Weak hydrogen bonding. Part 2.[1] The hydrogen bonding nature of short C–H ••• π contacts: crystallographic, spectroscopic and quantum mechanical studies of some terminal alkynes

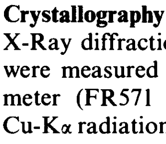
Thomas Steiner,*[†][a] Evgeni B. Starikov,[a] Ana M. Amado[b] and José J. C. Teixeira-Dias[b]
[a] *Institut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195 Berlin, Germany*
[b] *Molecular Physical Chemistry, University of Coimbra, P-3049 Coimbra, Portugal*

In a number of crystalline terminal alkynes, the alkyne C–H groups form short intermolecular contacts with other alkyne or with aromatic moieties. A particularly short C–H ••• phenyl contact is found in (±)-3-phenylbut-1-yn-3-ol, with an H ••• midpoint separation of only 2.51 Å. Crystallographic, spectroscopic and computational evidence is given to show that these contacts represent hydrogen-bond-type interactions. Quantum chemical calculations indicate hydrogen bond energies in the range 1–2.2 kcal mol^{-1}. Interconnected contacts such as C≡C–H ••• C≡C–H ••• C≡C–H exhibit a pronounced cooperativity effect, with energy increases of ~0.5 kcal mol^{-1} compared with isolated contacts. Based on these results, the role of the terminal alkyne group in cooperative hydrogen bond networks is described as topologically paralleling that of hydroxy groups.

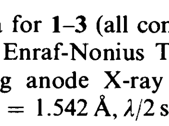
Acidic C–H groups are weak hydrogen bond donors, and hydrogen bonds from C–H to strong acceptors such as O, N, Cl$^-$ are abundant in organic, metal–organic and biological systems.[‡,2–5] Weaker hydrogen bond acceptors than O, N and Cl$^-$ are π-bonded functional groups such as C≡C, C=C, Ph, heteroarenes, *etc.* For these acceptors, hydrogen-bond-type interactions with the strong donors O–H, N–H and the hydrogen halides have been observed in various configurations[§,6–8] (usually called X–H ••• π *hydrogen bonds*, note that the π-bonded C-acceptors must be distinguished from the stronger carbene C-acceptors[9]). For fundamental reasons, one must also expect hydrogen-bond-like interactions to be formed between weak donors and weak acceptors, and this includes C–H ••• π hydrogen bonds. Actually, cohesive directional interactions between highly acidic C–H groups and π-bonded systems have been reported,[10] but it remains unclear as to what degree they parallel conventional O–H ••• O or N–H ••• O interactions, and if they really deserve the classification as 'hydrogen bonds'. Recently, in a preliminary communication, chains of short C≡C–H ••• C≡C–H ••• C≡C–H contacts in crystalline DL-prop-2-ynylglycine were interpreted as being cooperative C–H ••• π hydrogen bonds,[11] and it is the aim of the present study to put this view on solid ground.

To study C–H ••• π interactions, we have selected a model system with high acidity C–H donors and good π-bonded acceptors. Such a system is represented by the terminal alkynes, R–C≡C–H, which are, at the same time, strong C–H donors and strong π-acceptors. This potential to donate and accept *simultaneously* led us to hope to find cooperativity phenomena similar to those for conventional hydrogen bonding groups.

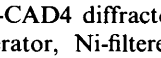
Crystal structures were determined for a series of such molecules,[¶] and for three of them (**1–3**) short C≡C–H ••• π contacts were actually found. For these compounds, additional vibrational spectroscopic experiments and quantum chemical calculations were performed. The results clearly show that the C–H ••• π interactions possess the essential characteristics of hydrogen bonds, including the property of cooperativity. The study was completed by a database analysis to quantify the frequencies with which the described interactions occur in crystal structures.



1



2



3

Experimental

Crystallography

X-Ray diffraction data for **1–3** (all commercially available[‖]) were measured on an Enraf-Nonius Turbo-CAD4 diffractometer (FR571 rotating anode X-ray generator, Ni-filtered Cu-Kα radiation with $\lambda = 1.542$ Å, $\lambda/2 \sin \theta_{max} = 0.89$ Å, room temperature). Structures were solved by direct methods and refined with standard techniques[12] (anisotropic refinement for non-H atoms and isotropic refinement for H atoms).[††] Relevant numerical data are given in Table 1.

[†] On leave from the *Max-Delbrück-Centrum für Molekulare Medizin, Forschungsgruppe Kristallographie*, Robert Rössle Straße 10, D-13122 Berlin, Germany.

[‡] For O acceptors, numerous crystal structures have been reported, where C–H ••• O hydrogen bonds play important roles in determining crystal packing arrangements and/or molecular conformations (a necessarily incomplete selection is given in ref. 3). The general structural properties of C–H ••• O hydrogen bonds are being extensively explored.[4,5]

[§] The phenomenon of X–H ••• π hydrogen bonding is not yet well studied even for the most common configurations with O–H and N–H donors. For example, it is still questionable whether the individual C atoms or the electrons of the π-bond should be regarded as the acceptor. X–H ••• π hydrogen bonds are neglected or overlooked in most publications of crystal structures, where they occur. Some overviews are given in ref. 6, a selection of individual spectroscopic and crystallographic studies in ref. 7, and some theoretical work in ref. 8.

[¶] In most of the structures, we observe 'normal' C≡C–H ••• O interactions. These crystal structures will be published elsewhere.

[‖] **1** was purchased from Aldrich; **2**, **3** from Lancaster.

[††] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details, see 'Instructions for Authors (1995),' *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

Table 1 Crystallographic data

	Compound		
	1	**2**	**3**
Formula	$C_{10}H_{10}O$	$C_{15}H_{10}O$	$C_5H_6O_2$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C2/c*	*I2/a*	*Pbca*
a/Å	19.817(2)	22.655(4)	6.862(1)
b/Å	8.5626(6)	8.6034(5)	5.7465(7)
c/Å	21.167(3)	24.256(2)	27.192(8)
β/°	101.43(1)	105.21(1)	90.0
V/Å^3	3520.5(7)	4562.3(9)	1072.2(4)
Z	16	16	8
Mol. per asymm. unit	2	2	1
D_{calc}/g cm^{-3}	1.10	1.20	1.22
Crystal size/mm^3	0.6 × 0.4 × 0.15	0.3 × 0.3 × 0.3	0.5 × 0.4 × 0.1
Unique reflections	2402	3060	656
σ-cut-off level	1.0	1.0	3.0
Reflections with $F_o > n\sigma(F_o)$	2284	2893	486
Reflections per parameter	8.2	7.9	5.6
R [for $F_o > n\sigma(F_o)$]	0.041	0.049	0.063

Table 2 Alkynyl stretching frequencies (cm^{-1}). ν_{CH} determined by FTIR spectroscopy, $\nu_{C≡C}$ determined by Raman spectroscopy. Standard errors are ~ 1 cm^{-1}

	Compound		
	1	**2**	**3**
ν_{CH}			
in apolar solution	3310^a	3305^b	3314^a
crystal^c	3272, 3288	3285, 3298	3281
shift $\Delta\nu_{CH}$	−38, −22	−20, −7	−33
$\nu_{C≡C}$			
in apolar solution	2115^a	2119^b	2123^a
crystal	2108, 2118	—^{d}	2114
shift $\Delta\nu_{C≡C}$	−7, +3	—^{d}	−9

^{a} In CCl_4. ^{b} In $CHCl_3$. ^{c} In KBr. ^{d} Crystal is unstable in the laser beam.

Vibrational spectroscopy

FTIR and Raman spectra were recorded for crystals (in KBr) and solutions in apolar solvents (Nicolet FTIR 7400 Spectrometer, equipped for the 4000–400 cm^{-1} region with a germanium on CsI beam splitter and with a DTGS detector with CsI windows. Raman spectroscopy: Jobin-Yvon T64000 Raman spectrometer, Coherent-Innova 300–05 Ar$^+$ laser, λ = 514.5 nm, 100 mW at the sample position). The intensity of the alkynyl ν_{CH} is high in the FTIR and low in the Raman spectra; for $\nu_{C≡C}$, the situation is *vice versa*. Numerical data of ν_{CH} (FTIR) and $\nu_{C≡C}$ (Raman) are given in Table 2.

Computations

The quantum-chemical calculations were performed at the *ab initio* MO LCAO SCF (HF + MP2) approximation using the GAUSSIAN 92/DFT routine package.[13] Hydrogen-bond energies and atomic partial charges were calculated using the 6-31G** basis set and by taking into account the BSSE (basis set superposition error) by means of the MASSAGE option of the program (hardware: CRAY Y-MP4D/464 of the Konrad-Zuse-Zentrum, Berlin). Calculations proceeded smoothly.

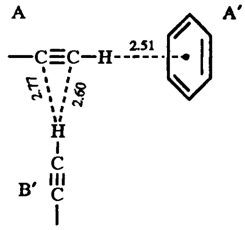
Database study

Cambridge Structural Database,[14] August 1994 update with 126 353 entries, ordered and error-free crystal structures of terminal alkynes, $R \le 0.07$, C≡C–H ··· X and Y–H ··· C≡C contacts with H ··· X separations < 2.8 Å (X = O, N, Cl, Br, F, S centroid of π-bonded systems including that of C≡C), normalized C–H bond based on C–H = 1.08 Å and a linear C≡C–H group.

Results and discussion

Experimental results

(*a*) **(±)-3-Phenylbut-1-yn-3-ol (1).** The crystal structure of **1** (Fig. 1) contains two symmetry-independent molecules **1A** and **1B**, which exhibit different intermolecular contacts (and also a different conformation of the phenyl ring with respect to the alkynyl group‡‡). The hydroxy groups of neighbouring molecules form four-sided ('quadrilateral') cooperative hydrogen-bonded rings, which nicely satisfy the hydroxy donor and acceptor potentials. This is certainly the dominating hydrogen bond motif of the structure. The alkynyl groups of molecules **1A** and **1B** form short intermolecular contacts as shown in Scheme 1. The C≡C–H group of molecule **1A** points almost linearly to the midpoint *M*(Ph) of the phenyl ring of molecule **1B** (angle at H = 171°). The H ··· *M*(Ph) separation of 2.51 Å is in the typical range for X–H ··· π hydrogen bonds with strong O–H and N–H donors[6] and is immediately suggestive of a significant bonding interaction (more detailed geometrical data are given in Table 3). To our knowledge, such a short C–H ··· Ph interaction has not been discussed before. At the same time, this C≡C–H group *accepts* a C≡C–H ··· π contact from molecule **1B**, with an H ··· *M*(C≡C) distance of 2.62 Å which is also in the range for weak hydrogen bonding [here *M*(C≡C) is the midpoint of the C≡C bond]. The alkynyl group of molecule **1B** does not accept a similar interaction, so that the arrangement as a whole is *finite*, C≡C–H ··· C≡C–H ··· Ph.



Scheme 1

To verify the bonding nature of these contacts, the IR and Raman spectra were recorded, Table 2. Generally, in a C≡C–H ··· X hydrogen bond, the C–H stretching frequency ν_{CH} is lowered. For C≡C–H ··· O hydrogen bonds, typical shifts of ν_{CH} compared with free C–H are −20 to −120 cm^{-1}, ref. 2(*f*). If a C≡C moiety *accepts* a significant hydrogen bond, the triple bond is weakened and $\nu_{C≡C}$ should decrease. In crystals of **1**, ν_{CH} and $\nu_{C≡C}$ are each split into two sharp bands, indicating the presence of two symmetry-independent molecules in the crystal lattice. Both ν_{CH} values are lowered compared with ν_{CH} in apolar solution, and the shifts of −22 and −38 cm^{-1} are indicative of two hydrogen bonding interactions of unequal strength. Of the $\nu_{C≡C}$ values, one is lowered by −7 cm^{-1}, whereas the other is marginally increased by +3 cm^{-1} compared with apolar solution. Looking at Scheme 1, these data can be easily interpreted as follows. Of the two C–H ··· π interactions, that with the molecule A acting as the donor is expected to be the stronger one, because (*i*) it has the shorter H ··· *M* distance, and (*ii*) its strength should be enhanced by

---

‡‡ Torsion angles C2–C3–C5–C6 are −23.3(3)° for molecule **A** and −9.1(3)° for molecule **B** (Table I-5 of the deposited material).

Table 3 Geometry of the C≡C–H ··· π contacts, for normalized H-positions based on a linear alkyne group with C–H = 1.08 Å. *M* designates the midpoint of the acceptor group

	Contact			
	H ··· *M* (Å)	H ··· C (Å)	C ··· *M* (Å)	C–H ··· *M* (°)
1; (±)-3-Phenylbut-1-yn-3-ol				
C2(A)≡C1(A)–H ··· Ph(B)	2.51	2.70–2.93	3.58	171
C2(B)≡C1(B)–H ··· C≡C(A)	2.62	2.60, 2.77[a]	3.67	164
2; 9-Ethynylfluoren-9-ol				
C14(A)≡C15(A)–H ··· Ph(A)	2.77	3.03–3.17	3.72	147
C14(B)≡C15(B)–H ··· C14(B)≡C15(B)		2.97[b]	3.31[b]	98[b]
3; Pent-4-ynoic acid				
C4≡C5–H ··· C4≡C5	2.67	2.75, 2.71[c]	3.70	159
4; DL-Prop-2-ynylglycine (ref. 11)				
C_γ≡C_δ–H ··· C_γ≡C_δ	2.71	2.99, 2.54[d]	3.78	172

[a] Acceptors C1(A) and C2(A), respectively. [b] Acceptor C15(B). [c] Acceptors C4 and C5, respectively. [d] Acceptors C_γ and C_δ, respectively.

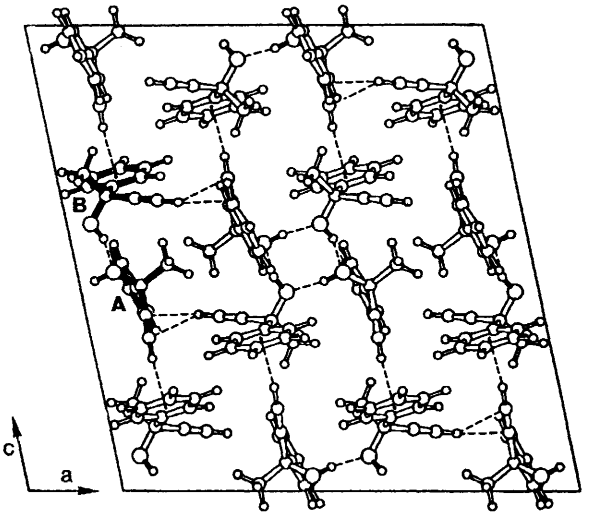


Fig. 1 Molecular and crystal structure of **1** [(±)-3-phenylbut-1-yn-3-ol)]. Projection is along the *b*-axis. Two symmetry-independent molecules are drawn with filled bonds. Hydroxy groups are indicated by filled O–H bonds.

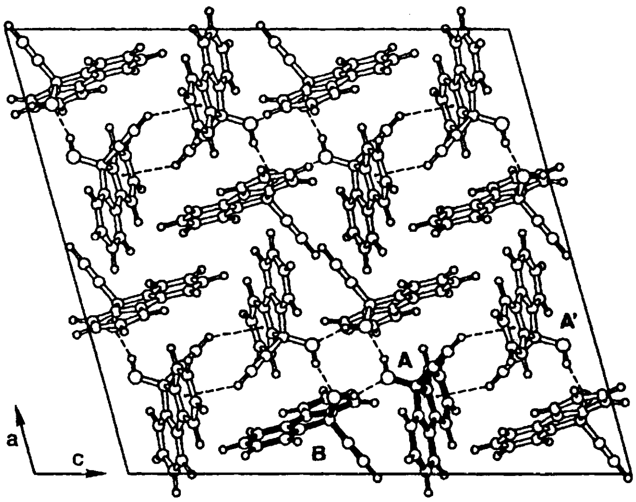
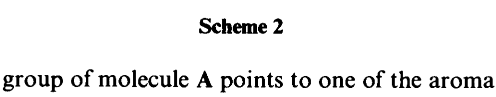


Fig. 2 Molecular and crystal structure of **2** (9-ethynylfluoren-9-ol). Projection is along the *b*-axis. Two symmetry-independent molecules are drawn with filled bonds. Hydroxy groups are indicated by filled O–H bonds.

the accepted interaction, *i.e.*, by the *cooperative effect*. Therefore, the alkynyl C–H band shifted by −38 cm^{-1} is assigned to molecule **A**, and that shifted by only −22 cm^{-1} to molecule **B**. This assignment is supported by the quantum-chemical calculations presented below. Only alkynyl group **A** accepts a C–H ··· π contact, and is therefore assigned the $\nu_{C\equiv C}$ downshift of −7 cm^{-1}.

(*b*) **9-Ethynylfluoren-9-ol (2).** In the crystal structure of **2**, there are two symmetry-independent molecules **2A** and **2B**, Fig. 2. Similar to the crystal structure of **1**, the hydroxy groups form a four-sided cooperative cycle which satisfies all O–H hydrogen bond potentials. The alkynyl groups of **2A** and **2B** form very different intermolecular interactions as shown in Scheme 2. The alkynyl group of molecule **A** points to one of the aromatic six-membered rings of a symmetry-related molecule **A'**, with an H ··· *M*(Ph) separation of 2.77 Å. The alkynyl group of molecule **B** forms a very long contact with an antiparallel alkynyl group of a symmetry-related molecule **B'** (H ··· C = 2.97 Å); this geometry has been referred to as the '*tandem*'-configuration,[2e] and should (if cohesive at all) be strengthened by mutual polarization of the engaged groups.



Scheme 2

The IR study on crystals of **2** is summarized as follows. Here, the alkynyl ν_{CH} is split into two bands with shifts of −20 and −7 cm^{-1}, as compared with apolar solution. This indicates weak hydrogen-bonding interactions of both symmetry-independent alkynyl groups, one of which, however, is only very weak. As will be seen below, quantum chemical calculations suggest the assignment of the stronger downshift to alkynyl residue **A**, and the marginal downshift of −7 cm^{-1} to residue **B**. Unfortunately, the crystals are unstable in intensive laser light, so that it was not possible to record Raman spectra to be able to deduce the behaviour of $\nu_{C\equiv C}$.

(*c*) **Pent-4-ynoic acid (3).** The crystal structure of **3** contains only one molecule per asymmetric crystal unit. As expected, the typical dimer structure of carboxylic acids is formed, Fig. 3. These dimers are arranged in layers stacked along the *a*-axis, in which the alkyne groups form an infinite zigzag pattern,

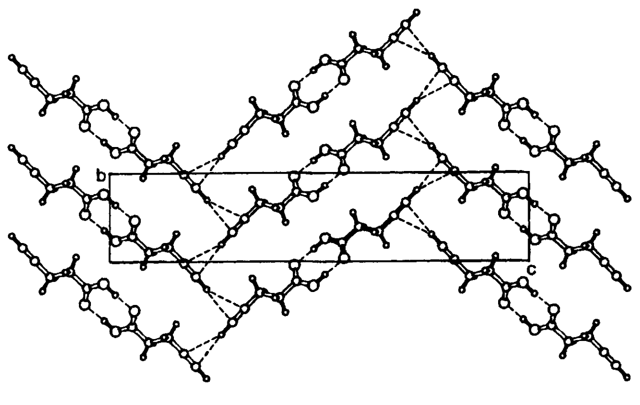
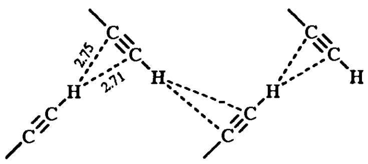


Fig. 3 Molecular and crystal structure of **3** (pent-4-ynoic acid). Projection is along the *a*-axis. One molecule is drawn with filled bonds.

Table 4 Database analysis: acceptors of the shortest intermolecular contact < 2.8 Å formed by terminal alkynes (141 C≡C–H residues in 113 crystal structures, present work included)

Acceptor	Number
O	66
N	8
Cl, Br, F	7
S	1
C≡C	18
C=C	5
Arene	8
No. contacts < 2.8 Å	28

Scheme 3. This zigzag chain parallels the pattern classified as cooperative hydrogen bonds for DL-prop-2-ynylglycine.[11]



Scheme 3

Analogous patterns are also formed by the lower homologues but-3-ynoic acid[10a] and prop-2-ynoic acid[15] (despite different space groups).

In the IR-spectrum of crystalline **3**, a single band for ν_{CH} is observed, which shows a downshift of -33 cm^{-1} compared with the apolar solution.§§ This is a significantly stronger shift than for the C≡C–H ··· C≡C contact in **1** (-20 cm^{-1}), which has very similar geometry (Table 3), but is not a part of an infinite cooperative pattern. This indicates that in the above zigzag pattern, the strength of the individual interactions significantly increases due to cooperativity, as compared with isolated contacts. In the Raman spectrum, a single band for $\nu_{C\equiv C}$ is observed, which is shifted by -9 cm^{-1} compared with apolar solution, indicating weakening of the C≡C bond.

Quantum chemical calculations

The energies of the intermolecular interactions discussed above were estimated by means of *ab initio* quantum chemical calculations. For reasons of limited computer capacity, such calculations must be restricted to polyatomic fragments with the total number of atoms ≤ 30. Therefore, the hydrogen-bonded patterns in question were approximated by contacts of identical geometry between appropriate smaller molecules: the alkyne residues were approximated by propyne (CH_3–C≡C–H), and the aromatic moieties by methylbenzene for **1** and by benzene for **2**. Owing to this gross but necessary simplification, the results can be taken as only (rough) estimates; however, they should reflect the general trends of the interactions in a qualitatively correct way.

(*a*) Isolated contacts (dimers). The bond energy of a T-shaped propyne dimer was calculated to be -0.9 kcal mol^{-1} with the geometry observed in **1** [H ··· *M*(C≡C) = 2.62 Å], -1.1 kcal mol^{-1} with the geometry observed in **3** [H ··· *M*(C≡C) = 2.67 Å], and -0.7 kcal mol^{-1} with the geometry found in DL-prop-2-ynylglycine[11] [H ··· *M*(C≡C) = 2.71 Å]. For a dimer propyne–methylbenzene with the geometry as in **1** [H ··· *M*(Ph) = 2.51 Å], a bond energy of -1.6 kcal mol^{-1} was calculated, and for propyne–benzene in the geometry as in **2** [H ··· *M*(Ph) = 2.77 Å], an energy of -1.4 kcal mol^{-1} was obtained.¶¶. These values indicate that aromatic moieties are somewhat stronger acceptors than alkynyl residues.

For a propyne dimer with antiparallel molecules as in **2** (Scheme 1, left), a bonding energy of only -0.1 kcal mol^{-1} was obtained, which can only be regarded as marginal or insignificant.

For **2**, both types of C–H ··· π contact are isolated and should not be (strongly) influenced by cooperativity effects. Therefore, the energy estimates of -1.4 and -0.1 kcal mol^{-1} can be directly applied to the realistic contacts shown in Fig. 2. This allows assignment of the alkynyl IR stretching frequencies: the band shifted by -20 cm^{-1} compared with apolar solution is assigned to residue **A**, and that shifted by only -7 cm^{-1} to residue **B**.

(*b*) Cooperative patterns. For **1** and **3**, the C–H ··· π contacts are interconnected. If they actually are of hydrogen-bonding type, they must possess the property of *cooperativity*, *i.e.*, the interactions must mutually increase each other's strengths, and the bond energy per contact must be greater than the sum of individual isolated contacts. Actually, for the finite chain of C–H ··· π contacts found in **1** (Scheme 1), energies of -1.4 kcal mol^{-1} are calculated for the C≡C–H ··· C≡C contact, and -2.2 kcal mol^{-1} for the C≡C–H ··· Ph contact. This means that the energy of the former contact is enhanced by -0.5, and that of the latter by -0.6 kcal mol^{-1} compared with isolated dimers, clearly showing a pronounced cooperativity effect (Sharma and Desiraju calculated energy increases of similar magnitudes for cooperative C–H ··· O hydrogen bonds[5]). In the IR spectrum, the alkynyl ν_{CH} value shifted by -38 cm^{-1} compared with apolar solution should therefore be assigned to residue **A**, and that shifted by -22 cm^{-1} to residue **B**.

For the zigzag chain of interconnected alkyne–alkyne contacts, Scheme 3, bond energies are calculated as -1.1 kcal mol^{-1} for the dimer, -1.6 kcal mol^{-1} for an additional contact, and -2.1 kcal mol^{-1} for the contact between two dimers (*i.e.*, for the central bond in a tetramer). Addition of a fifth residue produced no further increase in the energy of the central bonds, so that the energy per bond in the infinite chain is estimated to be around -2.1 kcal mol^{-1}, again clearly showing enhancement due to cooperativity.

Database studies

To see whether the above arrangements occur frequently in crystal structures, the closest contacts C–H ··· X formed by

---

§§ Crystals of **3** dissolve well in CCl_4. In the IR spectrum of the solution, the typical broad and intense band for hydrogen bonding O–H is observed, but no band for free O–H. This shows that **3** dissolves as a dimer (as is often found for carboxylic acids).

¶¶ For interactions of the stronger N–H donors with benzene, bond energies around 3 kcal mol^{-1} have been calculated.[8a]

Table 5 $C\equiv C-H\cdots Ph$ hydrogen bonds with $H\cdots M < 2.8$ Å found in the Cambridge Structural Database (M = midpoint). For normalized H position

Ref. code[a]	Ref.	$H\cdots M$ (Å)	$H\cdots C$ (Å)	$C\cdots M$ (Å)	$C-H\cdots M$ (°)
This work, **1**		2.51	2.70–2.93	3.58	171
This work, **2**		2.77	3.03–3.17	3.72	147
DIJZOL	16(*a*)	2.59	2.72–3.13	3.60	154
PENMAW	16(*b*)	2.53	2.72–3.03	3.60	170
PENTYN	16(*c*)	2.79	2.79–3.41	3.82	159
TADJUD	16(*d*)	2.58	2.58–3.23	3.63	162
VEFPIF[t]	16(*e*)	2.84	2.51–3.68	3.87	158
VUYXES	16(*f*)	2.71	2.75–3.30	3.76	165

[a] Reference code with the Cambridge Structural Database. [b] $H\cdots M > 2.8$ Å, but included because of the short $H\cdots C$ contact of 2.51 Å.

terminal alkynes were investigated in a crystallographic database analysis, Table 4. Of 141 $C\equiv C-H$ residues in 113 crystal structures (including those from the present work), 82 (=58%) form hydrogen bonds $H\cdots X < 2.8$ Å with the 'conventional' acceptors O, N, Cl, Br, F, S. The number of 31 $C-H\cdots\pi$ interactions (=22%) is surprisingly high; of these, the acceptor is 18 times $C\equiv C$, 5 times $C{=}C$ and 8 times an arene. 28 of the alkyne groups (=20%) form no intermolecular contact < 2.80 Å(for a longer $H\cdots X$ cut-off value, some of these would also fall into one of the other classes).

The conventional $C-H\cdots X$ hydrogen bonds need not be discussed here (only the eye-catching single $C-H\cdots S$ hydrogen bond in Table 4 should be mentioned, which is short and linear with $H\cdots S$ = 2.58 Å, $C-H\cdots S$ = 169°, and is found in VITYUS[17]). For the $C\equiv C-H\cdots C\equiv C$ contacts, no information going beyond the earlier study[11] is obtained. For the novel $C\equiv C-H\cdots Ph$ interactions, however, a number of examples with geometries similar to **1** are found, Table 5. The distances from H to the arene midpoint M(Ph) may be as short as 2.5 Å. In most of the cases, the $H\cdots M$(Ph) separation is significantly shorter than any of the individual $H\cdots C$ distances, *i.e.*, the $C\equiv C-H$ donor points actually at M(Ph). However, there are also exceptions with one or two $H\cdots C$ distances of lengths similar to or even shorter than $H\cdots M$(Ph). The shortest $H\cdots C$ distances observed are slightly above 2.50 Å, which is the same value as for the shortest $H\cdots C$ distances in $C\equiv C-H\cdots C\equiv C$ contacts[11] (and also in the $C\equiv C-H\cdots C{=}C$ contacts in Table 4, for which, however, the data quantity seems to be too small for an extended discussion).

Conclusions

The above results show that short contacts of sufficiently acidic C–H groups with π-bonded acceptor groups ($C\equiv C$, $C{=}C$, arenes) possess the essential properties of weak hydrogen bonds. (*i*) Geometrically, the contacts are directional with close to linear $C-H\cdots\pi$ angles, and short $H\cdots\pi$ (and $H\cdots C$) distances down to 2.5 Å; these are the typical geometries for weak hydrogen bonding. (*ii*) In the infrared spectrum, the donor C–H stretching frequencies are reduced by over 20 cm^{-1} compared with solutions in apolar solvents, which are the IR frequency shift values typically observed for $C-H\cdots O$ hydrogen bonds. (*iii*) *Ab initio* quantum chemical calculations suggest bonding energies in the range 1–2.2 kcal mol^{-1}, which again are similar to what is usually calculated for $C-H\cdots O$ interactions. (*iv*) Interconnected systems of $C-H\cdots\pi$ interactions possess the property of *cooperativity*, *i.e.*, the contacts enhance the strengths of each other, and the hydrogen-bond energy per contact is greater than the energy of an isolated interaction. Energy enhancements due to cooperativity are estimated ~0.5 kcal mol^{-1} per contact. Also this value parallels that from the calculations for interconnected $C-H\cdots O$ interactions.

The above conclusions should be valid not only for terminal alkynes, but also for other C–H groups that are capable of donating hydrogen bonds. However, the *simultaneous* donor and acceptor potential distinguishes $C\equiv C-H$ from most other types of C–H donor, making it an excellent model to study cooperativity phenomena. Actually, in crystal structures, $C\equiv C-H\cdots\pi$ interactions are often found as part of cooperative patterns. These patterns may be finite such as $C\equiv C-H\cdots C\equiv C-H\cdots Ph$ in **1** of the present study, or as $C\equiv C-H\cdots C\equiv C-H\cdots O$ in 1-ethynyl-2,7-dimethoxynaphthalene.[18] The cooperative patterns may also be infinite, such as the zigzag chain $C\equiv C-H\cdots C\equiv C-H\cdots C\equiv C-H$ in **3** and many other crystal structures,[11] or the two-dimensional network of $C\equiv C-H\cdots C\equiv C$ contacts in the orthorhombic phase of solid acetylene.[19]

These results complement earlier studies where infinitely hydrogen-bonded networks have been reported, in which terminal alkynes act as donors of 'normal' $C-H\cdots O$ interactions, such as $C\equiv C-H\cdots O-H\cdots C\equiv C-H\cdots O-H$ in donazole[6b] and $C\equiv C-H\cdots O-H\cdots O-H\cdots C\equiv C-H\cdots O-H$ in 2-ethynyladamantan-2-ol.[6d,20] Topologically, $C\equiv C-H$ may therefore play the same role in hydrogen-bond networks as the hydroxy group O–H.

Acknowledgements

We thank Wolfram Saenger for giving us the opportunity to carry out the crystallographic and theoretical part of this work in his laboratory. The study was supported by the *Deutsche Forschungsgemeinshaft* (T. S. by Sa 196/25-1; E. B. S. by Sta 354/2-1), by *Deutscher Akademischer Austauschdienst* (322-inida-dr), and by *Junta Nacional de Investigação Científica e Tecnológica*, Lisboa (A. M. A. and J. J. C. T. D.; Research Unit No. 70/94, *Química-Física Molecular*).

References

1 Part 1: Th. Steiner, *J. Chem. Soc., Perkin Trans. 2*, preceding paper; precursor studies of this series: refs. 4(*d*)–(*g*), 11, and also: Th. Steiner and W. Saenger, *Acta Crystallogr., Sect. D*, 1993, **49**, 592; Th. Steiner, *Acta Crystallogr., Sect. D*, 1995, **51**, 93.

2 (*a*) G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Freeman, San Francisco, 1960; (*b*) D. J. Sutor, *J. Chem. Soc.*, 1963, 1105; (*c*) R. D. Green, *Hydrogen Bonding by C–H Groups*, Macmillan, London, 1974; (*d*) R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063; (*e*) G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991; (*f*) G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290, and references cited therein.

3 (*a*) G. Ferguson and J. Tyrrell, *Chem. Commun.*, 1965, 195; (*b*) J. Sussman, N. C. Seeman, S.-H. Kim and H. M. Berman, *J. Mol. Biol.*, 1972, **66**, 403; (*c*) I. Goldberg, *Acta Crystallogr., Sect. B*, 1975, **31**, 754; (*d*) P. Seiler and J. D. Dunitz, *Helv. Chim. Acta*, 1989, **72**, 1125; (*e*) H. Bock, R. Dienelt, H. Schödel and Z. Havlas, *J. Chem. Soc., Chem. Commun.*, 1993, 1792; (*f*) C. V. K. Sharma, K. Panneerselvam, T. Pilati and G. R. Desiraju, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2209; (*g*) Th. Steiner, G. Koellner, K. Geßler and W. Saenger, *J. Chem. Soc., Chem. Commun.*, 1995, 511.

4 (*a*) G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1989, 179; (*b*) G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1990, 454; (*c*) V. R. Pedireddi and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1992, 988; (*d*) Th. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1992, **114**, 10156; (*e*) Th. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1993, **115**, 4540; (*f*) Th. Steiner, *J. Chem. Soc., Chem. Commun.*, 1994, 101; (*g*) Th. Steiner, *J. Chem. Soc., Chem. Commun.*, 1994, 2341.

5 C. V. K. Sharma and G. R. Desiraju, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2345.

6 (*a*) P. Hobza and R. Zahradnik, *Chem. Rev.*, 1988, **88**, 871, and references cited therein; (*b*) M. A. Viswamitra, R. Radhakrishnan, J. Bandekar and G. R. Desiraju, *J. Am. Chem. Soc.*, 1993, **115**, 4868,

and references cited therein; (*c*) M. F. Perutz, *Phil. Trans. R. Soc. London, Ser. A*, 1993, 105; (*d*) H. S. Rzepa, M. H. Smith and M. L. Webb, *J. Chem. Soc., Perkin Trans. 2*, 1994, 703.

7 (*a*) K. Nakatsu, H. Yoshioka, K. Kunimoto, T. Kinugasa and S. Ueji, *Acta Crystallogr., Sect. B*, 1978, **34**, 2357; (*b*) A. D. U. Hardy and D. D. MacNicol, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1140; (*c*) W. G. Read and W. H. Flygare, *J. Chem. Phys.*, 1982, **76**, 2238; (*d*) S. Ueji, K. Nakatsu, H. Yoshioka and K. Kinoshita, *Tetrahedron Lett.*, 1982, **23**, 1173; (*e*) H. S. Rzepa, M. L. Webb, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 765; (*f*) J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr and R. L. Vincent, *Nature* (*London*), 1991, **349**, 683; (*g*) D. Mootz and A. Deeg, *J. Am. Chem. Soc.*, 1992, **114**, 5887; (*h*) S. Suzuki, P. G. Green, R. E. Bumgarner, S. Dasgupta, W. A. Goddard III and G. A. Blake, *Science*, 1992, **257**, 942; (*i*) D. A. Rodham, S. Suzuki, R. D. Suenram, F. J. Lovas, S. Dasgupta, W. A. Goddard III and G. A. Blake, *Nature* (*London*), 1993, **362**, 735; (*j*) S. Liu, X. Ji, G. L. Gilliland, W. J. Stevens and R. N. Armstrong, *J. Am. Chem. Soc.*, 1993, **115**, 7910; (*k*) G. Ferguson, J. F. Gallagher, C. Glidewell and C. M. Zakaria, *Acta Crystallogr., Sect. C*, 1994, **50**, 70.

8 (*a*) M. Levitt and M. F. Perutz, *J. Mol. Biol.*, 1988, **201**, 751; (*b*) T.-H. Tang, W.-J. Hu, D.-Y. Yan and Y.-P. Cui, *J. Mol. Struct.* (*Theochem*), 1990, **207**, 319; (*c*) J. B. O. Mitchell, C. L. Nandi, I. K. McDonald, J. M. Thornton and S. L. Price, *J. Mol. Biol.*, 1994, **239**, 315.

9 A. J. Arduengo III, S. F. Gamper, M. Tamm, J. C. Calabrese, F. Davidson and H. A. Craig, *J. Am. Chem. Soc.*, 1995, **117**, 572.

10 (*a*) V. Benghiat and L. Leiserowitz, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1772; (*b*) L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1976, **32**, 775; (*c*) R. K. McMullan, Å. Kvick and P. Popelier, *Acta Crystallogr., Sect. B*, 1992, **48**, 726; (*d*) M. Nishio and M. Hirota, *Tetrahedron*, 1989, **45**, and references cited therein; (*e*) T. E. Müller, D. M. P. Mingos and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 1787; (*f*) G. T. Frazer, R. D. Suenram, F. J. Lovas, A. S. Pine, J. T. Hougen, W. J. Lafferty and J. S. Muenter, *J. Chem. Phys.*, 1988, **89**, 6028, and references cited therein; (*g*) G. T. Frazer, F. J. Lovas, R. D. Suenram, J. Z. Gillies and C. W. Gillies, *Chem. Phys.*, 1992, **163**, 91; (*h*) R. Hunter, R. H. Haueisen and A. Irving, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 566.

11 Th. Steiner, *J. Chem. Soc., Chem. Commun.*, 1995, 95.

12 (*a*) G. M. Sheldrick, SHELXS86, in *Crystallographic Computing*, 3rd edn., eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, 1986, pp. 175–189; (*b*) G. M. Sheldrick, SHELX76, *Program for Crystal Structure Determination*, University of Cambridge, UK, 1976; (*c*) N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Birkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. J. P. Stewart and J. A. Pople, GAUSSIAN92/DFT, *Revision G.3*, Gaussian, Inc., Pittsburgh PA, 1993.

14 F. H. Allen, J. E. Davies, J. E. Galloy, J. J. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187.

15 Z. Berkovitch-Yellin and L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1984, **40**, 159.

16 (*a*) M. Bohshar, H. Heydt, G. Maas, H. Gumbel and M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 597; (*b*) T. Kunstler, D. Schollmeyer, H. Singer and M. Steigerwald, *Tetrahedron: Asymmetry*, 1993, **4**, 1645; (*c*) A. Perez-Salazar, F. H. Cano, S. Martinez-Carrera and S. Garcia-Blanco, *Acta Crystallogr., Sect. B*, 1977, **33**, 2276; (*d*) V. E. Shklover, V. A. Igonin, Yu. T. Struchkov, I. R. Golding, N. A. Vasnyova, I. V. Chernoglazova, O. L. Lazareva and A. N. Shchegolikhin, *Mol. Cryst. Liq. Cryst.*, 1990, **180B**, 417; (*e*) K. L. Evans, G. W. Horn, F. R. Fronczek, R. D. Gandour and S. F. Watkins, *Acta Crystallogr., Sect. C*, 1990, **46**, 331; (*f*) J. A. Moore, F. R. Fronczek and R. D. Gandour, *Acta Crystallogr., Sect. C*, 1988, **44**, 2027.

17 A. E. Shalamov, O. V. Agashkin, A. I. Yanovskii, Yu. T. Struchkov, A. P. Logunov, G. P. Revenko and Yu. G. Bosyakov, *Zh. Strukt. Khim.*, 1990, **31**, 153.

18 P. Prince, F. R. Fronczek and R. D. Gandour, *Acta Crystallogr., Sect. C*, 1990, **46**, 1720.

19 R. K. McMullan, Å. Kvick and P. Popelier, *Acta Crystallogr., Sect. B*, 1992, **48**, 726.

20 (*a*) S. Y. Lin, Y. Okaya, D. M. Chiou and W. J. le Noble, *Acta Crystallogr., Sect. B*, 1982, **38**, 1669; (*b*) E. Steinwender, E. T. G. Lutz, J. H. van der Maas and J. A. Kanters, *Vib. Spectrosc.*, 1993, **4**, 217.

Paper 5/00796H
Received 9*th February* 1995
Accepted 21*st March* 1995