Weak hydrogen bonding. Part 5.[1] Experimental evidence for the long-range nature of C≡C–H ··· π interactions: crystallographic and spectroscopic studies of three terminal alkynes

Thomas Steiner,[*,a] **Matthias Tamm,**[b] **Alexander Grzegorzewski,**[b] **Niels Schulte,**[b] **Nora Veldman,**[c] **Antoine M. M. Schreurs,**[c] **Jan A. Kanters,**[c] **Jan Kroon,**[c] **John van der Maas**[d] **and Bert Lutz**[d]

[a] *Institut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195 Berlin, Germany*
[b] *Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstraße 34-36, D-14195 Berlin, Germany*
[c] *Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[d] *Department of Analytical Molecular Spectrometry, Faculty of Chemistry, Utrecht University, PO Box 80083, 3508 TB Utrecht, The Netherlands*

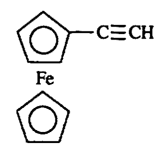
In the crystal structures of three terminal alkynes, long C≡C–H ··· C≡C contacts with H ··· C separations in the range 2.7–3.1 Å are observed. Despite the long distances, these contacts possess the characteristic infrared spectroscopic features of weak hydrogen bonds. This provides direct evidence that the range of C–H ··· π interactions donated by sufficiently acidic C–H groups extends beyond van der Waals separation. In two of the crystal structures, the C–H ··· π interactions form interconnected systems C≡C–H ··· C≡C–H ··· C≡C–H.

Introduction

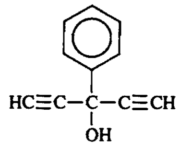
It is well known that acidic C–H groups like in C≡C–H or $CHCl_3$ can donate,[2] and that π-bonded systems like C≡C or Ph can accept hydrogen bonds.[†,3] Consequently, hydrogen-bond type interactions C–H ··· π must be expected to occur in systems that contain acidic C–H donors and suitable π-acceptors. Actually, in a number of crystal structures, short C≡C–H ··· π[4] and Cl_3C–H ··· π[5] contacts were observed and interpreted as weak bonding interactions (for a heteroarene acceptor, see ref. 6). Of particular interest is the observation of short C–H ··· Ph[7] and C–H ··· C≡C[8] contacts in the stabilisation of inclusion complexes. However, it remained unclear to what degree these interactions parallel conventional hydrogen bonds, and most authors cautiously characterized them just as 'C–H ··· π interactions'. Only recently, by a combination of crystallographic, IR spectroscopic and quantum-chemical techniques, could it be shown for the acidic C≡C–H donors that short contacts to C≡C and Ph acceptors have in fact the structural and spectroscopic properties of weak hydrogen bonds,[9] very similar to O–H ··· π and N–H ··· π interactions.

The previous studies of C–H ··· π bonds were focused on the shortest occurring contacts, in which the donor H-atom approaches the centroid M of π-acceptors to distances down to 2.5 Å.[9] The long-distance behaviour of these interactions has as yet not been investigated. Hydrogen bonds in general have a pronounced long-range character, and operate also far beyond van der Waals separations.[2d] This is of great importance for their role in steering molecular association. If they are of hydrogen-bond nature, C–H ··· π interactions should operate at similarly long ranges.

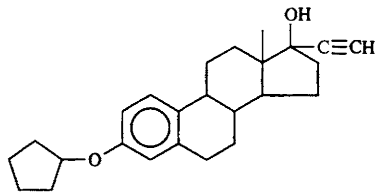
In the present study, we report structural and spectroscopic investigations of the crystalline compounds **1**–**3**, which shed light upon the nature of long C–H ··· π contacts occurring in these substances.



1



2



3

Ethynylferrocene 1

The crystal structure of ethynylferrocene, **1**, contains three symmetry-independent molecules, A, B, C (crystallographic data in Table 1). Since their conformations are virtually identical, the molecular structure and the atomic numbering scheme needs to be shown for only one molecule, Fig. 1(*a*). The crystal packing scheme is complex, with the ethynyl groups crowded around the inversion centre of the space group, Fig. 2. Each ethynyl residue points at the ethynyl residue of a neighbouring molecule, whereby a six-membered cyclic arrangement is formed, Fig. 3 (this pattern has not been reported for C–H ··· C≡C interactions before). In Fig. 3, the ethynyl groups alternately point 'up, down, up, down, up, down', *i.e.* they form a chair-type puckered ring with approximate S_6-symmetry, Scheme 1 (in Fig. 2, this ring is seen in side-view).

The contact geometries within the ring are unequal, Fig. 3 and Table 2. In all three independent contacts the ethynyl

---

[†] The π-bonded C-acceptors like C≡C or Ph should be distinguished from the chemically different carbene C-accceptors.[17]

Table 1 Crystallographic data

	Compound		
	1	**2**	**3**
Formula	$C_{12}H_{10}Fe$	$C_{11}H_8O$	$C_{25}H_{32}O_2 \cdot 0.5CH_4O$
M_w	210.1	156.2	380.5
Temperature	100 K	100 K	Room temp.
Crystal system	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$I\bar{4}$	$P2_1$
a/Å	9.4068(9)	16.270(2)	10.346(1)
b/Å	11.668(1)	16.270(2)	6.5114(4)
c/Å	13.626(1)	6.5893(6)	32.805(5)
α/°	74.598(6)	90	90
β/°	79.705(7)	90	92.79(2)
γ/°	70.815(7)	90	90
V/Å^3	1354.8(2)	1744.2(3)	2207.3(5)
Z	6	8	4
Mol. per asymm. unit	3	1	2
D_c/g cm^{-1}	1.55	1.19	1.15
Crystal size/mm^3	0.7 × 0.7 × 0.7	0.5 × 0.5 × 0.2	0.6 × 0.05 × 0.03
μ/mm^{-1}	1.61	0.08	0.56
Measured reflections	6661	1328	3690
R_{merge} (F^2)	0.048	0.031	0.047
Unique reflections	6205	1292	3621
Unique refl. $F^2 > 2\sigma(F^2)$	5893	1211	1919
$wR(F^2)$ [for $F^2 > 2\sigma(F^2)$]	0.078	0.083	0.148
R [for $F^2 > 2\sigma(F^2)$]	0.029	0.032	0.073

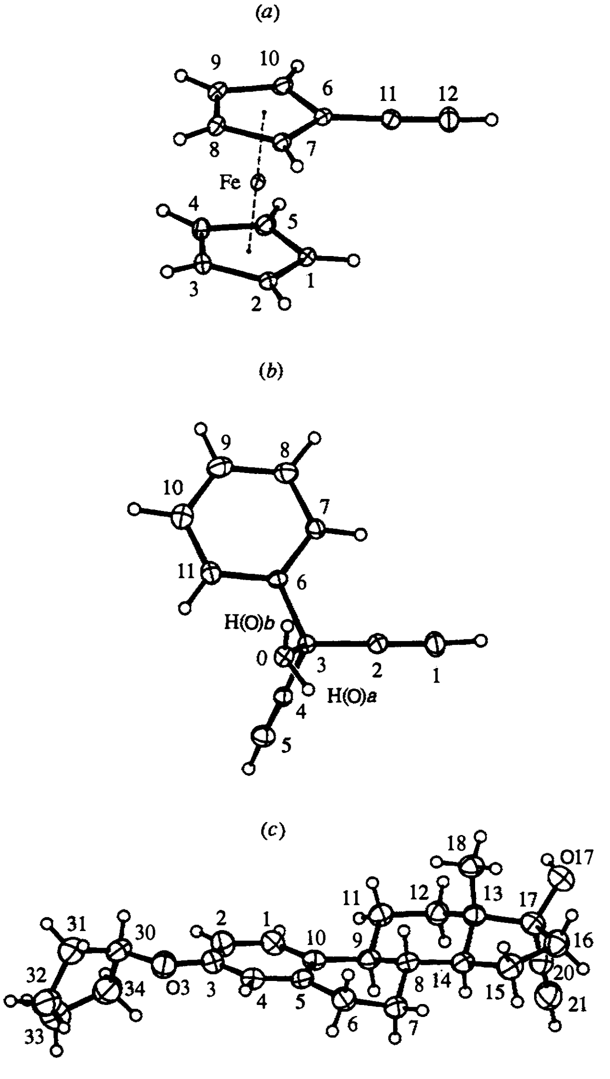


Fig. 1 Molecular structure and atomic numbering scheme for **1**, molecule A (top), **2** (centre) and **3**, molecule A (bottom). Displacement ellipsoids are drawn at the 50% probability level for **1** and **2**, and at the 30% probability level for **3**.

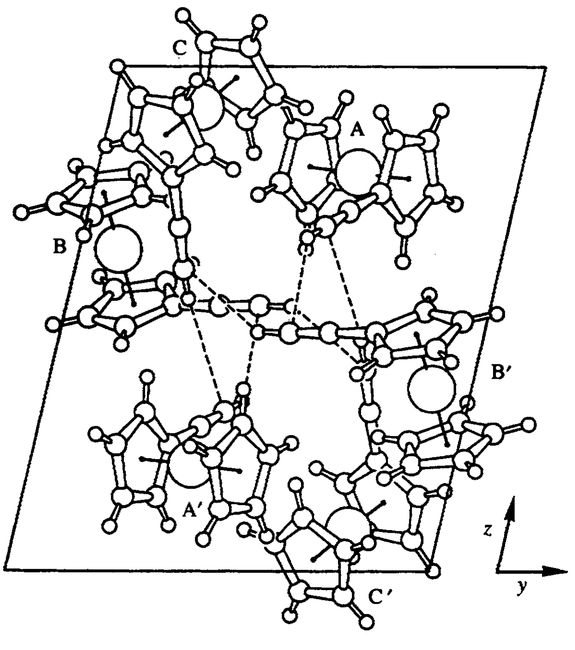
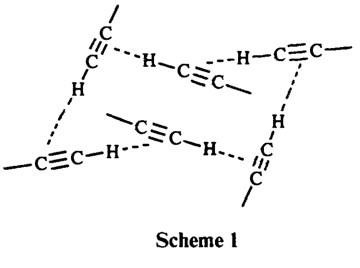


Fig. 2 Crystal structure for **1**. Projection is along the x-axis. Symmetry-independent molecules A, B and C are labelled near Fe.



Scheme 1

groups point at the neighbouring terminal C atom rather than at the midpoint of the C≡C bond. The shortest of the contacts, C(12A)–H···C(12B), is geometrically similar to the C–H···C≡C hydrogen bonds of the previous studies,[4c,9a] whereas the longest contact, C(12C)–H···C(12A′), is outside the normally accepted hydrogen bond ranges.

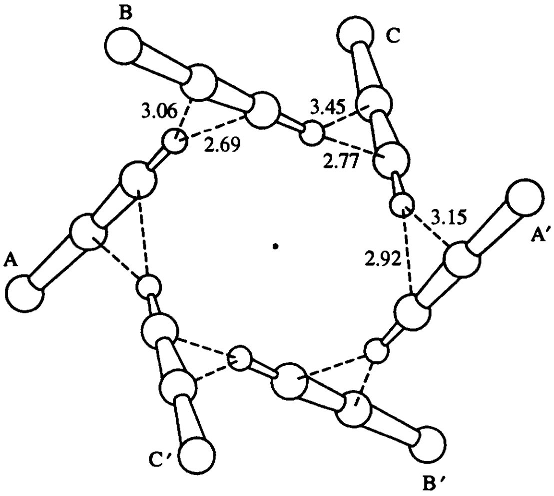


Fig. 3 The intermolecular contacts of the ethynyl groups, forming a cooperative cycle of six C–H ··· C≡C hydrogen bonds. For clarity, only the fragment C(6)–C(11)≡C(12)–H of each molecule is drawn. The crystallographic inversion centre in the midpoint of the arrangement is marked by a dot.

Table 2 Geometry of the C–H···C≡C interactions in **1** in Å and degrees. M = centre of the C≡C bond (for ideal H-position based on a C–H bond length of 1.09 Å)

	H···C	C···C	C–H···C
C(12A)–H···C(12B)	2.69	3.547(3)	135
···C(11B)	3.06	3.801(3)	126
···M(B)	2.82	3.628(3)	131
C(12B)–H···C(12C)	2.77	3.695(3)	142
···C(11C)	3.45	4.187(3)	127
···M(C)	3.07	3.903(3)	134
C(12C)–H···C(12A)	2.92	3.964(3)	160
···C(11A)	3.15	4.115(3)	147
···M(A)	2.98	3.996(3)	155

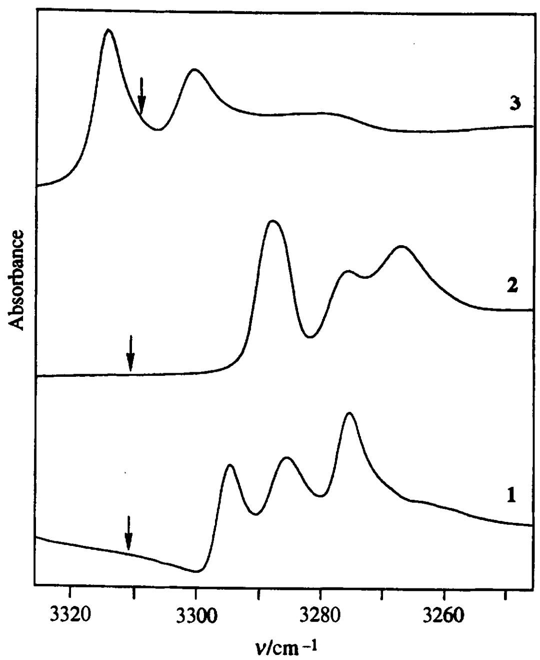


Fig. 4 IR spectra of crystalline **1** at 95 K (bottom curve) **2** at 95 K (middle curve) and **3** at room temp. (top curve). Only the spectral region of the alkynyl C–H stretching band is shown. The position of $\nu_{\equiv C-H}$ in dilute CCl_4 solution is indicated by an arrow. Numerical values are given in Table 3. Spectra 1 and 3 contain minor artifacts, presumably due to crystal inhomogeneity.

Table 3 Relevant IR stretching frequencies in cm^{-1}, for solutions in CCl_4 at room temp. and for crystals (for **1** and **2** at *ca.* 95 K, for **3** at room temp.)

	In CCl_4	Crystal	Shift $\Delta\nu_{\text{cryst-soln}}$
Compound **1**			
$\nu_{\equiv C-H}$	3311.2	3275.5	−35.7
		3285.6	−25.6
		3294.6	−16.6
Compound **2**			
$\nu_{\equiv C-H}$	3311.0	3288.1	−22.9
		3275.8	−35.3
		3267.1	−43.9
ν_{O-H}	3592.3	3207.1	−385.2
Compound **3**			
$\nu_{\equiv C-H}$	3309	3314.4	+5
		3300.4	−9
ν_{O-H}	3615	3171.9[a]	−443

[a] Very broad composed band.

If only the contact *pattern* is looked at, the regular motif of Fig. 3 immediately suggests that the arrangement represents a cooperative cycle of six C–H···C≡C hydrogen bonds, irrespective of the rather long contact distances. Such an image cannot, however, be taken as a proof. Conclusive interpretation of the arrangement requires experimental evidence for the bonding nature of the contacts. A most sensitive method to detect a bonding situation of an X–H group is IR spectroscopy: if of bonding nature, a given contact is normally associated with spectral red-shift of the X–H stretching frequency compared to 'free' X–H groups [see, *e.g.* ref. 3(*b*)]. For the weak C–H···X interactions, these red-shifts are typically ≤100 cm^{-1}.‡ For a dilute solution of **1** in CCl_4, the ethynylic C–H stretching vibration is found at 3311.2 cm^{-1}; this is the typical value for 'free' ethynyl groups.[10] Since the X-ray data of **1** was measured at *ca.* 100 K, the corresponding solid state IR spectra were taken at a similar temperature. The relevant spectral region is shown in Fig. 4 (curve 1); numerical data are given in Table 3. The $\nu_{\equiv C-H}$ band is split into a triplet, with the individual bands exhibiting shifts of $\Delta\nu = -35.7$, -25.6 and -16.6 cm^{-1}, respectively, compared to solution in CCl_4. These we associate with the three symmetry-independent C–H···C≡C contacts, the largest shift with the shortest contact and the smallest shift with the longest contact. All three values are indicative of a weak but significant bonding effect, and even the longest of the contacts (appreciably longer than van der Waals separation) must be assessed as hydrogen bonding in nature. This clearly supports the view that the arrangement in Fig. 3 represents a cycle of weak hydrogen bonds.

It is of importance that the three Δν values differ from each other, reflecting the differences of the contact geometries. The variation of *ca.* 0.23 Å in the H···C distance (Fig. 3) is associated with a variation of Δν by more than a factor of two. Although the three interactions are functionally equivalent within the pattern, they appear to have significantly different strengths.

3-Phenylpenta-1,4-diyn-3-ol 2

The conformation of **2** in the crystal structure is shown in Fig. 1(*b*). The phenyl ring is almost coplanar with one of the ethynyl groups [torsion angle C(2)–C(3)–C(6)–C(7) = 4.1(2)°]. The orientation of the hydroxy group is twofold disordered, with

---

‡ In some exceptionally strong C–H···O interactions, spectral downshifts appreciably larger than 100 cm^{-1} are observed.[10]

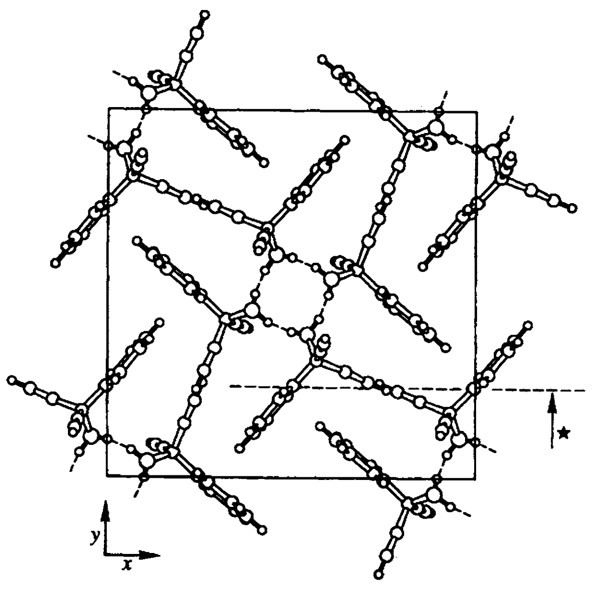


Fig. 5 Crystal structure of **2**, projection is along the tetragonal axis *z*. The section that is shown in Fig. 6, and the direction of view, is indicated by a dashed line and an arrow.

both orientations staggered with respect to the other residues.§ Although there is only one molecule per asymmetric crystal unit, the centred tetragonal symmetry causes a complex crystal packing scheme, Fig. 5. The dominant pattern of intermolecular interactions is a cooperative cycle of four O–H···O hydrogen bonds, which satisfies the hydroxy hydrogen bond potentials. The disorder of the hydroxy orientation results in disorder of the hydrogen bond orientation in the cycle.

The system of intermolecular contacts formed by the ethynyl groups is shown in Fig. 6 (numerical data in Table 4). C(2)≡C(1)–H donates a conventional C–H···O hydrogen bond to the hydroxy group of a neighbouring molecule. The other ethynyl group points directly into the central angle of an adjacent pentadiyne molecule, thereby contacting both C≡C moieties with long H···C distances *ca.* 2.9 Å. Of these contacts, crystal symmetry generates infinite chains (or ribbons) of molecules which chelate ethynyl groups of their neighbours. At a first glance, this arrangement could be interpreted as van der Waals contacts in a favourable close packing pattern. In the light of the previous observations (on **1** and in ref. 9), it is tempting to interpret the pattern as an infinite chain of cooperative three-centred ('bifurcated') C–H···π hydrogen bonds (again, a motif that has not been reported before).

To see if the ethynyl groups actually experience bonding effects, the IR spectra were recorded. In CCl_4 solution, the typical $\nu_{\equiv C-H}$ value for free C–H is found (Table 3).¶ In the solid state, the $\nu_{\equiv C-H}$ band is split into at least three components, which exhibit spectral red-shifts between −22.9 and −43.9 cm^{-1} [Table 3, Fig. 4(*b*)]. This complex behaviour for the two symmetry-independent C≡C–H groups is presumably due to the twofold hydroxy orientational disorder, which results in different intra- and inter-molecular environments of the two ethynyl groups. The intramolecular O–H···C≡C interactions, *gauche*-oriented, may enhance the donor properties of the accepting ethynyl groups. The important point is that the spectrum contains no band for free ethynylic C–H, *i.e.* both the C–H···O and the bifurcated C–H···π interactions cause appreciable spectral shifts. Even if the C–H···π contacts are associated with the band exhibiting the smallest shift, $\Delta\nu = -22.9$ cm^{-1}, it still is clearly of a weak hydrogen bonding nature.

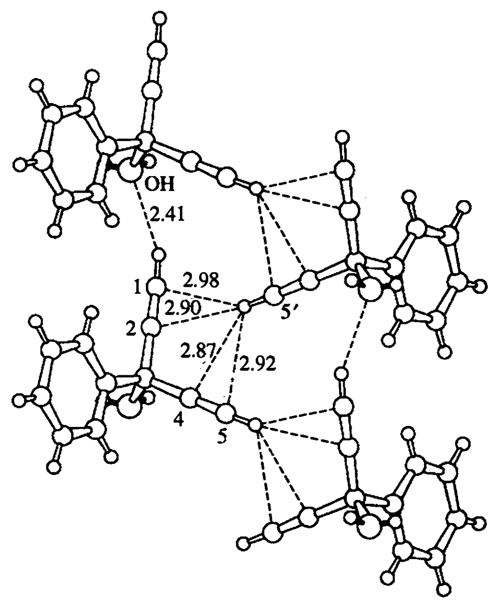


Fig. 6 The intermolecular contact pattern of the alkynyl groups of **2** (distances in Å)

Table 4 Geometry of the O–H···O, C–H···O and C–H···C≡C interactions in **2** in Å and degrees. M = centre of the C≡C bonds (for ideal H-position based on bond lengths of O–H = 0.98 and C–H = 1.09 Å)

	H···A	D···A	D–H···A
O–H···O bonds			
O–H(a)···O	1.80	2.737(2)	158
O–H(b)···O	1.80	2.737(2)	159
C–H···O bond			
C(1)–H···O	2.41	3.376(2)	147
C–H···π bonds			
C(5)–H···C(1)	2.98	3.919(3)	145
···C(2)	2.90	3.971(2)	168
···M(1,2)	2.88	3.900(2)	156
···C(4)	2.87	3.791(2)	142
···C(5)	2.92	3.577(2)	119
···M(4,5)	2.84	3.638(2)	130

Quinestrol hemi-methanolate 3

If grown from methanolic solution, crystals of the ethynylsteroid **3** contain two molecules per asymmetric crystal unit, and one additional MeOH molecule. The steroid molecules have very similar geometries, so that only one needs to be shown in Fig. 1(*c*). The steroid skeleton has virtually the same conformation as the parent molecule 17-α-ethynyl-estradiol (in ref. 11 described for the hemihydrate crystal form) and is therefore not further discussed here.

A section of the crystal packing scheme is shown in Fig. 7. The steroid and MeOH hydroxy groups form an infinite cooperative chain of O–H···O hydrogen bonds, O(17A)–H···O(17B)–H···OMe–H···O(17A′)–H, running in the direction of the crystallographic *y*-axis. This nicely satisfies the

---

§ O–H(*a*) is oriented *trans* with respect to the phenyl ring, and ± *gauche* with respect to the ethynyl groups. O–H(*b*) is oriented *trans* with respect to the ethynyl group C(4)≡C(5)–H, and *gauche* with respect to the other ethynyl group and the phenyl ring, Fig. 1(*b*). The hydroxy orientations are therefore associated with different intramolecular O–H···π interactions.[18]

¶ It is of interest that in CCl_4, the O–H stretching frequency, 3592.3 cm^{-1}, is reduced compared to free tertiary α-ethynyl alcohols, *ca.* 3610 cm^{-1}. Two effects may be responsible for this frequency red shift, intramolecular O–H···π interactions and through-bond effects of the π-substituents *via* C_α, respectively.[19]

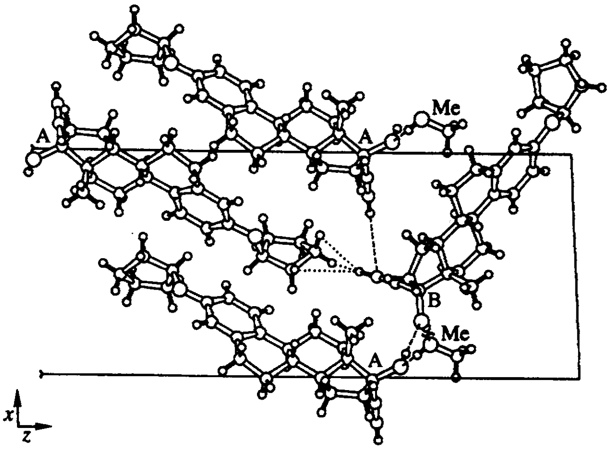


Fig. 7 Crystal structure of **3**, projection is along the monoclinic axis *y*. Symmetry independent molecules A and B are labelled near C17.

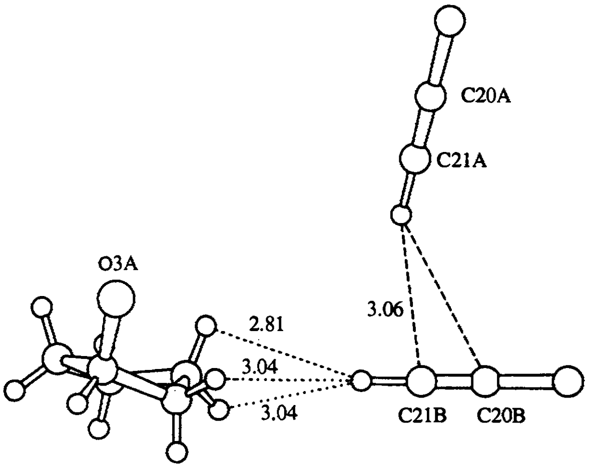


Fig. 8 The intermolecular contact pattern of the alkynyl groups of **3** (distances in Å)

Table 5 Geometry of the O–H···O and C–H···C≡C interactions in **3** in Å and degrees. M = centre of the C≡C bond (for ideal H-position based on bond lengths of O–H = 0.98 and C–H = 1.09 Å)

	H···A	D···A	D–H···A
O–H···O bonds			
O(17A)–H···O(17B)	1.92	2.893(9)	177
O(17B)–H···OM	1.75	2.720(11)	170
OM–H···O(17A)	2.00	2.792(9)	137
C–H···π bond			
C(21A)–H···C(21B)	3.06	4.05(1)	152
···C(20B)	3.41	4.26(1)	135
···M[C(21),C(20)]	3.19	4.12(1)	143

hydroxy hydrogen bond potentials. The two symmetry-independent ethynyl groups form only long intermolecular contacts: ethynyl residue A points in the direction of residue B, with an H···C(21) separation of 3.06 Å, Figs. 7 and 8, and Table 5. Residue B points at the edge of the cyclopentyl group of a neighbouring molecule, with all H···H separations >2.8 Å. These contacts are well beyond van der Waals separation, so that both ethynyl groups might be regarded as 'free' or 'undisturbed'. Such a view, however, contradicts with the IR absorption spectrum which shows a splitting of the $\nu_{\equiv C-H}$ band into two components. One component experiences a red-shift of −9 cm^{-1} compared to solution in CCl_4, and the other one a slight blue-shift of +5 cm^{-1}, Table 3. These are only small shifts, but they still indicate different effects from the intermolecular surrounding on the two ethynyl H-atoms. On the basis of Fig. 8, the spectral data can be interpreted as follows: the red-shifted component belongs to residue A and indicates a weakly bonding nature of the long C–H···C≡C contact. The other component belongs to residue B which forms C≡C–H···H–C(sp^3) contacts; the slight blue-shift might indicate a weakly repulsive character of these interactions. Additional evidence for a repulsive nature of the C–H···H–C(sp^3) contacts comes from low temperature IR spectra (*ca.* 100 K), where the blue-shift is increased to +7 cm^{-1} ($\nu_{\equiv C-H}$ = 3316 cm^{-1}).

Conclusions

The crystal structures of **1**, **2** and **3** contain long C≡C–H···C≡C contacts with H···C distances in the range 2.7–3.1 Å. Despite the long distances, these contacts exhibit the characteristic spectroscopic features of weak bonding interactions. Even for an H···C separation of 3.06 Å, an effect on the vibrational properties of ≡C–H is shown. This provides direct evidence that for sufficiently acidic C–H, the range of C–H···π interactions extends beyond van der Waals separation (*ca.* 2.7 Å), which is one of the essential characteristics of hydrogen bond-type forces.[2d] The previous classification of (much shorter) C–H···π contacts as weak 'hydrogen bonds'[9] is thereby confirmed.

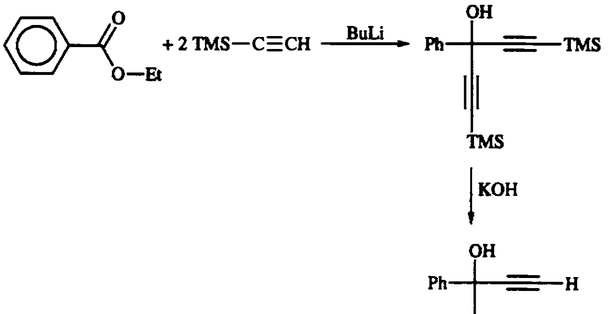
Topologically, the C–H···π contacts in **1** and **2** are fused into patterns that resemble the cooperative patterns formed by conventional hydrogen bonds.[12] These patterns can be composed of only C–H···π interactions, such as the six-membered ring in **1** (or the infinite chains reported previously[4c,9a]), or they can consist of different types of hydrogen bonds like the system of O–H···O, C–H···O and C–H···π bonds in **2**.

Experimental

Source of the compounds

Compound 1. Ethynylferrocene **1** was synthesised according to published procedures.[13] Bulky brown crystals were obtained by crystallization from hexane–diethyl ether (1 : 1, v : v) at −26 °C.

Compound 2 (3-phenylpenta-1,4-diyn-3-ol). The synthesis of **2** has been published previously.[14] In the present work, **2** was synthesized by a modified method from ethylbenzoate and trimethylsilylacetylene following Scheme 2; experimental details for this synthetic path have been published previously.[9b] Needle shaped colourless crystals were obtained by crystallization from diethyl ether at −26 °C.



Scheme 2

Compound 3. Quinestrol [3-*O*-cyclopentyl-17α-ethynylestradiol; 3-cyclopentyloxy-17α-ethynyl-1,3,5(10)-estratrien-17β-ol] **3** is commercially available (Sigma), and was recrystallized by slow evaporation of solutions in MeOH. Crystallization from EtOH yields a hemi-ethanolate with different crystal packing [$P2_1$, a = 13.950(6), b = 6.5945(8), c = 25.403(8) Å, β =

104.78(4)°, $V = 2260(1)$ Å^3, $Z = 4$; crystal structure unpublished].

Crystallography

Crystals of **1** are stable at ambient conditions, but decay in the X-ray beam within a few hours (at room temp.). Therefore, X-ray data collection had to be performed at liquid nitrogen temperature (*ca.* 100 K, Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation, $\lambda = 0.710\,73$ Å). X-Ray data for **2** were collected under the same conditions. X-Ray data for **3** were collected at room temp., Enfraf-Nonius Turbo-CAD4 diffractometer with Ni-filtered Cu-Kα radiation, $\lambda = 1.541\,84$ Å. The crystal structures were solved by direct methods[15] and refined with standard techniques[16] (refinement on F^2 of all reflections; H-atoms of **1** and **2** refined isotropically; for **3**, H-atoms bonded to C calculated to ideal positions, H-atoms bonded to O refined isotropically).|| Relevant numerical data are given in Table 1.**

Vibrational spectroscopy

IR spectra were recorded, *versus* open beam background, in transmission on a Mattson research Series FTIR spectrometer equipped with a DTGS detector and connected to a personal computer operating with standard WINFIRST software. Scanning parameters: spectral range 4000–4450 cm^{-1}, optical resolution 2 cm^{-1}; apodization: medium; number of scans averaged: 16. Solution spectra were recorded in 10 mm Infrasil Quartz cells at ambient temperature at a concentration $<10^{-5}$ mol dm^{-3} in CCl_4 (Merck; dried over 4 Å molecular sieves). (Micro)crystalline samples were prepared as KBr pellets for **1** and as a mull in poly(chlorotrifluoroethylene) oil for **2** and **3**. A programmable variable temperature vacuum cell (SPECAC 21525) connected to a microprocessor-based controller, and with nitrogen as coolant, was used to record spectra in the range between 95–300 K.

Acknowledgements

Part of this study was performed during a stay of T. S. at the Bijvoet Center, Utrecht, in the frame of the Research Network 'Molecular Recognition Phenomena' of the European Union (ERB-CHRX-CT94-0469). The study was also supported by the Deutsche Forschungsgemeinschaft (T. S. by Sa 196/25-1; M. T. by Ta 189/1-1 and Ta 189/1-2). T. S. is on leave from the Max-DelbrückCentrum für Molekulare Medizin, Forschungsgruppe Kristallographie (Professor U. Heinemann), Robert Rössle Straße 10, D-13122 Berlin, and thanks Wolfram Saenger (Freie Universität Berlin) for giving him the opportunity to initiate and complete the study in his laboratory.

|| Atomic coordinates, bond lengths and angles and thermal parameters of **1**, **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/27.

** Only after submission was it learned that the crystal structure of **1** has already been determined at room temperature in a different context; K. Wust, O. Elsner and H. Schottenberger, *Synlett*, 1995, 833.

References

1 Part 3. T. Steiner, E. B. Starikov and M. Tamm, *J. Chem. Soc., Perkin Trans. 2*, 1996, 67; Part 4. T. Steiner, M. Tamm, B. Lutz and J. van der Maas, *Chem. Commun.*, 1996, 1127.

2 (*a*) D. J. Sutor, *J. Chem. Soc.*, 1963, 1105; (*b*) R. D. Green, *Hydrogen Bonding by C-H Groups*, Macmillan, London, 1974; (*c*) R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063; (*d*) G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991; (*e*) G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290; (*f*) J. Bernstein, M. C. Etter and L. Leiserowitz, in *Structure Correlation*, ed. H.-B. Bürgi and J. D. Dunitz, VCH, Weinheim, 1994, vol. 2, pp. 431–507; (*g*) T. Steiner, *Crystallogr. Rev.*, 1996, **6**, 1.

3 (*a*) M. A. Viswamitra, R. Radhakrishnan, J. Bandekar and G. R. Desiraju, *J. Am. Chem. Soc.*, 1993, **115**, 4868; (*b*) E. Steinwender, E. T. G. Lutz, J. H. van der Maas and J. A. Kanters, *Vib. Spectrosc.*, 1993, **4**, 217; (*c*) M. F. Perutz, *Phil. Trans. R. Soc. Lond. A*, 1993, 105; (*d*) H. S. Rzepa, M. H. Smith and M. L. Webb, *J. Chem. Soc., Perkin Trans. 2*, 1994, 703; (*e*) P. K. Bakshi, A. Linden, B. R. Vincent, S. P. Roe, D. Adhikesavalu, T. S. Cameron and O. Knop, *Can. J. Chem.*, 1994, **72**, 1273.

4 (*a*) V. Benghiat and L. Leiserowitz, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1772; (*b*) R. K. McMullan, Å. Kvick and P. Popelier, *Acta Crystallogr., Sect. B*, 1992, **48**, 726; (*c*) T. Steiner, *J. Chem. Soc., Chem. Commun.*, 1995, 11.

5 T. E. Müller, D. M. P. Mingos and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 1787.

6 R. Hunter, R. H. Haueisen and A. Irving, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 566.

7 (*a*) D. A. Leigh, P. Linnane, R. G. Pritchard and G. Jackson, *J. Chem. Soc., Chem. Commun.*, 1994, 389; (*b*) T. Steiner and K. Gessler, *Carbohydr. Res.*, 1994, **260**, 27; (*c*) T. Fujimoto, R. Yanagihara, K. Kobayashi and Y. Aoyama, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2113.

8 T. Steiner and W. Saenger, *J. Chem. Soc., Chem. Commun.*, 1995, 2087.

9 (*a*) T. Steiner, E. B. Starikov, A. M. Amado and J. J. C. Teixeira-Dias, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1321; (*b*) T. Steiner, E. B. Starikov and M. Tamm, *J. Chem. Soc., Perkin Trans. 2*, 1996, 67.

10 B. Lutz, J. van der Maas and J. A. Kanters, *J. Mol. Struct.*, 1994, **325**, 203.

11 V. J. van Geerestein, *Acta Crystallogr., Sect. C*, 1987, **43**, 1206.

12 (*a*) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; (*b*) J. Bernstein, R. E. Davis, L. Shimoni and N.-L. Chang, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1555.

13 G. Doisneau, G. Balavoine and T. Fillebeen-Ichan, *J. Organomet. Chem.*, 1992, **425**, 113.

14 G. Märkl, R. Liebl and H. Baier, *Liebigs Amn. Chem.*, 1981, 1610.

15 G. M. Sheldrick, SHELXS86, in *Crystallographic Computing 3*, ed. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, 1986, pp. 175–189.

16 G. M. Sheldrick, SHELXL-93, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1993.

17 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.

18 T. Visser and J. H. van der Maas, *Spectrochim. Acta*, 1985, **41A**, 757.

19 T. Visser and J. H. van der Maas, *Spectrochim. Acta*, 1984, **40A**, 959.

Paper 6/02307J
Received 2nd *April* 1996
Accepted 16th *July* 1996