Complementary hydrogen bonding in diamides: a study on the influence of remote substituents using density functional theory

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Density functional calculations using gradient corrected functionals have been used to explore the factors which determine the strength of the intermolecular interaction in cyclic systems formed by complementary hydrogen bonding between amides. Optimised structures and interaction energies are presented for the simplest amide dimer, diformamide, and the results are compared with experimental and *ab initio* results available in the literature. Full optimisations are also performed on hydrogen bonded molecular pairs formed from the *N*-substituted derivatives of formamide, *N*-methylformamide (NMF) and *N*-formylformamide (NFF). The total interaction energy is found to decrease in the order NMF•NMF > NFF•NMF > NFF•NFF, the difference between successive pairs being approximately 10 kJ mol^{-1} in each case. The origin of this trend is traced to electrostatic repulsions between the spectator carbonyl groups in NFF and the carbonyl groups involved in the cyclic hydrogen bonded array.

The importance of hydrogen bonding in determining the three dimensional structures of biological molecules has long been recognised.[1] More recently, the stabilising effect of complementary hydrogen bonding networks has been used as a design principle in the rapidly expanding fields of supramolecular chemistry and molecular recognition.[2-4] The doubly hydrogen bonded diamide linkage is a particularly common structural motif in biological and supramolecular systems and has received considerable attention from experimentalists and theoreticians alike. Recent studies have shown that the strength of the interaction between the amide monomers is strongly dependent on the nature of groups external to the cyclic hydrogen bonded array. For example, self-association constants for imides (Fig. 1) are generally found to be significantly lower than those for the corresponding dilactams, with mixed imide•lactam complexes intermediate between the two.[5-7] In this paper, the electronic origins of this trend are elucidated with the aid of molecular orbital calculations.

Attempts to provide an adequate description of hydrogen bonding within a theoretical framework have been limited by the high level of theory required to calculate accurately such weak interactions. Within the *ab initio* methodology, an adequate description of hydrogen bonding requires both extended basis sets and an explicit treatment of electron correlation,[8] a combination of which makes treatment of large molecules prohibitively expensive. As a consequence, the majority of work on diamides has centred on the simplest possible example, the formamide dimer, $(NH_2CHO)_2$ [Fig. 2(*a*)].[9-11] To our knowledge, the only systematic study of the effects of remote substituents on the hydrogen bonded array has been performed using model potentials in a Monte Carlo-type simulation.[12] In addition to being computationally demanding, these calculations are dependent on the generation of an adequate model potential. It would clearly be desirable to identify a first principles methodology capable of describing the hydrogen bonding in relatively large systems and at a reasonable computational cost. This latter point is particularly important since many of the hydrogen bonded systems under investigation in our laboratory contain many atoms, including transition metals.

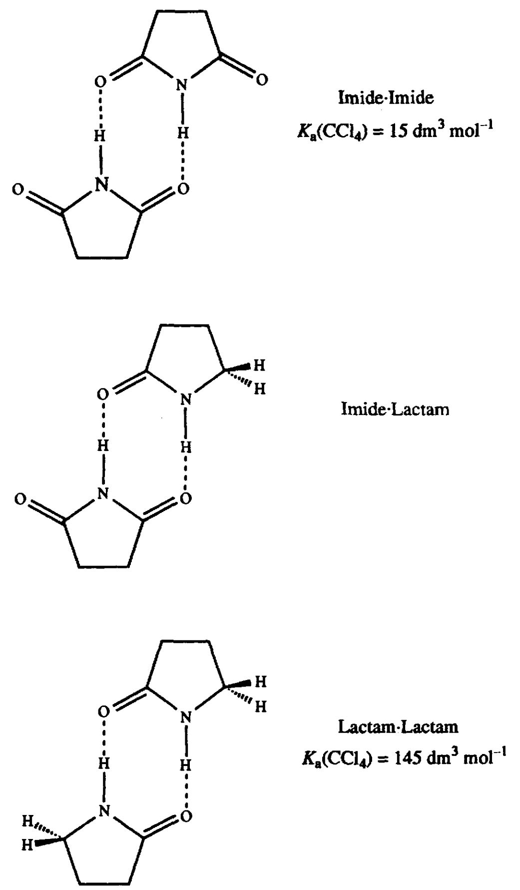
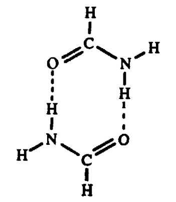
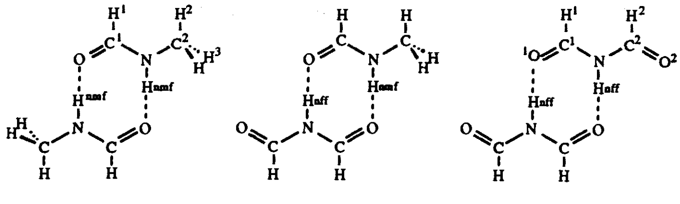


Fig. 1 Diimide, dilactam and mixed imide•lactam molecular pairs. Associations constants are taken from refs. 5 and 6.

Recent advances in density functional theory (DFT) have made possible the inclusion of electron correlation at a substantially lower cost than in traditional *ab initio* methods and several groups have shown that DFT, using gradient corrected functionals, can give estimates of hydrogen bond energies and



(a) Diformamide



(b) NMF:NMF (c) NFF:NMF (b) NFF:NFF

Fig. 2 Cyclic hydrogen bonded structures of (*a*) the formamide dimer, (*b*) the *N*-methylformamide dimer, (*c*) the mixed *N*-methylformamide·*N*-formylformamide molecular pair and (*d*) the *N*-formylformamide dimer

bond distances of comparable quality to correlated *ab initio* techniques.[13–16] In this contribution, we aim to illustrate the application of the relatively new DFT methodology to the study of the larger molecules of importance in the supramolecular field. The results of test calculations on the formamide dimer are reported, exploring the influence of both basis set size and gradient corrections to the density functional on the calculated properties of the hydrogen bonded array. The results are also compared with *ab initio*[16] and X-ray crystallographic[17] studies reported in the literature. Having established a satisfactory level of theory, we then examine the influence of remote substituents on the hydrogen bonded network. Two model monomeric fragments are derived from formamide by replacement of a proton by either a formyl (CHO) or a methyl (CH_3) group, giving *N*-formylformamide (NFF) and *N*-methylformamide (NMF), respectively. These two molecules are the smallest model systems which exhibit the essential structural features of the imide and lactam monomers shown in Fig. 1.

Computational details

All calculations described in this paper were performed using the Amsterdam Density Functional package (ADF 1.1.4).[18] The local density approximation (LDA) was employed in the parametrisation of Vosko *et al.*,[19] along with the gradient corrections to exchange (Becke)[20] and correlation (Perdew)[21] functionals. Basis sets of Slater-type functions were used, either of double zeta quality with a single polarisation function on each atom (DZP), or of triple zeta quality, with two polarisation functions (TZ2P). Geometry optimisations were performed in C_{2v}, C_{2h} or C_s symmetry.

Hydrogen bond energies were calculated in two ways. In the ΔSCF method, the total energies of the dimer and component monomers were calculated relative to those of their constituent atoms. The hydrogen bond energy was then obtained from the expression $E(\text{H-bond}) = E_{\text{dimer}} - \Sigma E_{\text{monomers}}$, corrected for the basis set superposition error using the counterpoise method of Boys and Bernardi.[22] In the alternative 'fragment' approach, the self-consistent molecular orbitals of the monomeric fragments, rather than those of the individual atoms, were used as a basis for the supermolecular calculation. In both the ΔSCF and fragment approaches, the total energy was decomposed according to the transition state approximation of Ziegler and Rauk [eqn. (1)].[23] ΔE_{el} represents the electrostatic interaction

$$\Delta E_{\text{tot}} = \Delta E_{\text{el}} + \Delta E_{\text{xrp}} + \Delta E_{\text{oi}} \qquad (1)$$

between the basis fragments, while ΔE_{xrp} is the exchange repulsion term between occupied orbitals. The orbital interaction term, ΔE_{oi}, arises through the redistribution of electrons in the molecular ground state wavefunction. In the ΔSCF approach, these three components are expressed relative to the atomic fragments and the electrostatic, exchange repulsion and orbital interaction terms associated with the hydrogen bond formation are masked by the larger changes associated with the formation of strong intra-fragment covalent bonds. In contrast, in the fragment approach the covalent bonds are already formed in the molecular fragments and the components of the total interaction energy reflect the formation of the hydrogen bond in isolation. Thus, through the use of the fragment approach, it is possible to gain further insight into the electronic origins of the trends outlined above, over and above that gained from a consideration of the total bonding energy in isolation.

Results and discussion

Formamide dimer

We have completed density functional calculations on the cyclic conformer of $(\text{formamide})_2$ shown in Fig. 2(*a*). Various other possible structures have been investigated by other authors, but this cyclic form is invariably found to be the most stable.[9,10] Full optimisations of the structure were completed using the local density approximation with both double zeta + polarisation (LDA/DZP) and triple zeta + double polarisation (LDA/TZ2P) basis sets. Calculations using the gradient corrections of Becke[20] and Perdew[21] were also performed using the same two basis sets (BP/DZP and BP/TZ2P).

Selected structural parameters for the formamide dimer, along with the hydrogen bond energies (calculated by the ΔSCF method) are summarised in Table 1. A detailed *ab initio* and density functional study of the formamide dimer using Gaussian basis sets has very recently been reported by Florian and Johnson.[16] The results of their *ab initio* calculations using a double zeta + polarisation basis set at both Hartree Fock (HF/DZP) and MP2 (MP2/DZP) levels are presented for comparison, along with those of an X-ray crystallographic determination of the formamide dimer.[17]

The O···N distances calculated at the HF and MP2 level span the experimentally determined distance of 2.948(3) Å, both values lying within 0.05 Å. In contrast, calculations performed using the LDA functional significantly underestimate the bond distances, calculated values lying some 0.4 Å shorter than those calculated at the HF/DZP level, and 0.35 Å lower than the experimentally determined value. Gradient corrections result in a significant increase in the hydrogen bond length and bring the calculated value more into line with experimental results, although still some 0.1–0.15 Å too short. The limitations of the LDA functional in calculating hydrogen bond distances and energies are well documented,[13–15] and the trends noted above are consistent with other studies of hydrogen bonded systems using *ab initio* and DFT methodologies. The choice of basis set has a smaller effect on hydrogen bond length than the choice of functional, the change from DZP to TZ2P causing an elongation of the hydrogen bond by only 0.03 Å.

The accuracy of the calculated interaction energies is rather more difficult to assess in the absence of an experimental estimate of the association energy. However, in systems such as the water dimer, where experimental data are available,

Table 1 Comparison of the calculated structural parameters and hydrogen bond energies for $(\text{formamide})_2$

	r O···H/Å	r O···N/Å	∠O···HN/degrees	∠CO···H/degrees	E(H-bond)/kJ mol^{-1}	E(H-bond)^a/kJ mol^{-1}
LDA/DZP	1.598	2.671	177.03	116.51	−106.7	−95.7
LDA/TZ2P	1.621	2.686	176.24	117.53	−95.9	−85.0
BP/DZP	1.760	2.812	176.07	117.06	−61.3	−51.5
BP/TZ2P	1.802	2.843	174.62	119.23	−53.7	−48.8
HF/DZP^b		2.995	171.56		−56.1	−48.9
MP2/DZP^b		2.900	175.04		−72.8	−51.9
Expt.^{c}		2.948				

[a] Corrected for BSSE using the counterpoise method. [b] Ref. 16. [c] Ref. 17.

Table 2 Structural parameters, total energies and hydrogen bond energies for NFF, NMF and the molecular pairs NFF•NFF, NFF•NMF and NMF•NMF

	NFF bond lengths/Å							NMF bond lengths/Å						
	rNH	rC′O′	rC^{2}O^2	rC′N	rC^{2}N	rC′H′	rC^{2}H^2	r/NH	rCO	rC′N	rC^{2}N	rC′H′	rC^{2}H^2	rC^{2}H^3
NFF	1.031	1.214	1.214	1.389	1.389	1.113	1.113							
NMF								1.025	1.224	1.362	1.454	1.118	1.103	1.100
NFF•NFF	1.055	1.229	1.212	1.366	1.395	1.111	1.115							
NFF•NMF	1.071	1.231	1.213	1.365	1.393	1.113	1.116	1.043	1.243	1.340	1.454	1.113	1.102	1.100
NMF•NMF								1.053	1.244	1.339	1.453	1.115	1.103	1.101

	H-bond lengths/Å		H-bond angles/degrees		Energies/kJ mol^{-1}		
	rO···H^{nff}	rO···H^{nmf}	∠O···H^{nff}N	∠O···H^{nmf}N	E_{tot}	E(H-bond)	E(H-bond)^a
NFF					−4816.6		
NMF					−4892.6		
NFF•NFF	1.764		173.81		−9677.9	−44.7	−34.5
NFF•NMF	1.680	1.816	176.92	176.45	−9765.0	−55.8	−45.9
NMF•NMF		1.749		180.85	−9849.8	−64.6	−54.5

[a] Corrected for BSSE using the counterpoise method.

calculations performed with the LDA functional consistently overestimate bond energies, while the addition of gradient corrections provides values more consistent with experiment.[13,14] These general trends are apparent in the calculated interaction energies shown in Table 1, where the values calculated using the LDA functional are almost twice as large as those obtained with the gradient corrections. Like the bond lengths, interaction energies are less sensitive to basis size and the expansion from DZP to TZ2P causes a reduction of only *ca.* 6 kJ mol^{-1}. In the remainder of this paper, where we consider the differences between a series of structurally similar molecules, the effect of increasing basis size should be relatively consistent. Consequently all additional calculations are performed using the smaller DZP basis, in conjunction with the BP functional. This level of theory represents the best available compromise between accuracy and computational efficiency. The calculations summarised in Table 1 suggest that this should lead to satisfactory estimates of the bond energy, but interaction distances may be underestimated by *ca.* 0.15 Å.

Effects of remote substituents on the hydrogen bonding

Having described the hydrogen bonding in the simplest amide dimer, $(\text{formamide})_2$, we now examine in detail the influence on the hydrogen bonded network of substitution of one of the NH protons by either CHO or CH_3. The resultant monomers, *N*-formylformamide (NFF) or *N*-methylformamide (NMF) may be combined to form three distinct molecular pairs, NMF•NMF, NFF•NMF and NFF•NFF [Fig. 2(*b*), (*c*) and (*d*)]. All three pairs display the same hydrogen bonding motif as diformamide and differ only in the nature of the 'spectator' groups, CHO in NFF and CH_3 in NMF.

The geometries of the two monomers, NMF and NFF, along with the NMF•NMF, NMF•NFF and NFF•NFF dimers, were optimised at the BP/DZP level. All atoms other than the protons of the CH_3 groups were constrained to lie in a plane, resulting in overall C_{2v} (NFF), C_{2h} (NFF•NFF, NMF•NMF) or C_s (NMF, NFF•NMF) symmetry. Selected structural parameters and total energies for the optimised species are summarised in Table 2. The corresponding hydrogen bond energies, with and without counterpoise correction, are also shown in Table 2.

The hydrogen bond energy for the NMF•NMF dimer is very similar to that of the formamide dimer, from which it differs only by the addition of two non-polar methyl groups in the 'spectator' positions. Sequential replacement of these two methyl groups with negatively polarised CHO groups results in a decrease in hydrogen bond energy by 11.4 (NFF•NMF) and 8.6 (NFF•NFF) kJ mol^{-1}, respectively. Thus we may assign a destabilising influence of *ca.* 10 kJ mol^{-1} per spectator oxygen in diamide systems, slightly larger than the estimate of 7.5 kJ mol^{-1} derived from model potentials.[12]

The structural influence of the remote groups is minor, the spectator oxygen groups causing only a small deviation of the NH···O hydrogen bonds away from linearity. The average bond lengths for all three species are almost unchanged, values in all three cases lying in the range 1.748–1.764 Å. Note that within each of the monomeric NFF or NMF fragments, bond lengths are relatively unperturbed by the formation of the hydrogen bonds. In each case, the N–H and C–O bonds involved in the cyclic hydrogen bonded rings lengthen only slightly, and the C–N bond contracts a little, but the changes are less than 0.05 Å in each case. In order to investigate the energetic significance of these geometric changes, an additional series of optimisations was performed where the NFF and

Table 3 Comparison of hydrogen bond lengths and energies for NFF•NFF, NFF•NMF and NMF•NMF obtained from full and partial optimisation

		rO ••• H$^{\rm nff}$/Å	rO ••• H$^{\rm nmf}$/Å	E(H-bond)/kJ mol^{-1}	E(H-bond)^a/kJ mol^{-1}
Full optimisation	NFF•NFF	1.764		−44.7	−34.5
	NFF•NMF	1.680	1.816	−55.8	−45.9
	NMF•NMF		1.749	−64.6	−54.5
Frozen monomers	NFF•NFF	1.835		−39.5	−30.8
	NFF•NMF	1.765	1.878	−47.2	−38.7
	NMF•NMF		1.818	−56.7	−46.8

[a] Corrected for BSSE using the counterpoise method.

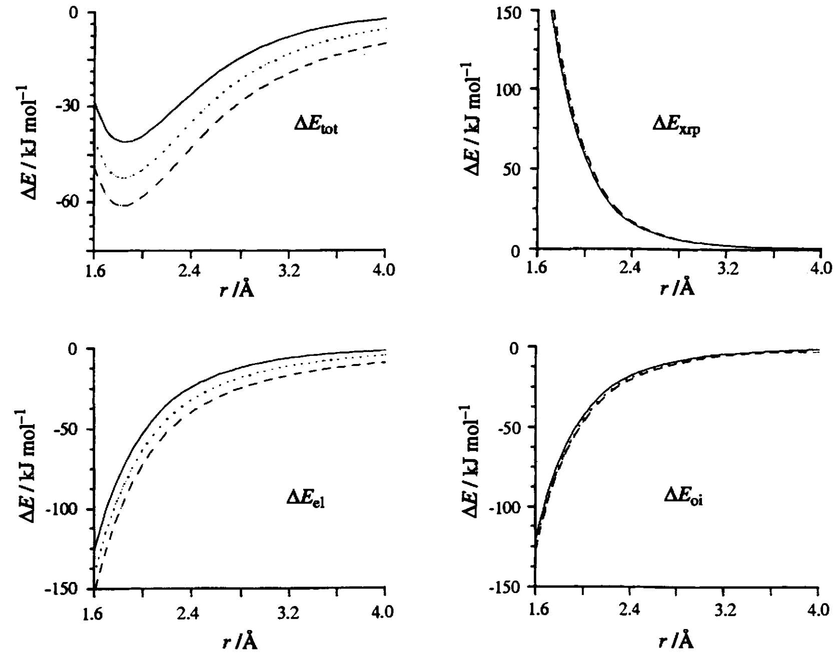


Fig. 3 Components of the total interaction energy, $\Delta E_{\rm tot}$, for the molecular pairs NFF•NFF (——), NFF•NMF (• • • •) and NMF•NMF (– – –)

NMF fragments were not permitted to relax from the geometries obtained for the monomeric fragment in isolation. Only the three parameters directly associated with the hydrogen bond (∠CO ••• H, rO ••• H and ∠O ••• HN) were varied. The structural parameters and hydrogen bond energies for the molecular pairs with 'frozen' monomeric structures are compared with their counterparts from the full optimisation in Table 3. The hydrogen bond energy is reduced by 4–8 kJ mol^{-1} in each case and the average O ••• H distance increased by *ca.* 0.08 Å. More significantly in the context of the present study, the magnitude of this relaxation term is similar in all three cases and the trend in the interaction energies remains the same, with NFF•NFF < NFF•NMF < NMF•NMF. We conclude, therefore, that differences in the intra-fragment relaxation energy are not responsible for the influence of the spectator groups and consequently that the origin of the trend can be examined using frozen monomeric geometries.

The interaction energies summarised in Table 3 confirm that the DFT methodology is capable of modelling the gross destabilising effect of the spectator oxygen atoms, but give no insight into the electronic origins of the phenomenon. A simple electrostatic repulsion between neighbouring oxygen atoms has been proposed,[12] but alternative explanations are possible. For example, the spectator groups may change the electronic properties of the proton donor (N–H) and acceptor (C=O) groups, thereby altering the strength of the primary hydrogen bonds. Alternatively, the origin of the effect may simply lie in the different steric requirements of the spectator groups, the bulkier carbonyl group being more demanding than a methyl group in this respect. In order to distinguish between these possibilities, we must turn to the fragment approach described in the introduction, where the hydrogen bond energy is calculated using the self-consistent orbitals of the monomers as a basis. As noted above, the components of the total energy in the fragment approach reflect the formation of the hydrogen bond in isolation and are not masked by the changes associated with the formation of strong covalent bonds. In Fig. 3, the variation of the hydrogen bond energy and its components is shown as a function of the average bond distance, r, for all three molecular pairs, NFF•NFF, NFF•NMF and NMF•NMF. The frozen monomer geometries given in Table 2 were used in all cases, and the NH$^{\rm nmf}$ ••• O angle was set at 180°. In the $C_{\rm 2h}$ symmetry of the NFF•NFF and NMF•NMF dimers, the geometry is fully defined by these two parameters alone. In the NFF•NMF pair ($C_{\rm s}$ symmetry), the H ••• OC angle must also be defined and is set at 120°, resulting in a difference of 0.1 Å between rO ••• H$^{\rm nff}$ and rO ••• H$^{\rm nmf}$ (*cf.* 0.11 Å in the optimised structure).

First, it is important to note that the calculations performed using the fragment approach reproduce the trends described previously, with the total interaction energy again increasing in the order NFF•NFF < NFF•NMR < NMF•NMF. Small differences between the optimised total energy in Fig. 3 and the values reported in Table 3 (frozen monomers) arise from the enforcement of a linear NH ••• O bond in the former.

Table 4 Decomposition of the total interaction energies for the molecular pairs imide•imide, imide•lactam and lactam•lactam (see Fig. 1)

	ΔE_{el}/kJ mol^{-1}	ΔE_{xrp}/kJ mol^{-1}	ΔE_{oi}/kJ mol^{-1}	ΔE_{tot}/kJ mol^{-1}
Imide•imide	−85.5	108.5	−71.4	−48.4
Imide•lactam	−95.4	112.2	−73.8	−57.0
Lactam•lactam	−105.7	115.4	−75.5	−65.8

Within the transition state approximation, two distinct attractive contributions to the total energy are identified, ΔE_{el} and ΔE_{oi}, countered by the repulsive ΔE_{xrp} term. A comparison of the three components of the total energy indicates that across the series NFF•NFF, NFF•NMF and NMF•NMF, variations in ΔE_{xrp} and ΔE_{oi} are relatively minor, and changes in the electrostatic term, ΔE_{el}, dominate the overall trend in total energy. Of the three possible explanations for the destabilising effect of the spectator oxygen groups noted above, only the secondary electrostatic repulsion hypothesis is consistent with the results summarised in Fig. 3. If the electronic properties of the proton donor and acceptor groups were significantly influenced by the remote substituents, different degrees of charge transfer within the cyclic hydrogen bonded array would be reflected in changes in ΔE_{oi}. Similarly, different steric requirements of the methyl and carbonyl groups would cause variations in the exchange repulsion term, ΔE_{xrp}. Thus the identification of the electrostatic term as the dominant factor in determining the total energy lends considerable weight to the hypothesis that repulsive electrostatic interactions between adjacent oxygen groups are responsible for the destabilising effect on cyclic hydrogen bonded arrays.

Finally, we have performed test calculations using the fragment approach on molecular pairs containing the cyclic imide and lactam molecules shown in Fig. 1. The geometries of the monomers were again optimised at the BP/DZP level and frozen at these values in the fragment calculations. Total energies and their components for imide•imide, imide•lactam and lactam•lactam, at an average hydrogen bond distance of 1.80 Å in each case, are summarised in Table 4. The total interaction energy decreases in the order lactam•lactam > imide•lactam > imide•imide, in accordance with experimental observations and the differences are due principally to changes in the electrostatic term. Thus the trends observed are identical to those in the series NFF•NFF, NFF•NMF, NMF•NMF and we are confident that the conclusions described for these simple model systems may be extended directly to the larger species of direct relevance to supramolecular chemistry.

Conclusions

In this paper we have examined the electronic origins of the influence of remote groups on cyclic hydrogen bonded arrays which are relevant to systems of current interest in supramolecular chemistry. In common with previously reported studies, density functional theory is found to produce accurate estimates of hydrogen bond lengths and energies, provided that gradient corrections are made to the local density approximation. The DFT methodology has been applied to cyclic eight-membered rings derived from complementary hydrogen bonding in monomeric amides. The calculations accurately modelled the destabilising influence of remote carbonyl groups on the hydrogen bonding interactions. Furthermore, the breakdown of the hydrogen bond energy into its components according to the transition state approximation identifies variations in the electrostatic interaction between the fragments as the dominant factor in determining this trend.

The results are therefore consistent with the hypothesis that electrostatic interactions between adjacent carbonyl groups destabilise the hydrogen bonded array. The importance of these secondary electrostatic interactions in a wide variety of supermolecular arrays has been emphasised by several authors[3,4,12,24] and the incorporation and elimination of such remote groups provides an important mechanism for fine-tuning the strength of the intermolecular hydrogen bonding. The nature of these remote groups is consequently an important variable in the successful design of supramolecular aggregates.

The fragment approach used in this paper represents a particularly powerful and chemically attractive method for delineating the important contributions to the interaction energy in hydrogen bonded dimers. In forthcoming papers we will illustrate the application of DFT, and particularly this fragment approach, to triply hydrogen bonded systems and also to the influence of coordinated metal ions on the hydrogen bonded array.

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