	9.1736(7)	18.3835(19)	10.493(8)
c(Å)	4.1182(15)	14.2042(16)	20.485(2)	19.088(14)
α(°)	90.00	90.00	90.00	102.52(3)
β(°)	90.00	126.398(3)	96.746(4)	93.32(3)
γ(°)	90.00	90.00	90.00	95.97(3)
V (Å^3)	2427.1(15)	1862.2(3)	1819.0(3)	913.6(12)
Z	8	4	4	1
D(g/cm^3)	1.403	1.243	1.243	1.237
$R_1(I > 2\sigma(I))$	0.0387	0.0426	0.0744	0.0773
wR_2(on F^2, all data)	0.0563	0.0622	0.2397	0.2400

Table 2. Geometrical parameters of hydrogen bonds in **1a**, **2c**, **2d** and **3d**.

Molecules	Type	H···A (Å)	D···A (Å)	D-H···A (°)
1a	N-H···N	2.26	3.035(3)	150
	C-H···O	2.37	3.245(3)	156
2c	N-H···O(W)	2.08	2.830(3)	159
	O(W)-H···N	2.04	2.874(3)	166
2d	N-H···O	2.03	2.808(5)	150
	N-H···O	1.99	2.821(5)	161
	C-H···O	2.57	3.208(7)	127
3d	N-H···N	2.18	3.017(7)	164
	N-H···O	2.04	2.892(6)	170
	C-H···O	2.48	3.365(8)	151

2d, Yield = 52%, M.p 125–127 °C. Anal. Calcd for $C_{19}H_{24}N_4O_2$: C, 67.04%; H, 7.11%; N, 16.46%; Found: C, 67.32%; H, 7.54%; N, 16.23%.

2.3c *Procedure for synthesis of **3d***: Tetrahydrofuran (THF) solution of 3-aminopyridine (2 mmol) and triethylamine (2 mmol) was cooled to 0°C under nitrogen atmosphere and to this solution azeloyl chloride (1 mmol) in THF was added drop wise with continuous stirring. The solution was stirred overnight. THF was distilled off and the resulting solid was washed three times with water and dried under vacuum.

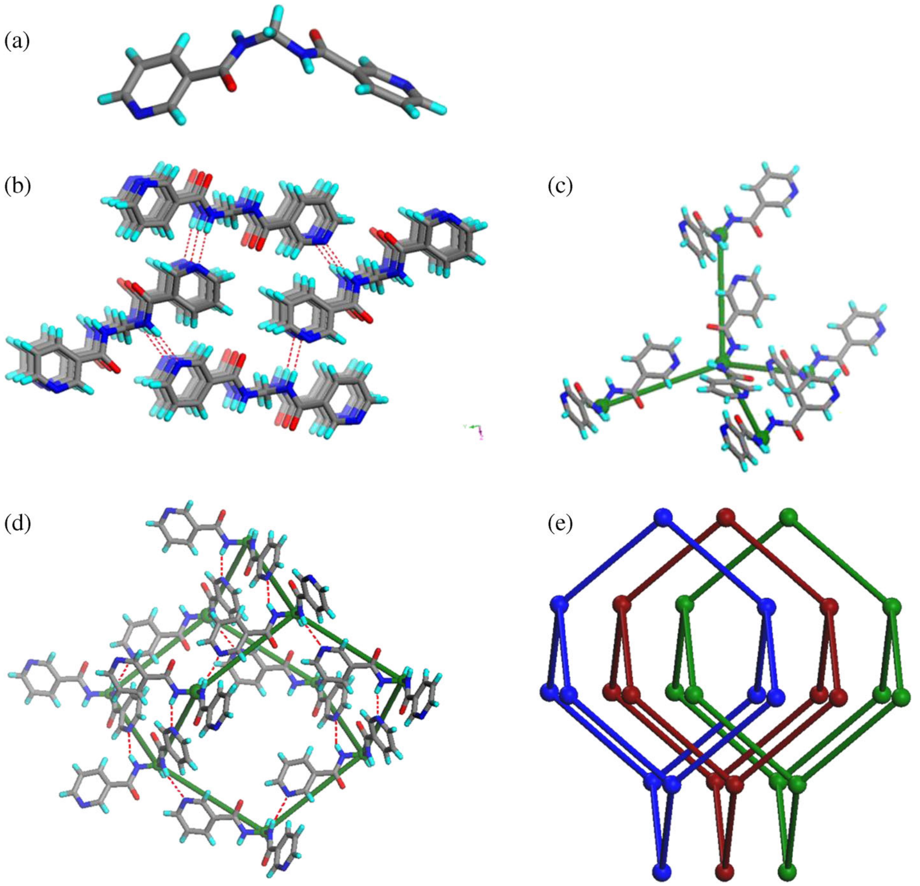

Figure 1. Illustrations for the crystal structure of **1a**: Molecular geometry of (a) **1a**, (b) fourfold helix via N-H···N hydrogen bonds (top view) (c) tetrahedral node formation, (d) single supramolecular adamantanoid cage, and (e) three-fold interpenetrated adamantanoid network; the central C-atom of alkyl spacer was considered as a node.

3d, Yield = 65%, M.p 155–160 °C. Anal. Calcd for $C_{19}H_{24}N_4O_2$: C, 67.04%; H, 7.11%; N, 16.46%; Found: C, 66.83%; H, 7.92%; N, 16.98%.

3. Results and Discussion

The molecule **1a**, **2c**, **2d** and **3d** (scheme 1) were synthesized by employing two well known procedures of amide syntheses. The amide derivatives (**1a**, **2c** and **2d**) were prepared by the reaction of corresponding α, ω-alkanediamines with pyridine acid in the presence of pyridine and triphenylphosphite, while the reverse amide derivative (**3d**) was prepared by the coupling of α, ω-alkanediacid chlorides and the corresponding amine. The crystallizations of molecules **1a**, **2c**, **2d** and **3d** in various solvents resulted in single crystals suitable for X-ray diffraction. In this contribution, the crystal structures of **1a**, **2c**, **2d** and **3d** will be analyzed in comparison to the previously reported structures of both amide and reverse amide derivatives. Molecule **1a** exhibits three-fold interpenetrated diamondoid network.[8] **2c** is found to include water molecule and afforded a tubular network. **2d** forms honeycomb network supported by amide-to-amide recognition and **3d** exhibits 1D- network based on alternate N-H$\cdots$O and N-H$\cdots$N interactions. The pertinent crystallographic details and geometrical parameters of strong hydrogen bonds involving amide functionality of derivatives of **1a**, **2c**, **2d** and **3d** are given in tables 1 and 2, respectively.

Molecule **1a** crystallizes in orthorhombic space group *Fdd*2 and the asymmetric unit is composed of half unit of molecule **1a**. Interestingly, the molecule exhibits arclike geometry as observed previously with other members of the bis-amide series having odd number of alkyl chain (figure 1). The amide groups and the pyridyl N are aligned *trans* to each other making the molecule to act as 4-connected node. Designating the molecule as node and hydrogen bond as nodal connection revealed that the network exhibits diamondoid topology. The diamondoid units are composed of two distances 9.322 and 9.336 Å, respectively. The molecules are assembled exclusively by N-H$\cdots$N interactions in a four-fold helical fashion to form a three-dimensional network and the voids are filled through three-fold interpenetration. The interpenetration occurs through aromatic interactions of pyridyl rings. This structure bears a striking resemblance with previously reported organic diamondoid network of bis(4-pyridinecarboxamido)methane, (**4a**) which exhibited four-fold interpenetration in contrast to the three-fold interpenetration observed here. Despite similar arm length (~9.3 Å) of diamondoid networks, the change in four-fold to three-fold interpenetration could be due to the differences in the geometry of the molecules which ultimately fill the voids. Also, in the present one the tetrahedral node is found to be more distorted compared

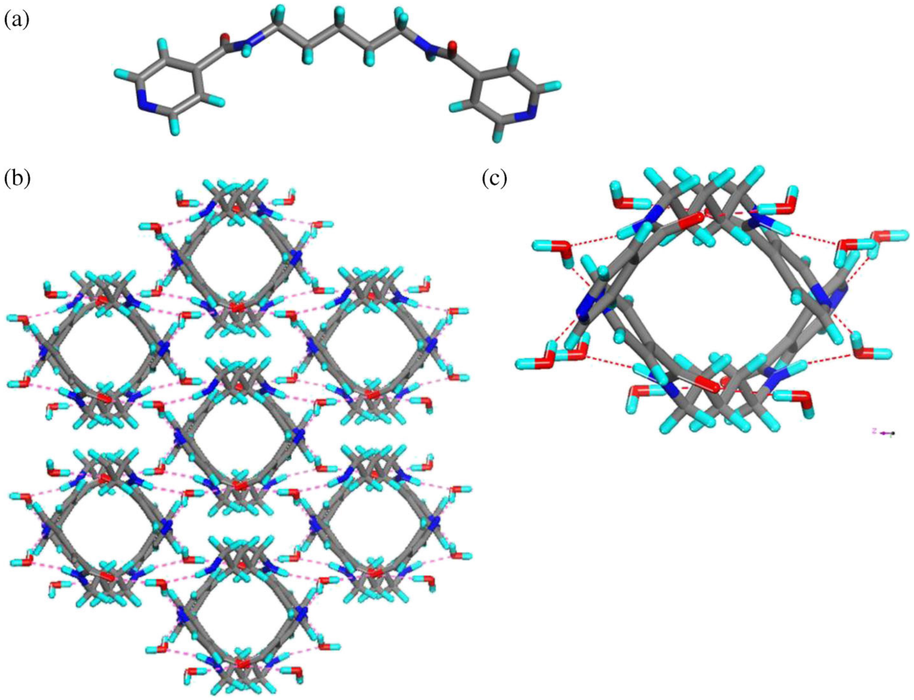

Figure 2. Illustrations for the crystal structure of **2c**: Molecular geometry of (a) **2c**, (b) tubular structure, and (c) hydrogen bonding between the tubes by water molecules.

to the previous one. The angles of the tetrahedral connection in **1a** vary from 80° to 140° in contrast to 102° to 125° in case of **4a.**

Molecule **2c** also exhibits a twisted geometry and crystallizes in monoclinic space group $C2/c$ as hydrate. The asymmetric unit is composed of half unit of molecule **2c** and one unit of water molecule. This structure is the only example of inclusion of water molecule in crystal lattices out of nine bis-amide derivatives having odd number of -$(CH_2)_n$- studied (figure 2). Water molecules exhibit 3-centred hydrogen bonding interactions, one each with amide CO, amide NH and pyridine N-atom from three different molecules, whereas the molecule **2c** is engaged in hydrogen bond with six water molecules through two each of pyridine N-atoms, amide CO, amide NH, leads to a tubular structure. These tubular units further interact with each other through water molecules. It is to note here that previously the bis(4-pyridyl)alkanediamides (reverse amide) derivatives with $(CH_2)_6$ (**4g**) and $(CH_2)_8$ (**4h**) were found to flaunt similar types of tubular structure with inclusion of water molecules, the only difference is that previously four water molecules were observed to be connected with each ligand in contrast to six water molecules per ligand here.

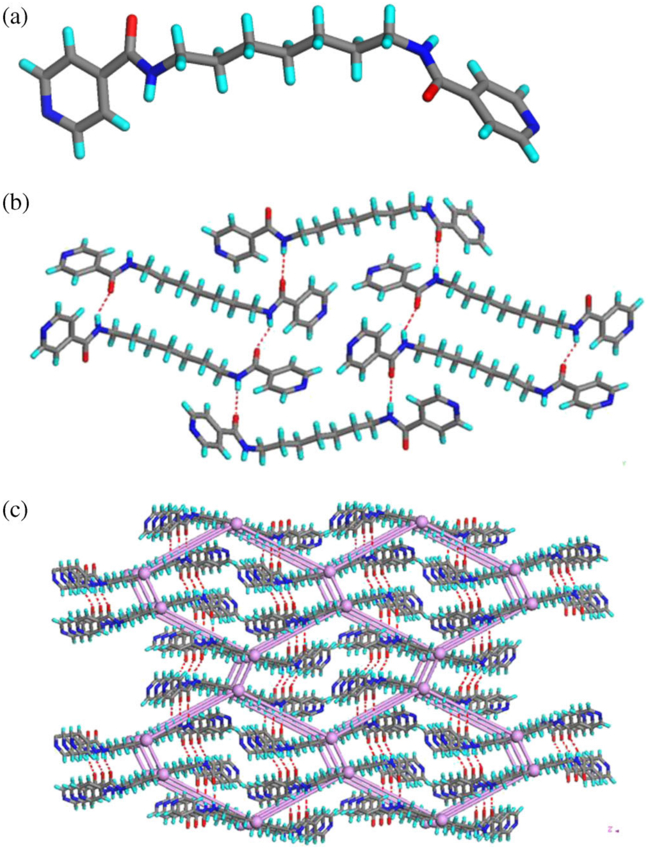

Figure 3. Illustrations for the crystal structure of **2d**: Molecular geometry of (a) **2d**, (b) formation of 2D layer via amide-to-amide hydrogen bonds, and (c) honeycomb network through connection of the central C-atom of alkyl spacer considered as a node.

In contrast to molecules **1a** and **2c**, molecule **2d** is assembled exclusively via N-H$\cdots$O interaction which is the first example of occurrence of amide-to-amide recognition in this series having odd number of alkyl chain derivatives. The molecule **2d** crystallizes in monoclinic space group $P2_1/c$. Each molecule connects with three other molecules through four N-H$\cdots$O interactions and an unique (6,3) network is observed (figure 3). The geometry of the network is honeycomb with arm lengths 4.338 and 11.561 Å. It is to be noted here that previously in the case of even spacer amide derivatives (**1f**, **2f**), 2D layer with (4,4) topology was observed.

The molecule **3d** bears iso-structurality with the bis(3-pyridyl)alkanediamides having six (**3g**) and eight (**3h**) spacers and all the three homologous molecules crystallize in identical space group P-1 (figure 4). However there is a subtle difference in geometry of ligands. The angle between the amide plane and pyridine plane (θ) for molecule **3d** are 6.99° and 5.90° whereas those for **3g** are 33.4° and 26.5° and for **3h** are 27.9° and 4.3°, respectively. Despite large differences in θ values, the trio exhibit similar hydrogen bonding pattern in which the molecules are assembled via alternate N-H$\cdots$O and N-H$\cdots$N interactions and results a 1 D network.

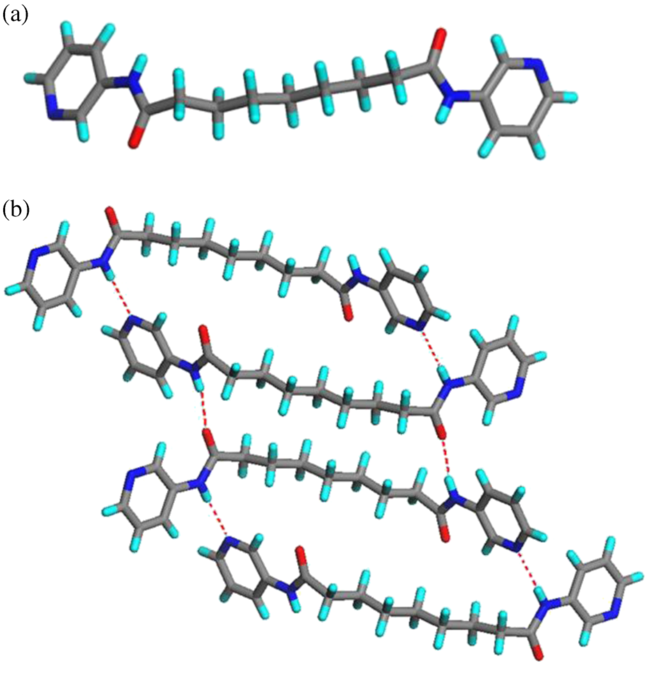

Figure 4. Illustrations for the crystal structure of **3d**: Molecular geometry of (a) **3d**, and (b) formation of 1D chain via amide-to-amide hydrogen bonds.

4. Conclusions

In our previous studies on the homologous series of bis(pyridinecarboxamido)alkane (amide) and bis(pyridyl)alkanediamides (reverse amide), it was shown that the odd members display more propensities to adopt 3-dimensional structures compared to the even ones and reverse amides show greater tendencies to exhibit pyridine interferences in amide-to-amide hydrogen bonding, i.e., N-H$\cdots$N hydrogen bond is more prevalent. However, structural studies on the higher analogues of series show that the odd-even alteration of dimensionality of network and hydrogen bonding patterns gradually fades away with increase in chain length. The lower analogues (n = 1, 3, 5) of the series mainly exhibits diamondoid or quartz type topology formed by N-H$\cdots$N hydrogen bond. But in case of seven membered (n = 7) derivatives of both the series, we see that either 1D or 2D network is exhibited. Further, pyridine interference in amide-to-amide hydrogen bonding reduces and N-H$\cdots$O interactions play more important role in assembling the network as we observed earlier in case of even analogues. For example, molecule **2d** of amide series has 2D network and **3d** of reverse amide series has 1D structure which is iso-structural with its even member analogues having -(CH_2)-group one less (n = 6, **3g**) or one more (n = 8, **3h**). Although there are only two crystal structures with higher spacers, the structural trend is pretty clear from these structures.

Supplementary Information

The electronic supporting information can be seen at www.ias.ac.in/chemsci.

Acknowledgements

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References

1. (a) Desiraju G R and Steiner T 1999 In *The weak hydrogen bond in structural chemistry and biology* (Oxford: Oxford University Press); (b) Zaworotko M J 2001 *Chem. Commun*. p1
2. (a) Desiraju G R 1989 In *Crystal Engineering: The design of organic solids* (Amsterdam: Elsevier); (b) Desiraju G R 1995 *Angew. Chem. Int. Ed*. **34** 2311; (c) Etter M C 1990 *Acc. Chem. Res*. **23** 120
3. (a) Nguyen T L, Fowler F W and Lauher J W 2001 *J. Am. Chem. Soc*. **123** 11057; (b) Das D and Desiraju G R 2006 *Chem. Asian J*. **1** 231; (c) Bis J A, Vishweshwar P, Middleton R A and Zaworotko M J 2006 *Cryst. Growth Des*. **6** 1048
4. (a) Sarkar M and Biradha K 2006 *Cryst. Growth Des*. **6** 202; (b) Rajput L, Singha S and Biradha K 2007 *Cryst. Growth Des*. **7** 2788; (c) Mukherjee G and Biradha K 2011 *Cryst. Growth Des*. **11** 924; (d) Sarkar M and Biradha K 2005 *Chem. Commun*. 2229; (e) Biradha K and Rajput L 2010 In *Organic crystal engineering: Frontiers in crystal engineering* E R T Tiekink, J J Vittal and M J Zaworotko (Eds.) (Chichester: John Wiley Publishers)
5. (a) Boese R, Weiss H-C and Bläser D 1999 *Angew. Chem. Int. Ed*. **38** 988; (b) Thalladi V R, Boese R and Weiss H-C 2000 *J. Am. Chem. Soc*. **122** 1186; (c) Thalladi V R, Boese R and Weiss H-C 2000 *Angew. Chem. Int. Ed*. **39** 918; (d) Thalladi V R, Nüsse M and Boese R 2000 *J. Am. Chem. Soc*. **122** 9227
6. (a) Lauher J W, Chang Y L and Fowler F W 1992 *Mol. Cryst. Liq. Cryst*. **211** 99; (b) Zhao Y L and Wu Y D 2002 *J. Am. Chem. Soc*. **124** 2002
7. Batten S R and Robson R 1998 *Angew. Chem. Int. Ed*. **37** 1460
8. (a) Craig D C, Dance I G and Garbutt R 1986 *Angew. Chem. Int. Ed. Engl*. **25** 165; (b) Ermer O 1988 *J. Am. Chem. Soc*. **110** 3747; (c) Ermer O and Eling A 1988 *Angew. Chem. Int. Ed. Engl*. **27** 829; (d) Hoskins B F and Robson R 1990 *J. Am. Chem. Soc*. **112** 1546; (e) Simard M, Su D and Wuest J D 1991 *J. Am. Chem. Soc*. **113** 4696; (f) Copp S B, Subramanian S and Zaworotko M J 1992 *J. Am. Chem. Soc*. **114** 8719; (g) Brunet P, Simard M and Wuest J D 1997 *J. Am. Chem. Soc*. **119** 2737; (h) Reddy D S, Dewa T, Endo K and Aoyama Y 2000 *Angew. Chem. Int. Ed*. **39** 4266; (i) Men Y B, Sun J, Huang Z-T and Zheng Q Y 2009 *CrystEngComm* **11** 978
9. Sheldrick G M 1997 In *Program for the Solution and Refinement of Crystal Structures, SHELX-97* (Germany: University of Gottingen)