ORGANIC COMPOUNDS

Acta Cryst. (1996). C**52**, 1684–1686

TAPSO at Low Temperature

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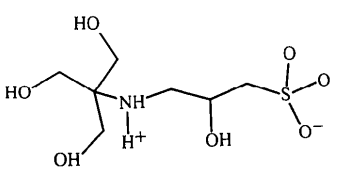
(*Received 30 August 1995; accepted 25 January 1996*)

Abstract

The crystal structure of TAPSO, 2-hydroxy-3-[tris-(hydroxymethyl)methylamino]propane-1-sulfonic acid, $C_7H_{17}NO_7S$, was determined at 153 K. This widely used buffer crystallizes as a zwitterion, 2-hydroxy-3-[tris(hydroxymethyl)methylammonio]propane-1-sulfonate, and crystal cohesion is provided by a dense network of hydrogen bonds. The molecular conformation of TAPSO is compared with the structure of TRIS (or TRIZMA), another commonly used buffering agent in protein crystallization. Cell parameters reported in the literature for a series of biological buffers used in protein crystallography are also provided.

Comment

TAPSO is a widely used biological buffer presenting a useful pH range between 7.0 and 8.2 (pK_a = 7.6). It crystallizes as a zwitterion, the proton of the sulfonic acid group being transferred to the N atom. The positions of the H atoms at the N atom were unambiguously located from difference Fourier maps and no residual electron density remained near the O atoms of the sulfonic acid group.



TAPSO

TAPSO adopts an extended conformation (see Fig. 1 and the torsion angles in Table 2). The S1—O bond lengths are 1.445 (2), 1.459 (3) and 1.468 (3) Å for O1, O2 and O3, respectively. The shortest S—O bond involves O1; this O atom is not involved in any hydrogen bonding. Slight deviation from an ideal tetrahedral configuration around S1 is found, the angles which deviate most being O1—S1—O2 113.9 (1) and C1—S1—O1 105.8 (1)°. C10 also displays tetrahedral coordination with bond lengths of 1.510 (4), 1.515 (4), 1.533 (4) and 1.530 (4) Å for N1, C11, C21 and C31, respectively, and bond angles around 109.5°: N1—C10—C11 108.7 (2), N1—C10—C21 111.7 (2), N1—C10—C31 110.1 (2), C11—C10—C21 111.8 (2), C11—C10—C31 109.7 (2) and C21—C10—C31 111.8 (2)°.

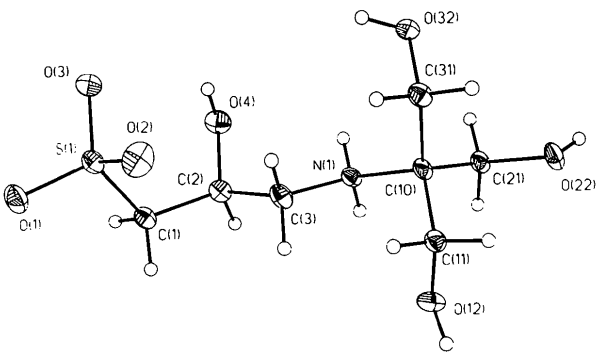


Fig. 1. The atomic numbering scheme, molecular structure and conformation of TAPSO. Non-H atoms are represented by displacement ellipsoids at the 50% probability level.

The conformation of the tris(hydroxymethyl)methylamino part of TAPSO is comparable with the structure of other pentaerythritol compounds, in particular, with the geometry of neutral TRIS, $(HOCH_2)_3CNH_2$ (Kendi, 1982). The average r.m.s. deviation between the two molecules, calculated using the *OFIT* option in *SHELXTL/PC* (Sheldrick, 1992), is 0.076 Å (Fig. 2). This suggests that the propanesulfonic acid moiety in TAPSO does not significantly modify the conformation of the tris(hydroxymethyl)methylamino part.

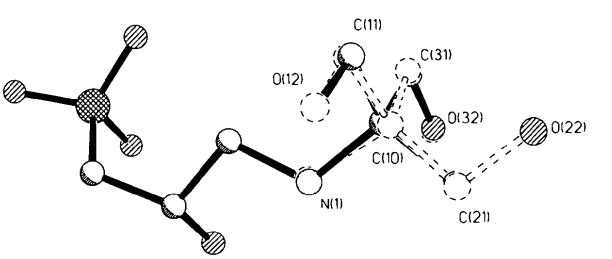


Fig. 2. Comparison of the conformation of the pentaerythritol part of TAPSO with the structure of TRIS, $(HOCH_2)_3CNH_2$. The coordinates for TRIS were obtained from the Cambridge Structural Database (refcode: THXMAM01).

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Molecular cohesion in the crystal structure of TAPSO is provided by a dense network of hydrogen bonds (Jeffrey & Saenger, 1991) involving the sulfate group, the protonated amine group and the four hydroxyl groups (O4, O12, O22, O32) of the molecule. In Table 3, the geometries of these hydrogen bonds are compared with the patterns reported for TRIS (Rudman, Eilerman & La Place, 1978) and $TRISH^+.X^-$ (X = Cl, Br, I; Rudman, Lippman, Sake Gowda & Eilerman, 1983). Of the five independent hydrogen bonds, four connect the molecules into sheets parallel to the *ac* plane (Fig. 3), whereas the fifth (O12···O22) links these sheets parallel to the *y* axis.

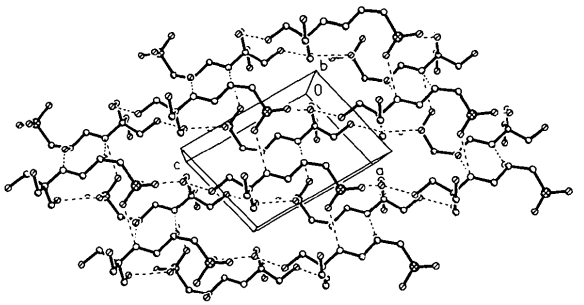

Fig. 3. A packing diagram for TAPSO viewed perpendicular to the *ac* plane. H atoms are omitted and hydrogen bonds are indicated by broken lines. The molecules form sheets, of which one is shown, involving four of the five independent hydrogen bonds; the sheets are linked by further hydrogen bonds O12···O22 (not shown).

The differences in the hydrogen-bonding patterns of these two molecules may reflect distinct solvation properties of the buffering agents, which provide a similar useful pH of around 8. These structural differences are rarely taken into account when a buffer is chosen, although it is clear that they may play a crucial role, for example, during crystallization of macromolecules.

Although biochemical and biophysical methods can be used to establish the nature of crystals (see, for example, Lorber & Giege, 1992), lucky macromolecular crystal growers usually prefer X-ray diffraction methods to obtain crystallographic parameters directly. We present here (Table 4) a short list of cell parameters of common biological buffers. Note that the volume of the cell may become important, particularly in the presence of some ions (Mg^{2+}, Cu^{2+}).

Experimental

Crystals formed in a 10 ml drop during an experiment designed to crystallize a small peptide from a solution buffered with TAPSO. The cell parameters ($V \approx 500$ Å^3) deduced from a first set of 20 reflections collected on a crystal clearly indicated that the peptide has not crystallized.

Crystal data

$C_7H_{17}NO_7S$
M_r = 259.28
Triclinic
$P\bar{1}$
a = 6.689 (6) Å
b = 8.790 (9) Å
c = 9.447 (8) Å
α = 95.23 (9)°
β = 104.88 (7)°
γ = 92.21 (6)°
V = 533.5 (9) Å^3
Z = 2
D_x = 1.614 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 28 reflections
θ = 20–25°
μ = 0.326 mm^{-1}
T = 153 (2) K
Prism
0.5 × 0.4 × 0.4 mm
Colourless

Data collection

Stoe $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1789 measured reflections
1394 independent reflections
1263 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0342
θ_{max} = 22.49°
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0379
$wR(F^2)$ = 0.1401
S = 1.074
1391 reflections
166 parameters
H(N) and H(O) refined freely, other H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 0.4316P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.119
$\Delta\rho_{max}$ = 0.256 e Å^{-3}
$\Delta\rho_{min}$ = −0.456 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
S1	0.06814 (10)	0.74988 (8)	0.39123 (7)	0.0153 (3)
O1	0.1552 (3)	0.8261 (2)	0.2894 (2)	0.0241 (5)
O2	0.1714 (3)	0.7968 (2)	0.5458 (2)	0.0263 (5)
O3	0.0546 (3)	0.5826 (2)	0.3589 (2)	0.0226 (5)
C1	−0.1915 (4)	0.8043 (3)	0.3601 (3)	0.0156 (6)
C2	−0.3278 (4)	0.7309 (3)	0.4452 (3)	0.0167 (6)
O4	−0.3483 (3)	0.5685 (2)	0.4197 (2)	0.0210 (5)
C3	−0.2625 (4)	0.7832 (3)	0.6085 (3)	0.0172 (6)
N1	−0.4175 (4)	0.7194 (3)	0.6806 (3)	0.0145 (6)
C10	−0.3658 (4)	0.7426 (3)	0.8466 (3)	0.0143 (6)
C11	−0.3088 (4)	0.9110 (3)	0.8964 (3)	0.0159 (6)
C21	−0.5649 (4)	0.6884 (3)	0.8842 (3)	0.0153 (6)
C31	−0.1837 (4)	0.6485 (3)	0.9127 (3)	0.0165 (6)
O12	−0.4754 (3)	0.9932 (2)	0.8241 (2)	0.0201 (5)
O22	−0.5323 (3)	0.7111 (2)	1.0399 (2)	0.0197 (5)
O32	−0.2291 (3)	0.4900 (2)	0.8673 (2)	0.0209 (5)

Table 2. *Selected geometric parameters (Å, °)*

S1—O1	1.445 (2)	N1—C10	1.510 (4)
S1—O2	1.459 (3)	C10—C11	1.515 (4)
S1—O3	1.468 (3)	C10—C21	1.533 (4)
S1—C1	1.778 (3)	C10—C31	1.530 (4)
C1—C2	1.522 (4)	C11—O12	1.412 (4)
C2—O4	1.422 (4)	C21—O22	1.424 (3)
C2—C3	1.514 (4)	C31—O32	1.417 (4)
C3—N1	1.497 (4)		
O1—S1—O2	113.86 (14)	C3—N1—C10	117.3 (2)
O1—S1—O3	112.03 (14)	N1—C10—C11	108.7 (2)
O2—S1—O3	111.3 (2)	N1—C10—C21	104.6 (2)
O1—S1—C1	105.82 (14)	N1—C10—C31	110.1 (2)
O2—S1—C1	107.19 (14)	C11—C10—C31	109.7 (2)
O3—S1—C1	106.06 (14)	C11—C10—C21	111.8 (2)
C2—C1—S1	117.5 (2)	C31—C10—C21	111.8 (2)
O4—C2—C3	110.9 (2)	O12—C11—C10	107.4 (2)
O4—C2—C1	113.5 (2)	O22—C21—C10	108.5 (2)
C3—C2—C1	113.0 (2)	O32—C31—C10	111.7 (2)
N1—C3—C2	109.4 (2)		
O1—S1—C1—C2	175.6 (2)	S1—C1—C2—C3	69.0 (3)
O2—S1—C1—C2	−62.6 (2)	S1—C1—C2—O4	−58.4 (3)
O3—S1—C1—C2	56.4 (2)	C1—C2—C3—N1	173.8 (2)
C3—N1—C10—C11	51.8 (3)	N1—C10—C11—O12	55.4 (3)
C3—N1—C10—C21	171.4 (2)	N1—C10—C21—O22	−178.1 (2)
C3—N1—C10—C31	−68.3 (3)	N1—C10—C31—O32	−59.6 (3)
C10—N1—C3—C2	172.6 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °) for TAPSO, TRIS and TRISH$^+$.X$^-$ (X = Cl, Br, I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
TAPSO[a]				
O12—H12···O22^{i}	0.824	1.967	2.785 (4)	171.7
O22—H22···O32^{ii}	0.767	1.928	2.688 (4)	170.8
O32—H32···O3^{iii}	0.834	1.893	2.725 (4)	176.1
N1—H1N···O2^{iv}	0.881	2.001	2.854 (4)	162.9
N1—H2N···O4^{v}	0.827	2.149	2.872 (4)	146.0
TRIS[b]				
O12—H12···O32	0.739	2.021	2.723 (2)	159.0
O22—H22···N1	0.984	1.737	2.718 (2)	155.6
O32—H32···O22	0.878	1.797	2.674 (2)	176.0
N1—H···O12	0.835	2.338	3.051 (4)	143.7
TRISH$^+$.X$^-$[c]				
X = Cl				
N···O*	0.69 (3)		2.818 (3)	167 (4)
O*···X	0.73 (5)		3.031 (3)	112 (4)
X = Br				
N···O*	0.61 (4)		2.812 (3)	164 (4)
O*···X	0.91 (4)		3.217 (3)	169 (4)
X = I				
N···O*			2.886 (15)	
O*···X			3.489 (13)	

Symmetry codes: (i) $-1-x, 2-y, 2-z$; (ii) $-1-x, 1-y, 2-z$; (iii) $-x, 1-y, 1-z$; (iv) $x-1, y, z$; (v) $1-x, 1-y, 1-z$.

References: (*a*) this work; (*b*) Rudman, Eilerman & La Place (1978); (*c*) Rudman, Lippman, Sake Gowda & Eilerman (1983). * Along a threefold axis.

Table 4. *Cell parameters (Å, °) for widely used biological buffers*

Cell parameters were determined at room temperature except for TAPSO.

		a	*b*	*c*	α	β	γ	Refcode
TAPSO[a]	$P\bar{1}$	6.689	8.790	9.447	95.23	104.88	92.21	-
BICINE	$P2_1/n$	9.963	11.045	7.667	90	111.78	90	BICINE
MES	$P2_1/c$	8.632	9.985	11.150	90	93.77	90	YATVUK
HEPES[b]	$Pbca$	11.804	11.392	16.256	90	90	90	-
TRIS	$Pn2_1a$	8.844	7.794	8.795	90	90	90	THXMAM10
TRISHCl	$R\bar{3}$	7.569	7.569	24.694	90	90	120	TRISHC10
TRISHBr	$R\bar{3}$	7.701	7.701	25.447	90	90	120	BUZGAE
TRISHI	$I2_13$	11.627	11.627	11.627	90	90	90	BUZFUX
TRISNi	$P2_1/c$	11.725	12.235	6.335	90	92.86	90	BEWKIX
TRISCu	$C2/c$	14.287	10.945	11.192	90	96.29	90	BITCAI
TRIS/PO$_4$	$P2_1$	8.179	6.170	9.576	90	106.32	90	GEXRUW

References: (*a*) this work; (*b*) Wouters, Häming & Sheldrick (1996).

The structure was solved by direct methods and refined anisotropically. Coordinates of widely used biological buffers were retrieved from the Cambridge Structural Database (Allen & Kennard, 1993). Reference codes are provided in Table 4.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

JW thanks the National Foundation for Scientific Research (FNRS Belgium) for his Research Assistant position and the Boehringer Ingelheim Fonds for partial financial support for his postdoctoral stay in Professor Sheldrick's laboratory. DS thanks the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. JW acknowledges comments and help from Dr P. G. Jones, Co-editor.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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