

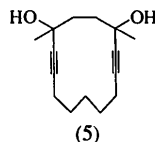
Molecular Structure Corporation (1992a). *MSC/AFC Diffractometer Control Software*. Revised edition. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1992b). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Ramnathan, A., Sivakumar, K. & Subramanian, K. (1995). *Acta Cryst. C* **51**, 2446–2450.

Wei-Xing, C. (1993). *Advances in Organic Synthesis*, edited by D. Li-Xin & Q. Yan-Long, pp. 469–491. Beijing: Chemical Industry Press.

tionalized reagents and for comparison of different ring sizes and substitution patterns at the propargylic centres of homologous ring compounds.



Acta Cryst. (1997). **C53**, 322–325

meso-1,11-Dimethylcyclotrideca-2,9-diyne-1,11-diol

CHRISTOPH BOSS,^a HELEN STOECKLI-EVANS^b AND REINHART KEESE^a

^aInstitut für Organische Chemie, Universität Bern, Freiestr. 3, CH-3012 Bern, Switzerland, and ^bInstitut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland. E-mail: keese@ioc.unibe.ch

(Received 21 August 1996; accepted 5 November 1996)

Abstract

The title compound, C₁₅H₂₂O₂, (5), has been prepared and its structure determined. At room temperature, two conformations are observed, but at 193 K, the compound shows only the conformation which has 67% occupancy at room temperature. The appearance of two conformations and the low symmetry of compound (5) are in accordance with the general structural behaviour of 13-membered-ring systems. *meso*-(5) crystallizes in the monoclinic space group *I2/a*. The lengths of the triple bonds are close to 1.175 Å at room temperature and 1.188 Å at 193 K. The bond angles at the triple bonds deviate by less than 7° from being linear and are almost temperature independent.

Comment

Medium-sized ring compounds are of considerable interest because of their unique structure and transannular reactivity (Dunitz & Meyer, 1965; Johnson, 1986; Gleiter, Merger, Irgartinger & Nuber, 1993; Meier, 1991). The cyclotridecadienediol (5), as well as the recently published substituted cyclododecadiynes (Boss, Keese & Förtsch, 1996; Boss, Stoeckli-Evans & Keese, 1996), have been prepared both for investigation of the reactions of the juxtaposed triple bonds with doubly func-

In the crystalline state at 193 K, the unit cell contains two enantiomeric forms of *meso*-(5) in a ratio of 1:1. The population of the two conformations at room temperature corresponds to the general conformational behaviour of unsubstituted cyclotridecane (Dale, 1978). Quite different from the 12-membered-ring compounds where the racemic form crystallizes (Boss, Stoeckli-Evans & Keese, 1996), it is the *meso*-(5) compound that affords crystals which are composed of layers with the hydrophilic and hydrophobic areas separated.

In *meso*-(5), the lengths of the two triple bonds at room temperature are 1.174 (5) (C2≡C3) and 1.177 (5) Å (C9≡C10). At 193 K, the triple bonds show lengths of 1.187 (5) (C2≡C3) and 1.189 (5) Å (C9≡C10), and are exactly within the range of triple-bond lengths found for the cyclododecadiyne diols (Boss, Stoeckli-Evans & Keese, 1996). The angles at the triple bonds [173.9 (4) (C1—C2≡C3), 175.0 (5) (C2≡C3—C4), 176.1 (5) (C8—C9≡C10) and 176.2 (4)° (C9≡C10—C11) at room temperature; 173.3 (4) (C1—C2≡C3), 175.3 (4) (C2≡C3—C4), 175.2 (4) (C8—C9≡C10) and 175.9 (4)° (C9≡C10—C11) at 193 K] show practically no temperature dependence and lie within the same range as those determined for 12-membered-ring systems. The transannular distances of the two alkyne moieties in *meso*-(5) are 4.126 (5) (C2···C10) and 4.333 (6) Å (C3···C9) at 193 K, and 4.155 (5) and 4.384 (6) Å, respectively, at room temperature.

These structural features are well within the range found for other cycloalkadiynes in the Cambridge Structural Database (Allen *et al.*, 1979). Other salient features of diol (5) are the bond angles at the other centres. The C2—C1—C13 bond angle at the quaternary C atom is 110.1 (3)° and the value at the corresponding centre (C10—C11—C12) is 109.2 (3)°, whereas the adjacent bond angles C1—C13—C12 and C11—C12—C13 are 117.7 (3) and 112.4 (3)°, respectively. This is reminiscent of the bond angles at the quaternary C atoms of type (H₃C)₂C(C)₂ (Keese & Meyer, 1993). The values determined at 193 K are very similar to those obtained at room temperature.

The disordered part of the molecule shows very different values for bond angles at the CH₂ groups [C4—C5—C6 124.8 (3) and C4—C5—C6A 91.1 (7)°]. At 193 K, the corresponding angle is 118.0 (4)°. In the cell packing diagram of *meso*-(5) (Fig. 2), hydro-

gen bonding is observed. The molecules are linked by hydrogen bonds to form a two-dimensional chain extending in the **b** direction. The hydrogen-bond lengths at room temperature are 2.02(4) (H1...O11) and 2.24(4) Å (H11...O1), with the hydrogen-bond angles

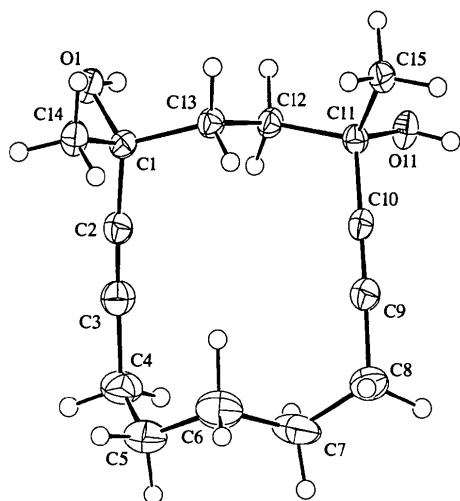


Fig. 1. The molecular structure of the title compound showing the labelling of the non-H atoms at 193 K. Displacement ellipsoids are shown at the 50% probability level.

being 164(4) (O1—H1...O11) and 174(4)° (O11—H11...O1). At 193 K, the hydrogen-bond lengths and angles differ only slightly from those determined at room temperature. By lowering the temperature, the *a*, *b* and *c* axes shrink by 0.033, 0.044 and 0.183 Å, respectively, and the unit-cell volume decreases by 46.7 Å³. This results in a higher density (+1.75%); the molecules

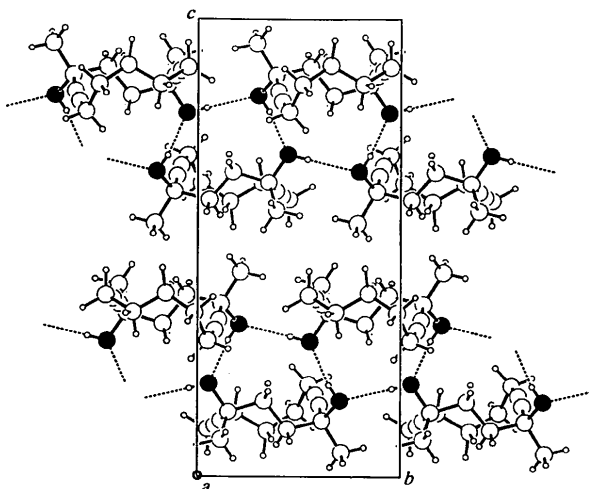
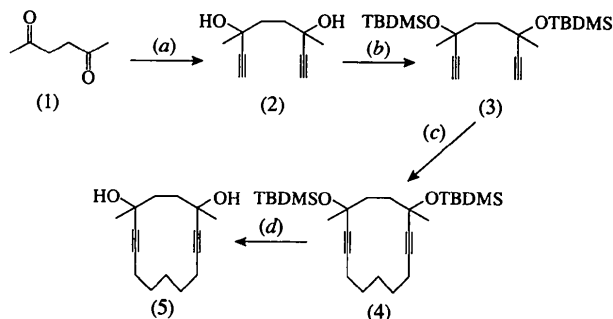


Fig. 2. Packing diagram of the title compound at 193 K down the *a* axis. Hydrogen-bonded chains extend in the **b** direction.

are now able to pack more closely as they are fixed in only one conformation.

Experimental



- (a) $\text{ClMg}\equiv\text{CH}$, THF; 92%,
 (b) TBDMS-triflate, NEt_3 , THF; 96%,
 (c) (i) 2^tBuLi , THF; (ii) DMPU, 1,5-dibromopentane; 35%,
 (d) TBAF, THF; 66%

Compound (5) was prepared by a four-step sequence. Addition of acetylacetone, (1), to ethynylmagnesium chloride gave a 1:1 mixture of *meso*- and *rac*-(2). After silylation of the hydroxy groups with *tert*-butyldimethylsilyl trifluoromethanesulfonate, compound (3) was deprotonated with $^t\text{BuLi}$ and alkylated with 1,5-dibromopentane to give compound (4) in 35% isolated yield. After deprotection with TBAF in THF, a diastereomeric mixture of (5) was isolated in 66% yield. Pure *meso*-(5) was obtained by flash chromatography, followed by recrystallization from ether at room temperature. *meso*-(5) forms colourless crystal plates (m.p. 372–374 K) which can be easily separated from the white powder of the racemic isomer (5).

meso-(5) at 293 K

Crystal data

$\text{C}_{15}\text{H}_{22}\text{O}_2$
 $M_r = 234.33$
 Monoclinic
 $I2/a$
 $a = 17.812(2)$ Å
 $b = 8.2826(11)$ Å
 $c = 19.064(4)$ Å
 $\beta = 99.878(14)^\circ$
 $V = 2770.8(8)$ Å³
 $Z = 8$
 $D_x = 1.123$ Mg m⁻³
 D_m not measured

Data collection

Stoe AED-2 four-circle diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 4876 measured reflections
 2438 independent reflections
 1452 reflections with $I > 2\sigma(I)$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 17 reflections
 $\theta = 14\text{--}19^\circ$
 $\mu = 0.073$ mm⁻¹
 $T = 293(2)$ K
 Transparent block
 $0.53 \times 0.23 \times 0.17$ mm
 Colourless

$R_{\text{int}} = 0.0602$
 $\theta_{\text{max}} = 25^\circ$
 $h = -21 \rightarrow 21$
 $k = 0 \rightarrow 9$
 $l = -22 \rightarrow 22$
 2 standard reflections
 frequency: 60 min
 intensity decay: 4.4%

Refinement

Refinement on F^2 $R(F) = 0.074$ $wR(F^2) = 0.1908$ $S = 1.109$

2424 reflections

176 parameters

H atoms placed in calculated positions

 $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 4.9313P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.029$ $\Delta\rho_{\max} = 0.282 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.290 \text{ e } \text{\AA}^{-3}$

Extinction correction:

SHELXL93

Extinction coefficient:

0.0015 (4)

Scattering factors from

International Tables for Crystallography (Vol. C)

meso-(5) at 193 K

Crystal data

C₁₅H₂₂O₂ $M_r = 234.33$

Monoclinic

I2/a

 $a = 17.779 \text{ (2) } \text{\AA}$ $b = 8.238 \text{ (1) } \text{\AA}$ $c = 18.881 \text{ (3) } \text{\AA}$ $\beta = 99.92 \text{ (1)}^\circ$ $V = 2724.1 \text{ (6) } \text{\AA}^3$ $Z = 8$ $D_x = 1.143 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 28 reflections

 $\theta = 14\text{--}19^\circ$ $\mu = 0.074 \text{ mm}^{-1}$ $T = 193 \text{ (2) K}$

Transparent block

 $0.53 \times 0.23 \times 0.17 \text{ mm}$

Colourless

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (5) at 293 K
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.8953 (2)	-0.1194 (4)	0.6215 (2)	0.0379 (9)
C2	0.8263 (2)	-0.1077 (4)	0.6551 (2)	0.0479 (10)
C3	0.7686 (3)	-0.0912 (5)	0.6762 (2)	0.0636 (12)
C4	0.6941 (3)	-0.0610 (7)	0.6972 (3)	0.089 (2)
C5	0.6423 (2)	0.0263 (6)	0.6432 (2)	0.100 (2)
C6	0.6641 (2)	0.1574 (6)	0.6016 (2)	0.058 (2)
C7	0.6662 (5)	0.3271 (14)	0.6418 (5)	0.077 (3)
C6A†	0.6821 (8)	0.199 (2)	0.6711 (11)	0.085 (7)
C7A‡	0.6590 (2)	0.3178 (6)	0.6043 (3)	0.110 (12)
C8	0.7077 (2)	0.4472 (6)	0.6014 (3)	0.090 (2)
C9	0.7898 (2)	0.4119 (5)	0.6108 (2)	0.0550 (11)
C10	0.8554 (2)	0.3827 (4)	0.6225 (2)	0.0410 (9)
C11	0.9375 (2)	0.3428 (4)	0.6421 (2)	0.0347 (8)
C12	0.9459 (2)	0.1655 (4)	0.6654 (2)	0.0386 (9)
C13	0.9218 (2)	0.0494 (4)	0.6039 (2)	0.0399 (9)
C14	0.8767 (2)	-0.2158 (4)	0.5526 (2)	0.0525 (11)
C15	0.9811 (2)	0.3793 (4)	0.5819 (2)	0.0488 (10)
O1	0.95517 (14)	-0.2077 (3)	0.6661 (2)	0.0459 (7)
O11	0.9704 (2)	0.4365 (3)	0.70377 (14)	0.0503 (8)

† Site occupancy = 0.673 (11). ‡ Site occupancy = 0.327 (11).

Table 2. Selected geometric parameters (\AA , $^\circ$) for (5) at 293 K

C1—O1	1.443 (4)	C7—C8	1.524 (12)
C1—C2	1.484 (5)	C6A—C7A	1.60 (2)
C1—C14	1.524 (5)	C7A—C8	1.386 (6)
C1—C13	1.531 (4)	C8—C9	1.472 (5)
C2—C3	1.174 (5)	C9—C10	1.177 (5)
C3—C4	1.472 (6)	C10—C11	1.483 (5)
C4—C5	1.451 (6)	C11—O11	1.446 (4)
C5—C6	1.437 (6)	C11—C15	1.522 (5)
C5—C6A	1.64 (2)	C11—C12	1.534 (4)
C6—C7	1.598 (12)	C12—C13	1.521 (5)
C2—C1—C14	109.4 (3)	C7A—C8—C9	117.2 (3)
C2—C1—C13	110.1 (3)	C9—C8—C7	111.5 (5)
C14—C1—C13	108.6 (3)	C10—C9—C8	176.1 (5)
C3—C2—C1	173.9 (4)	C9—C10—C11	176.2 (4)
C2—C3—C4	175.0 (5)	O11—C11—C10	109.3 (3)
C5—C4—C3	112.6 (4)	O11—C11—C15	108.6 (3)
C6—C5—C4	124.8 (3)	C10—C11—C15	112.0 (3)
C4—C5—C6A	91.1 (7)	C10—C11—C12	109.2 (3)
C5—C6—C7	112.7 (4)	C15—C11—C12	111.8 (3)
C8—C7—C6	107.8 (6)	C13—C12—C11	112.4 (3)
C7A—C6A—C5	103.9 (11)	C12—C13—C1	117.7 (3)
C8—C7A—C6A	115.4 (6)		
C1—C2—C3—C4	-10 (9)	C8—C9—C10—C11	10 (12)
C2—C3—C4—C5	10 (6)	C11—C12—C13—C1	-155.0 (3)

Data collection

Stoe AED-2 four-circle-diffractometer

 $2\theta/\omega$ scans

Absorption correction: none

2398 measured reflections

2398 independent reflections

1583 reflections with

 $I > 2\sigma(I)$ $\theta_{\max} = 25^\circ$ $h = -21 \rightarrow 20$ $k = 0 \rightarrow 9$ $l = 0 \rightarrow 22$

2 standard reflections

frequency: 60 min

intensity decay: 5%

Refinement

Refinement on F^2 $R(F) = 0.072$ $wR(F^2) = 0.1997$ $S = 1.159$

2371 reflections

175 parameters

H atoms placed in calculated positions

 $w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 8.7395P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.031$ $\Delta\rho_{\max} = 0.731 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.239 \text{ e } \text{\AA}^{-3}$

Extinction correction:

SHELXL93

Extinction coefficient:

0.0011 (4)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (5) at 193 K
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.8951 (2)	-0.1147 (4)	0.6221 (2)	0.0233 (8)
C2	0.8271 (2)	-0.1024 (5)	0.6569 (2)	0.0283 (9)
C3	0.7694 (2)	-0.0822 (5)	0.6794 (2)	0.0346 (10)
C4	0.6951 (2)	-0.0491 (6)	0.7020 (2)	0.0437 (11)
C5	0.6377 (2)	0.0159 (6)	0.6415 (2)	0.0441 (11)
C6	0.6605 (3)	0.1573 (7)	0.5998 (2)	0.0499 (13)
C7	0.6645 (2)	0.3179 (6)	0.6408 (3)	0.0509 (13)
C8	0.7055 (2)	0.4515 (6)	0.6042 (3)	0.0472 (12)
C9	0.7878 (2)	0.4165 (5)	0.6114 (2)	0.0313 (9)
C10	0.8543 (2)	0.3871 (4)	0.6225 (2)	0.0238 (8)
C11	0.9370 (2)	0.3495 (4)	0.6419 (2)	0.0212 (8)
C12	0.9466 (2)	0.1723 (4)	0.6662 (2)	0.0234 (8)
C13	0.9214 (2)	0.0552 (4)	0.6034 (2)	0.0239 (8)
C14	0.8749 (2)	-0.2118 (4)	0.5525 (2)	0.0292 (9)
C15	0.9803 (2)	0.3874 (5)	0.5810 (2)	0.0278 (9)
O1	0.95556 (15)	-0.2033 (3)	0.66658 (14)	0.0282 (7)
O11	0.9694 (2)	0.4454 (3)	0.70410 (13)	0.0288 (7)

Table 4. Selected geometric parameters (\AA , $^\circ$) for (5) at 193 K

C1—O1	1.443 (4)	C7—C8	1.548 (7)
C1—C2	1.475 (5)	C8—C9	1.475 (5)
C1—C14	1.527 (5)	C9—C10	1.189 (5)
C1—C13	1.536 (5)	C10—C11	1.486 (5)
C2—C3	1.187 (5)	C11—O11	1.450 (4)
C3—C4	1.483 (5)	C11—C15	1.522 (5)
C4—C5	1.495 (6)	C11—C12	1.531 (5)
C5—C6	1.500 (6)	C12—C13	1.533 (5)
C6—C7	1.528 (7)		
C2—C1—C14	109.2 (3)	C9—C8—C7	110.8 (4)
C2—C1—C13	110.2 (3)	C10—C9—C8	175.2 (4)
C14—C1—C13	108.4 (3)	C9—C10—C11	175.9 (4)
C3—C2—C1	173.3 (4)	C10—C11—C15	112.3 (3)
C2—C3—C4	175.3 (4)	C10—C11—C12	109.1 (3)
C3—C4—C5	111.7 (3)	C15—C11—C12	112.1 (3)
C4—C5—C6	118.0 (4)	C11—C12—C13	111.5 (3)
C5—C6—C7	113.6 (4)	C12—C13—C1	117.1 (3)
C6—C7—C8	112.0 (4)		
C1—C2—C3—C4	4 (9)	C11—C12—C13—C1	-154.6 (3)
C8—C9—C10—C11	0 (10)		

Space group $I2/a$ was used, which is the third choice for space group $C2/c$ (No. 15; *International Tables for Crystallography*, 1983, Vol. A), in order to avoid large correlation coefficients between the $sc + z$ coordinates when β is much larger than 90° . At 193 K, there are fewer measurable reflections (*ca* 2%) as N is proportional to the volume of the unit cell, however, the number of observed reflections increased by *ca* 8%.

For both measurements, data collection: *STADI-4* (Stoe & Cie, 1996a); cell refinement: *STADI-4*; data reduction: *X-RED* (Stoe & Cie, 1996b); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL93*.

This work has been supported by the Swiss National Science Foundation (Project Nos. 20-43565.95 and 20.37270.93) and the Stipendienfonds der Schweizerischen Chemischen Industrie.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1269). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* B35, 2331–2339.
- Boss, C., Keese, R. & Försch, M. (1996). *Acta Cryst.* C52, 2370–2372.
- Boss, C., Stoeckli-Evans, H. & Keese, R. (1996). *Acta Cryst.* C52, 3069–3073.
- Dale, J. (1978). *Stereochemie und Konformationsanalyse*, pp. 174–182. Weinheim: Verlag Chemie.
- Dunitz, J. D. & Meyer, E. F. Jr (1965). *Helv. Chim. Acta*, 48, 1441–1449.
- Gleiter, R., Merger, R., Irgartinger, H. & Nuber, B. (1993). *J. Org. Chem.* 58, 2025–2028, and references therein.
- Johnson, R. P. (1986). *Mol. Struct. Energ.* 3, 85–140.
- Keese, R. & Meyer, M. (1993). *Tetrahedron*, 49, 2055–2064.

- Meier, H. (1991). *Adv. Strain Org. Chem.* 1, 215–272.
- Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* A46, C-34.
- Stoe & Cie (1996a). *STADI-4. Diffractometer Control Program*. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1996b). *X-RED. Data Reduction Program*. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1997). C53, 325–327

2-Amino-5-methyl-10bH-1,3,4-thia-diazolo[3,2-c]quinazolin-6-ium-10b-carboxylate Hydrate

QI ZHANG,^{a,b} SHUBEN LI,^a LIUFANG WANG,^{b*} JIACHENG LIU^b AND XIAOYING HUANG^c

^aState Key Laboratory of Oxo-Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China, ^bState Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China, and ^cState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

(Received 21 February 1996; accepted 8 November 1996)

Abstract

The $C_{11}H_{10}N_4O_2S$ molecule in the title compound, $C_{11}H_{10}N_4O_2S \cdot H_2O$, is a new heterocycle. It comprises three fused rings and exists in a zwitterionic form. The two six-membered rings are approximately coplanar, but the presence of a saturated C_{sp^3} atom at the junction of the five-membered and central six-membered rings imposes a marked non-coplanarity on these, with a dihedral angle of $23.1(2)^\circ$. The molecule is thus chiral and the crystal structure is a racemate incorporating two molecules of water for each *R/S* pair of molecules. There is an extensive hydrogen-bonding network.

Comment

Many heterocyclic compounds exhibit bioactivity (Grayson, 1982), especially as antifungal, antitumour and antiviral agents (Irdyan *et al.*, 1990). Several heterocyclic compounds with a composition similar to that of the tricyclic CAM molecule in the title compound, $CAM \cdot H_2O$, are essentially planar and hence achiral. We have determined the structure of $CAM \cdot H_2O$ by X-ray diffraction methods (Gilmore, 1983) as part