6603 measured reflections
1579 independent reflections
1310 observed reflections
[$I > 2.5\sigma(I)$]

3 standard reflections
frequency: 60 min
intensity variation: 2.1%

Refinement

Refinement on *F*
$R = 0.0386$
$wR = 0.0395$
$S = 0.43$
1310 reflections
92 parameters
All H-atom parameters refined
Calculated weights
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.086$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.0128 (1)	0.4348 (1)	$\frac{3}{4}$	0.0418 (4)
N1	0.1375 (1)	0.0982 (2)	$\frac{3}{4}$	0.0401 (5)
N2	0.1218 (1)	0.4234 (2)	$\frac{3}{4}$	0.0424 (5)
C1	0.1466 (2)	0.3132 (2)	$\frac{3}{4}$	0.0369 (6)
C2	0.0731 (2)	0.2094 (2)	$\frac{3}{4}$	0.0360 (5)
C3	0.2037 (1)	0.0937 (2)	0.5703 (3)	0.0539 (6)
C4	0.2775 (2)	0.1999 (2)	0.5697 (3)	0.0663 (6)
C5	0.2584 (2)	0.2767 (2)	$\frac{3}{4}$	0.0527 (8)
C6	−0.0133 (2)	0.5597 (2)	$\frac{3}{4}$	0.0463 (6)
Cl1	0.47766 (5)	0.36551 (5)	$\frac{1}{4}$	0.0509 (2)

Table 2. *Geometric parameters* (Å, °)

O1—N2	1.411 (2)	C1—C2	1.497 (3)
O1—C6	1.434 (3)	C1—C5	1.498 (4)
N1—C2	1.493 (3)	C3—C4	1.520 (3)
N1—C3	1.493 (2)	C4—C5	1.518 (3)
N2—C1	1.271 (3)		
N2—O1—C6	108.7 (2)	C2—C1—C5	113.5 (2)
C2—N1—C3	110.2 (1)	N1—C2—C1	106.9 (2)
C2—N1—C3$^{\rm i}$	110.2 (1)	N1—C3—C4	109.5 (2)
C3—N1—C3$^{\rm i}$	110.1 (1)	C3—C4—C5	109.7 (2)
O1—N2—C1	109.7 (2)	C1—C5—C4	108.0 (2)
N2—C1—C2	126.2 (2)	C1—C5—C4$^{\rm i}$	108.0 (2)
N2—C1—C5	120.4 (2)	C4—C5—C4$^{\rm i}$	108.0 (2)

Symmetry code: (i) $x, y, \frac{3}{2} - z$.

The systematic extinctions ($h0l$, h odd; $0kl$, $k + l$ odd) are consistent with space groups $Pna2_1$ and $Pnam$ (alternative setting of $Pnma$, No. 62). The structure was solved in space group $Pna2_1$, which resulted in a model having mirror symmetry. Therefore, the analysis was continued in space group $Pnam$ [general positions: $\pm(x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; x, y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, -z)$], which, in contrast to $Pna2_1$, yielded normal non-deviating geometries. The positions of the H atoms were located from $\Delta\rho$ syntheses and included in the refinement with an overall isotropic thermal parameter, which refined to 0.074 (2) Å^2. Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *EUCLID* (Spek, 1982). Software used to prepare material for publication: *PLATON* (Spek, 1990*a*).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71500 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1095]

References

Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.

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

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

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467-473.

Spek, A. L. (1982). *The EUCLID Package*. *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Spek, A. L. (1990*a*). *Acta Cryst.* A**46**, C-34.

Spek, A. L. (1990*b*). *HELENA*. *Program for Data Reduction*. Laboratorium voor Kristal- en Structuurchemie, Univ. of Utrecht, The Netherlands.

Acta Cryst. (1994). C**50**, 129–131

2,7-Dimethyl-3,5-octadiyne-2,7-diol Dichloromethane Solvate: a Clathrate Comprising Hydrogen-Bonded Supramolecular Tunnels Containing Dichloromethane Guest Molecules

D. A. Leigh, A. E. Moody and R. G. Pritchard

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

(*Received* 15 *October* 1992; *accepted* 21 *July* 1993)

Abstract

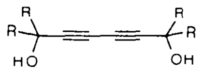
The title molecule, $C_{10}H_{14}O_2.0.06CH_2Cl_2$, forms an unusual tubular structure in which double-walled channels of approximately 5 Å internal diameter extend throughout the crystal. Groups of three molecules are positioned around a threefold axis to form a section of the tube. These molecules are configured so that methyl and acetylene groups line the tube and hydroxyl groups form the outer wall. As each hydroxyl group is near to a threefold screw axis, the channel walls are reinforced by infinite hydrogen-bonded columns parallel to *c* [O···O 2.68 (1), 2.771 (9) Å]. Although dichloromethane fits well in the channels, the final guest-to-host ratio of 0.06:1 indicates

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

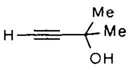
that the open structure is unable to retain these molecules in ambient conditions.

Comment

2,7-Dimethyl-3,5-octadiyne-2,7-diol (1) is a member of a family of diacetylenic alcohols, some of which are able to form crystalline inclusion complexes with a variety of guest molecules. Studies by Toda (1987) have shown that 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol (2) is the most versatile of these complexing reagents, leading to its utilization in the isolation of caffeine from tea, nicotine from tobacco and cholesterol from gallstones *via* complexation in the solid state. Compound (2) has been used to separate strychnine and sparteine from brucine using a similar method (Segawa, Mori & Toda, 1988). However, in other studies, Toda & Akagi (1968) report that (1) does not appear to participate in similar crystalline clathrate complexation. During the course of work employing 2-methyl-3-butyn-2-ol (3) as an acetylenic coupling reagent, we produced (1) as a highly crystalline by-product. The title molecule is seen to self associate *via* hydrogen bonds (Fig. 1) to form an extended tubular structure (Fig. 2) containing 6% dichloromethane of crystallization. By contrast to the ordered 2:1, 1:1 or 1:2 inclusion complexes formed by (2) with similar molecules, the dichloromethane in (1) is disordered and resembles water in zeolitic cavities.



(1) R = Me
(2) R = Ph



(3)

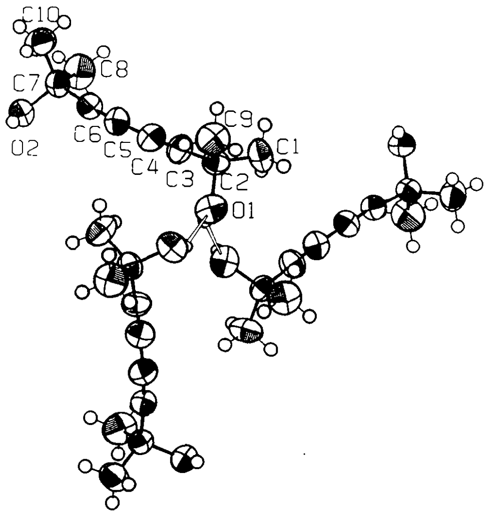


Fig. 1. The title molecule, including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976) and showing part of a hydrogen-bonded column.

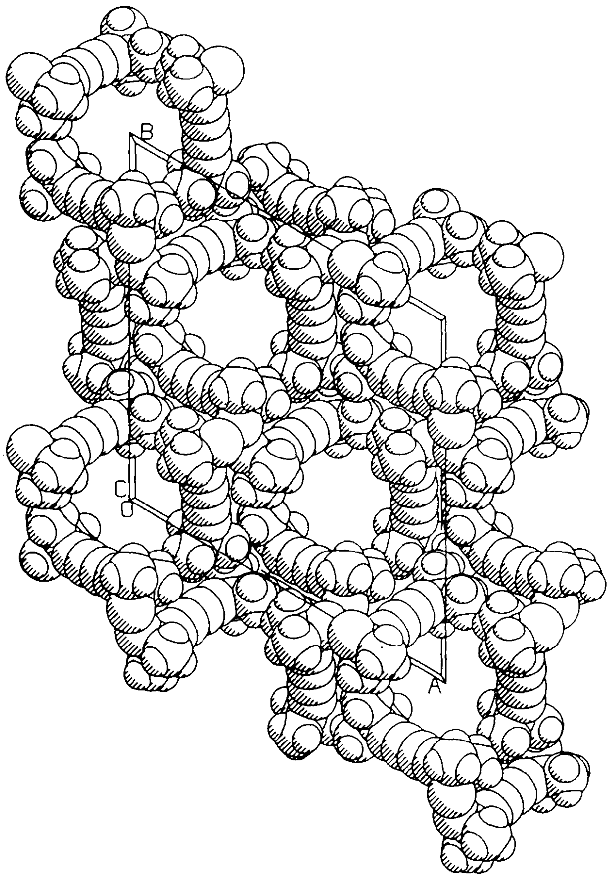


Fig. 2. A cross section of the channel system, drawn using *PLUTO* (Motherwell & Clegg, 1978).

Experimental

Crystal data

$C_{10}H_{14}O_2.0.06CH_2Cl_2$
$M_r = 171.32$
Trigonal
$R3$ (hexagonal axes)
$a = 22.426$ (5) Å
$c = 6.395$ (4) Å
$V = 2785$ (2) Å^3
$Z = 9$
$D_x = 0.919$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 14.3\text{–}20.6°$
$\mu = 0.084$ mm^{-1}
$T = 296$ K
Needle
0.40 × 0.20 × 0.20 mm
Colourless

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.83$, $T_{\max} = 1.00$
1255 measured reflections
1098 independent reflections
502 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.040$

$\theta_{\max} = 25°$
$h = -22 \rightarrow 21$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 7$
3 standard reflections monitored every 150 reflections intensity variation: not significant

Refinement

Refinement on F
$R = 0.0609$
$wR = 0.0736$
$S = 2.56$
502 reflections
117 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.05$
$\Delta\rho_{\max} = -0.23$ e Å^{-3}
$\Delta\rho_{\min} = 0.36$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
O1	1.0130 (5)	0.7134 (5)	1.3216	0.0688
O2	0.7192 (4)	0.6949 (4)	0.592 (1)	0.0551
C1	1.0889 (6)	0.8229 (6)	1.175 (2)	0.0755
C2	1.0201 (6)	0.7786 (7)	1.278 (2)	0.0552
C3	0.9643 (6)	0.7692 (6)	1.138 (2)	0.0581
C4	0.9204 (7)	0.7626 (7)	1.024 (2)	0.0615
C5	0.8677 (6)	0.7580 (6)	0.889 (2)	0.0571
C6	0.8253 (7)	0.7573 (6)	0.777 (2)	0.0534
C7	0.7753 (6)	0.7618 (6)	0.641 (2)	0.0515
C8	0.8091 (7)	0.7947 (8)	0.436 (2)	0.0891
C9	1.0154 (7)	0.8081 (7)	1.484 (3)	0.0837
C10	0.7482 (7)	0.8026 (7)	0.753 (3)	0.0899
Cl11 †	1.0	1.0	0.673 (8)	0.17 (2)
Cl12 †	0.918 (1)	0.936 (2)	1.042 (8)	0.17 (2)
C11 †	1.0	1.0	0.950 (8)	0.17 (2)

† The coordinates of these atoms were constrained in the manner described below.

Table 2. *Geometric parameters* (Å, °)

O1—C2	1.42 (2)	C4—C5	1.42 (2)
O2—C7	1.43 (1)	C5—C6	1.19 (2)
C1—C2	1.50 (2)	C6—C7	1.46 (2)
C2—C3	1.46 (2)	C7—C8	1.51 (2)
C2—C9	1.50 (2)	C7—C10	1.51 (2)
C3—C4	1.18 (2)		
O1—C2—C3	108.8 (9)	C4—C5—C6	177 (1)
C2—C3—C4	179 (1)	C5—C6—C7	176 (1)
C3—C4—C5	177 (2)	O2—C7—C6	111 (1)

2,7-Dimethyl-3,5-octadiyne-2,7-diol (1) was isolated (by flash chromatography; silica, methanol-dichloromethane as eluent) as a by-product of a palladium-catalysed coupling reaction of the parent acetylene (3) with an aryl halide. Good quality crystals were obtained by subsequent recrystallization from dichloromethane.

Disorder of the dichloromethane guest molecule was treated by constraining the C—Cl bonds to 1.77 Å and the Cl—C—Cl angles to 109°. H atoms were ignored. A C atom and one Cl atom were constrained to lie on the threefold axis parallel to c with the molecular z coordinate, rotation about z and overall vibrational parameter being allowed to refine. The group multiplicity was allowed to vary but not at the same time as the above parameters and not during the final least-squares cycle. Site occupancies for the C, Cl11 and Cl12 atoms were tied in the ratio 2:1:1, *i.e.* the dichloromethane Cl atoms were completely disordered among four tetrahedrally arranged sites. This resulted in a guest-to-host ratio of 0.060 (6):1 and site occupancy of 0.18 (2).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *TEXSAN FINISH*. Literature search: *CSSR* (1984).

We are grateful to the SERC and GEC Marconi for a Studentship (to AEM).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71517 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1038]

References

CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual*. SERC Daresbury Laboratory, Warrington, England.
Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42-46.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.
Segawa, M., Mori, K. & Toda, F. (1988). *Chem. Lett.* pp. 1755-1758.
Toda, F. (1987). *Top. Curr. Chem.* **140**, 43-69.
Toda, F. & Akagi, K. (1968). *Tetrahedron Lett.* pp. 3695-3698.

Acta Cryst. (1994). C**50**, 131-133

Structure of *trans*-Methyl {2-[(Cyano)(phenylthio)methyl]-3-oxocyclopentyl}acetate, $C_{16}H_{17}NO_3S$

M. NIERLICH, M. LANCE AND D. VIGNER

CEN-Saclay, SCM, Bâtiment 125,
91191 Gif-sur-Yvette CEDEX, France

T. STRZALKO AND L. WARTSKI

ICMO, Laboratoire des carbocycles, CNRS-URA 478,
Bâtiment 420, Orsay CEDEX, France

(*Received* 3 *February* 1993; *accepted* 30 *June* 1993)

Abstract

The X-ray analysis confirms the *trans* relationship between the C(2) and C(3) substituents of the cyclopentanone ring and allows us to determine the rela-