Eric C. Hosten and Richard Betz*

The crystal structure of bis(1,3-dihydroxy-2-methylpropan-2-aminium) carbonate, $C_9H_{24}N_2O_7$

<https://doi.org/10.1515/ncrs-2020-0521>

Received October 3, 2020; accepted October 30, 2020;

published online November 13, 2020

Abstract

$C_9H_{24}N_2O_7$, monoclinic, $P2_1/n$ (no. 14), $a = 11.1646(7)$ Å, $b = 6.3264(4)$ Å, $c = 18.6926(9)$ Å, $\beta = 97.5994(18)^\circ$, $V = 1308.69(13)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0385$, $wR_{ref}(F^2) = 0.1057$, $T = 200$ K.

CCDC no.: 2041499

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was provided as 2-amino-2-methylpropane-1,3-diol by Merck, possibly in the 1960s. Crystals used for the diffraction study were taken directly from the stock present in store as-is.

*Corresponding author: Richard Betz, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa, E-mail: Richard.Betz@mandela.ac.za. <https://orcid.org/0000-0002-5730-2152>

Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa. <https://orcid.org/0000-0003-4173-2550>

Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	0.23 × 0.21 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.12 mm ⁻¹
Diffraction, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	12136, 3249, 0.028
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2469
$N(param)_{refined}$:	182
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U_{eq}(C)$. The H atoms of the methyl and ammonium groups were allowed to rotate with a fixed angle around the C–C bond to fit the experimental electron density (HFIX 137 in the SHELX program [3]), with $U(H)$ set to $1.5U_{eq}(C)$. The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C–O bond to fit the experimental electron density (HFIX 147 in the SHELX program [3]), with $U(H)$ set to $1.5U_{eq}(O)$.

One of the hydroxyl groups shows well-behaved disorder over two orientations that could be handled by a two-component model with the major position being present in 72.1% of cases.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
O11	0.77200 (9)	0.81957 (18)	0.10955 (6)	0.0263 (3)
H11	0.831458	0.833996	0.141749	0.039*
O12	0.41969 (9)	0.96624 (16)	0.15114 (6)	0.0225 (2)
H12	0.417472	0.862414	0.178947	0.034*
O21	0.35589 (9)	0.16714 (19)	0.32775 (6)	0.0312 (3)
H21	0.404831	0.247626	0.310690	0.047*
O31	0.41551 (8)	0.61718 (16)	0.23120 (5)	0.0191 (2)
O32	0.54009 (9)	0.37582 (16)	0.28729 (5)	0.0203 (2)
O33	0.61127 (9)	0.68927 (17)	0.26064 (6)	0.0249 (2)
N1	0.65427 (10)	1.07429 (19)	0.20594 (6)	0.0164 (2)
H1A	0.639417	0.941698	0.221468	0.025*
H1B	0.610961	1.169640	0.228424	0.025*
H1C	0.734476	1.103442	0.216482	0.025*
N2	0.24971 (10)	−0.21694 (19)	0.32594 (6)	0.0187 (3)
H2A	0.207204	−0.102970	0.306806	0.028*
H2B	0.197541	−0.318170	0.337388	0.028*
H2C	0.295251	−0.269506	0.293121	0.028*
C3	0.52251 (11)	0.5622 (2)	0.25950 (7)	0.0154 (3)
C11	0.61794 (12)	1.0876 (2)	0.12594 (7)	0.0176 (3)
C12	0.58464 (13)	1.3153 (2)	0.10642 (8)	0.0238 (3)
H12A	0.566637	1.328608	0.053863	0.036*
H12B	0.652413	1.408104	0.124096	0.036*
H12C	0.513381	1.355973	0.128712	0.036*
C13	0.72545 (13)	1.0214 (3)	0.08771 (8)	0.0238 (3)
H13A	0.699756	1.019909	0.034953	0.029*
H13B	0.790529	1.127741	0.097822	0.029*
C14	0.51213 (12)	0.9346 (2)	0.10694 (7)	0.0198 (3)
H14A	0.478100	0.954580	0.055736	0.024*
H14B	0.542092	0.787535	0.112789	0.024*
C21	0.33099 (12)	−0.1510 (2)	0.39298 (7)	0.0195 (3)
C22	0.39630 (15)	−0.3447 (3)	0.42720 (8)	0.0282 (3)
H22A	0.447081	−0.405819	0.393558	0.042*
H22B	0.336827	−0.449674	0.438222	0.042*
H22C	0.447036	−0.303355	0.471830	0.042*
C23	0.42043 (13)	0.0081 (2)	0.36985 (8)	0.0235 (3)
H23A	0.467937	0.071969	0.412916	0.028*
H23B	0.477055	−0.063650	0.341271	0.028*
C24 ^a	0.24965 (15)	−0.0482 (3)	0.44325 (8)	0.0294 (4)
H24A ^a	0.212620	0.080716	0.419838	0.035*
H24B ^a	0.183542	−0.147274	0.450266	0.035*
O22 ^a	0.31043 (15)	0.0048 (3)	0.50929 (8)	0.0301 (5)
H22 ^a	0.308137	−0.097034	0.537918	0.045*
C25 ^b	0.24965 (15)	−0.0482 (3)	0.44325 (8)	0.0294 (4)
H25A ^b	0.303496	0.036001	0.478740	0.035*
H25B ^b	0.197749	0.054124	0.413444	0.035*
O23 ^b	0.1837 (4)	−0.1468 (8)	0.4774 (2)	0.0389 (14)
H23 ^b	0.225425	−0.214587	0.510386	0.058*

^aOccupancy: 0.721 (3), ^bOccupancy: 0.279 (3).

Comment

Synthesis and analysis are the two major aspects of historic and contemporary chemistry. For a large variety of reactions well-established standard synthesis procedures are

apparent that form the basis of vast sections of practical laboratory courses during undergraduate student training. Against this backdrop it then seems improbable that one specific synthesis reaction (whose nature is known and understood) would then-all of a sudden-yield surprising results contradicting experience. The latter is a particularly suspicious development if the unexpected results coincide with a change in reagent supply as the historic example of the Simmons-Smith reaction has shown when success or failure during the early years of this reaction being applied could be attributed to the catalytic effects of silver present in one of the starting materials [7–11]. In our case, coordination reactions involving 2-amino-2-methyl-propane-1,3-diol as a ligand started providing unexpected results. As the onset of the changed behaviour coincided with an older batch of the reagent being used in our laboratories, the nature of the compound was checked by means of a diffraction study. The unit cell dimensions of the aminole are apparent in the literature [12] but differed from the ones found in our case.

The title structure showed a surprising result – instead of the expected pure aminole, the material constituted the carbonate salt of its protonated form, the latter most likely having formed over the decades of storage and – *via* a loose lid – subsequent gradual sequestration of atmospheric carbondioxide and moisture.

The asymmetric unit contains two aminium cations (see the Figure). The two positive charges are balanced by the presence of a carbonate anion. One of the hydroxyl groups present in one of the cations is disordered over two positions with the major orientation being present in 72.1% of cases. C–N bond lengths of 1.4990(17) and 1.5056(17) Å as well as C–O bond lengths within the carbonate ion covering a range of 1.2742(16)–1.2928(17) Å are in good agreement with comparable bonds in other compounds deposited with the Cambridge Structural Database [13]. The C–O distances for the hydroxyl groups span a narrow range of 1.369(2)–1.4190(17) Å, however, the shortest value in this context is established towards the disordered OH group and might show a systematic shortening caused by the chosen disorder model.

In the crystal structure, classical hydrogen bonds of the O–H...O and the N–H...O type supported by all hydrogen atoms bonded to these heteroatoms are apparent. All oxygen atoms of the carbonate ion as well as some of the hydroxyl groups act as acceptors for these hydrogen bonds. In terms of graph-set analysis [14, 15], the descriptor for these hydrogen bonds is DDDDDDDDDD on the unary level. In total, the entities present in the crystal structure are connected to a three-dimensional network.

The results of this study strengthen the notion that even simple, solid organic compounds that enjoy a – supposedly! – infinite shelf-life and are impervious

to decomposition can undergo chemical alterations over prolonged storage.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: National Research Foundation.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *APEX2*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
2. Bruker. *SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
3. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, *A64*, 112–122.
4. Farrugia L. J. *WinGX and ORTEP for Windows*: an update. *J. Appl. Crystallogr.* 2012, *45*, 849–854.
5. Macrae C. F., Bruno I. J., Chisholm J. A., Edgington P. R., McCabe P., Pidcock E., Rodriguez-Monge L., Taylor R., van de Streek J., Wood P. A. *Mercury CSD 2.0* – new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* 2008, *41*, 466–470.
6. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, *D65*, 148–155.
7. Simmons H. E., Jr., Smith R. D. A new synthesis of cyclopropanes from olefins. *J. Am. Chem. Soc.* 1958, *80*, 5323–5324.
8. Simmons H. E., Smith R. D. A new synthesis of cyclopropanes. *J. Am. Chem. Soc.* 1959, *81*, 4256–4264.
9. Denis J. M., Girard J. M., Conia J. M. Improved Simmons–Smith reactions. *Synthesis* 1972, *10*, 549–551.
10. Charette A. B., Beauchemin A. Simmons–Smith cyclopropanation reaction. *Org. React.* 2001, *58*, 1–415.
11. Lévesque E., Goudreau S. R., Charette A. B. Improved zinc-catalyzed Simmons–Smith reaction: access to various 1,2,3-trisubstituted cyclopropanes. *Org. Lett.* 2014, *16*, 1490–1493.
12. Rose H. A., Van Camp A. Crystallographic data. 139. 2-amino-2-methyl-1,3-propanediol. *Anal. Chem.* 1956, *28*, 1790–1791.
13. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
14. Bernstein J., Davis R. E., Shimon L., Chang N.-L. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. *Angew. Chem. Int. Ed. Engl.* 1995, *34*, 1555–1573.
15. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* 1990, *B46*, 256–262.