# Cooperative C≡C–H···C≡C–H Interactions: Crystal Structure of DL-Prop-2-ynylglycine and Database Study of Terminal Alkynes

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In the crystal structure of DL-prop-2-ynylglycine, the alkyne groups form a zigzag pattern with intermolecular H···C distances of 2.54 Å, which is suggestive of cooperative C–H···C≡C (C–H···π) hydrogen bonding; alkyne–alkyne contacts with similar geometries are found in a number of other crystal structures.

It has been shown repeatedly from gas phase experiments,[1] crystal structure analyses,[2–4] solid state IR data[2,5] and theoretical calculations[6–8] that C≡C moieties and other π-bonded systems can accept interactions from O–H, N–H and hydrogen halides, which possess the essential properties of hydrogen bonds (usually called X–H···π hydrogen bonds). For C≡C acceptors, the gas phase geometry is T-shaped with the X–H donor pointing towards the centre of the triple bond.[1] In the crystalline state, this symmetrical geometry is observed only rarely (as in[4] but-2-yne·HCl); in most cases, one H···C separation is significantly shorter than the other.[3] Related interactions with acidic C–H groups were proposed early on[7,9] but could be definitely found in a crystal structure only very recently[10] (with chloroform as the donor and –Au–C≡C–Au– as the acceptor).† In this context, the terminal alkynes are particularly interesting: they are among the strongest C–H hydrogen bond donors[11–13] and should therefore be capable of donating and accepting C–H···π interactions *simultaneously*. In the study below, a chain of C≡C–H···C≡C–H···C≡C–H interactions is actually found in crystalline DL-prop-2-ynylglycine (DL-2-aminopent-4-ynoic acid), which is believed to be the first example of interconnected C–H···π hydrogen bonds described as a cooperative pattern.

In the crystal structure of the α-amino acid DL-prop-2-ynylglycine,‡ the $NH_3^+$, $C_\alpha$–H and $CO_2^-$ groups of neighbouring molecules are connected by a complex spatial network of N–H···O and $C_\alpha$–H···O hydrogen bonds. Unlike most crystal structures of terminal alkynes, the prop-2-ynyl residue does not act as a C–H···O hydrogen bond donor, but points almost linearly at the terminal C atom ($C_\delta$) of a symmetry related prop-2-ynyl residue, whereby an infinite chain of C≡C–H···C≡C–H contacts is formed (Fig. 1). In these contacts, the H···$C_\delta$ separation is only *ca.* 2.54 Å (Table 1; based on the normalized C–H bond length of 1.08 Å). This is a value typical for hydrogen bonds donated from C–H to the stronger acceptors O and N, and is even shorter than the average H···C separation reported for O–H···C≡C and N–H···C≡C interactions.[2] On geometric grounds, this suggests that the pattern can be classified as a chain of hydrogen bond type interactions§ (note that H···C is over 0.4 Å shorter than in the herringbone-packing interaction[14] of *e.g.* benzene).

The occurrence of similar contacts in other crystal structures was checked by a search through the Cambridge Structural Database[15] (only ordered and error-free organic structures with $R < 0.07$, H···C≡C < 2.8 Å). Actually, a number of short C≡C–H···C≡C contacts could be identified, the shortest in CELFAA[16] with H···C 2.51 Å (Table 1). The two H···C separations in the H···C≡C–H contacts may be almost equal, or very different (as

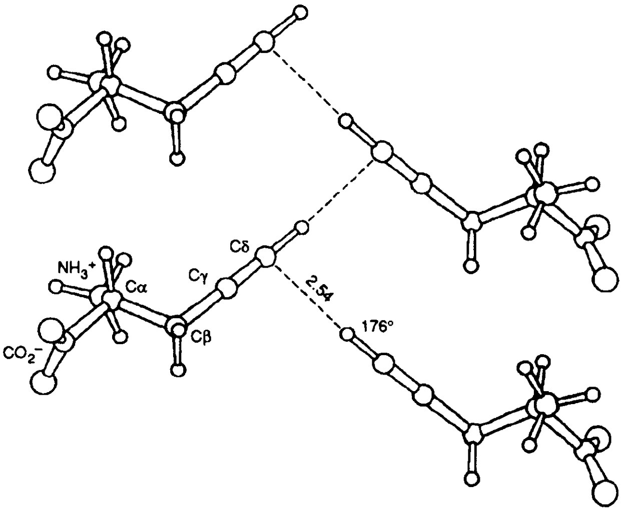

**Fig. 1** Molecular conformation and cooperative C≡C–H···C≡C–H interactions in crystalline DL-prop-2-ynylglycine. For clarity, conventional hydrogen bonds are not shown. H-atoms are drawn in normalized positions (*i.e.* shifted along the X–H bond to neutron-determined bond lengths).

**Table 1** C≡C–H···C≡C geometries[a] in DL-prop-2-ynylglycine and in crystal structures of terminal alkynes in the Cambridge Structural Database (acceptor groups labelled C1≡C2–H, Mid = midpoint of triple bond; distances in Å, angles in °)

| Substance | H···C1 | H···Mid | H···C2 | C···C1 | C···Mid | C···C2 | $\theta_{CH\cdots C1}$ | $\theta_{CH\cdots Mid}$ | $\theta_{CH\cdots C2}$ |
|---|---|---|---|---|---|---|---|---|---|
| This work[b] | 2.99 | 2.71 | 2.54 | 4.03 | 3.78 | 3.62 | 163 | 172 | 176 |
| CELFAA[c] | 2.51 | 2.51 | 2.66 | 3.58 | 3.56 | 3.65 | 171 | 164 | 152 |
| VEVBON[d] | 2.68 | 2.57 | 2.60 | 3.59 | 3.58 | 3.65 | 143 | 154 | 165 |
| DEYNAP[e] | 2.65 | 2.59 | 2.66 | 3.71 | 3.66 | 3.71 | 166 | 172 | 165 |
| BUYNAC[f] | 2.91 | 2.76 | 2.74 | 3.95 | 3.83 | 3.79 | 163 | 168 | 164 |
| PASZAK[g] | 2.68 | 2.79 | 2.68 | 3.68 | 3.73 | 3.87 | 154 | 166 | 175 |
| | 2.68 | 2.61 | 2.67 | 3.63 | 3.63 | 3.72 | 147 | 157 | 165 |
| | 2.67 | 2.63 | 2.71 | 3.63 | 3.63 | 3.72 | 146 | 153 | 158 |
| | 2.69 | 2.67 | 2.79 | 3.69 | 3.73 | 3.87 | 154 | 166 | 175 |
| DADPAZ[h] | 3.20 | 2.87 | 2.63 | 4.19 | 3.81 | 3.49 | 152 | 146 | 136 |
| BIYVEK[i] | 2.66 | 2.67 | 2.81 | 3.61 | 3.59 | 3.67 | 147 | 143 | 137 |

[a] For normalized H positions based on linear C≡C–H groups and C–H = 1.08 Å. [b] Donor and acceptor $C_\gamma{\equiv}C_\delta$–H. [c] Bis- cyclohexylammonium) prop-2-ynyl phosphate dihydrate;[16] donor and acceptor C2≡C3–H. [d] 1-Ethynyl-2,7-dimethoxynaphthalene;[17] donor C11B≡C12B–H, acceptor C11A≡C12A–H. [e] 1,4-Diethynylnaphthalene;[18] donor C27≡C28–H, acceptor C11≡C12–H. [f] But-3-ynoic acid;[10] donor C3′≡C4′–H, acceptor C3≡C4–H. [g] Tetraprop-2-ynylmethane;[19] first to fourth line: donor C2≡C1–H, acceptor C12≡C11–H; donor C6≡C7–H, acceptor C9≡C8–H; donor C9≡C8–H, acceptor C6≡C7–H; donor C12≡C11–H, acceptor C2≡C1–H. [h] Methyl-4(propyn-2-yloxy)-7-chromen-2-one;[20] donor and acceptor C13≡C14–H. [i] Diethynyl-2α,16α Nor-*A* 5α-androstanediol-2β,16β;[21] donor and acceptor CE12≡CE22–H.

in the present study: 2.54 and 2.99 Å, respectively, Table 1); in the latter case, either of the C atoms may accept the shorter contact. The substances in Table 1 belong to very different compound classes. Some carry charges (as prop-2-ynylglycine) and/or strong conventional hydrogen bond donors and acceptors, whereas for others C≡C–H is the most polar residue. For molecules R–C≡C–H, no particular chemical requirement for R is obvious to allow the discussed interaction to be formed.

In most of the crystal structures in Table 1, the C≡C–H···C≡C–H contacts are not isolated, but form zigzag patterns as shown in Fig. 1. Topologically they are equivalent with conventional cooperative hydrogen bonds O–H···O–H···O–H. In these, the polarisation of the O–H groups is enhanced compared to isolated O–H···O hydrogen bonds, thereby increasing the hydrogen bond energy per contact[22] ('cooperative effect'). It can be assumed that in the alkynyl zigzag chains, the strength of the interaction is analogously increased compared to isolated C–H···π contacts. Also patterns involving conventional hydrogen bond partners are observed, such as a finite chain C≡C–H···C≡C–H···O in VEVBON.[17] The depicted ability to participate in hydrogen bond networks with the same topological functionality as O–H distinguishes the terminal alkynes from all other C–H donors and C≡C acceptors.

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## Footnotes

† For arene acceptors, interactions of type C–H···π···H–C were recently found in crystal structures: Th. Steiner and K. Gessler, *Carbohydr. Res.*, 1994, **260**, 27; R. Hunter, R. H. Haueisen and A. Irving, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 566.

‡ *Crystal data*: $C_5H_7NO_2$, Commercial material (Sigma) recrystallized from water, room temp., space group $P2_1/a$, $a = 9.881(2)$, $b = 4.734(1)$, $c = 13.017(3)$ Å, $\beta = 108.04(1)°$, $V = 578.9(2)$ Å$^3$, $Z = 4$, $D_c = 1.30$ g cm$^{-3}$, Enraf-Nonius CAD4 diffractometer, Ni-filtered Cu-Kα X-rays, $\lambda/2\sin\theta_{max} = 0.89$ Å, 847 unique reflections with $F_o > \sigma(F_o)$, programs SHELXS[23] and SHELX76,[24] H-atom positions refined isotropically, $R = 0.050$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ A spectroscopic indication for the bonding nature of the contacts is given by the solid state IR spectrum, in which the alkynyl stretching frequency $\nu_{CH} = 3286$ cm$^{-1}$ is slightly but significantly shifted downwards from the typical values around 3310 cm$^{-1}$ of free alkynyl groups.[11] This is only an indication and not a proof because, due to insolubility of the polar molecule in $CCl_4$, a comparative spectrum in apolar surroundings could not be determined.

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