

Role of weak hydrogen bonds in the crystal structures of phenazine, 5,10-dihydrophenazine and their 1 : 1 and 3 : 1 molecular complexes†

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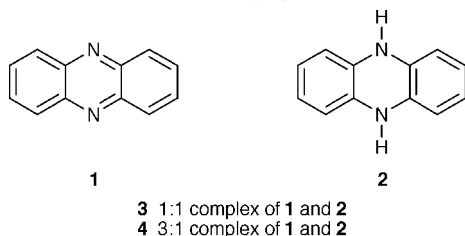
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Phenazine (**1**) and 5,10-dihydrophenazine (**2**) form not only a 1 : 1 complex (**3**), as expected from N–H···N hydrogen bond requirements, but surprisingly also a 3 : 1 complex (**4**). Single crystal X-ray analyses of compound **2** and complexes **3** and **4** have been carried out. While the overall packing in complex **3** is as efficient as in pure **1** and **2**, acidic C–H groups, which contribute actively to the structural assembly in pure **2**, are not involved in hydrogen bonding in **3**. It is shown that the quest for hydrogen bonding by these C–H groups steers the formation of complex **4** with an unprecedented N–H···N and C–H···N hydrogen bond mediated tape structure.

The hydrogen bond is the most versatile intermolecular interaction responsible for molecular aggregation in the biological and material worlds.¹ Conventionally strong hydrogen bonds such as O–H···O, N–H···O and O–H···N have been extensively used in the area of supramolecular chemistry and crystal engineering.² In contrast, conventionally well-known, but somewhat weaker, N–H···N hydrogen bonds have been scarcely studied. Combined use of N–H···O and N–H···N hydrogen bonds in biomimetic three-point recognition has recently attracted much interest in self-assembly.³ However, supramolecular design based solely on N–H···N hydrogen bonding has not been explored thus far.⁴ With this background and with our continuing interest in structures exhibiting photochromic properties⁵ we have studied N–H···N hydrogen-bond based supramolecular systems of phenazine (**1**) and 5,10-dihydrophenazine (**2**). Compounds **1** and **2** are known to form molecular complexes **3** and **4** in 1 : 1 and 3 : 1 stoichiometries, respectively,⁶ and their UV/Vis spectra have been studied.^{6a} Single crystal X-ray analyses of compound **2** and complexes **3** and **4** have now been performed. These three structures, together with the structure of **1**,⁷ reveal interesting features of weak hydrogen bonds that are useful in current crystal engineering approaches.⁸

Experimental

Compound **2** is synthesised by reducing **1** according to a literature procedure.^{6a} Since **2** is highly sensitive towards oxida-



3 1:1 complex of **1** and **2**
4 3:1 complex of **1** and **2**

tion the crystals of **2**, **3** and **4** were grown under Ar atmosphere from deoxygenated solutions of methanol and their X-ray data were collected (Table 1) on Nicolet R3 (for **2**) and Bruker SMART (for **3** and **4**) diffractometers. The structures were solved and refined using the SHELXTL suite of programs. Differential scanning calorimetry (DSC) experiments were carried out on a Du Pont 910 differential scanning calorimeter.

CCDC reference number 440/161. See <http://www.rsc.org/suppdata/nj/a9/a908744c/> for crystallographic files in .cif format.

Results and discussion

Compound **2** crystallises in the space group *Pbca* (*Z* = 8, Table 1) and the molecules adopt a bent geometry in the crystal. Fig. 1 illustrates the packing features of **2**. While one of the N–H groups is involved in an N–H···N bridge ($d_{\text{H}\cdots\text{N}} = 2.33 \text{ \AA}$, $\theta = 176^\circ$),[‡] the other forms an N–H··· π ($d_{\text{H}\cdots\pi} = 2.57 \text{ \AA}$, $\theta = 136^\circ$) interaction. Molecules linked by N–H···N are also linked by two C–H··· π ($d_{\text{H}\cdots\pi} = 2.57$, 2.71 \AA ; $\theta = 136$, 151°) interactions,⁹ resulting in a three-point recognition [Fig. 1(a)]. Molecules connected with N–H··· π are also linked by a C–H···N ($d_{\text{H}\cdots\text{N}} = 2.66 \text{ \AA}$, $\theta = 160^\circ$) interaction. In effect, each molecule is linked to four other molecules through ten intermolecular interactions. These interactions extend to a two-dimensional network of molecules parallel to the *ab* plane [Fig. 1(c)]. One way of describing this 2D-network is that N–H···N/C–H··· π mediated corrugated tapes [which run along the *b* axis, Fig. 1(b)] are cross-linked by N–H··· π /C–H···N interactions. Close-packing along the *c* axis completes the three-dimensional structure.

The X-ray data for complex **3** were collected in a triclinic system and in the initial attempts the structure was solved and refined in the space group *P* $\bar{1}$. During the analysis of packing patterns it was noticed that adjacent N–H···N linked molecules could be related by a pseudo-glide symmetry. Search for higher symmetry revealed a monoclinic system and finally the structure was solved and refined in the space group *I2/a*. However, molecules **1** and **2** now occupy the same site with

† Dedicated to Professor Peter Paetzold on the occasion of his 65th birthday.

Electronic supplementary information (ESI) available: ORTEP views of compounds **2**–**4**. See <http://www.rsc.org/suppdata/nj/a9/a908744c/>

Table 1 Crystal data and measurement details for 2–4

	2	3	4
Emp. Formula	C ₁₂ H ₁₀ N ₂	C ₁₂ H ₈ N ₂ · C ₁₂ H ₁₀ N ₂	(C ₁₂ H ₈ N ₂) ₃ · C ₁₂ H ₁₀ N ₂
Formula wt.	182.22	362.42	722.83
MP/K	449	504	491
T/K	123	300	300
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pbca</i>	<i>I2/a</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.7727(14)	11.6466(3)	9.026(2)
<i>b</i> /Å	7.5924(9)	6.2335(2)	9.676(2)
<i>c</i> /Å	21.775(3)	12.5573(5)	11.242(2)
α /°	90	90	72.522(2)
β /°	90	97.612(2)	80.196(3)
γ /°	90	90	77.597(3)
<i>Z</i>	8	2	1
<i>U</i> /Å ³	1781.0(4)	903.61(5)	908.7(3)
<i>N</i> /total ^a	2482	6224	3221
<i>N</i> /indep. ^b	1458	895	2294
<i>R</i> _{int}	0.020	0.022	0.053
<i>R</i> ₁	0.035	0.056	0.063
<i>wR</i> ₂	0.095	0.152	0.158
<i>C</i> _k ^c	0.72	0.70	0.69

^a Number of reflections collected. ^b Number of independent reflections. ^c Packing coefficient.

equal occupancies resulting in a domain disorder. Molecules of **1** and **2** are connected with N–H···N ($d_{\text{H} \cdots \text{N}} = 2.10$ Å, $\theta = 162^\circ$) hydrogen bonds, as expected, and extend to a chain pattern along the *a* axis [Fig. 2(a)]. The packing in the other two dimensions, that is in the *bc* plane, is governed by aromatic···aromatic interactions [Fig. 2(b)], with stacking (3.49 Å, interplanar distance) along the *b* axis and C–H··· π ($d_{\text{H} \cdots \pi} = 2.62$ Å, $\theta = 143^\circ$) interactions along the *c* axis.

A structural comparison of complex **3** (Fig. 2) and compound **1**⁷ (Fig. 3) is interesting. Comparison of Figs. 2(a) and 3(a) reveals that, in the absence of N–H donors, translation related molecules along the *a* axis are linked through C–H···N dimer synthons¹⁰ in **1** and extend to a linear tape structure. Replacement of a single N–H···N hydrogen bond in **3** by a C–H···N dimer synthon leads to a parallel arrangement of successive molecules in **1**, as opposed to the inclined orientation seen in complex **3**. The packing in the *bc* plane [Fig. 3(b)] is similar to that in complex **3** [Fig. 2(b)] governed by stacking (3.50 Å, interplanar distance) and C–H··· π ($d_{\text{H} \cdots \pi} = 3.23$ Å, $\theta = 133^\circ$) interactions. Effectively, the crystal packing of **1** resembles that of **3** in these two dimensions.

At this juncture it is important to recall that compounds **1**

and **2** also form a 3 : 1 complex, **4**.⁶ This is surprising and unusual. Consideration of N–H···N hydrogen bond requirements suggests that only a 1 : 1 complex can be expected (two N acceptors in **1** and two N–H donors in **2**). Similar packing coefficients for **1**, **2** and **3** (0.70, 0.72§ and 0.70, respectively) indicate that the gross packing in complex **3** is as efficient as in pure **1** and **2**. Structural comparison between complex **3** and compound **1** suggests that the interaction environment of **1** molecules in complex **3** is as good as in pure **1**. A question then remains. Is the interaction environment of **2** molecules in complex **3** equally good? A closer look at the structures of **2** and **3** reveals that this is not the case. Consider Fig. 4. The C–H groups that are involved in C–H···N and C–H··· π interactions in pure **2** [Fig. 4(a)] are not involved in hydrogen bonding in complex **3** [Fig. 4(b)]. Indeed, these C–H groups are involved in C–H···N hydrogen bonds with the additional two molecules of **1** present in complex **4** [Fig. 4(c)].¹¹

Fig. 5 displays the linear tapes along [110] in complex **4**. As in **3**, N–H···N ($d_{\text{H} \cdots \text{N}} = 2.12$ Å, $\theta = 176^\circ$) hydrogen-bonded chains link alternating molecules of **1** and **2**. However, the two accompanying C–H groups of **2** also link to two additional molecules of **1** through C–H···N ($d_{\text{H} \cdots \text{N}} = 2.47, 2.57$ Å

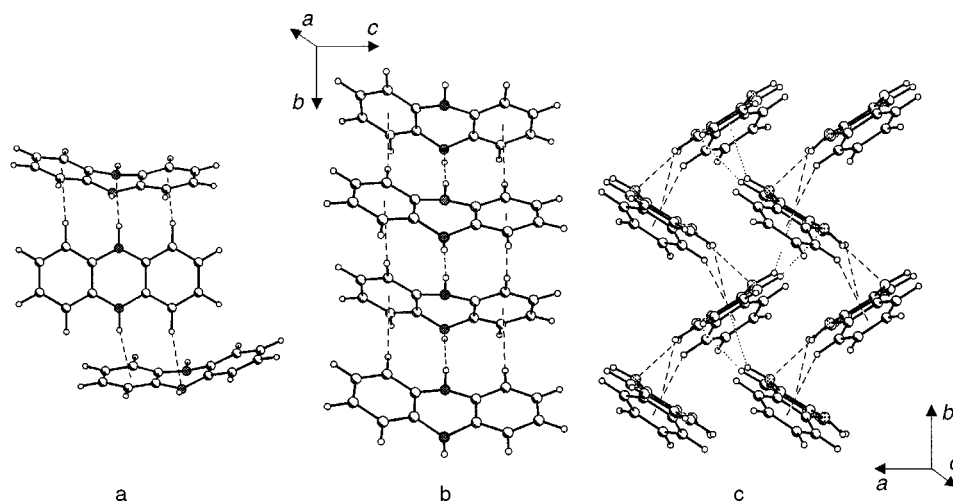


Fig. 1 Crystal structure of **2**. (a) N–H···N and C–H··· π interactions on one side and N–H··· π and C–H···N on the other side of the molecule. Notice the bent geometry. (b) N–H···N/C–H··· π mediated corrugated tape motif along the *b* axis. (c) Two-dimensional network parallel to the *ab* plane. Notice the tapes shown in (b) in a different view and also the cross-linking N–H··· π /C–H···N interactions (shown as dotted lines).

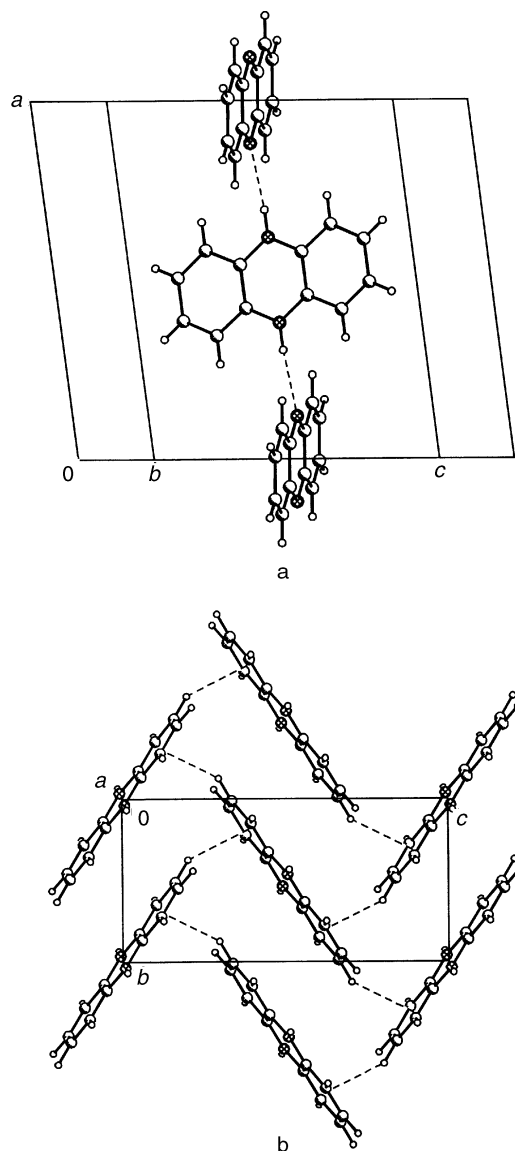


Fig. 2 Crystal structure of **3**. (a) N-H...N hydrogen-bonded chain of **1** and **2** molecules. For clarity only one of the positions of the H atoms of the N-H groups are shown. (b) Aromatic packing in the *bc* plane. Notice the $\pi \cdots \pi$ stacking and C-H... π interactions.

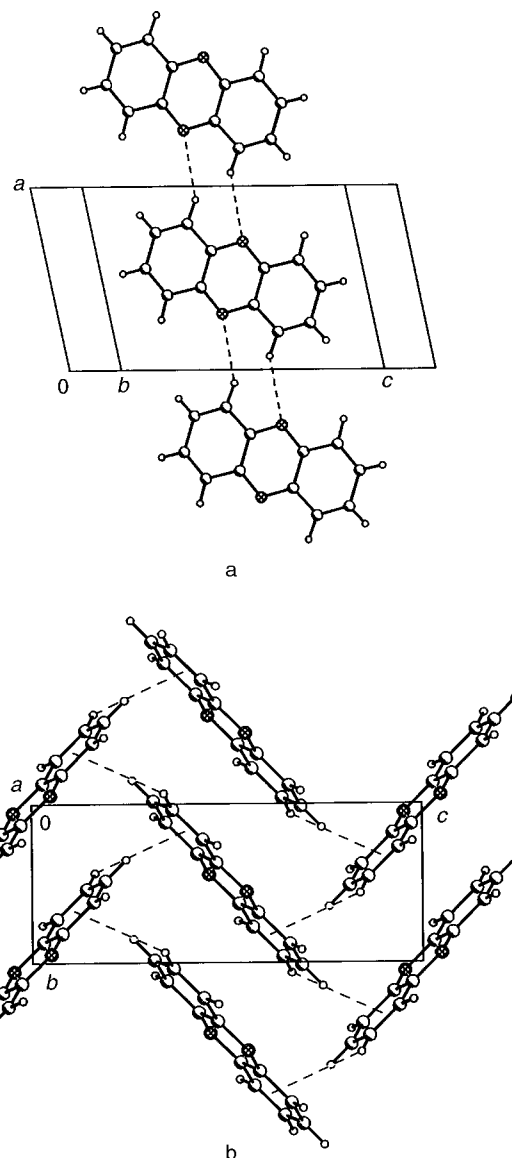


Fig. 3 Crystal structure of **1**. (a) C-H...N mediated tape motif along *a* axis. (b) Aromatic packing in *bc* plane. Notice the $\pi \cdots \pi$ stacking and C-H... π interactions. Notice the similarity to Fig. 2(b).

$\theta = 152, 138^\circ$) hydrogen bonds. A three-point hydrogen bond donation is observed. It should be noted that while three-point donation occurs at both edges of **2** in complex **4** (Fig. 5), it takes place only at one edge in the structure of pure **2** [Fig. 4(a)]. The recognition through three-point donation in complex **4** is unusual in that it leads to an assembly of four molecules. This is in contrast to the classical three-point recognition observed in the structure of **2** where two molecules are held together by three hydrogen bonds.³ A further note of interest is that the recognition in both cases involves conventional (N-H...N) and non-conventional (C-H... π or C-H...N) hydrogen bonds.^{1c}

The geometrical disposition of N-H and C-H groups in **2**, coupled with the quest for N-H...N and C-H...N hydrogen bonding, requires the formation of stacked triads of **1** in complex **4**. The stacking of these stacked triads continues along [001] and results in an infinite columnar stack of **1** (Fig. 6). The packing in the third dimension, that is along [1 $\bar{1}$ 0] is maintained by edge-to-face interactions between **1** and **2**, respectively (Fig. 6).¶

It is interesting to note that the N-H...N hydrogen-bonded chains in complexes **3** and **4** have similar topology and geometry. Adjacent molecules of **1** and **2** within these chains

are inclined to the same extent [68° and 69° in **3** and **4**, respectively, Fig. 2(a) and Fig. 5]. It may then be perceived that complex **4** is formed from complex **3** with two additional molecules of **1**, which are positioned above and below the one that is already present in the N-H...N chain. As described above, these additional molecules allow C-H...N, C-H... π and $\pi \cdots \pi$ interactions resulting in an efficient packing. At a much deeper level, it appears in hindsight that the main pattern of N-H...N chains is identical in the pre-nucleation stages of both the complexes, with further differences arising during the next stages of crystallisation.

DSC experiments were performed with finely ground mixtures of **1** and **2** in varied proportions. An analysis of the thermograms clearly revealed two distinct peaks corresponding to complexes **3** and **4**. These experiments indicate no other complex of a different composition. Further, it is observed that even when the proportion of **1** is as little as 6%, complex **4** is formed (it cannot be completely ruled out that some portion of **2** is oxidised to **1** during the experiments). However, when **1** is in excess ($\geq 75\%$) complex **4** is the exclusive product. These observations are further corroborated by complexation experiments that were carried out with varying proportions of **1** and **2**.

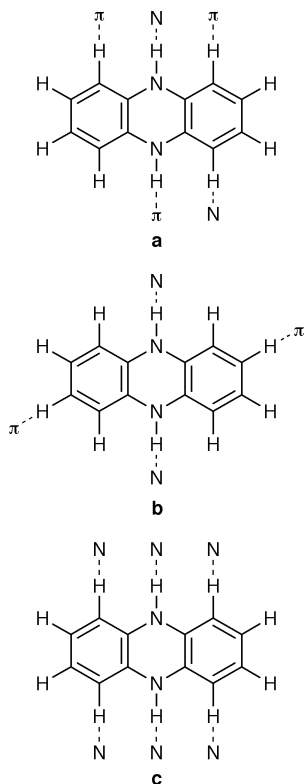


Fig. 4 Interaction environment of a molecule of **2** in the crystal structures of pure **2** (a) and complexes **3** (b) and **4** (c). Only the donor situations are shown.

Conclusion

In summary, since N-H...N hydrogen bonds and aromatic...aromatic interactions are observed in both the 1 : 1 and 3 : 1 complexes, the structure-discriminating interactions between these two complexes are weak C-H...N hydrogen bonds. Again, if N-H...N hydrogen bonds were solely operative, only the 1 : 1 complex **3** would be expected. The fact that complex **4** is formed with a 3 : 1 stoichiometry, with the tape structure described above, underscores the structure-steering character of C-H...N hydrogen bonds.¹² Structures **1–4** present a special case for understanding how weak interactions can steer a distinct packing of their own, when not satisfied with a packing in which only the stronger ones are realised. This is not always discernible. Many weak interactions that fortify the stronger interactions in structural assembly are usually unnoticed. It is shown here that strong and weak interactions work in harmony and result in a 3 : 1 molecular complex, which in the beginning seemed anomalous, but when one realises the crucial role played by the weaker hydrogen bonds, turns out to be normal.¹³ These weak hydrogen bonds have the directionality similar to their stronger counterparts (O-H...O, N-H...O, O-H...N and N-H...N)¹⁴ but because of their inherent softness they can still be formed with bent geometries. This reflects the adaptability while maintaining the directionality, a feature unique to weak hydrogen bonds. Indeed, it is this special character of weak hydrogen bonds that makes 3 : 1 complexation possible. Such soft character of C-H...N(O) hydrogen bonds is still waiting to be exploited in the supramolecular construction of functional materials.

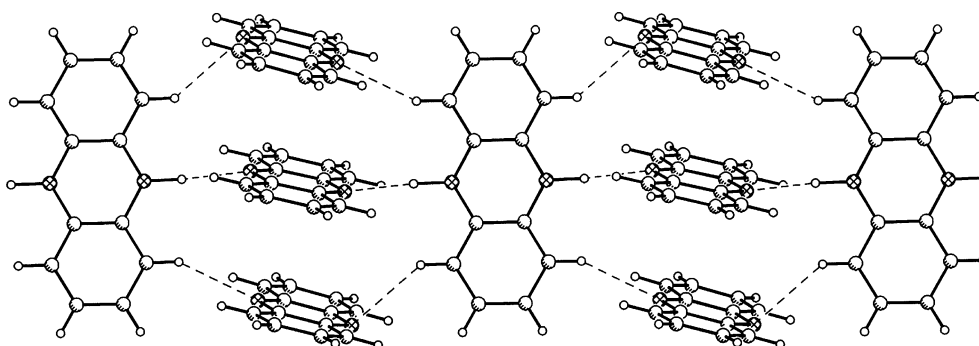


Fig. 5 N-H...N and C-H...N mediated linear tapes in complex **4**. Notice the trimolecular stacks of **1**.

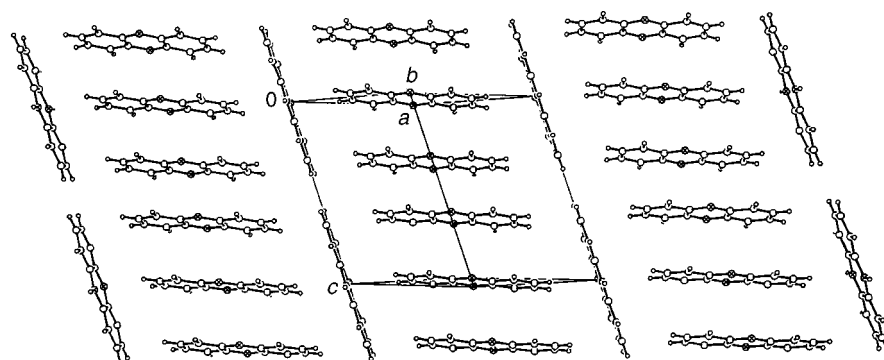


Fig. 6 Aromatic...aromatic interactions in complex **4**: face-to-face between molecules of **1**, edge-to-face between molecules of **1** and **2**, and edge-to-edge between molecules of **2**.

Acknowledgements

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Notes and references

‡ Throughout the paper the N–H and C–H bond lengths are normalised to 1.009 and 1.083 Å, respectively. The N–H... π and C–H... π geometries are calculated to the centroids of the aromatic rings. The angle at the H atom is given as θ .

§ The data for **2** were collected at a much lower temperature (123 K, Table 1) than those for **1** and **3** (300 K) and therefore it has a seemingly higher packing coefficient.

¶ It may be noted that **2** adopts a flat molecular geometry in the structures of **3** and **4** in contrast to the bent geometry found in pure **2**. This may be attributed to the pyramidalisation at the N–H groups in pure **2** because they act as hydrogen bond donors and acceptors simultaneously. In **3** and **4** the N–H groups of **2** act merely as donors.

- (a) G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin, 1991; (b) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997; (c) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999.
- Some selected reviews: (a) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; (b) J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383; (c) M. C. T. Fyfe and J. F. Stoddart, *Acc. Chem. Res.*, 1997, **30**, 393; (d) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397.
- (a) J.-M. Lehn, M. Mascal, A. DeCain and J. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1992, 461; (b) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen and D. M. Gordon, *Acc. Chem. Res.*, 1995, **28**, 37; (c) S. V. Kolotuchin and S. C. Zimmerman, *J. Am. Chem. Soc.*, 1998, **120**, 9092.
- M. C. Etter and D. A. Admond, *J. Chem. Soc., Chem. Commun.*, 1990, 589; P. S. Corbin and S. C. Zimmerman, *J. Chem. Soc., Chem.*, 1998, **120**, 9710.
- (a) A. Reyes-Arellano, R. Boese, I. Steller and R. Sustmann, *Struct. Chem.*, 1995, **6**, 391; (b) M. Felderhoff, I. Steller, A. Reyes-Arellano, R. Boese and R. Sustmann, *Adv. Mater.*, 1996, **8**, 402; (c) T. Smolka, R. Sustmann and R. Boese, *J. Prakt. Chem.*, 1999, **341**, 378; (d) M. Felderhoff, T. Smolka, R. Sustmann, I. Steller, H.-C. Weiss and R. Boese, *J. Prakt. Chem.*, 1999, **341**, 639.
- (a) A. Claus, *Liebigs Ann.*, 1873, **168**, 1; (b) W. Schlenk and E. Bergmann, *Liebigs Ann.*, 1928, **463**, 306; (c) G. R. Clemon and H. McIlwain, *J. Chem. Soc.*, 1934, 1991; (d) E. Toromanoff, *Ann. Chim.*, 1956, **1**, 115; (e) G. A. Wheaton, L. J. Stoel, N. B. Stevens and C. W. Frank, *Appl. Spectrosc.*, 1970, 339.
- (a) F. H. Herbstein and G. M. J. Schmidt, *Acta Crystallogr.*, 1955, **8**, 406; (b) K. Wozniak, B. Kariuki and W. Jones, *Acta Crystallogr., Sect. C*, 1991, **47**, 1113.
- (a) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; (b) G. R. Desiraju, *Curr. Opin. Solid State Mater. Sci.*, 1997, **2**, 451; (c) C. B. Aakeröy, *Acta Crystallogr. Sect. B*, 1997, **53**, 569.
- M. Nishio, M. Hirota and Y. Umezawa, *The CH/ π Interaction: Evidence, Nature and Consequences*, Wiley-VCH, New York, 1998.
- (a) C. E. Marjo, M. L. Scudder, D. C. Craig and R. Bishop, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2029; (b) V. R. Pedireddi, W. Jones, A. P. Chorlton and R. Docherty, *Chem. Commun.*, 1996, 997.
- It is known that acidic C–H groups, when not content with normal packing patterns, produce structural anomalies. See: (a) G. R. Desiraju, B. N. Murthy and K. V. R. Kishan, *Chem. Mater.*, 1990, **2**, 447; (b) G. R. Desiraju and C. V. K. Sharma, *J. Chem. Soc., Chem. Commun.*, 1991, 1239; (c) C. V. K. Sharma, K. Panneerselvam, T. Pilati and G. R. Desiraju, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2209; (d) S. S. Kuduva, D. C. Craig, A. Nangia and G. R. Desiraju, *J. Am. Chem. Soc.*, 1999, **121**, 1936.
- A recent controversy raised on the nature of these hydrogen bonds (F. A. Cotton, L. M. Daniels, G. T. Jordan IV and C. A. Murillo, *Chem. Commun.*, 1997, 1673) has been successfully rebutted [see: (a) M. Mascal, *Chem. Commun.*, 1998, 303; (b) T. Steiner and G. R. Desiraju, *Chem. Commun.*, 1998, 891].
- Sometimes the demands of weaker interactions completely change the patterns of stronger ones. See e.g.: F. H. Allen, V. J. Hoy, J. A. K. Howard, V. R. Thalladi, G. R. Desiraju, C. C. Wilson and G. J. McIntyre, *J. Am. Chem. Soc.*, 1997, **119**, 3477.
- (a) G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441; (b) T. Steiner, *Chem. Commun.*, 1997, 727.

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