A computational investigation of cooperativity in weakly hydrogen-bonded assemblies

Douglas Philp* and James M. A. Robinson

School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT

The non-covalent forces present in ethyne oligomers and ethyne–water aggregates containing $C-H\cdots\pi(C\equiv C)$ interactions, are investigated using *ab initio* calculations. The $C-H\cdots\pi(C\equiv C)$ interaction is found to be a very weak hydrogen bonding interaction, in accordance with previously reported work, with an enthalpy of interaction of around -4 kJ mol^{-1}. The potential surface of this interaction in the ethyne T-shaped dimer demonstrates that the interaction energy is relatively insensitive to the position of the donating proton along the bond vector of the accepting triple bond as well as to the tilt angle of the major axis of the acetylene molecule.

The strength of the $O-H\cdots\pi(C\equiv C)$ contact is found to be consistent with a very weak hydrogen bonding interaction with an enthalpy of interaction of around -6 kJ mol^{-1} which is very similar to that of the ethyne T-shaped dimer although ethyne is a much poorer hydrogen bond donor. The interaction energy per $C-H\cdots\pi(C\equiv C)$ interaction in ethyne trimers, both cyclic and linear, as compared to that in the ethyne dimer does not appear to suggest that there are large gains in stabilisation through cooperativity and the use of a more polarised surface—that of a water molecule—to create larger polarisation effects again resulted in small cooperative gains (0–10% range) suggesting that hydrogen-bonded arrays containing terminal alkynes are incapable of exhibiting significant cooperative enhancements. It is demonstrated that the shifts in the stretching frequency of the C–H bond of propyne in different intermolecular $C-H\cdots O$ hydrogen bonding environments are insignificant relative to the effects of the accepting strength of the oxygen and therefore infra-red spectroscopic data may not provide sufficient evidence to prove that large cooperative effects operate in these hydrogen bonding arrays.

Introduction

The continuing development of the field of supramolecular chemistry is heavily dependent on a thorough understanding of intermolecular interactions. The nature of stronger, conventional hydrogen bonds such as $N-H\cdots O$ and $O-H\cdots O$ has been the subject of extensive study. However, more recently, weaker interactions such as $C-H\cdots O$,[1] $C-H\cdots\pi(Ar)$,[2] $O-H\cdots\pi(Ar)$,[3] halogen $X\cdots X$[4] and $\pi\cdots\pi$[2a,b,5] have attracted increasing attention. Recently, there has been considerable interest[6] in the hydrogen bonding patterns found in solids containing terminal alkyne functionalities. Terminal alkynes possess a polarised C–H bond, with the acidic hydrogen acting as a hydrogen bond donor and the triple bond as a hydrogen bond acceptor. Most of these structures contain traditional hydrogen bonds (*e.g.* $O-H\cdots O$) as the dominant intermolecular interaction, with terminal alkynes also interacting with C≡C, O–H and aromatic functionalities to form a wide range of interactions such as $C\equiv C-H\cdots\pi(C\equiv C)$, $C\equiv C-H\cdots\pi(Ar)$, $C\equiv C-H\cdots O$ and $O-H\cdots\pi(C\equiv C)$. More recently, the crystal structures[7] of 1,4-di- and 1,3,5-tri-ethynylbenzene have demonstrated that $C\equiv C-H\cdots\pi(C\equiv C)$ can serve as the dominant intermolecular interaction in the solid state giving rise to different, but predictable, molecular packing arrangements.

The ability of the terminal alkyne functionality to participate simultaneously as a hydrogen bond acceptor and donor in a similar fashion to the hydroxy group is of particular interest. Several crystal structures have provided evidence[6c–h] (Fig. 1) that suggests cooperative effects exist in non-covalent bonding arrays containing alkyne and hydroxy functional groups—forming $C\equiv C-H\cdots\pi(C\equiv C)$, $O-H\cdots\pi(C\equiv C)$ and $C-H\cdots O$ interactions—which are similar to the mutual polarisation found[8] in arrays of $^{\delta-}O-H^{\delta+}\cdots{}^{\delta-}O-H^{\delta+}\cdots$ hydrogen bonds. The cooperative effects evident in the $O-H\cdots O-H\cdots$ arrays have been studied by analysis of neutron and X-ray diffraction data[9] and by quantum mechanical calculations.[10] These calculations have suggested that the strength of $O-H\cdots O$ hydrogen bonds in the cyclic water trimer is enhanced by as much as 50% with respect to the hydrogen bond in the water dimer through cooperativity. The evidence for the existence of cooperative effects involving terminal alkynes has been supported[6h] by infra-red spectroscopic analysis of the effect of intermolecular bonding environments on the frequency of the C–H stretching vibration. Additionally, *ab initio* calculations[6c] have suggested that cooperative effects account for as much as 25% of the interaction energy—or a 50% enhancement—in the $C\equiv C-H\cdots\pi(C\equiv C)$ interaction between two propyne dimers.

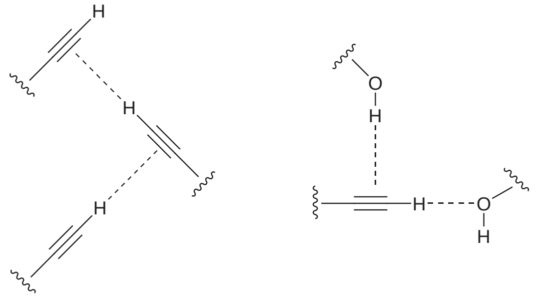

Fig. 1 Potentially cooperative hydrogen bonding networks involving alkyne functional groups

In this paper we describe a series of *ab initio* calculations designed to focus on the characteristics of the hydrogen bonding interactions involving terminal alkynes. Our aim is the examination of the potential surface of the $C\equiv C-H\cdots\pi(C\equiv C)$ interaction so the increasing number of crystallographic $C\equiv C-H\cdots\pi(C\equiv C)$ contacts can be put in perspective in terms of their energetics. We also wish to investigate the existence of the cooperativity phenomenon operating in hydrogen-bonded arrays containing these interactions. We have undertaken this study using calculations of the interaction energies of complexes containing ethyne molecules as a representation of the C≡C–H···π(C≡C) interaction. Initially, cooperative effects in oligomers of ethyne were analysed, although in addition, complexes of ethyne and water have also been studied, since the larger polarisation of the O–H bond as compared to the C–H bond should facilitate larger cooperative effects. Finally, we have explored the manifestation of cooperative effects on the vibrational stretching frequency of the C–H bond in complexes of water and propyne.

Computational methods

All *ab initio* calculations described in this paper were performed using either GAMESS[11] or CADPAC.[12] Initial starting geometries were generated by the graphical interface of SPARTAN.[13] All the internal coordinates were then optimised fully using GAMESS to an rms gradient of less than 2×10^{-5} a.u. Calculations of zero-point energies (ZPE) were performed using GAMESS by the analytical calculation of second derivatives. The ZPEs were scaled by a factor of 0.89 to account[14] for the overestimation of vibrational frequencies.

Corrections for basis set superposition error (BSSE) for the optimised coordinates were obtained by the full counterpoise[15] procedure using CADPAC. Thus, for a complex between three molecules, the BSSE correction is described by eqn. (1), where

$$\mathrm{BSSE(A{-}B{-}C)} = E(\mathrm{A})_\mathrm{A} - E(\mathrm{A})_\mathrm{ABC} + E(\mathrm{B})_\mathrm{B} - E(\mathrm{B})_\mathrm{ABC} + E(\mathrm{C})_\mathrm{C} - E(\mathrm{C})_\mathrm{ABC} \quad (1)$$

$E(\mathrm{X})_\mathrm{X}$ (X = A, B or C) represents the energy of molecule X using its own basis functions and $E(\mathrm{X})_\mathrm{ABC}$ represents the energy of molecule X using the complete set of basis functions (A + B + C).

Intermolecular stabilisation energies at 0 K (ΔE_int) were calculated using the supramolecular approach, which is described as the difference between the energy of the supramolecular aggregate and that of the isolated monomers, corrected for BSSE. Accordingly, correction of this value for differences in zero-point energies between the aggregate and monomers gave the enthalpies of interaction at 0 K (ΔH_0).

The study of interactions as weak as those described in this paper requires calculations which are highly accurate, especially if subtle effects such as cooperativity are to be analysed successfully. It is widely acknowledged that calculations on weak intermolecular interaction energies at the self-consistent-field molecular orbital (SCF-MO) Hartree–Fock level of theory tend to underestimate enthalpies of association as a result of the lack of correlation terms inherent in the theoretical method. Attempts made to apply density functional theory (DFT), increasingly successful in the modelling of stronger hydrogen bonds, to C–H···π(C≡C) interactions,[16] demonstrate that interaction energies calculated by DFT are significantly smaller than MP2 energies. Additionally, the calculation of interaction energies at one level of theory does not guarantee a correct answer, whereas the comparison of the results obtained from a number of levels of theory allows an assessment of the validity of the interaction energies to be made. All calculations have therefore been performed at the Møller–Plesset (MP*n*) ($n = 2$) level using the Gaussian basis sets; 6-31G(d,p), 6-311G(d,p), 6-311G(2d,2p) and additionally one basis set of triple-zeta quality; TZ2P.[17] Calculations performed using the 6-311G(2d,p) basis set gave such similar energies and geometries to the 6-311G(2d,2p) basis set, that for the sake of brevity the results are not reported here. Gaussian basis sets that include diffuse functions such as 6-311++G(d,p) resulted in difficulties in obtaining convergence in the SCF, as well as giving unreasonably large BSSE errors.

The three-dimensional potential surface for the T-type interaction between two molecules of C_2H_2 was calculated at the MP2/TZ2P level. Two molecules of C_2H_2, with internal coordinates optimised at the MP2/TZ2P level, were placed such that the major axis of one molecule was perpendicular to that of the second molecule and these vectors intersected at the midpoint of the C–C bond. The molecules were then moved with respect to each other in two dimensions by varying the C–H···π(C≡C) midpoint distance and the offset of one major axis with respect to the midpoint of the second molecule. Single point energy calculations were performed at each point on the grid affording a potential energy surface for this interaction.

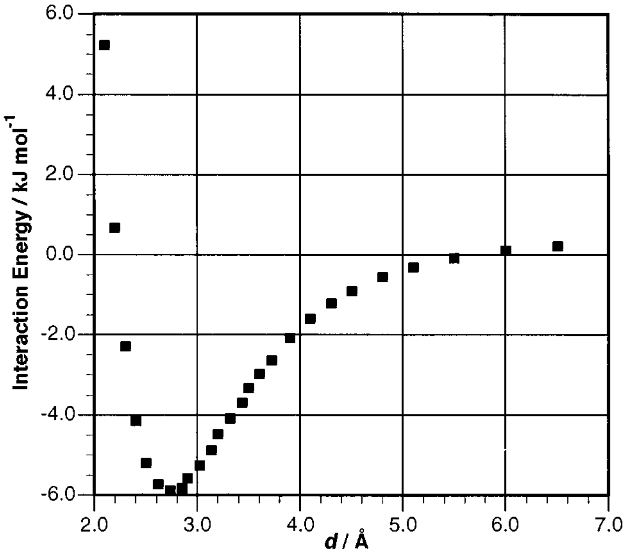

Fig. 2 Interaction potential for the symmetrically bifurcated T-shaped ethyne dimer; *d* represents the C–H···π(M) distance where M is the midpoint of the triple bond

Results and discussion

C–H···π(C≡C) interactions in ethyne complexes

Theoretical investigations of C≡C–H···π(C≡C) interactions, predominantly in the form of ethyne complexes, have been restricted to calculations utilising moderately sized basis sets on the stationary points on the potential energy surfaces of ethyne[18] dimers, trimers, tetramers and on propyne[6c] oligomers. Although the interaction potential surface of the ethyne dimer is widely regarded to be relatively shallow, we believe that the increasing attention that is directed towards crystal structures containing C≡C–H···π(C≡C) interactions warrants a more systematic and thorough examination of the interaction potential. The minimum energy structure is the C_{2v} symmetrically bifurcated T-shaped dimer although the change in interaction energy with respect to the C–H···M distance *d*, where M is the midpoint of the triple bond between the two molecules (Fig. 2), reflects the assumed shallowness of the interaction potential. The minimum stabilisation energy ($d \approx 2.75$ Å, interaction energy ≈ -6.0 kJ mol^{-1}) is comparable with the previously determined[18e] MP2/DZ+(2df,2p) energy (-5.69 kJ mol^{-1}).

The interaction potential of the unsymmetrically bifurcated dimer [Fig. 3(a)], in which the distance *x* represents the offset with respect to midpoint of the triple bond, shows the interaction energy is relatively insensitive to the position of the hydrogen atom along the C≡C bond vector. Therefore, the energy difference between a symmetrically bifurcated motif and one in which the direction of the donating C–H bond is biased towards an individual carbon atom is small—when x is $\leqslant 0.6$ Å, the change in the interaction energy is < 1 kJ mol^{-1}.

This observation is reflected in the crystal structures containing C≡C–H···π(C≡C) interactions which often show no strong preference for the direction of the C–H bond vector towards the midpoint of the triple bond. A search, using the Cambridge Structural Database,[19] of C≡C–H···π(C≡C) contacts found 37

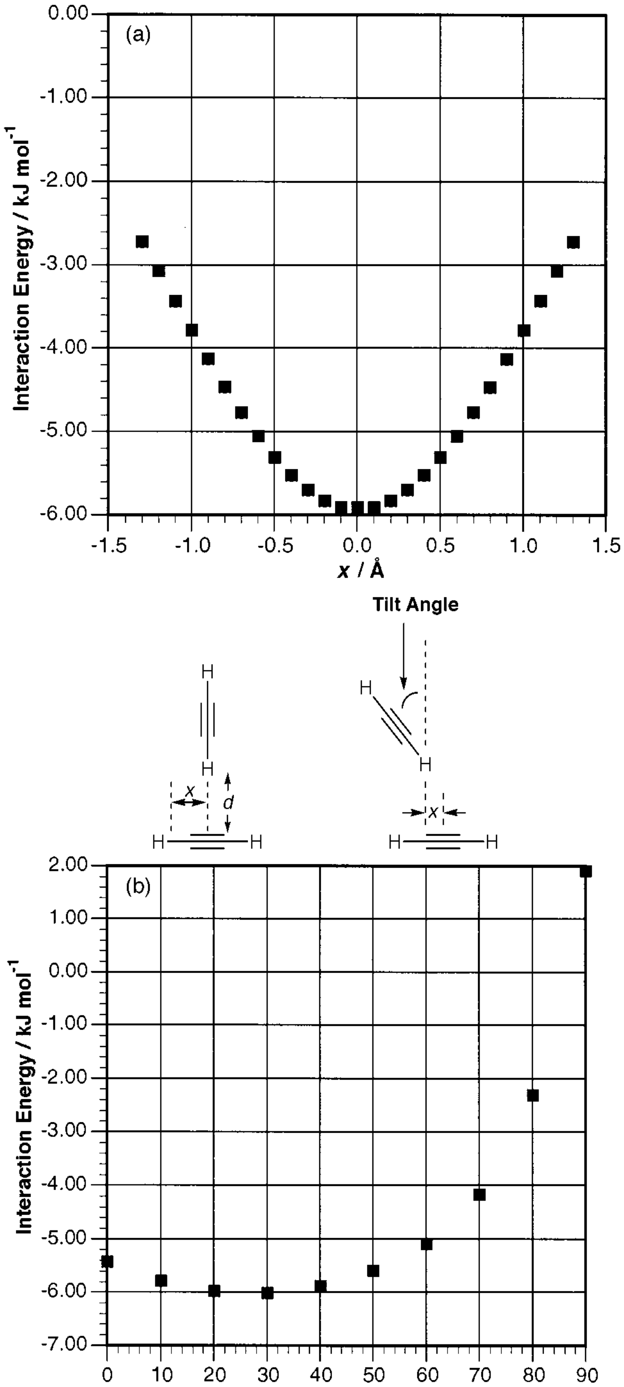

Fig. 3 Interaction potential for (a) the unsymmetrically bifurcated T-shaped ethyne dimer where the C–H · · · π(M) distance is kept constant at 2.70 Å and x represents the offset distance from the midpoint of the triple bond, (b) the unsymmetrically bifurcated tilted dimer where the offset distance x is set so that the donating C–H bond is directed towards an individual carbon atom of the accepting triple bond

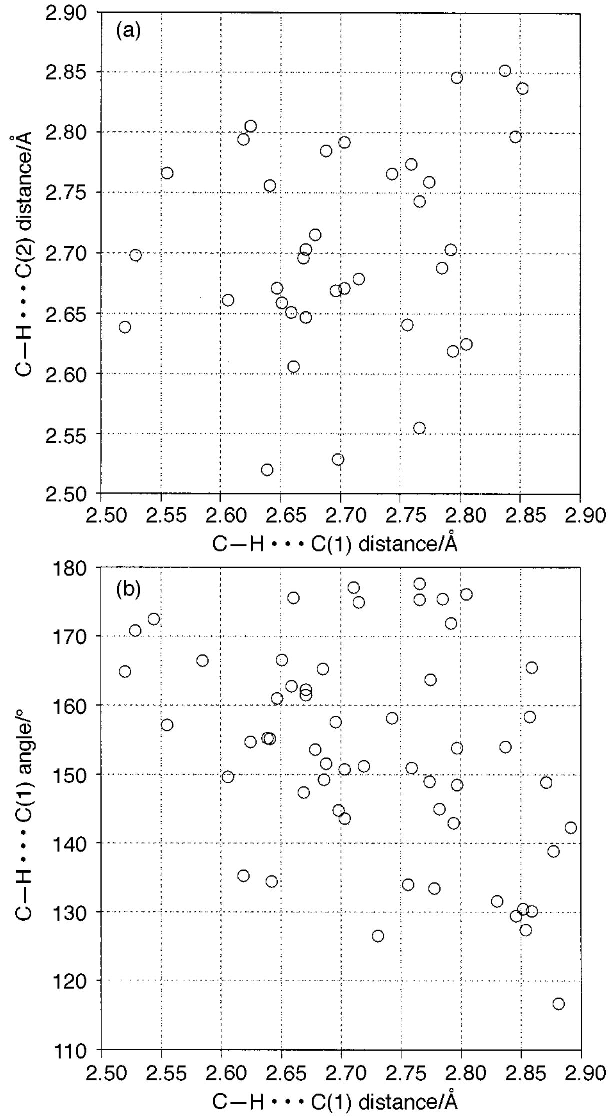

Fig. 4 (a) Scattergram for the C–H · · · C(1) *vs.* C–H · · · C(2) distances in C≡C–H · · · π(C≡C) interactions where C(1) and C(2) are the two carbon atoms of the alkyne triple bond. (b) Scattergram for the C–H · · · C(1) distance *vs.* C–H · · · C(1) angle.

contacts of less than 2.9 Å in length. A comparison of the two C–H · · · π(C) distances within each contact [Fig. 4(a)] clearly demonstrates that there is no strong preference for the interaction to be bifurcated symmetrically.

The distance–angle relationship [Fig. 4(b)] shows no significant correlation for the shorter contacts to be most linear as in the case[20] of stronger, shorter hydrogen bonds (*e.g.* N–H · · · O=C). Although there are no shorter contacts (<2.70 Å) with C–H · · · π(C≡C) angles of less than 130°, there is no obvious preference for short contacts to be linear. The distance–angle correlation apparent in the N–H · · · O=C shorter hydrogen bonds is presumed to arise[21] from the need to minimise the repulsive non-bonded (N · · · O) interactions when the N · · · O distance is small. The poor distance–angle correlation in alkyne systems can be rationalised in terms of the longer nature of the C≡C–H · · · π(C≡C) interaction with the relatively large C · · · C distances (typically 3.5–4.0 Å) resulting in insignificant non-bonded interactions even when the H · · · π(C≡C) distance is towards the lower end of the observed range and the angle between the major axes of the two acetylene molecules is small. This assertion is supported by the change in interaction potential of the unsymmetrical T-shaped ethyne dimer with varying angle of inclination of the molecular axis of one molecule with respect to the molecular axis of the other [Fig. 3(b)]. The interaction energy varies little with respect to the angle at inclination up to an angle of 60° and even shows a shallow minimum at around 30°. This outcome is reflected in the analysis of the microwave spectrum[22] of the ethyne dimer in the gas phase which has suggested that the ground state has the angle of inclination at 27° contradicting earlier reports that the T-shaped dimer possessed C_{2v} symmetry.

The calculation of stabilisation energies after correction for BSSE (ΔE_{int}) for the ethyne dimer using a number of basis sets (Table 1) shows a reasonable agreement between the smallest basis set [6-31G(d,p)] and the largest (TZ2P) with a difference of about 1.0 kJ mol^{-1} between them. The intermolecular

Table 1 Structural parameters and interaction energies for ethyne oligomers

	Basis	C–H···π(M)/Å	$^a\Delta E_{\mathrm{uncor}}$/ kJ mol^{-1}	$^b\Delta E_{\mathrm{int}}$/ kJ mol^{-1}	$^c\Delta H_0$/ kJ mol^{-1}	$^dC(\Delta E_{\mathrm{uncor}})$ (%)	$^dC(\Delta E_{\mathrm{int}})$ (%)	$^dC(\Delta H_0)$ (%)
$(C_2H_2)_2$	6-31G(d,p)	2.629	−8.974	−4.305	−0.780			
	6-311G(d,p)	2.738	−7.052	−4.562	−3.533			
C_{2v}	6-311G(2d,2p)	2.680	−7.540	−5.590	−3.502			
	TZ2P	2.695	−6.579	−5.263	−4.328			
$(C_2H_2)_3$	6-31G(d,p)	2.656	−8.800	−4.541	−1.840	−1.9	5.5	57.6
	6-311G(d,p)	2.757	−7.013	−4.742	−3.672	−0.6	4.0	3.8
C_{3h}	6-311G(2d,2p)	2.693	−7.683	−5.853	−4.478	1.9	4.7	21.8
	TZ2P	2.693	−6.642	−5.450	−4.270	1.0	3.6	−1.4
$(C_2H_2)_3$	6-31G(d,p)	2.614/2.607	−9.486	−4.718	−1.324	5.7	9.6	41.1
	6-311G(d,p)	2.719/2.703	−7.511	−4.907	−3.610	6.5	7.6	2.1
C_s	6-311G(2d,2p)	2.666/2.641	−8.056	−6.031	−3.968	6.8	7.9	11.7
	TZ2P	2.644/2.640	−7.060	−5.688	−4.399	7.3	8.1	1.6

^{a} $\Delta E_{\mathrm{uncor}}$, interaction energy per hydrogen bond at 0 K = $[E(C_2H_2)_n - nE(C_2H_2)]/n$. ^{b} ΔE_{int}, interaction energy per hydrogen bond at 0 K after correction for BSSE. ^{c} ΔH_0, enthalpy of interaction after correction for zero point energies. ^{d} The cooperative enhancement, C, is the % increase in interaction energy per hydrogen bond of the trimer as compared to that of the dimer. $C(\Delta E_{\mathrm{uncor}})$ is the cooperative enhancement for the $\Delta E_{\mathrm{uncor}}$ energies, $C(\Delta E_{\mathrm{int}})$ the enhancement for the ΔE_{int} energies and $C(\Delta H_0)$ the enhancement for the ΔH_0 energies.

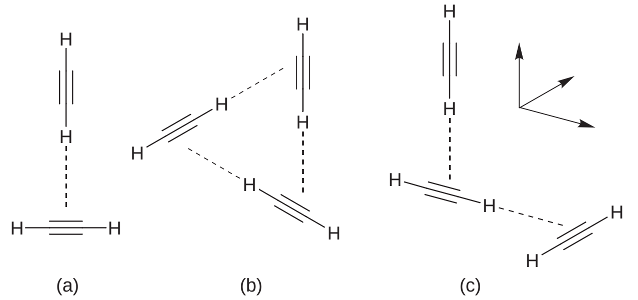

Fig. 5 Ethyne (a) T-shaped C_{2v} dimer; (b) C_{3h} trimer and (c) C_s trimer

geometries obtained from all the basis sets are also very similar, with C≡C–H···π(M) distances, where M is the midpoint of the accepting C≡C bond, of 2.6–2.7 Å and are in stark contrast to the 3.03 Å obtained[23] from a Hartree–Fock [6-311G(d,p)] calculation, confirming the need for the computational theory to encompass terms for electron correlation. In all cases, the BSSE correction is extremely large with respect to the total binding energy, although the effect is less pronounced for the larger basis sets, emphasising the fact that the implementation of this correction is especially important for weaker intermolecular interactions. The inclusion of the correction for the differences in zero-point energies (ZPEs) between the dimer and two isolated monomers lowers the interaction energy and gives a wide range of values for the enthalpy of dimerisation (ΔH_0), the effect being most evident for the 6-31G(d,p) value (−0.78 kJ mol^{-1}). The ZPE of the dimer is derived from the values of the vibrational frequencies and is highly sensitive to the precision of the smaller frequencies—in this case the intermolecular vibrations (typically <100 cm^{-1}). Therefore, inadequate description of the intermolecular interactions by the smaller basis sets between the dimer has presumably resulted in imprecise intermolecular frequencies and thus a significantly inaccurate value for the ZPE correction. The energies for the larger basis sets (−4.33 kJ mol^{-1} for TZ2P) suggest that the C≡C–H···π(C≡C) interaction is akin, at best, to a very weak hydrogen bond, thus indicating that the electrostatic contribution to the binding energy is unlikely to be much greater than the dispersive contribution, in contrast to stronger hydrogen bonds. The lack of a large electrostatic contribution to the total binding energy would also impose a restriction on the magnitude of any cooperative enhancements which are dependent on polarisation arising from the proximity of strongly charged electrostatic potential surfaces.

The cooperative effect in C≡C–H···π(C≡C) chains can be described as the enhancement in the strength of the intermolecular interactions arising from the alkyne residues participating simultaneously as hydrogen bond acceptors and donors. This effect can be investigated simply by the comparison of the energy of the C≡C–H···π(C≡C) interaction in the ethyne dimer with the presumably enhanced C≡C–H···π(C≡C) interaction in ethyne oligomers. We have undertaken studies on two stationary points of the $(C_2H_2)_3$ potential surface—the C_{3h} global and C_s local minima (Fig. 5). The C_s trimer has only two C≡C–H···π(C≡C) interactions compared to the three in the C_{3h} (cyclic) trimer, and thus no ···(C≡C)–H···π(C≡C)–H··· (*a*···***da***···***da***···*d*) interaction arrays,† as shown in Fig. 6, as compared to the three in the cyclic trimer. However, the C≡C–H···π(C≡C) interactions in the C_s trimer are more comparable to those in the T-shaped C_{2v} dimer since the linear trimer can be considered to contain two symmetric T-shaped interactions whereas the cyclic trimer is built up from tilted dimers. The difference in the interaction energy (ΔE_{int}) per C≡C–H···π(C≡C) contact (Table 1) between the ethyne trimer and the ethyne dimer—the so-called cooperative enhancement—is 4–6% for the C_{3h} trimer and 8–10% for the C_s trimer. When the correction is made for zero-point energies, again, as in the case for the enthalpy of dimerisation, there are large fluctuations in the values for the cooperative enhancement, $C(\Delta H_0)$. For the C_s trimer, the values lie in the range of 2–41%, with the larger basis sets giving smaller values. The C_{3h} trimer also shows a similar range of enhancements (−1 to 58%) with a good agreement with the C_s values for each individual basis set. Again, these fluctuations can be attributed to inaccurate values of the ZPE of the dimer and trimer arising from the inaccurate description of the intermolecular vibrational frequencies. The effect of the ZPE correction is more pronounced for weakly bound complexes such as the ethyne oligomers and thus we believe the calculated values using smaller basis sets should be discounted. In principle, the ZPE corrections obtained from the largest basis set (TZ2P) should be the most accurate—if these values are applied to correct the ΔE_{int} energies obtained from the other basis sets (Fig. 7), then the

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† Where *ad* represents an entity that can behave simultaneously as a hydrogen bond acceptor and donor (*e.g.* O–H, C≡C–H), *a*···*d* a non-covalent interaction and ***a***···***d*** a cooperatively 'doubly enhanced' non-covalent interaction where *both* the molecules participating in the ***a***···***d*** interaction are themselves accepting or donating additional hydrogen bonds. The C_s trimer contains no molecules of ethyne participating in an ***a***···***d*** type interaction whereas all the interactions in cyclic trimers are of this type. The *a*···***da***···***da***···*d* interaction also exists in linear oligomers where there are $n - 3$ type interactions for a chain containing *n* molecules. Therefore, the minimum oligomer chain length for such a 'doubly enhanced' *a*···***da***···***da***···*d* is an ethyne tetramer, the calculations of which surpassed our computational resources. However, the C_s trimer still has cooperatively enhanced *a*···*da*···*d* interactions—the first *a*···*d* interaction accepts from an enhanced donor whereas the second *a*···*d* interaction donates to an enhanced acceptor.

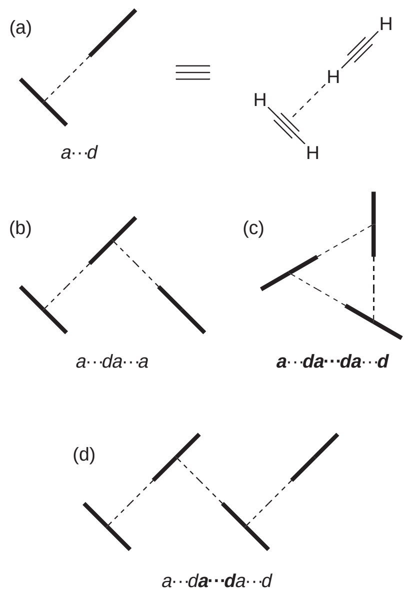

Fig. 6 Cartoon representation of ethyne oligomers; (a) dimer, (b) linear trimer, (c) cyclic trimer, (d) linear tetramer, demonstrating how 'doubly enhanced' *a* ··· ***da*** ··· ***da*** ··· *d* interactions arise

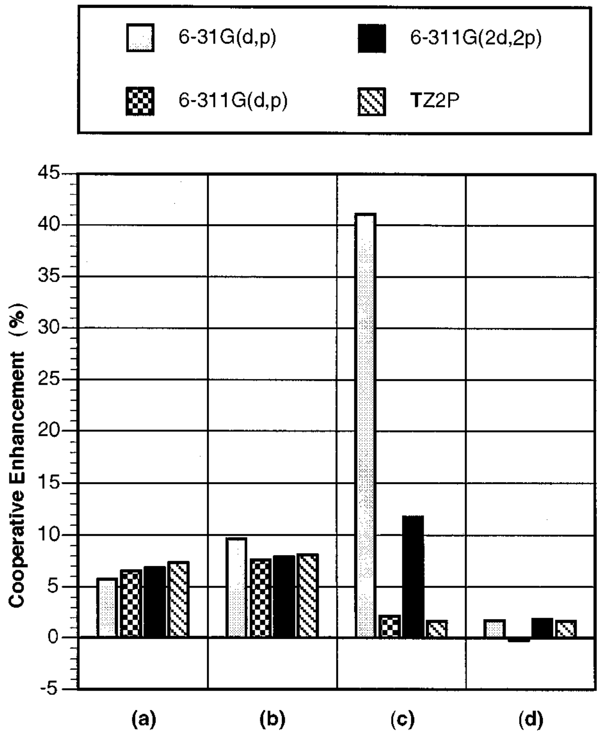

Fig. 7 Plot showing the cooperative enhancement in the C_s ethyne trimer obtained from different basis sets where the interaction energies are (a) uncorrected for BSSE and ZPE, (b) corrected for BSSE but not ZPE, (c) corrected for BSSE and ZPE, (d) corrected for BSSE and using the ZPE correction obtained from the calculations using the TZ2P basis set

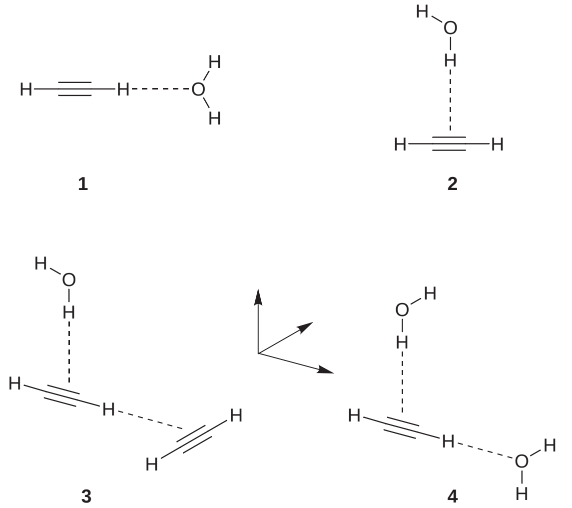

Fig. 8 Ethyne–water complexes containing C–H···O, O–H···π-(C≡C) and C≡C–H···π(C≡C) interactions

cooperative enhancement appears to be close to 0%. Cooperative enhancement, and thus strengthening of the C≡C–H···π(C≡C) interaction, in the ethyne trimers should also manifest itself in shorter C–H···π(M) distances.‡ However, a comparison of the C–H···π(M) distance in the dimer with the enhanced interactions in the C_s trimer (Table 1), shows that the differences are very small (<0.06 Å, <2%).

C≡C–H···O, O–H···π(C≡C) and C–H···π(C≡C) interactions in ethyne–water complexes

Calculations have been reported[24] previously for the interaction of terminal alkynes with an O–H group through the C≡C–H···O interaction in the ethyne–water complex. In principle, the acidity of terminal alkynes makes the C–H···O interaction one of the strongest in this class, and this is reflected in the relatively large reported enthalpy of interaction ($\Delta H_0 = 7.4$ kJ mol^{-1}). In numerous[6,25] crystal structures containing alkynes and O–H groups, the alkyne can also behave as the hydrogen bond acceptor and thus participate in O–H···π(C≡C) interactions. Many of the cooperative arrays containing alkyne residues arise through chains of C≡C–H···O and O–H···π(C≡C) interactions, although as far as we are aware, no computational investigations have yet been carried out on O–H···π(C≡C) interactions. Of particular interest is the propensity of the C≡C centre to be polarised by a strong hydrogen bond donor (*i.e.* O–H) so that the more strongly polarised C–H bond allows the alkyne to behave as a more powerful hydrogen bond donor—resulting in a cooperative enhancement. We have therefore investigated the C≡C–H···O and O–H···π(C≡C) interactions in the ethyne–water complexes **1**–**4** (Fig. 8).

The difference in the binding energy of the C≡C–H···O interaction in complex **1** from that for the O–H···π(C≡C) interaction in complex **2** (Table 2) provides a qualitative indication that the alkyne is a more powerful (C–H···) hydrogen bond donor than it is a [···π(C≡C)] hydrogen bond acceptor with the TZ2P ΔH_0 energy for the C≡C–H···O interaction (-9.3 kJ mol^{-1}) being nearly twice as large as that for the O–H···π(C≡C) interaction (-5.5 kJ mol^{-1}). However, the differences could also be attributed to the nucleophilicity of water being considerably larger[26] than its electrophilicity, although the importance of this effect is unclear.

The magnitude of any cooperative enhancement arising from O–H···π(C≡C)–H··· arrays can be described by the difference between the energy of the two interactions in the trimers **3** and **4** and the energy of the isolated interactions as found in the two dimers that represent the interactions present in the trimer [*i.e.* $(C_2H_2)_2$, **1** and **2**]. The pattern of the interactions in both **3** and **4** is similar to that in the ethyne C_s trimer in that they can be described as an array of *ad*···*ad*···*ad* interactions. In both complexes **3** and **4**, the O–H···π(C≡C) *d*···*a* interaction donates to an enhanced C≡C acceptor whereas the C–H···X *a*···*d* interaction (where X is C≡C or OH$_2$) accepts from an enhanced ≡C–H donor.

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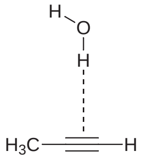
‡ The cooperative enhancement apparent in the global minimum of the water trimers shows[10b] that O–H···O bond lengths shorten by only about 0.1 Å as compared to the C_s dimer and therefore the smaller cooperative effects in the weakly bound complexes described in this paper might be expected to exhibit even smaller shortenings. However, given that the interaction potentials for these interactions are shallower, a large cooperative effect should be accompanied by relatively large intermolecular contractions.

Table 2 Structural parameters and energies for the ethyne–water complexes

	Basis	**C–H···O**, *O–H···π(M)*, C–H···π(M)/Å	${}^a\Delta E_{\text{uncor}}$/ kJ mol^{-1}	${}^b\Delta E_{\text{int}}$/ kJ mol^{-1}	${}^c\Delta H_0$/ kJ mol^{-1}	${}^d C(\Delta E_{\text{uncor}})$ (%)	${}^d C(\Delta E_{\text{int}})$ (%)	${}^d C(\Delta H_0)$ (%)
1	6-31G(d,p)	**2.153**	−17.102	−12.164	−8.663			
	6-311G(d,p)	**2.144**	−18.150	−12.145	−9.966			
	6-311G(2d,2p)	**2.158**	−19.594	−11.037	−7.672			
	TZ2P	**2.197**	−12.804	−11.599	−9.313			
2	6-31G(d,p)	*2.458*	−11.636	−6.900	−2.547			
	6-311G(d,p)	*2.538*	−9.885	6.509	−3.412			
	6-311G(2d,2p)	*2.428*	−10.932	−7.614	−4.911			
	TZ2P	*2.420*	−10.470	−8.207	−5.494			
3	6-31G(d,p)	*2.458*/2.595	−21.579	−11.809	−4.606	4.5	5.1	27.8
	6-311G(d,p)	*2.487*/2.677	−17.656	−11.156	−6.626	4.1	0.8	−4.8
	6-311G(2d,2p)	*2.411*/2.642	−19.455	−13.592	−8.080	5.0	2.9	−4.1
	TZ2P	*2.404*/2.630	−17.764	−13.928	8.693	4.0	3.3	13.0
4	6-31G(d,p)	*2.423*/**2.118**	−31.983	−21.545	−14.227	10.1	11.5	21.2
	6-311G(d,p)	*2.444*/**2.107**	−31.162	−20.124	−14.884	10.0	7.3	10.1
	6-311G(2d,2p)	*2.392*/**2.112**	−33.459	−20.263	−14.033	8.8	8.0	10.3
	TZ2P	*2.403*/**2.163**	−25.816	−21.697	−14.841	9.8	8.7	0.2

[a] ΔE_{uncor}, stabilization energy of the complex at 0 K = [E(complex) − E(constituent monomers)]. [b] ΔE_{int}, interaction energy per hydrogen bond at 0 K after correction for BSSE. [c] ΔH_0, enthalpy of interaction after correction for zero point energies. [d] The cooperative enhancement, C, is the % increase in interaction energy per hydrogen bond of the trimer as compared to that of the dimers. $C(\Delta E_{\text{uncor}})$ is the cooperative enhancement for the ΔE_{uncor} energies, $C(\Delta E_{\text{int}})$ the enhancement for the ΔE_{int} energies and $C(\Delta H_0)$ the enhancement for the ΔH_0 energies.

The cooperative enhancements calculated with (ΔE_{int}), and without correction (ΔE_{uncor}) for BSSE (Table 2) suggest that the cooperative enhancement in complex **3** is very small (<5%). The inclusion of the ZPE corrections results in a wide range of enhancements (+28 to −13%), which can again be attributed to the inadequate description of the intermolecular vibrational frequencies of the weakly bound complex. With the assumption that the 6-31G(d,p) value is significantly inaccurate and should be discounted, the results indicate that the overall cooperative enhancement may actually be a *negative* effect. As with the ethyne oligomers, cooperative enhancements of the interactions should result in shorter intermolecular bond lengths.§ The C–H···π(C≡C) intermolecular distances in **3** (Table 2) show little contraction from those in the ethyne dimer (<0.03 Å). Indeed, the changes are smaller than those found between the ethyne dimer and the ethyne C_s trimer despite the fact that the effect of cooperativity on the C–H···π(C≡C) distance should be more evident in **3** than the C_s trimer since the polarising power of the water, either as a hydrogen bond acceptor or donor, should be much greater than ethyne. The magnitude of the cooperative effects in **4** should be greater than those seen in **3** or the ethyne trimers because the alkyne is forming two relatively strong O–H···π(C≡C) and C–H···O hydrogen bonds to two strongly polarising water molecules. The differences between the cooperative enhancements (Table 2) for the ΔE_{uncor}, ΔE_{int} and ΔH_0 energies for each basis set are quite similar, as is the variation between basis sets. The cooperative enhancement is estimated to be about 0–10% in all cases, except for the 6-31G(d,p) $C(\Delta H_0)$ value, which is again probably due to an inaccurate value for the ZPEs of the complexes.



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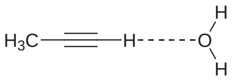

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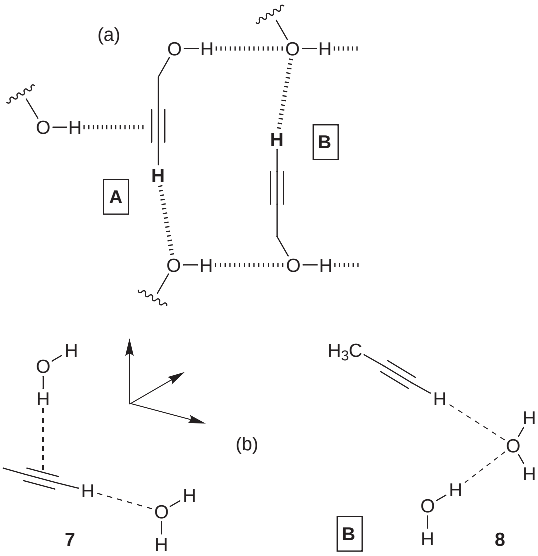

Fig. 9 (a) Differing C–H···O intermolecular interaction environments, **A** and **B**, in crystalline mestranol. (b) The two environments **A** and **B** can be represented by the complexation of a molecule of propyne with two molecules of water.

The study of cooperative effects using infra-red spectroscopy

The effect of the C–H···O interaction upon the donating strength of the ≡C–H bond can also be analysed by examining the difference between the ≡C–H stretching frequency of an isolated alkyne and that of an alkyne participating in a C–H···O interaction. In principle, the hydrogen bonding-type interaction weakens the C–H bond and thus shifts the ≡C–H stretching vibration to a lower frequency.

The crystal structure[6h] of mestranol (ethynylestradiol 3-methyl ester) contains two types of C≡C–H···O bonding environments (Fig. 9), one where the alkyne is simultaneously accepting an O–H···π(C≡C) interaction (**A**), and one where the alkyne accepts no bonds (**B**). The large difference in the corresponding shifts in the C–H stretching frequency,¶ brought about by the different intermolecular environments, has been attributed to the cooperative effect enhancing the C≡C–H donor ability in environment **A**. However, there are two other factors which may have a significant effect on the C–H stretch-

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§ We have not compared the O–H···π(M) distances in complexes **2**, **3** and **4** because of the variations of the position of the OH group along the triple bond vector and thus the difficulties of defining the criteria for the description of the O–H···π(C≡C) separation that can be applied to all the complexes.

¶ The $\nu_{\equiv\text{C–H}}$ red-shifts in crystalline mestranol with respect to a dilute solution in CCl$_4$ were reported to be −59.8 and −21.3 cm^{-1} for the residues **A** and **B** respectively.

Table 3 Structural parameters and C–H stretching frequencies for propyne complexes

Complex	$\mathrm{C{-}H\cdots O/Å}$	$\nu_{\equiv C-H}{}^{a}/\mathrm{cm^{-1}}$	$\Delta\nu_{\equiv C-H}{}^{b}/\mathrm{cm^{-1}}$
Propyne		3571	
5		3555	16
6	2.187	3464	107
7	2.174	3455	116
8	2.357	3533	38

[a] All vibrational frequencies quoted are uncorrected (*cf.* experimental $\nu_{\equiv C-H} \approx 3300\ \mathrm{cm^{-1}}$) and are therefore overestimated by about 8%. [b] Where $\Delta\nu_{\equiv C-H}$ is the difference between the C–H stretching frequency in the complex and for isolated propyne.

ing frequencies. The $\mathrm{C{\equiv}C{-}H}$(**B**)$\cdots$O interaction is to an oxygen already accepting an $\mathrm{O{-}H\cdots O}$ hydrogen bond whereas the $\mathrm{C{\equiv}C{-}H}$(**A**)$\cdots$O interaction is to an oxygen *donating* an $\mathrm{O{-}H\cdots O}$ hydrogen bond. These two factors are almost certainly more important than the presence of an $\mathrm{O{-}H\cdots\pi(C{\equiv}C)}$ interaction for it has been demonstrated that water, and thus hydroxy groups in general, behaving as a bisacceptor has a destabilising effect,[9e,27] whereas water that is donating hydrogen bonds facilitates[9e,28] a considerably enhanced hydrogen bond acceptor.

We have therefore compared the C–H stretching frequencies for the propyne–$2H_2O$ complexes **7** and **8** that represent, albeit to a limited extent,‖ the respective intermolecular environments **A** and **B** found in crystalline mestranol. Additionally, we have also analysed the C–H stretching frequencies for isolated propyne and the propyne–H_2O complexes **5** and **6**.

The values for the propyne $\nu_{\equiv C-H}$ in the propyne–water complexes (Table 3) are all red-shifted with respect to isolated propyne since the $\mathrm{C{-}H\cdots O}$ hydrogen bond weakens the C–H bond. The difference between the $\nu_{\equiv C-H}$ values for **6** and **7** is small (9 $\mathrm{cm^{-1}}$), suggesting that the effect of the additional $\mathrm{O{-}H\cdots\pi(C{\equiv}C)}$ interaction in the environment **A**, and hence any cooperative interaction, is also small. However, the difference between the red-shift in these complexes and that for **8** is relatively large (>60 $\mathrm{cm^{-1}}$) suggesting that the effect of the bisaccepting interaction in environment **B** is extremely significant. This observation could also be attributed to the fact that the $\mathrm{C{-}H\cdots O}$ distance in **8** (2.36 Å) is significantly longer than in **7** (2.17 Å), although the difference emphasises again the reduced accepting strength of the bisaccepting oxygen in the environment **B**.

Conclusions

In this paper, we have investigated the non-covalent interactions in $\mathrm{C{-}H\cdots\pi(C{\equiv}C)}$ complexes, comprising both ethyne oligomers and ethyne–water aggregates, using *ab initio* calculations. The $\mathrm{C{-}H\cdots\pi(C{\equiv}C)}$ interaction is found to be a very weak hydrogen bonding interaction, in accordance with previously reported work, with an enthalpy of interaction of around −4 kJ $\mathrm{mol^{-1}}$. The potential surface of this interaction in the ethyne T-shaped dimer demonstrates that the interaction energy is relatively insensitive to the position of the donating proton along the bond vector of the accepting triple bond as well as to the tilt angle of the major axis of the acetylene molecule. Therefore, the many crystallographic examples of $\mathrm{C{-}H\cdots\pi(C{\equiv}C)}$ interactions in which the $\mathrm{C{-}H\cdots M}$ angles deviate significantly from linearity do not necessarily represent significantly weaker interactions—an assertion which is supported by the poor distance–angle correlation for this contact.

The strength of the $\mathrm{O{-}H\cdots\pi(C{\equiv}C)}$ contact is again consistent with a very weak hydrogen bonding interaction with an enthalpy of interaction of around −6 kJ $\mathrm{mol^{-1}}$. It is noteworthy that the strength of this interaction, with a good hydrogen bond donor (*i.e.* water) is very similar to that of the ethyne T-shaped dimer although ethyne is a much poorer hydrogen bond donor. This observation suggests that the triple bond of the alkyne is a very poor hydrogen bond acceptor and interactions with it are largely governed by dispersion forces (*i.e.* van der Waals type) rather than electrostatic attractions (*i.e.* hydrogen bond type).

The interaction energy per $\mathrm{C{-}H\cdots\pi(C{\equiv}C)}$ interaction in ethyne trimers, both cyclic and linear, as compared to that in the ethyne dimer does not appear to suggest that there are large gains in stabilisation through cooperativity. This could be rationalised in terms of the electrostatic surface surrounding the hydrogen bond donating area of the molecule (*i.e.* the C–H bond) being only moderately positive thus making the surface a poor polariser of the (C≡C)–H bond it is donating to. Similarly, the electrostatic surface surrounding the accepting area of the molecule (*i.e.* the C≡C bond) is moderately negative making the surface a poor polariser of the C–H bond it is accepting from. However, the use of a more polarised surface—that of a water molecule—to create larger polarisation effects again resulted in small cooperative gains (0–10% range).

The shifts in the stretching frequency of the C–H bond of propyne in different intermolecular $\mathrm{C{-}H\cdots O}$ hydrogen bonding environments such as those reported for crystalline mestranol demonstrate that differences brought about by the effects of the $\mathrm{C{\equiv}C{-}H\cdots O}$ triple bond accepting a hydrogen bond, and thus any cooperative effects, are small. More importantly, they are insignificant relative to the effects of the accepting strength of the oxygen and therefore the infra-red spectroscopic data reported previously do not provide sufficient evidence to prove that large cooperative effects are operating in these hydrogen bonding arrays.

Given the evidence presented here, it is reasonable to conclude that hydrogen-bonded arrays containing terminal alkynes do not exhibit significant cooperative enhancements. In effect, the terminal alkyne cannot be polarised by other hydrogen bond acceptors/donors to enhance its own accepting/donating powers in a similar manner to the hydroxy group.

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Paper 8/00931G
Received 3rd *February* 1998
Accepted 30*th April* 1998