KS thanks the Deutscher Akademischer Austauschdienst for a grant to stay in Berlin, and LS is grateful to CSIR, New Delhi, India, for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Brown, C. J. (1967). *J. Chem. Soc. A*, pp. 60–65.
Brown, C. J. & Gash, D. J. (1984). *Acta Cryst.* C**40**, 562–564.
Brown, C. J. & Sengier, L. (1984). *Acta Cryst.* C**40**, 1294–1295.
Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthfhazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Acta Cryst. (1995). C**51**, 2325–2327

Alkynyl Contacts in 1β-Hydroxy-1α-propargyl-2α-(2-ethoxycarbonylvinyl)-2,4,4-trimethylcyclopentane

S. Lakshmi and K. Subramanian*

Department of Physics, Anna University, Madras 600 025, India

K. Rajagopalan

Department of Organic Chemistry, University of Madras, Madras 600 025, India

G. Koellner and Th. Steiner

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14159 Berlin, Germany

(*Received* 9 *March* 1995; *accepted* 6 *June* 1995)

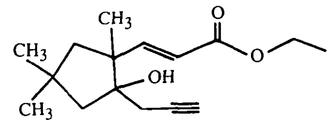
Abstract

In the crystal structure of the title compound [ethyl 2-hydroxy-1,4,4-trimethyl-2-(2-propynyl)cyclopentane-1-propenoate, $C_{16}H_{24}O_3$] the propynyl residue only acts as a donor in a long and severely bent C—H···O interaction, with an H···O distance of 2.92 Å. It is engaged in a short alkyne–alkyne C—H···H—C contact, with an H···H distance of 2.38 Å; such a short contact distance is unprecedented (numerical values are for normalized H-atom positions).

©1995 International Union of Crystallography
Printed in Great Britain – all rights reserved

Comment

Terminal alkynes of the type described here are used as starting materials in the syntheses of insect pheromones (Morrison & Boyd, 1989). The crystal structure of the title compound, (I), was determined in order to study the solid-state interactions of the propargyl residue. Normally, terminal alkynes act as weak hydrogen-bond donors with various acceptors such as O, N or even C (Desiraju, 1991; Steiner, 1994; Steiner, Starikov, Amado & Teixeira-Dias, 1995).



(I)

The molecular geometry of the title compound is shown in Fig. 1. The cyclopentane ring adopts an envelope conformation, with the *cis* torsion angle C2—C3—C4—C5 having a value of 3.2 (4)° (Table 2). The crystal packing arrangement is shown in Fig. 2. The hydrogen-bond pattern is not a favourable one as the O19—H hydroxy group donates an intermolecular hydrogen bond to the carbonyl O17 atom, which accepts an additional contact from the propargyl C—H group (Table 3). However, the latter contact is very long and bent (H···O 2.92 Å, angle at H 124°), so that its classification as a hydrogen bond is questionable. The resulting finite arrangement O—H···O···H—C≡C is a much weaker pattern than the cooperative hydrogen-bond chain C≡C—H···O—H···O=C, which was

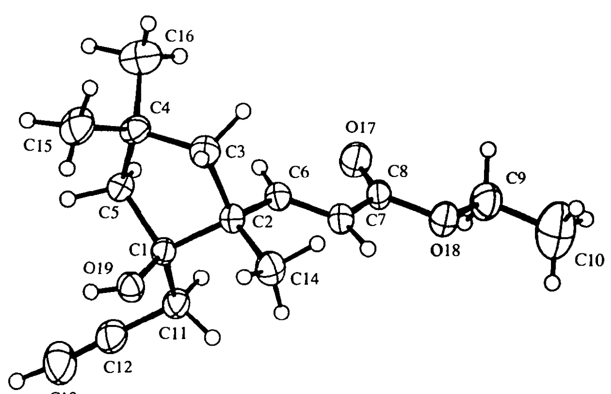


Fig. 1. Molecular structure and atomic numbering scheme of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

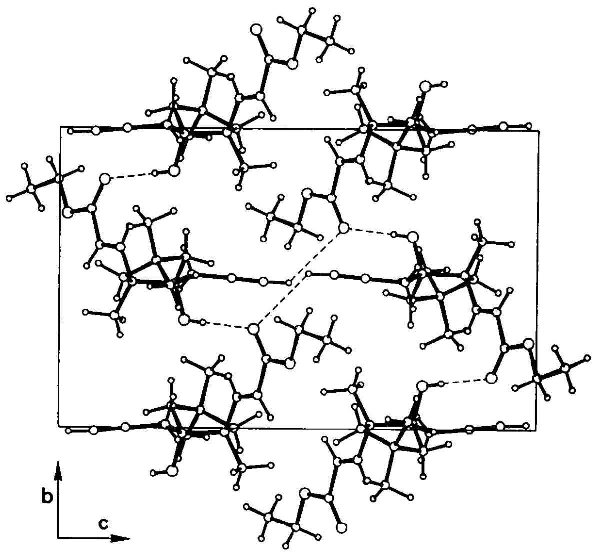


Fig. 2. Crystal-packing projection along the *a* axis. Hydrogen bonds are shown as dashed lines.

found in a related compound having the same hydrogen-bonding functional groups (Lakshmi, Subramanian, Rajagopalan, Koellner & Steiner, 1995).

It is worth noting that the shortest intermolecular contact of the propargyl C—H group is not to a hydrogen-bond acceptor, but to a symmetry-related propargyl H atom ($-x$, $-y$, $2-z$), *i.e.* C≡C—H···H—C≡C with an H···H distance of 2.38 Å and a C—H···H angle of 100° (Fig. 3) [H···C 2.78 and C···C 3.487 (7) Å; values are for normalized H-atom positions with a C—H distance of 1.08 Å and a linear alkynyl residue]. Due to the acidic properties of terminal alkynes and the pronounced $C^{\delta-}$—$H^{\delta+}$ polarization, these contacts must be repulsive. The arrangement should be energetically unfavourable and therefore should occur only rarely in crystal structures. Indeed, in a search of the Cambridge Structural Database (Allen *et al.*, 1987), no similarly short alkyne–alkyne C≡C—H···H—C≡C contacts could be found. This shows that the present arrangement is in fact an exceptional and unprecedented case.

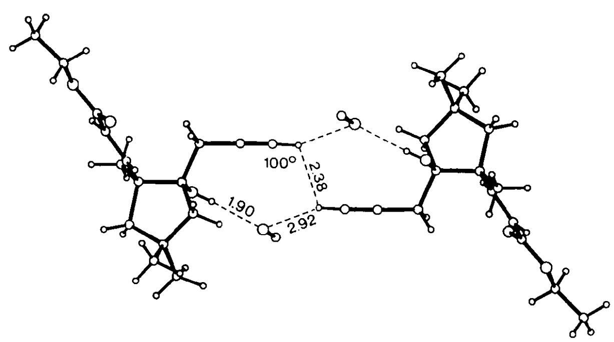


Fig. 3. Detailed view of the intermolecular alkynyl contacts (Å). Projection is onto the *ac* plane.

Experimental

The compound was synthesized by Wittig's reaction and crystallized from a mixture of ethyl acetate and hexane. The density D_m was measured by flotation in a KI–water solution.

Crystal data

$C_{16}H_{24}O_3$
$M_r = 264.35$
Monoclinic
$P2_1/c$
$a = 8.526\,(6)$ Å
$b = 10.815\,(5)$ Å
$c = 17.547\,(9)$ Å
$\beta = 90.40\,(6)°$
$V = 1618\,(2)$ Å^3
$Z = 4$
$D_x = 1.085$ Mg m^{-3}
$D_m = 1.090$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 14$–25°
$\mu = 0.585$ mm^{-1}
Room temperature
Needle
1.0 × 0.25 × 0.1 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
2487 measured reflections
2256 independent reflections
2173 observed reflections [$F > 2\sigma(F)$]

$R_{int} = 0.026$
$\theta_{max} = 60°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 30 min
intensity decay: 4.8%

Refinement

Refinement on F
$R = 0.057$
$wR = 0.057$
$S = 0.82$
2173 reflections
250 parameters
Unit weights applied

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C1	−0.0283 (3)	0.0193 (3)	0.7412 (2)	0.043 (3)
C2	−0.0280 (3)	0.0146 (3)	0.6521 (2)	0.046 (3)
C3	−0.2060 (4)	0.0010 (4)	0.6339 (2)	0.059 (4)
C4	−0.2883 (3)	−0.0574 (3)	0.7033 (2)	0.055 (3)
C5	−0.1568 (3)	−0.0705 (3)	0.7639 (2)	0.047 (3)
C6	0.0554 (3)	−0.1009 (3)	0.6273 (2)	0.046 (3)
C7	0.1810 (3)	−0.1085 (3)	0.5841 (2)	0.051 (3)
C8	0.2542 (3)	−0.2288 (3)	0.5667 (2)	0.051 (3)
C9	0.4587 (4)	−0.3273 (4)	0.4977 (2)	0.077 (4)
C10	0.5757 (6)	−0.2926 (5)	0.4400 (3)	0.145 (8)
C11	0.1330 (4)	−0.0104 (4)	0.7765 (2)	0.056 (3)
C12	0.1350 (4)	0.0014 (4)	0.8599 (2)	0.068 (4)
C13	0.1341 (5)	0.0128 (6)	0.9259 (3)	0.105 (7)
C14	0.0419 (5)	0.1305 (3)	0.6158 (2)	0.063 (4)
C15	−0.4199 (5)	0.0258 (5)	0.7316 (3)	0.084 (6)
C16	−0.3577 (7)	−0.1843 (5)	0.6845 (3)	0.095 (6)
O17	0.2211 (3)	−0.3277 (2)	0.5937 (1)	0.069 (3)
O18	0.3714 (2)	−0.2148 (2)	0.5168 (1)	0.064 (2)
O19	−0.0709 (3)	0.1433 (2)	0.7612 (1)	0.053 (2)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

C1—C2	1.566 (4)	C4—C16	1.530 (6)
C1—C5	1.519 (4)	C6—C7	1.319 (4)
C1—C11	1.538 (4)	C7—C8	1.476 (5)
C1—O19	1.434 (4)	C8—O17	1.204 (4)
C2—C3	1.556 (4)	C8—O18	1.341 (4)
C2—C6	1.503 (4)	C9—C10	1.476 (6)
C2—C14	1.529 (5)	C9—O18	1.466 (4)
C3—C4	1.545 (5)	C11—C12	1.469 (5)
C4—C5	1.546 (4)	C12—C13	1.165 (6)
C4—C15	1.524 (6)		
C11—C1—O19	108.9 (3)	C3—C4—C5	104.4 (3)
C5—C1—O19	110.4 (3)	C15—C4—C16	108.4 (4)
C5—C1—C11	114.0 (3)	C5—C4—C16	110.1 (3)
C2—C1—O19	106.1 (2)	C5—C4—C15	111.2 (3)
C2—C1—C11	112.8 (2)	C1—C5—C4	106.4 (2)
C2—C1—C5	104.3 (2)	C2—C6—C7	127.3 (3)
C1—C2—C14	113.1 (3)	C6—C7—C8	121.3 (3)
C1—C2—C6	108.6 (2)	C7—C8—O18	110.7 (3)
C1—C2—C3	101.5 (3)	C7—C8—O17	126.9 (3)
C6—C2—C14	112.0 (3)	O17—C8—O18	122.4 (3)
C3—C2—C14	112.0 (3)	C10—C9—O18	107.0 (3)
C3—C2—C6	109.0 (3)	C1—C11—C12	112.7 (3)
C2—C3—C4	108.9 (3)	C11—C12—C13	178.5 (5)
C3—C4—C16	111.9 (3)	C8—O18—C9	115.9 (3)
C3—C4—C15	110.8 (3)		
C1—C2—C3—C4	−24.5 (3)	C5—C1—C2—C6	−78.0 (3)
C2—C3—C4—C5	3.2 (4)	C11—C1—C2—C6	46.2 (4)
C2—C1—C5—C4	−36.4 (3)	C11—C1—C2—C14	−78.9 (4)
C5—C1—C2—C3	36.8 (3)	O19—C1—C2—C6	165.3 (3)
C3—C4—C5—C1	20.5 (3)	O19—C1—C2—C14	40.3 (4)
C2—C1—C11—C12	176.5 (3)	C14—C2—C6—C7	4.5 (5)

Table 3. *Hydrogen-bond parameters* (Å, °)

Data for the normalized H-atom position were based on bond lengths of O—H = 0.98 Å and ≡C—H = 1.08 Å.

D—H···O	D—H	H···O	D···O	H_{norm}···O	D—H_{norm}···O
O19—H···O17[i]	0.78 (3)	2.10 (3)	2.874 (3)	1.90	175
C13—H···O17[ii]	0.91 (4)	2.97 (4)	3.634 (5)	2.92	124

Symmetry codes: (i) $-x, y+\frac{1}{2}, \frac{3}{2}-z$; (ii) $x, -\frac{1}{2}-y, z+\frac{1}{2}$.

H atoms were refined isotropically, except those bonded to atoms C9 and C10. These did not refine realistically and were included in the model in their ideal positions (Sheldrick, 1976).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296, and references therein.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lakshmi, S., Subramanian, K., Rajagopalan, K., Koellner, G. & Steiner, Th. (1995). *Acta Cryst.* C**51**, 2327–2329.

Morrison, R. T. & Boyd, R. T. (1989). In *Organic Chemistry*. New Delhi: Prentice Hall.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Steiner, Th. (1994). *J. Chem. Soc. Chem. Commun.* pp. 101–102.

Steiner, Th., Starikov, E. B., Amado, A. M. & Teixeira-Dias, J. C. C. (1995). *J. Chem. Soc. Perkin Trans.* 2, pp. 1321–1326.

©1995 International Union of Crystallography
Printed in Great Britain – all rights reserved

Acta Cryst. (1995). C**51**, 2327–2329

1β-Hydroxy-1α-propargyl-2β-methyl-2-(2-ethoxycarbonylvinyl)cycloheptane

S. Lakshmi and K. Subramanian*

Department of Physics, Anna University, Madras 600 025, India

K. Rajagopalan

Department of Organic Chemistry, University of Madras, Madras 600 025, India

G. Koellner and Th. Steiner

Institut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-14159 Berlin, Germany

(*Received* 20 *February* 1995; *accepted* 12 *April* 1995)

Abstract

In the crystal structure of the title compound [ethyl 2-hydroxy-1-methyl-2-(2-propynyl)cycloheptane-1-prop-2-enoate, $C_{16}H_{24}O_3$] the hydroxy and the propargyl groups of neighbouring molecules form cooperative finite hydrogen-bonded chains, C≡C—H···O—H···O=C. In the C—H···O interaction, the H···O separation is 2.32 Å.

Comment

The terminal alkyne residue, C≡C—H, is among the most acidic C—H groups (Pedireddi & Desiraju, 1992) and is, therefore, an excellent model system for gaining insight into C—H···X hydrogen-bond interactions (Desiraju, 1991; Steiner, 1994). In the title compound, (I), the strongest hydrogen-bond donors are a hydroxy and a propargyl group. For these, three O atoms are available as good acceptors. Therefore, C ≡C—H···O hydrogen bonding can be expected to occur in the solid state.