Pholani Manana, Eric C. Hosten and Richard Betz*

The crystal structure of di-*tert*-butyl dicarbonate, $C_{10}H_{18}O_5$

<https://doi.org/10.1515/ncrs-2021-0228>

Received June 3, 2021; accepted June 30, 2021;

published online August 5, 2021

Abstract

$C_{10}H_{18}O_5$, monoclinic, $P2_1/c$ (no. 14), $a = 11.3561(7)$ Å, $b = 11.4569(7)$ Å, $c = 10.9762(6)$ Å, $\beta = 116.087(2)^\circ$, $V = 1282.58(13)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0547$, $wR_{ref}(F^2) = 0.1677$, $T = 200$ K.

CCDC no.: 2093269

The molecular structure is shown in Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.58 \times 0.43 \times 0.38$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11805, 3182, 0.016
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2386
$N(\text{param})_{\text{refined}}$:	235
Programs:	BRUKER [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

mounting the crystal under a constant stream of cold nitrogen.

Source of material

The compound was obtained commercially (Merck Schuchardt). Crystals suitable for the diffraction study were obtained upon cooling the compound to 0 °C and selecting and

Experimental details

The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [3]), with $U(\text{H})$ set to $1.5 U_{\text{eq}}(\text{C})$.

The central dicarbonate moiety shows well-behaved orientational disorder that could be resolved by a three-component model with occupancies of 85.1, 12.2 and 2.7%.

Comment

The synthesis of di- and polypeptides is one of the most widespread reactions found in synthetic, bio-inspired

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

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

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.52863 (15)	0.40516 (15)	0.76473 (17)	0.0618 (4)
C2	0.5373 (2)	0.3373 (2)	0.8852 (2)	0.0955 (7)
H2A	0.602527	0.275066	0.905995	0.143 [*]
H2B	0.451652	0.302985	0.864812	0.143 [*]
H2C	0.563527	0.389595	0.963441	0.143 [*]
C3	0.6564 (3)	0.4691 (3)	0.7976 (4)	0.1295 (11)
H3A	0.728741	0.412841	0.828337	0.194 [*]
H3B	0.672335	0.526404	0.869456	0.194 [*]
H3C	0.650420	0.509189	0.716236	0.194 [*]
C4	0.4893 (3)	0.3307 (2)	0.6404 (2)	0.0945 (7)
H4A	0.558053	0.272942	0.655477	0.142 [*]
H4B	0.477248	0.380044	0.562836	0.142 [*]
H4C	0.406965	0.290390	0.621608	0.142 [*]
C7	−0.00964 (14)	0.75511 (15)	0.68634 (15)	0.0575 (4)
C8	0.06147 (18)	0.81784 (17)	0.82089 (17)	0.0696 (5)
H8A	−0.001432	0.864227	0.839283	0.104 [*]
H8B	0.128511	0.869420	0.816858	0.104 [*]
H8C	0.103285	0.760391	0.893454	0.104 [*]
C9	−0.1066 (2)	0.66714 (19)	0.6889 (2)	0.0805 (5)
H9A	−0.180418	0.707761	0.693531	0.121 [*]
H9B	−0.063860	0.616630	0.768449	0.121 [*]
H9C	−0.138662	0.619613	0.606289	0.121 [*]
C10	−0.0730 (2)	0.8400 (2)	0.5704 (2)	0.0873 (6)
H10A	−0.142392	0.883038	0.581133	0.131 [*]
H10B	−0.110742	0.797090	0.484426	0.131 [*]
H10C	−0.006851	0.894976	0.570410	0.131 [*]
O1A ^a	0.43765 (13)	0.50715 (11)	0.73432 (17)	0.0555 (4)
O2A ^a	0.25815 (15)	0.40045 (13)	0.6966 (2)	0.0818 (6)
O3A ^a	0.2532 (2)	0.59567 (17)	0.6721 (3)	0.0692 (5)
O4A ^a	0.17181 (14)	0.57709 (12)	0.82467 (14)	0.0658 (4)
O5A ^a	0.09014 (15)	0.70265 (12)	0.64805 (14)	0.0541 (4)
C5A ^a	0.3147 (4)	0.4878 (3)	0.7046 (5)	0.0556 (6)
C6A ^a	0.1668 (3)	0.6206 (2)	0.7246 (4)	0.0499 (8)
O1B ^b	0.3916 (9)	0.4374 (9)	0.7597 (10)	0.066 (3)
O2B ^b	0.3397 (10)	0.5534 (10)	0.5778 (11)	0.077 (3)
O3B ^b	0.2003 (9)	0.5234 (8)	0.6676 (13)	0.078 (3)
O4B ^b	0.2330 (8)	0.7173 (7)	0.6996 (10)	0.061 (2)
O5B ^b	0.0433 (7)	0.6268 (7)	0.6669 (9)	0.052 (2)
C5B ^b	0.3226 (14)	0.5105 (14)	0.6679 (17)	0.050 (3)
C6B ^b	0.1670 (17)	0.6332 (14)	0.689 (3)	0.052 (6)
O1C ^c	0.413 (2)	0.486 (3)	0.676 (3)	0.040 (5)
O2C ^c	0.292 (3)	0.425 (3)	0.777 (4)	0.040 (5)
O3C ^c	0.262 (3)	0.601 (3)	0.666 (5)	0.040 (5)
O4C ^c	0.046 (2)	0.550 (3)	0.568 (3)	0.040 (5)
O5C ^c	0.1257 (18)	0.701 (3)	0.710 (4)	0.040 (5)
C5C ^c	0.312 (7)	0.488 (5)	0.702 (9)	0.040 (5)
C6C ^c	0.133 (2)	0.613 (3)	0.636 (4)	0.040 (5)

^aOccupancy: 0.851 (3), ^bOccupancy: 0.122 (2), ^cOccupancy: 0.027 (2).

organic chemistry. To prevent the formation of mixed links between the various amino acids to be connected protection groups are employed that only leave the desired amino and carboxy groups accessible for condensation reactions. The protection of the amino group is frequently achieved

by means of the so-called Boc group (short for *tert*-butyl oxycarbonyl) that is conveniently introduced to an amino acid by reacting it with di-*tert*-butyl dicarbonate [7]. The latter reagent can be regarded as a diester derivative of pyrocarbonic acid. Structural information about ester derivatives of this illusive parent acid is scant with only one report apparent in the literature for its symmetric diester of trifluoromethanol [8]. In continuation of our interest in structural aspects of esters of carboxylic acids [9–13] we sought to determine the molecular and crystal structure of the title compound to extend the structural knowledge of dicarbonic acid diesters.

The structure solution shows the presence of the symmetric diester of *tert*-butyl alcohol and dicarbonic acid. The atoms of the central dicarbonate chain show well-behaved orientational disorder over three orientations with the major orientation present in 85.1% of cases. C–O double bond distances in the major component are measured at 1.171(4) and 1.184(4) Å which is in good agreement with other esters of carbonic acid whose metrical parameters have been deposited with the Cambridge Structural Database [14]. The least-squares planes as defined by the four atoms of each individual carbonate moiety intersect at an angle of 59.27(15) Å.

In the crystal, a number of C–H...O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them are observed. These exclusively involve one of the carbonyl-type oxygen atoms as acceptor. In terms of graph-set analysis [15, 16], the descriptor for these interactions is C₁¹(6) C₁¹(8) C₁¹(8) on the unary level. In total, the molecules are connected to zig-zag chains along the crystallographic *b* axis.

Acknowledgements: The corresponding author thanks the National Research Foundation for financial support.

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

Research funding: The study was financially supported by National Research Foundation.

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

References

1. Bruker. *APEX2 and SAINT*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
2. Bruker. *SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.

4. Farrugia L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, 45, 849–854.
5. Macrae C. F., Sovago I., Cottrell S. J., Galek P. T. A., McCabe P., Pidcock E., Platings M., Shields G. P., Stevens J. S., Towler M., Wood P. A. Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Crystallogr.* 2020, 53, 226–235.
6. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, D65, 148–155.
7. Wakselman M. Di-*t*-butyl dicarbonate. In *Encyclopedia of Reagents for Organic Synthesis*; Charette A., Bode J., Rovis T., Shenvi R., Eds. Wiley & Sons: New York, 2004.
8. Garcia P., Willner H., Paci M. B., Arguello G. A., Berends T. Bis(trifluoromethyl)dicarbonate, $CF_3OC(O)OC(O)OCF_3$. *J. Fluor. Chem.* 2005, 126, 984–990.
9. Betz R., Herdlicka S., Klüfers P. Ethyl dicyclohexylglycolate. *Acta Crystallogr.* 2007, E63, o3916.
10. Garudachari B., Isloor A. M., Satyanarayan M. N., Gerber T., Hosten E., Betz R. Diethyl 2-[[2-(trifluoromethyl)anilino]methylidene]propanedioate. *Acta Crystallogr.* 2012, E68, o514–o515.
11. Isloor A. M., Rai U. S., Shetty P., Gerber T., Hosten E., Betz R. Methyl 2-[(2-methylphenoxy)methyl]benzoate. *Acta Crystallogr.* 2012, E68, o728.
12. Odame F., Hosten E. C., Tshentu Z. R., Betz R. Crystal structure of 3,5-diaza-methyl-2-methyl-6-oxo-6-phenyl-4-thioxohexanoate, at 200 K, $C_{12}H_{14}N_2O_3S$. *Z. Kristallogr. NCS* 2015, 230, 9–10.
13. Betz R., Gerber T., Schalekamp H., Hosten E. Refinement of the crystal structure of l-valinemethylester hydrochloride, $C_6H_{13}NO_2 \cdot HCl$, at 200 K. *Z. Kristallogr. NCS* 2011, 226, 637–638.
14. Groom C. R., Allen F. H. The Cambridge Structural Database in retrospect and prospect. *Angew. Chem. Int. Ed.* 2014, 53, 662–671.
15. 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.
16. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* 1990, B46, 256–262.