The Hydrogen Bond and Crystal Engineering[†]

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1 Introduction

The purpose of this review is to present a philosophy of crystal engineering. The chemist is comfortable and familiar with intramolecular bonding; our advanced knowledge of synthetic chemistry (which could almost be considered as the *raison d'être* of the chemist) is constructed around our understanding of the essential principles of covalent bonding. Less well-known and acceptable are the concepts of intermolecular bonds between molecules and/or ions (even the field of supramolecular chemistry has only just established itself),[1,2] and our understanding of the factors which control crystal habit and morphology is rudimentary. The chemist, in designing molecules, rarely turns his attention to the crystalline form which that molecule will adopt in the solid state. The crystal form is usually a matter of serendipity; the ubiquitous occurrence of polymorphism (see Section 4.4) is either ignored or treated as a problem beyond control.

We present here our thoughts on the field of 'crystal engineering', which has been advanced in recent years by the elegant synthetic work and shrewd topological analysis of Margaret Etter.[3] This is a field in its infancy; it is at the interface between a number of demanding disciplines, and has all the challenge and excitement expected of interdisciplinary research. We present the hydrogen bond as a synthetic 'vector' for granting topological control over crystalline form, and hence control over such crucial physical phenomena as optical properties, thermal stability, solubility, colour, conductivity, crystal habit, and mechanical strength. The significance of this area to industry and academia cannot be overstated.

2 The Hydrogen Bond

The object of this section is not to define in detail what a hydrogen bond is, nor to exhaustively record experimental techniques for studying it, but to raise healthy questions in the mind of the reader. The field of hydrogen bonding tends to be clouded by preconception and prejudice about the nature, strength, occurrence, and importance of the hydrogen bond. It is hoped that, by the end of this review, the reader will not dismiss it as a weak bond of relatively marginal importance to material chemists.

2.1 What is a Hydrogen Atom?

This is not a rhetorical question, and nor are we the first to raise it. The following is quoted verbatim from a recent paper by Cotton and Luck:[4]

'There is a kind of conventional wisdom that neutron diffraction finds hydrogen atoms better than X-ray diffraction does. But is this even a meaningful statement, let alone a true one? It can be argued that it is not meaningful and thus incapable of being true. The simple facts are that neutrons and X-rays see two different parts of the hydrogen atom and that these parts do not coincide. It is then a Solomonic question whether either technique is justifiably considered to 'see' the hydrogen atom. The neutron experiment sees, with considerable accuracy (*ca.* ± 0.001 Å), the location of the hydrogen atom's *nucleus, the proton.* In a very favourable case [...], the X-ray experiment sees, with less accuracy (*ca.* ± 0.02 Å), the hydrogen atom's *electron cloud.* Which of these is '*the* hydrogen atom'? Both the nucleus and the electron density of an atom are essential parts, and it is therefore impossible to assert rationally that the position of either the one or the other is 'the' position of the atom.'

Only Cotton has the standing, insight, and gall to ask questions like this in a manuscript primarily concerned with the crystal and molecular structure of {diethylbis(1-pyrazolyl)borato)allyldicarbonylmolybdenum(II)! It is a pity that this manuscript, principally of interest to organometallic chemists, may not attract the universal readership that it deserves. The question raised is of fundamental importance, and should be considered carefully and seriously by all chemists, especially those with a

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central interest in hydrogen bonding. If there is not universal agreement about the absolute positon of a hydrogen atom in a molecule or lattice, how can serious qualitative and quantitative studies of its bonding be made? In other words, if we are not sure what we mean by a hydrogen atom, how can we enter detailed discussions and calculations on hydrogen bonding?

2.2 What is a Hydrogen Bond?

Again, this is not a rhetorical question: currently, a definitive answer does not exist. Ideas of what constitutes a hydrogen bond are in a constant state of flux. The following quotes, arranged chronologically, may illustrate the nature of the problem of producing even a simple definition:

Latimer and Rodebush (1920)[5]
'Water [...] shows tendencies both to add and give up hydrogen, which are nearly balanced. Then [...] a free pair of electrons on another water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together. [...]. Indeed the liquid may be made up of large aggregates of molecules, continually breaking up and reforming under the influence of thermal agitation. [...]. Such an explanation amounts to saying that the hydrogen nucleus held between two octets constitutes a weak 'bond'.'

Pauling (1940)[6]
'It has been recognized in recent years that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the *hydrogen bond*. It is now recognized that [...] the hydrogen bond is largely ionic in character, and is formed only between the most electronegative atoms. [...]. Although the hydrogen bond is not a strong bond (its bond energy [...] being only about 5 kcal/mole†), it has great significance in determining the properties of substances.'

Pimentel and McClellan (1960)[7]
'A hydrogen bond exists between a functional group A–H and an atom or a group of atoms B in the same or a different molecule when:
  (a) there is evidence of bond formation (association or chelation),
  (b) there is evidence that this new bond linking A–H and B specifically involves the hydrogen atom already bonded to A.'

Zeegers-Huyskens and Huyskens (1991)[8]
'Specific interactions are short-range site-bounded cohesion forces that considerably weaken a given chemical bond of one of the partners. Hydrogen bonding constitutes a particular case of specific interactions where the weakened chemical bond involves a hydrogen atom and a more electronegative one (in general O, N, S, halogens).'

Attempts at simpler explanations seem doomed to failure. The following quotation could form the basis of a critical finals examination question:

Atkins (1989)[9]
'A hydrogen bond is a link formed by a hydrogen atom lying between two strongly electronegative atoms.'

This has the seductive appeal of appearing correct at first sight, but being in error in almost every detail and at every level of understanding.

The problems of defining the hydrogen bond are manifest. All too frequently, current descriptions of hydrogen bonds include phrases which refer to them as 'involving hydrogen bonded to an electronegative atom', 'thermodynamically weak', or 'essentially ionic in nature'. As can be seen, these hark back to Pauling,[6] a definition that was insightful and visionary when proposed, but now should be viewed with the hindsight of fifty years of chemical progress: although many hydrogen bonds do

† 5 cal mol⁻¹ = 20.92 kJ mol⁻¹.

fall within Pauling's definition, it is now too restrictive, and precludes many examples of intermolecular bonding now universally accepted as hydrogen bonding (*e.g.* C–H···O). Many definitions are empirical, usually boiling down to 'a hydrogen bond exists where there is evidence that it exists'. Theoretical descriptions of the hydrogen bond are rapidly improving, but are extraordinarily sensitive to details of the basis set, and to electron-correlation effects: there is not yet general agreement as to whether, in weak hydrogen bonds, D–H···A, there is any significant electron density in the H···A bond (*i.e.* is a hydrogen bond essentially electrostatic in nature, or is there a significant covalent contribution). This review is not the correct place to extend this controversy, fascinating though it is. A detailed, multidisciplinary study of this area is greatly needed – an updated and expanded version of the seminal volumes edited by Schuster *et al.*[10] is long overdue.

Perhaps the last words in this Section should go to Samuel Butler:

'A definition is the enclosing a wilderness of idea within a wall of words.'

Notebooks (1912)

We will thus not attempt a formal definition here, but draw from the descriptions above as appropriate, recognizing that the value of the hydrogen-bond concept lies in the wilderness of idea, and not within the wall of words.

2.3 Occurrence of Hydrogen Bonds

Hydrogen bonds occur between atoms, molecules, or ions (positive or negative) in the gas, liquid, solid, or supercritical phases. Hydrogen bonds may be simple (involving only one donor and one acceptor), bifurcated (three-centre), or trifurcated (four-centre) (see Figure 1). Some hydrogen bond donors and acceptors are given in Table 1. However, there are now examples of aliphatic methylene protons acting as hydrogen bond donors,[4] and transition metals,[4] alkenes,[11] alkynes,[11] and aromatic π-clouds[12] acting as hydrogen bond acceptors. Moreover, it could be convincingly argued that even the hydrogen atom is not essential to a hydrogen bond, and that lithium could be considered to enter into multi-centred bonds which could be described, in the wilderness of idea, as 'hydrogen bonds'.[13]
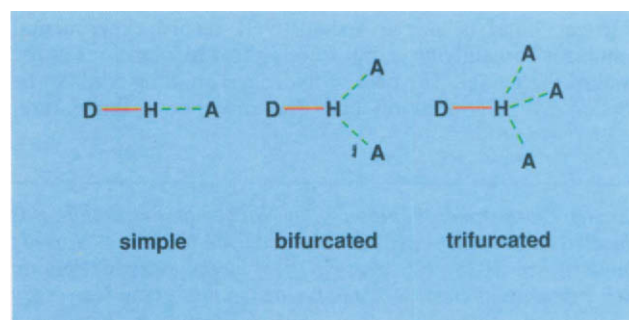

Figure 1 Common hydrogen bond arrangements: note that the simple bond is rarely linear.

2.4 Characterization and Effects of Hydrogen Bonding

Let us consider the simple, and most common, arrangement for a hydrogen bond (see Figure 1). In this description, where r(D–H) is shorter than r(H···A), the element D is referred to as a hydrogen bond donor, and the element A as a hydrogen bond acceptor. Most hydrogen-bond acceptors (see Table 1) have one feature in common: they formally possess a lone-pair of electrons in conventional formalisms. Some unusual acceptors, such as transition metals, alkenes, and aromatic π-clouds, all have centres of high electron density (an occupied d_z orbital, or the π-molecular orbitals). Similarly, the elements, D, of the hydrogen

Table I Some hydrogen bond donors and acceptors

Donors	Acceptors
C–H	C=C, C≡C, arenes
N–H	N
P–H	P
O–H	O
S–H	S
F–H	F
Cl–H	Cl
Br–H	Br
I–H	I

bond donors (or, to be more precise, the functional groups or moieties of which D is a part) have the effect of removing electron density from the hydrogen atom, leaving it with a significant partial positive charge. Note, however, that this has little to do with our outmoded ideas of electronegativity (a concept that is perhaps best left for heated tutorial debates about the validity of imprecise definitions, and about the use of terms such as 'atoms within molecules'), and a lot more to do with the overall electronic structure of the molecule of which D–H forms a part. Thus, methane does not readily form strong directional hydrogen bonds (although methane activation WILL occur via a mechanism involving initial hydrogen bond formation, when a viable system is discovered), whereas all the C–H ring protons of the imidazolium cation form three-dimensional, structure-determining hydrogen-bonded networks.[14]

Clearly, then, a hydrogen bond cannot be defined in terms of the elements which might partake in it. Nevertheless, certain elements and functional groups exhibit a higher propensity than others to form hydrogen bonds, and it is these (which were, of course, the earliest recognized and most easily detected) which formed the basis of the Pauling definition (see Section 2.2).

So, how is a hydrogen bond detected? Its nett effect, in the system D–H···A is to weaken the D–H bond (compared with D–H in an isolated system), and this is the basis of the Zeegers–Huyskens and Huyskens definition (see Section 2.2).[8] Thus, a wide ranging collection of spectroscopic, structural, and thermodynamic techniques can be used to study the nature of hydrogen bonding, the most common being IR and NMR spectroscopy, and single-crystal X-ray diffraction (see Section 3). The use of these techniques, and many others, has been extensively reviewed elsewhere.[7,8,10]

2.5 Strength of the Hydrogen Bond

The thermodynamic strength of a hydrogen bond is, as might be expected, extremely variable.[7,8,10] For neutral molecules, it normally lies in the range of 10—65 kJ mol⁻¹, being greater than that found for van der Waals interactions (< 8 kJ mol⁻¹), but weaker than conventional covalent bonds. However, when one component of the hydrogen bond is ionic, the range of bond strengths rises to 40—190 kJ mol⁻¹. In order to place the strength of a hydrogen bond in perspective, a summary of some typical σ-bond strengths is presented in Figure 2, along with some of the stronger characterized hydrogen bonds (between an ion and a neutral molecule).[8,15] It is clear that a strong hydrogen bond is energetically on a par with a weak covalent bond.

3 Hydrogen Bonding in Crystals

3.1 Philosophy

In many areas of chemistry, an X-ray single-crystal structure determination of a novel compound represents the solution to a particular problem, or the end of a specific project: the cynosure is usually the identity of the molecule itself, or some particular feature within its molecular structure. An alternative view, however, would be to treat the structural information as the beginning of a new venture, leading to questions of far reaching
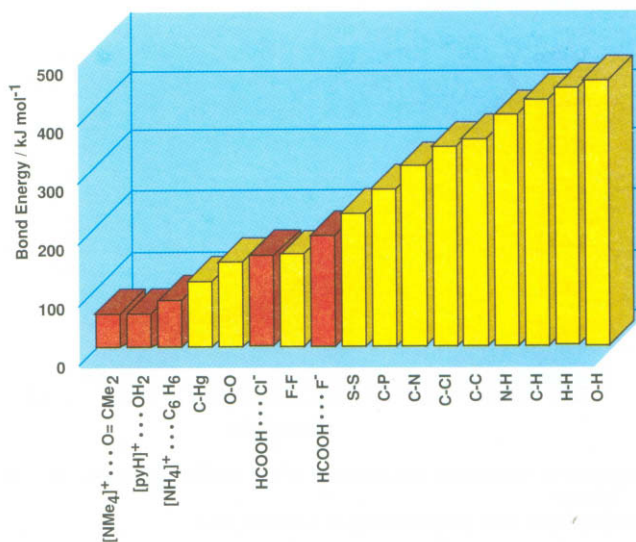
Figure 2 Bond energies for a range of common σ-bonds compared with a number of the stronger hydrogen bonds.

and fundamental importance regarding the interrelationships between molecules and ions in the solid state.

Since the crystal structure represents a situation where all the bonding and non-bonding forces are poised at an energetic minimum (not necessarily a global minimum!), it contains all the information regarding the importance of, and balance between, intermolecular forces. If this information could be extracted and deconvoluted, then prospects of designing materials with specific properties would be vastly enhanced. Consequently, it is of great importance to improve our understanding of the forces that determine the structures of crystalline materials, and single-crystal data provide a natural starting point.

3.2 Hydrogen-bond Geometry in Crystals

The existence of hydrogen bonds in solids is often detected and determined purely by applying geometric criteria.[7,16] These criteria, when based solely upon estimated van der Waals radii, are somewhat controversial,[17] and there have been several suggestions as to which radii are 'correct'.[6,18,19] Depending upon which set is chosen, certain interactions may, or may not, be regarded as 'legimate' hydrogen bonds. This is clearly not an ideal situation, but there are no better ways to discriminate between very weak hydrogen bonds and close contacts generated by lattice forces, especially since this question is difficult to answer unambiguously with current experimental techniques.

Nevertheless, several important publications containing tabulated data and statistical analyses of the known geometries of a wide range of hydrogen-bonded materials are available.[10,16] These studies, in combination with the information available in the Cambridge Structural Database,† constitute a vital base from which our understanding of solid-state hydrogen bonds can be developed.

Many surveys have correlated geometries of hydrogen bonds in the solid state with the nature and environment of the donor and acceptor groups, and some important trends have been identified.[7,10,11,16] It has been demonstrated that longer, weaker hydrogen bonds are more likely to deviate from a linear arrangement. Furthermore, it is more common for N–H···O bonds to deviate from linear arrangements than it is for O–H···O bonds, even when their bond distances are similar. In addition, the covalent D–H bond is also found to be influenced by the H···A

distance: a shorter H···A bond will lead to a longer D—H bond, as shown in Figure 3.
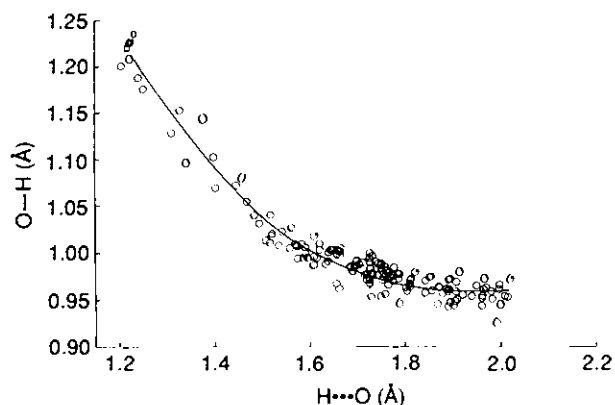

Figure 3 O—H distance as a function of H···O distance in a O—H···O system.
(Reproduced with permission from reference 10.)

In recent years, the importance, and frequency, of relatively weak interactions have been widely recognized, e.g. it has become clear that C—H···X hydrogen bonds (where X = F, O, N, Cl, Br, or I)[14,16,20] may be of significant importance to the organization of the solid-state. Situations where C—H groups are found to participate in C—H···X hydrogen bonds, are particularly common when they are found adjacent to a nitrogen atom (aliphatic or aromatic) and, hence, such hydrogen bonds may be very important in amino acid and nucleoside chemistry.

3.3 The Influence of Hydrogen Bonding on the Lattice Energy of Crystals

3.3.1 Introduction

Before the hydrogen bond can be 'employed' as a regiospecific, structure-controlling agent (i.e. as a synthetic vector), the energetic contribution made by hydrogen bonding to the lattice energy of a crystalline ionic material must be evaluated. Unless the hydrogen bond is seen to make a significant energetic contribution, the underlying assumptions about its usefulness in crystal engineering will be invalidated.

The lattice energy, U, of an ionic crystalline material, MX, is often defined as the energy change associated with the process described by equation 1.

$$MX(s) \rightarrow M^+(g) + X^-(g) \qquad (1)$$

The lattice energy of a solid is generally assumed to receive contributions from four main components: electrostatic, E_C; repulsive, E_r; dispersive, E_d; and zero-point energy, E_o, (equation 2).

$$U = -E_C + E_r - E_d + E_o \qquad (2)$$

The main dilemma with lattice energy calculations (see Section 3.3.3) results from the problems associated with the evaluation of the repulsive and the dispersive contributions. Such calculations are normally based upon extensive empirical parameterizations and, consequently, accurate lattice energy calculations require substantial effort.

3.3.2 Experimental Lattice Energies

Direct measurements of lattice energies are not feasible, but it is possible to relate the lattice energy of an ionic compound to various measurable thermodynamic quantities using a Born–Haber cycle, such as that illustrated for a Group 1 halide in Figure 4, where ΔH_{VM} and ΔH_{DX} are the enthalpies of vaporization and dissociation for the respective elements M and X, ΔH_{IE}
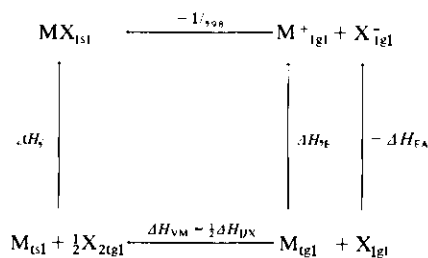

Figure 4 A typical Born–Haber cycle for a Group 1 halide.

is the ionization energy, $-\Delta H_{EA}$ is the electron affinity, ΔH_f is the enthalpy of formation of the crystalline salt, and U_{298} is the lattice energy of MX at 25 °C and 1 atm. The lattice energy at 0 K, U_o, is obtained by combining U_{298} with the appropriate heat capacity correction. Contributions arising from the heat capacities, C_v, of the species involved are normally small enough to be ignored.

It is worth noting that values for lattice energies obtained from a Born–Haber cycle are often referred to as 'experimental' data, U_{exp}, even though these data have only been deduced from the experimental values for the various steps involved in the cycle. The accuracy of 'experimental' lattice energies is therefore determined by the reliability of the available data for the enthalpies of ionization, vaporization, etc. Consequently, 'experimentally' determined lattice energies are not necessarily accurate and, in many cases, a situation exists where only simulations/calculations can give an indication of the lattice energy of a material.

3.3.3 Lattice Energy Calculations

Recent years have seen considerable interest in nonlinear optical materials, notably those capable of second harmonic generation (SHG).[21] Such materials, and the basis of their properties, have attracted both academic and commercial investigators.

The structural investigation of a series of SHG-active dihydrogenphosphate salts of organic cations[22] prompted our own interest in the role played by hydrogen bonding in the crystal structures of such salts, specifically concerning the energetic contribution made by hydrogen bonding to their lattice energies. Further, from the discussion in Section 3.3.2, it should be clear that accurate lattice energy calculations require much time and effort, and there would appear to be little point in developing separate potential models for all pair-wise interactions within these materials, if appropriate simplifications would yield an approximate value. Furthermore, since it is also impossible to assign an accurate value to the energy associated with each hydrogen bond in the solid state, the quality of the comparison will always be limited by estimates of hydrogen bond strengths. Hence, to a first approximation, it was assumed that in these ionic materials, the electrostatic forces would dominate, and the dispersive and repulsive forces would be of equal magnitude and, hence, would cancel each other. This approximation simplifies the lattice energy calculation significantly, as it has now been reduced to an Ewald summation of point charges. In the Ewald method, each point charge is replaced by a Gaussian charge distribution at the appropriate lattice site, resulting in a smoothly varying charge distribution, which leads to a quickly converging series. As the charge of an ion is a periodic function throughout the lattice, the Coulombic potential can be evaluated using a Fourier transformation of the charge.

A justification for the approximations adopted in this approach was provided by calculating the lattice energy, U_{cal}, for two salts with experimentally determined lattice energies, $[NH_4]_2[SnCl_6]$ and $[NH_4]_2[ReCl_6]$: the results are presented in Table 2, and justify the approximation that the dispersive and repulsive forces cancel. This approach has also been validated by extensive work carried out by Lubkowski et al. on a range of halide salts of mononitrogen bases.[23]

Table 2 Lattice energies (kJ mol^{-1}) and atomic charges for [NH$_4$]$_2$[MCl$_6$]^a

M	$z_{Cl}{}^b$	$z_H{}'$	U_{Cal}	U_{exp}	ΔU^d
Sn	−0.66	0.35	1329	1334	+0.4%
Re	−0.56	0.35	1397	1390	−0.5%

^{a} Energy terms are defined in the main text. ^{b} z_{Cl} = atomic charge on chloride (H. D. B. Jenkins and K. F. Pratt, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 1). ^{c} z_H = atomic charge on hydrogen (A. Pullman and A. M. Armbruster, *Int. J. Quam. Chem. Symp.*, 1974, **8S**, 69). ^{d} $\Delta U = 100(U_{xp} - U_{al})/U_{xp}$.

3.3.4 Lattice Energies of Organic Dihydrogenphosphates

As the organic salts of dihydrogenphosphate consist of structurally complex ions without either a symmetrical, or a centralized, charge distribution, it was necessary to perform *ab initio* calculations on the participating ions in order to obtain the desired information; charges obtained with the STO-3G basis set were used in these lattice energy calculations.[24]

Following the method outlined in Section 3.3.3, the lattice energies of a series of organic dihydrogenphosphate salts were calculated and compared with the strength of the hydrogen bonds present in each structure (Table 3).[24]

Table 3 Minimum calculated hydrogen bond contributions (kJ mol^{-1}) to the total lattice energy of four dihydrogenphosphate salts, [AH][H$_2$PO$_4$]

A	$U_{Cal}{}^a$	$E_{HB}{}^b$	$U_{tot}{}^c$	$\delta_{HB}{}^d$
Piperidine	500	130	630	21%
3-hydroxypyridine	545	135	680	20%
3-hydroxy-6-methylpyridine	410	135	545	25%
4-hydroxypyridine	515	135	650	21%

^{a} Calculated lattice energy. ^{b} Hydrogen bond energy. ^{c} Total lattice energy, $U_{ca} + E_{HB}$. ^{d} $100(E_{HB}/U_{tot})$.

Based upon extensive experimental and theoretical data,[25] each O−H⋯O interaction was assigned an energy content of 35 kJ mol^{-1}, and each N−H⋯O interaction was assigned a value of 30 kJ mol^{-1} (both values are significantly lower – by a factor of two - than those found experimentally and theoretically for ionic hydrogen bonds of this type). By adding these values for each structure to give a total hydrogen bond energy, E_{HB}, depending upon the number of hydrogen bonds, and comparing this with the total lattice energy, an estimate of the minimum contribution made by hydrogen bonding is obtained (Table 3).

It should be pointed out that some of the hydrogen bond energy (*i.e.* the electrostatic part) has, in reality, already been included in the calculated lattice energy, U_{cal}. Hence, an incorrect value (i.e. too large) for the total lattice energy U_{tot} will be the result if U_{cal} and E_{HB} are simply added together. As no attempt has been made to estimate the relative magnitude of the electrostatic part of the hydrogen bond energy, it is not possible to obtain an accurate value for the contribution made by hydrogen bonding to the total lattice energy. However, the minimum level of contribution can be estimated.

The results displayed in Table 3 show that hydrogen bonding provides a notable energetic contribution, 20—25%, to the total lattice energy of dihydrogenphosphates of organic cations. It is also likely that the true values are significantly higher than that, given the significant underestimation of E_{HB}, and the overestimation of U_{tot}. Consequently, hydrogen bonding *can* act as a regiospecific, controlling and directing, structural tool in the crystal engineering of ionic and molecular solids.

3.4 Effects of Hydrogen Bonding on Charge Density

The fundamental nature of chemical bonding and molecular structure is determined by the electron density distribution in the

system. Information regarding this feature can be made available through quantum mechanical calculations, but it can also be observed experimentally using high-intensity X-ray diffraction measurements.[26] By combining such experiments with neutron diffraction data, it is possible to gain added insight into the redistribution of electron density that occurs upon bond formation, including hydrogen bonding.[27] Such X-N maps, based upon structure factor amplitudes and thermal parameters from neutron data, can furnish information about the deviation of electron density around the nuclei from spherical symmetry.

Electron-density distribution studies of hydrogen-bonded complexes can be divided into two groups, (a) those involving weak or moderately strong hydrogen bonds, and (b) those containing strong hydrogen bonds. This division is made because of the presence of some distinctly different features within the two groups.

The observable changes in electron distribution that take place in materials with weak, or moderately strong, hydrogen bonds are close to the limit of current experimental techniques, but many studies have obtained a good agreement between X-N maps and theoretical deformation maps, both showing the general features of such hydrogen bonded systems. These features are, commonly, a build up of electron density in the D−H bond, and in a space close to the acceptor atom in the H⋯A interaction, which is accompanied by a decrease in the electron density closer to the hydrogen atom in the D−H⋯A bond,[28] see Figure 5.
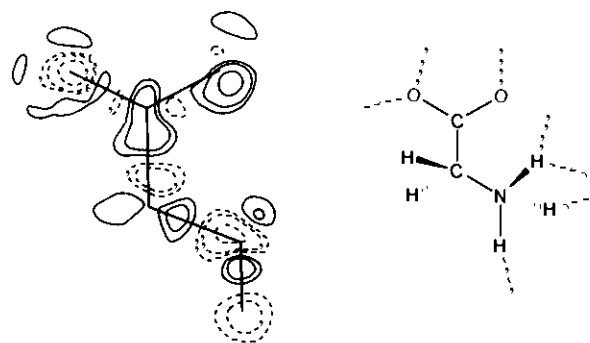
Figure 5 The difference density map for glycine, between a molecule in the crystal field and a free molecule. A schematic (right) shows the hydrogen-bond pattern.
(Reproduced with permission from reference 28.)

However, the same features can be obtained, qualitatively, by superimposing deformation maps of the isolated, unperturbed molecules in the system. Consequently, a weak or moderately strong hydrogen bond can be represented by a simple electrostatic model, since contributions from charge transfer and exchange repulsion effects are significantly smaller and tend to cancel each other. The accuracy of this description is also supported by the fact that the strength of these hydrogen bonds (the total hydrogen bond energy) correlates well with the electrostatic energy of the interaction. Detailed theoretical calculations have indicated, though, that some electron migration does take place as a second-order effect.[26b]

The situation regarding strong hydrogen bonds [most studies have been performed on systems with short O−H⋯O bonds, with r(O⋯O) in the range of 0.24—0.25 nm], however, is more complex. Normally, the charge distribution is more symmetrically arranged around the centre of the hydrogen bond and there is less charge build up both in the O−H bond and in the H⋯O region, see Figure 6.[29] It also becomes much more difficult to separate contributions from various components, *e.g.* polarization *vs.* charge-transfer effects, as well as trying to partition the electron distribution arising from the different molecules/ions in the complex.

Another question regarding electron distribution and hydrogen bonding, which has attracted much attention, concerns the role played by the lone-pair as a hydrogen-bond acceptor. Both
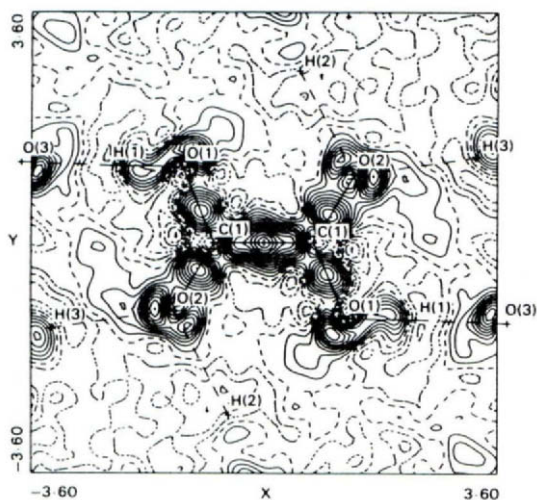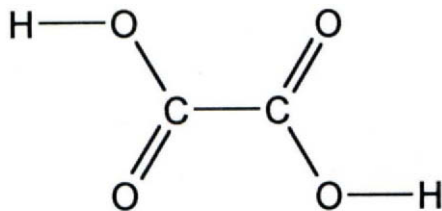
Figure 6 The experimental deformation density for α-$C_2O_4H_2$ $2H_2O$ in the plane of the oxalic acid molecule (schematic top)
(Reproduced with permission from reference 29)

theoretical and experimental studies have been carried out in order to clarify the stereoelectronic effect caused by lone-pair regions around acceptor atoms in hydrogen-bond interactions, and the main issue has been whether, or not, it is possible always to view a lone-pair as the distinct acceptor of a hydrogen bond

Theoretical studies of the electron density around $C=O$ groups normally reveal a double maximum of electron density corresponding to the lone-pair regions, although it should be pointed out that because of the very nature of these deformation-density calculations, only the difference between the molecular electron density and the superpositioning of spherical densities is evaluated, not an absolute location of excess electron density due to a specific orbital

Attempted correlations of solid-state bond angles and lone-pair directionality have not been completely conclusive [10][16] An extensive study of neutron-diffraction data of $C=O\cdots H$ angles found an accumulation of data around 120°, albeit with several large variations Other studies have also highlighted the importance of correlating such data with steric factors, which may otherwise bias the existing data On the whole, however, double bonded oxygen atoms in certain groups, $-C(O)OH$ and $-C(O)O^-$, appear to favour a hydrogen bond approach at an angle of 120°

In contrast, theoretical investigations of the water molecule and hydroxy groups normally only reveal one broad electron-density maximum, and a study of a large number of crystalline ROH compounds[30] found a tendency for the acceptor atom to occupy a position in the plane of the lone-pairs, although there was no accumulation of acceptor atoms in the tetrahedral direction within the plane

Overall, there is no absolute correlation between lone-pair regions and acceptor angles and, hence, it would seem somewhat simplistic to view the 'classical' lone-pairs as specific receivers of hydrogen bonds Instead, it is probably more fruitful, albeit more complex, to investigate both steric factors and the whole electrostatic potential energy surface, in order to elucidate the preferred approach for a hydrogen-bond donor

4 Crystal Engineering

4.1 Rationale

Within the fields of supramolecular chemistry, molecular recognition, and crystal engineering, it has been recognized that hydrogen bonding is an indispensable tool for designing molecular aggregates [1][31]

It is our firm belief that an improved understanding of hydrogen bonding in general, and hydrogen bonds in ionic solids in particular, can strengthen our awareness of the tools with which we may be able to 'persuade' molecules and ions to form specific aggregate structural units Since the properties of a solid are critically dependent upon its structure, it is feasible to design materials with desired characteristics by incorporating specific properties into the subunits There are clearly numerous diverse areas where such an approach could be very fruitful, e g studies of biomolecular substrate binding and recognition, reactivity and catalysis, development of improved detergents, the petrochemical industry, and the synthesis of novel nonlinear optical and ferroelectric materials

4.2 Pattern Recognition

Probably the most well known, and most easily identifiable, hydrogen-bonded aggregate is a monocarboxylic acid dimer (Figure 7) Several groups have carried out extensive studies of solid-state structures of a wide range of related molecular and ionic solids, and these studies have led to the realization that hydrogen-bond aggregation is not random patterns do exist Certain functional groups, and ions, display a clear pattern preference, and this insight will have important consequences for the development of crystal engineering If certain molecular building blocks tend to crystallize in specific, energetically favourable, arrangements, then molecules containing these blocks can be encouraged to form aggregates with specific structural features
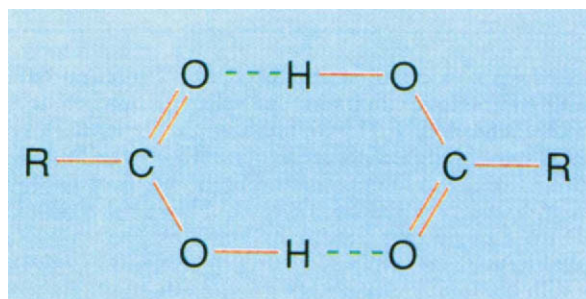

Figure 7 The common hydrogen-bonded dimeric form of a carboxylic acid

Lehn and co-workers have studied, inter alia, macromolecular recognition involving cryptands and other macrocyclics, interactions between phosphates and carboxylates with polyammonium macrocyclics, the formation of helical metal complexes of bipyridine strands, and supramolecular liquid crystalline polymers [1] Other groups have investigated molecular tweezers, organometallics, and small organic molecules as subunits of extended structures [32] Although all of these studies fall into the broad categories of molecular recognition or crystal engineering, the discussion in the remainder of this review will be focused upon relatively small organic/inorganic systems in the absence of preorganized, custom-designed cavities Such systems are more amenable to an examination and evaluation of hydrogen-bond selectivity, preference, and topology, without an a priori directional bias

The most extensive studies of organic hydrogen-bonded solid-state structures have been carried out by Etter and co-workers [33] Their work has identified the pattern preference displayed by a range of functional groups and molecular types, e g amides, diaryl ureas, imides, nitroanilines, and 2-aminopyrimidines A

detailed description of some of these patterns will be found in Section 4.3.2. As a result of this work, a method for describing hydrogen-bond patterns has been developed, in addition to several general rules (guide-lines) regarding expected hydrogen-bond organization in organic solid-state structures.[3]

Ionic compounds, both inorganic–organic salts and pure organic salts, have also been studied recently. A series of organic salts with the dihydrogenphosphate anion, $[H_2PO_4]^-$, displayed certain specific, reoccurring, arrangements of the anionic network; the anions were lined together by short, strong hydrogen bonds into specific chains (Figure 8), sheets, or three-dimensional infinite arrangements.[22] It is likely that the character of the cation, and the nature of its hydrogen-bond interactions with the anionic matrix, will discriminate between the three possible structures. Similarly, a structural study of organic salts of hydrogen-L-tartrates[34] showed that the anionic network was remarkably consistent, regardless of the nature of the cation. The strongly hydrogen-bonded sheet of anions created a matrix, see Figure 9, which dominated the structure and only allowed limited flexibility regarding the positioning and packing of the cations.[34]

The presence of rigid, frequently occurring, hydrogen-bonded aggregate structures in both molecular and ionic compounds, creates a necessary platform for intermolecular synthesis. By identifying, classifying, and rationalizing such networks, it may be possible to utilize them as active design tools in the crystal engineering of novel materials with specific structural features.

4.3 Encoding Hydrogen-bonded Networks

4.3.1 Pattern Designation

Once it has been established, via crystallographic data, that there are several different hydrogen bonds within a material, how can this information be translated into a form, or code, which allows for the classification and recognition of hydrogen-bond interac-

Figure 8 Chains of dihydrogenphosphate anions within the crystal structure of the piperidinium dihydrogenphosphate.[22] Covalent bonds, red; hydrogen bonds, yellow and green.
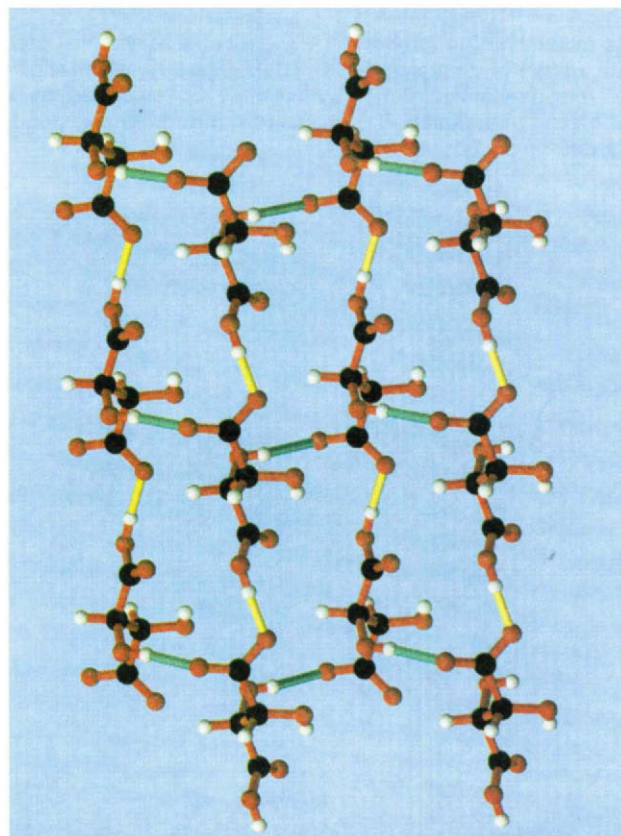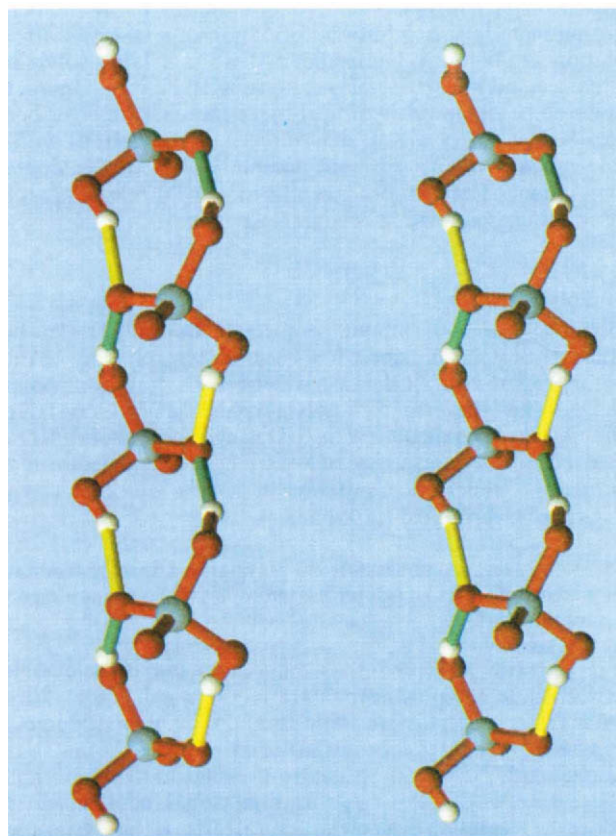

Figure 9 A two-dimensional sheet of hydrogen-L-tartrate anions, as found in piperazinium(2+) bis-hydrogen-L-tartrate.[34] Covalent bonds, red; hydrogen bonds, yellow and green.

tions as aggregate structures? Furthermore, how can this information be communicated in a precise fashion? Clearly, in order to achieve this objective, it is essential to find a way of describing even complex hydrogen-bond patterns in a simple, yet comprehensive, language.

The most successful method for encoding hydrogen-bond patterns of organic solids has been developed by Margaret Etter and co-workers,[3] who have demonstrated that, by analysing hydrogen-bond interactions in organic molecular solids in a systematic and consistent fashion, it is possible to establish the pattern-preference displayed by many functional groups. The methodology, loosely based upon graph-theory, adopts a topological approach to analysing hydrogen-bond patterns, but instead of viewing molecules as points and hydrogen bonds as lines, chemical structure and functionality have been retained.

A graph set is specified using the pattern designator (G), its degree (n) and the number of donors (d) and acceptors (a):

$$G_d^a(n)$$

G, the descriptor referring to the pattern of hydrogen bonding, can be either S (for intramolecular bonds), C (for infinite chains), R (for intermolecular rings), or D (for non-cyclic dimers and other finite structures), and the parameter n refers to the number of atoms in a ring, or the repeat unit of a chain. Graph sets are assigned initially to motifs (hydrogen-bond patterns constructed by only one type of hydrogen bond), and then to higher-level networks (combinations of the relevant motifs). Thus, if the compound contains four different hydrogen bond types, then the first-level graph set, N_1, is a sequential listing of these four motifs. Higher-level graph sets are assigned to networks generated by combinations of different hydrogen bond types (e.g. the second-level graph set is created by combinations of two hydrogen-bond types, the third-level set by, combinations of three etc.).

4.3.2 Encoding in Practice

The method outlined in Section 4.3.1 will now be demonstrated with a series of examples, illustrated in Figure 10, which shows the four fundamental motifs that may be generated by a hydrogen bond; dimers (D), chains (C), intramolecular bonds (S), and rings (R).
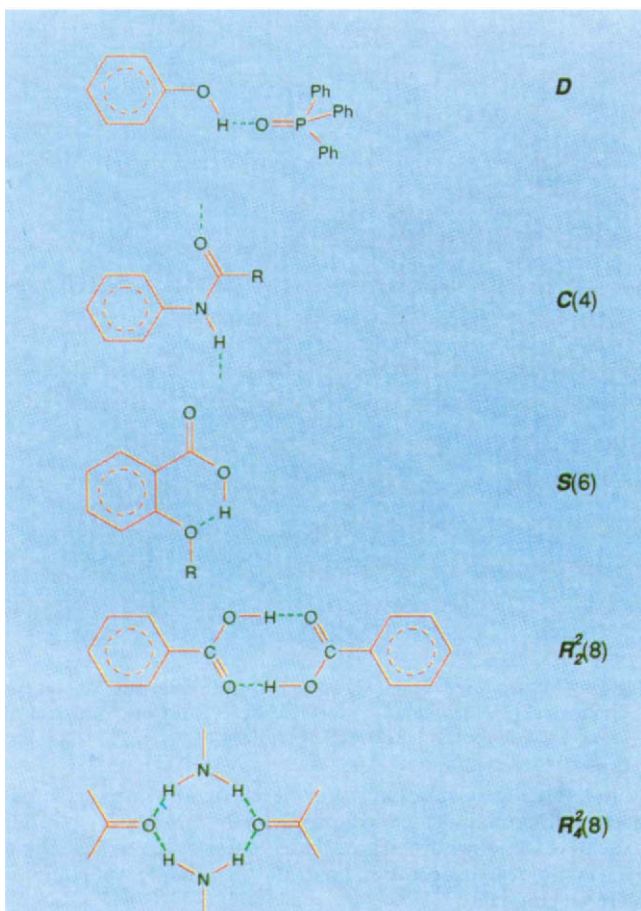
Figure 10 Some examples of assigning graph sets to simple hydrogen-bonded systems.[3]

Figure 11 Some examples of assigning graph sets to more complex hydrogen-bonded systems.[5]

Examples of higher-level graphs sets are presented in Figure 11, where several hydrogen bonds are combined to form specific patterns. The compounds depicted in Figure 11 each contain two unique hydrogen bonds and, therefore, their first-level graph sets, N_1, contain two motifs. The second-level graph sets, N_2, describe patterns that are created by combining the unique hydrogen bonds within each structure.

By applying this procedure in a systematic fashion, it is possible to characterize and recognize patterns that appear within crystals containing fundamentally different, as well as closely related, molecules. By correlating pattern preference with functional groups or molecular types, certain specific aggregate structures may be induced to form, and may be incorporated into a material by the introduction of a specific functionality.

This encoding technique has also been employed in the analysis of closely related hydrogen-bond networks in poly-morphs,[35] where subtle differences in various hydrogen-bond arrangements can be very difficult to detect and describe. Furthermore, the realization that specific hydrogen-bonded aggregates occur very frequently should also influence the way in which we investigate and approach topics like protein recognition and nucleation processes, as the 'active' species involved in such interactions may be hydrogen-bonded aggregates, and not isolated molecules or ions.
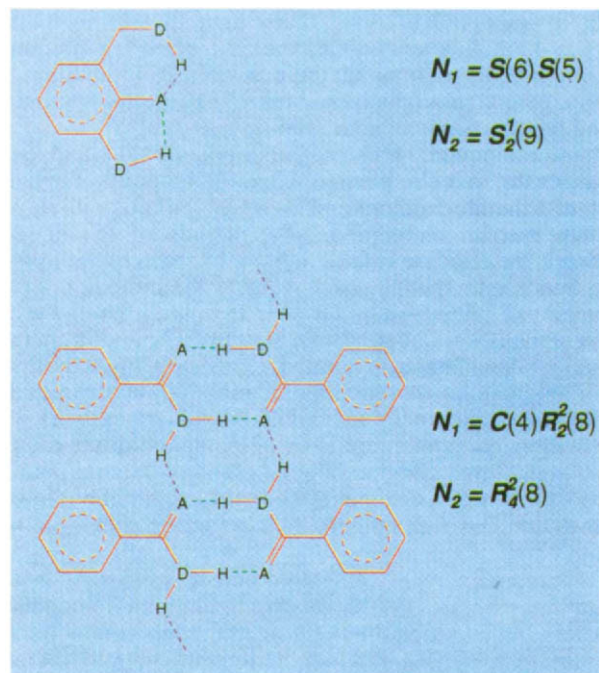
4.3.3 Hydrogen-bond Directed Co-crystallization

Etter and co-workers have employed co-crystallization techniques extensively, in order to identify competition in hydrogen-bond accepting/donating capability between different molecular types and functional groups.[3]

The co-crystals were prepared not only by traditional methods (involving evaporation of a solution containing two, or more, components), but also by grinding the starting materials together in the solid-state. A prerequisite for the formation of co-crystals is that the heteromeric species, the co-crystal, contains stronger hydrogen-bonds than either of the homomeric starting materials. In addition, formation of a co-crystal from solution is obviously hampered if there is a large solubility differences between the various starting materials. Figure 12 shows some common hydrogen-bond motifs that have been identified in co-crystals of diarylurea derivatives (top) with a wide range of hydrogen-bond acceptors (e.g. triphenylphosphine oxide).[3] Each pattern is identified with the relevant graph-set notation, described in Section 4.3.1.

4.4 Polymorphism

Polymorphism is a unique feature of the solid-state, but although this phenomenon has been known for more than a century, surprisingly little use has been made of it in solid-state studies. The true extent of polymorphism among crystalline materials is very difficult to gauge. However, as it has been more often encountered in areas of research where structure is of paramount importance, we are in strong agreement with McCrone[36] who stated (in 1965):

'[...] every compound has different polymorphic forms [...] and the number of forms known for a given compound is proportional to the time spent in research on that compound.'

It is generally accepted that differences in lattice energies between different polymorphs are in the region of 5—20 kJ mol⁻¹, and, especially for ionic compounds, these differences are small compared to the total lattice energies of such materials. Consequently, it would be fair to assume that, for example, different methods of recrystallization would be sufficient to induce the formation of a new structural form. If this is true, then
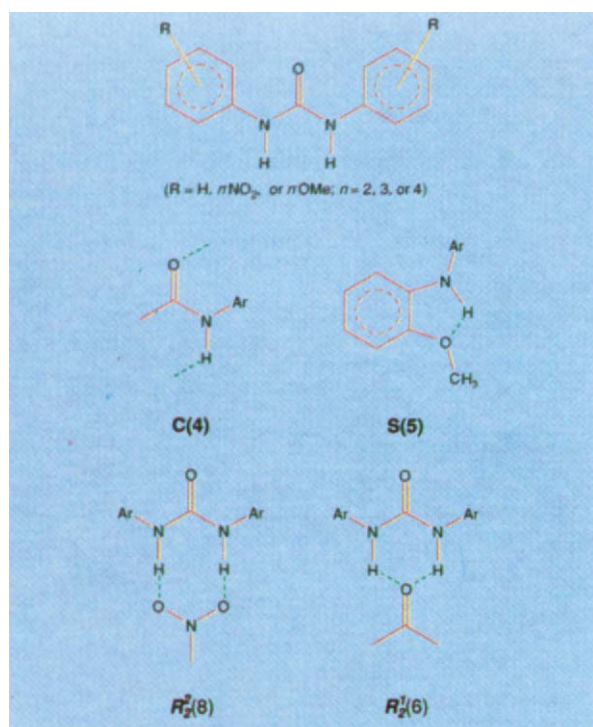
Figure 12 Some common hydrogen-bond patterns found in diaryl urea crystals and co-crystals.[55c]

4.5 Design of Crystals with Specific Structural Features and Properties

Although we are still a long way away from being able to predict the precise structure of an unknown material, several imaginative efforts have been made at utilizing hydrogen bonding as a means of creating specific structural features.

Wuest and co-workers[37] have utilized the well known cyclic dimeric motif of lactams, cf. 2-pyridones, in combination with rigid spacers, in order to create new extended structural motifs (Figure 13). Ureylendicarboxylic acids have been employed by Fowler and co-workers[32c] as building blocks for several infinite two-dimensional hydrogen-bonded layer structures. Whitesides and co-workers[38] have synthesized co-crystals of melamin derivatives and barbituric acids which contain extended hydrogen-bonded 'tapes'.
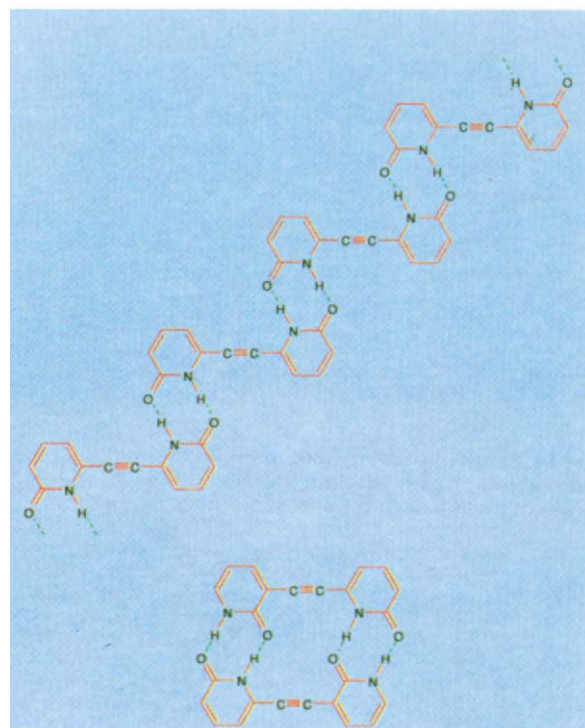

Figure 13 Novel structural motifs generated by isomeric derivatives of 2-pyridone.[37]

the whole process of identifying and classifying a material, based upon a single-crystal study, may, on its own, be less than satisfactory. When selecting individual crystals for structure determination, it is not necessarily true that the chosen crystals are representative of the structure of the bulk material. In fact, normally, the 'best' crystal is chosen – by definition, that must be atypical of the majority of the material. It would therefore seem critical always to compare the structure of the single-crystal with that of the bulk material, obtainable from powder diffraction. By simulating a diffraction pattern from the single-crystal data, and comparing that with the powder pattern recorded experimentally on the bulk sample, it is very easy to make an assessment as to the structural purity of, and agreement between, single-crystal and bulk material. We strongly believe that this procedure should be carried out routinely, in parallel with single-crystal structure determinations. The question of structural purity is, in many areas of chemistry, as important as that of chemical purity.

Polymorphic systems provide excellent opportunities to study specific chemical entities in different crystalline environments. Hence, information about the interplay between ionic or molecular geometry, and intermolecular and crystalline forces, may be extracted from such studies, e.g. the lattice energies of the observed structures can be calculated and evaluated against DSC measurements, the energy differences between observed ionic conformations can be estimated, and an analysis of the results may be correlated to a partitioning of the lattice energies into its individual atomic contributions.

A careful investigation of closely related polymorphic salts facilitates a comparison between the relative differences displayed by measurable thermodynamic quantities (obtainable from DSC techniques), and trends displayed by theoretically determined lattice energies. In this case, experimental and theoretical chemistry are combined into a very powerful probe of intermolecular interactions. Such an approach will also highlight the relative effects and importance of different ionic, or molecular, subunits, on the overall crystalline arrangement of each material.
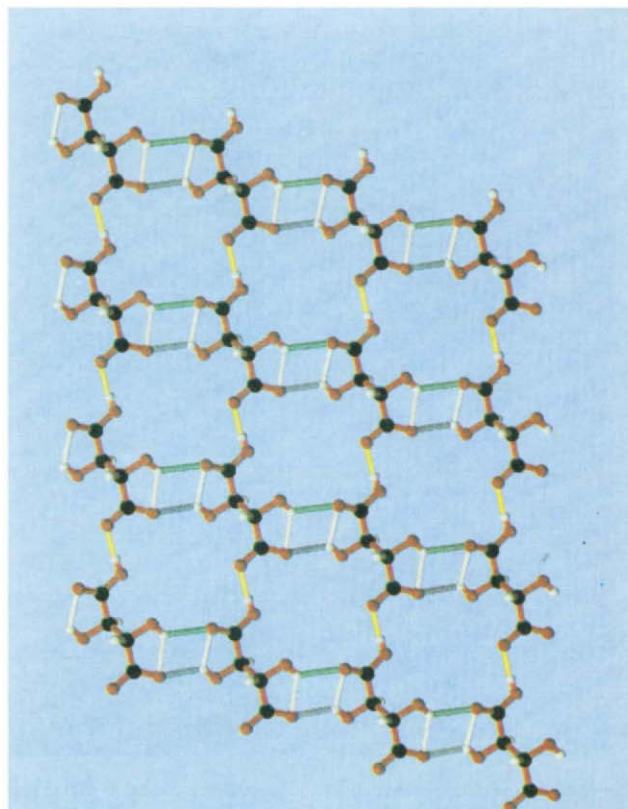
Our own work has focused on the preparation of salts with predictable structural features, and recent efforts include the use of infinite sheets of hydrogentartrate[34] anions as a means of imposing structural consistency within a series of non-linear optical salts (Figure 14 and Figure 15).

Furthermore, in an attempt to produce transparent, colourless, non-centrosymmetric crystals (a non-centrosymmetric medium is an absolute condition for certain non-linear optical effects) with a needle-like morphology (a condition required for the successful incorporation into thermally aligned polymer films),[39] 3- and 4-hydroxybenzoic acids were treated with a chiral amine, (S)-1-phenylethylamine, to produce crystals with the desired properties.[40] It was assumed that the anions would create infinite chains by a head-to-tail hydrogen bond, and that this aggregate structure would manifest itself macroscopically as needle-like crystals. Single-crystal studies of these two materials, both of which had a needle-like habit, revealed the presence of infinite chains of anions (Figure 16 and Figure 17), and, in the case of 1-phenylethylammonium 4-hydroxybenzoate, the direction of the infinite chain coincided with the long-axis of the needle.[40]

Further studies are also needed in order to identify correlations between microscopic structure and macroscopic appearance. Will the regions of strong hydrogen-bonds or the hydro-
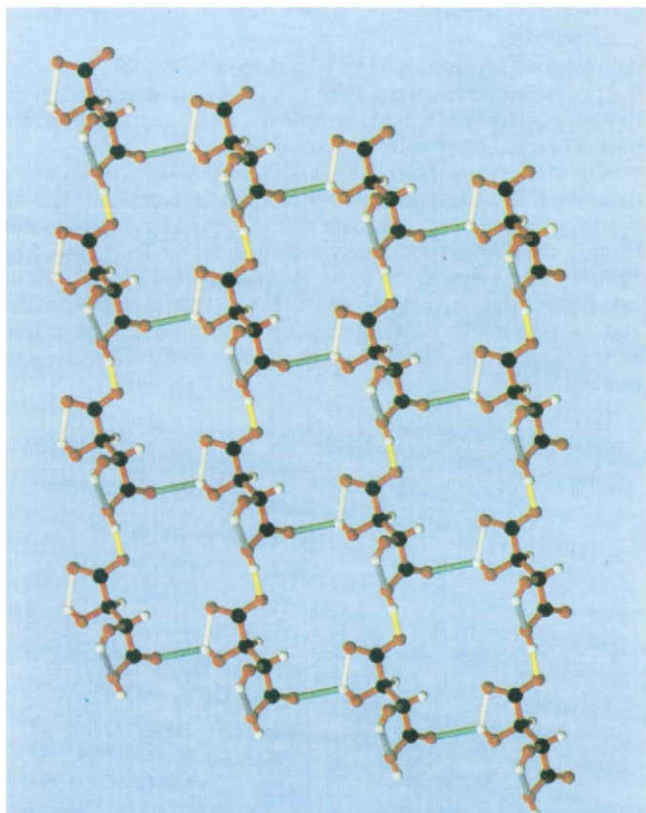
Figure 14 The two-dimensional sheet formed by the hydrogen-L-tartare anion in its (S)-1-phenylethylammonium salt.[34] Covalent bonds, red; hydrogen bonds, yellow, green, grey, and white.

Figure 15 The two-dimensional sheet formed by the hydrogen-*meso*-tartrate anion in its (S)-1-phenylethylammonium salt.[34] Covalent bonds, red; hydrogen bonds, yellow, green, grey, and white.
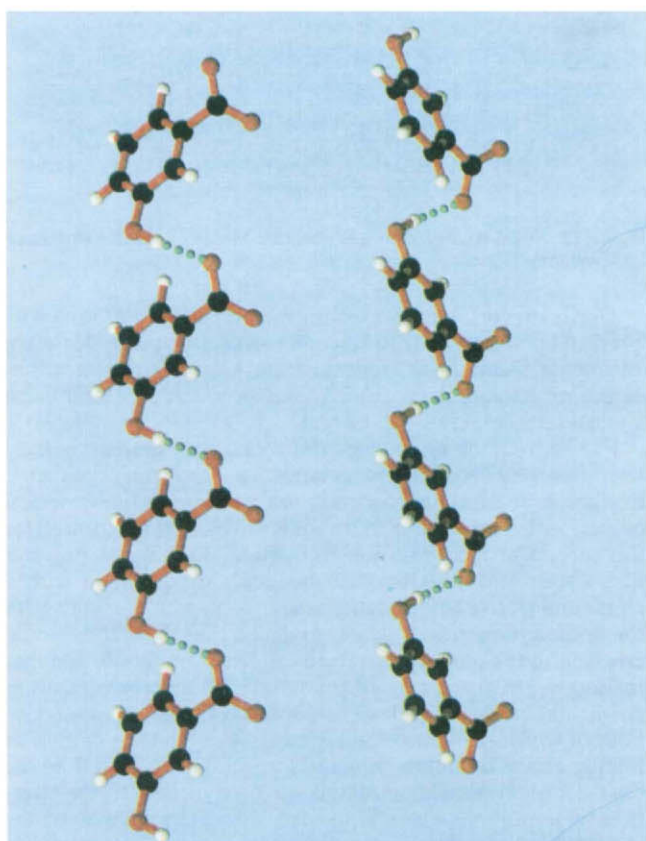
Figure 16 Infinite chains of anions, parallel to the *a* axis, in (S)-1-phenylethylammonium 3-hydroxybenzoate, viewed down *b*.[40] Hydrogen bonds indicated by dotted lines.
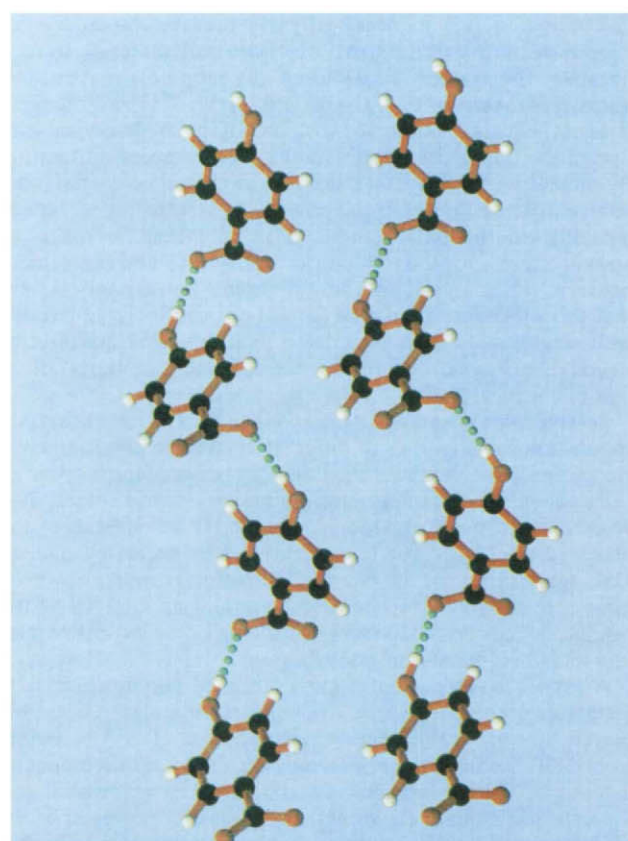
Figure 17 Infinite chains of anions, parallel to the *b* axis, in (S)-1-phenylethylammonium 4-hydroxybenzoate, viewed down *c*.[40] Hydrogen bonds indicated by dotted lines.

phobic regions crystallize more quickly upon precipitation from aqueous solvent? Answers to such questions are also likely to cast more light on the path towards successful crystal engineering

5 The Future

The last five years have witnessed a significantly increased awareness of the importance of being able to understand and rationalize the effects of hydrogen bonding on the solid state As a consequence, several groups, worldwide, have made very important and useful contributions to the field of crystal engineering by employing hydrogen bonds as active design elements in the synthesis of novel materials and extended aggregates In the past few years, Zyss and co-workers have developed an independent parallel approach to the design of novel materials for non-linear optics, of combining organic cations (to carry the high optical polarizability) with hydrogen-bonding inorganic (or organic) anions (to provide thermal and structural stability), similar to that which we proposed in 1989 [22] The resulting crystalline salt, 2-amino-5-nitropyridinium dihydrogenphosphate, shows significant SHG-activity [41]

Clearly, because of the potential impact that crystal engineering may have on a range of areas with significant commercial interests, we are likely to see substantial advances being made, both theoretical and practical, during the next few years Control of crystalline structure is an ambitious, but achievable, target, and the next decade promises to be extremely exciting

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