Journal of Chemical Crystallography, Vol. 35, No. 9, September 2005 (© 2005)
DOI: 10.1007/s10870-005-3479-7

C—H···O hydrogen bond networks in *E*- and Z-unsaturated esters of C-glycosides

Agneš Kapor,(1)* **Dieter Zobel,**(2) **Marianna Strümpel,**(2) **Ljilja Torović,**(1)
and Mirjana Popsavin(1)

Received October 15, 2004; accepted February 10, 2005

Methyl *E*(*Z*)-4,7 anhydro-5-benzamido-6,8-di-*O*-benzoyl-2,3,5-trideoxy-D-allo-oct-2-enoate have been synthesized like intermediates and isolated as single crystals during the synthesis of pyrazole-related C nucleosides as synthetic product with cytotoxic activity.[1] Crystal structures of *E*(*Z*) isomers were determined by X-ray analysis. *E* isomer crystallizes in the triclinic crystal system, space group P1, $a = 5.319(1)$ Å, $b = 10.758(2)$ Å, $c = 12.229(2)$ Å, $\alpha = 72.38(2)°$, $\beta = 89.97(2)°$, $\gamma = 87.07(2)°$, $D_x = 1.320$ Mgm^{-3} and *Z* isomer in the orthorhombic crystal system, space group $P2_12_12_1$, $a = 5.1297(13)$ Å, $b = 19.667(5)$ Å, $c = 25.871(6)$ Å, $D_x = 1.348$ Mgm^{-3}. The molecular structure was solved by direct method on the basis of 2609 and 2727 unique reflections recorded at the temperature 293 K (*E*-isomer) and 173 K (*Z*-isomer) up to the final *R*-factor 0.0378 and 0.0435, respectively. C—H···O contact networks were analyzed and the correlation established between the existence of the weak C—H···O hydrogen bonds and the melting point of the single crystals.

KEY WORDS: X-Ray crystallography; C-glycosides; weak C—H···O hydrogen bond networks.

Introduction

C-Nucleosides and their analogues constitute targets in synthesis because of their biological and pharmacological properties. As part of our programme on the synthesis of pyrazole-related *C*-nucleoside **5**[1] from D-glucose (Scheme 1), we have prepared two *C*-glycosyl derivatives **3** and **4**, bearing the α,β-olefinic ester function at C4 of the 2-benzamido-2-deoxy-β-D-ribofuranosyl moiety. The free aldehyde **2** was liberated from its ethylene acetal derivative **1** by treatment with a mixture of CF_3COOH-HCl-H_2O and reacted with carbomethoxymethylenetriphenylphosphorane in methylene chloride to give the *Z*- and *E*-unsaturated esters **3** and **4** as 2:1 mixture. After effective separation on a column of silica gel, pure *Z*- and *E*-isomers **3** and **4** were isolated in 56 and 29% yields, respectively. Herein we report the X-ray structure and hydrogen-bonding network in the *E* and *Z*-isomer.

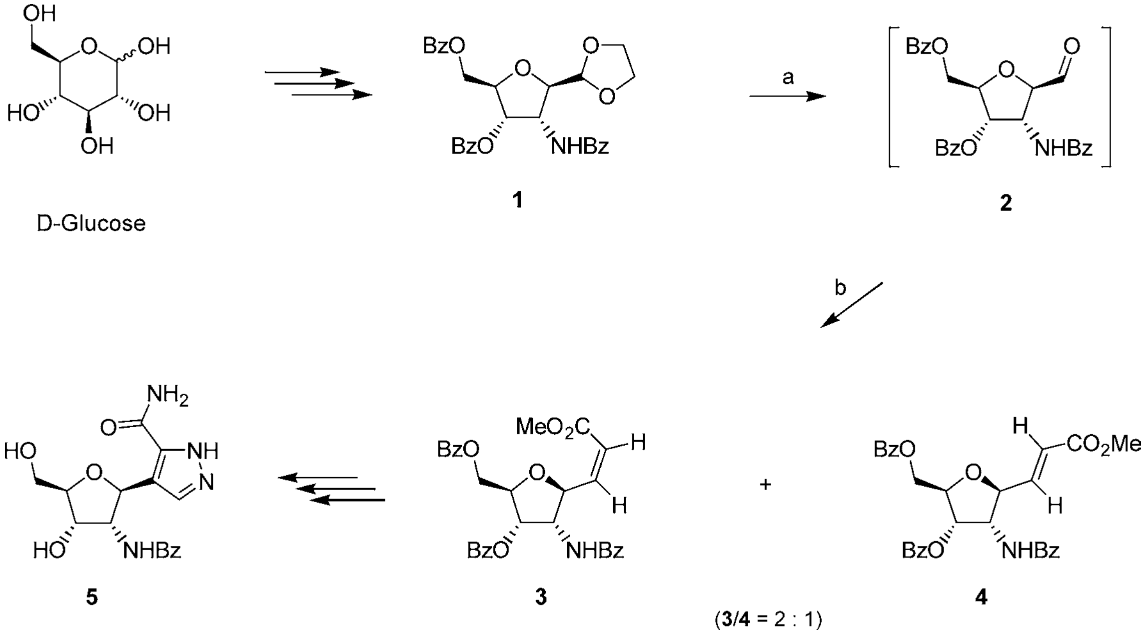
Experimental

Pure *Z*-isomer **3** was isolated as a white crystalline solid. Recrystallization from CH_2Cl_2-hexane gave an analytical sample (m.p. 114–115°C). Further elution with 5:1 toluene-EtOAc gave pure *E*-isomer **4** which crystallized from CH_2Cl_2-hexane to produce colorless needless

---

(1) Faculty of Natural Sciences and Mathematics, Trg D. Obradovića 4, 21000 Novi Sad, Serbia and Montenegro.
(2) Institute für Kristallographie, Freie Universität, Berlin, Takustraße 6, D-14195 Berlin, Germany.
* To whom correspondence should be addressed; e-mail: akapor@uns.ns.ac.yu.

1074-1542/05/0900-0687/0 © 2005 Springer Science+Business Media, Inc.



Scheme 1. (a) 4:1 CF_3CO_2H-6M HCl, +4°C, 96 h; (b) $Ph_3P{:}CHCO_2Me$, CH_2Cl_2, rt, 19 h, 85% from **1**.

(m.p. 165°C). The colorless crystal of *E*-isomer of dimension 0.93 mm × 0.40 mm × 0.12 mm was analyzed first at STOE four-circle diffractometer equipped with CuK_α radiation and Ni-filter at room temperature. Since we were dealing with an organic crystal of small dimensions, no absorption correction was performed. Very small white needle-shaped crystals of *Z*-isomer were rather fragile for the manipulation. Single crystal of dimension 0.15 mm× 0.08 mm× 0.05 mm was mounted at the STOE four circle diffractometer with graphite-monochromated MoK_α radiation. The intensity of 14,271 reflections was recorded with a CCD camera at the temperature of 173 K. Recording conditions data and crystal unit cell parameters are given in Table 1 for *E* and *Z*-isomer. In both cases, reflections were recorded with ϖ-2θ scan. Data were corrected for Lorentz and polarization effects.

The structure of isomers was solved by a direct method using program SHELXS86.[2] The E-map computed from the phase set with best combined figure of merit revealed the positions of all non-hydrogen atoms. Full-matrix least squares refinement of the fractional coordinates of the non-hydrogen atoms with anisotropic atomic displacement parameters was performed with SHELXL93[3] and WinGX.[4] Positions of H atoms were generated from the assumed geometry, checked in difference Fourier map and refined isotropically with common displacement parameters for methyl hydrogen $U_1 = 0.140(14)$ Å^2 (*E*-isomer), 0.067(12) Å^2 (*Z*-isomer), for phenyl hydrogen $U_2 = 0.107(5)$ Å^2 (*E*-isomer) 0.035(4) Å^2 (*Z*-isomer), and for other hydrogen's $U_3 =$ 0.049(3) Å^2 (*E*-isomer), 0.016(5) Å^2 (*Z*-isomer). Final *R*-factor was $R = 0.0378$, for 357 parameters for *E*-isomer and $R = 0.0435$ for 423 parameters for *Z*-isomer, using the F^2 values of 2609 and 2727 ($I > 2\sigma(I)$) reflections. The highest and the lowest peaks in the final difference map were 0.157 (0.17) and −0.143(−0.18) eÅ^{-3}, respectively for *E* and *Z*-isomer. Scattering factors were taken from SHELXL93. Details of structure solution and refinement are given in Table 1.

Atomic coordinates and equivalent isotropic displacement coefficients for non-hydrogen atoms are collected in Tables S1 and S2. Bond distances

Table 1. Crystal Data and Structure Refinement of *E*- and *Z*-isomer of $C_{30}H_{27}NO_8$

CCDC deposit no.	252513	252512
Empirical formula	$C_{30}H_{27}NO_8$,-*E*-isomer	$C_{30}H_{27}NO_8$,-*Z*-isomer
Formula weight	529.53	529.53
Melting point (K)	m.p. 438	m.p. 387–388
Temperature (K)	293(2)	173(2)
Wavelength (Å)	1.54178	0.71073 (on CCD)
Crystal system, space group	Triclinic, $P1$	Orthorhombic, $P2_12_12_1$
Unit cell dimensions		
a (Å)	5.319(1)	5.1297(13)
b (Å)	10.758(2)	19.6673(49)
c (Å)	12.229(2)	25.8714(62)
α (°)	72.38(1)	90
β (°)	89.97(2)	90
γ (°)	87.07(2)	90
Volume (Å^3)	665.9(3)	2610.1(11)
Z, Calculated density (Mg/m^3)	1, 1.320	4, 1.348
Absorption coefficient (mm^{-1})	0.799	0.098
$F(000)$	278	1112
Crystal size (mm)	0.93 × 0.40 × 0.12	0.15 × 0.08 × 0.05
θ range for data collection (°)	3.79 to 67.03	1.30 to 20.81
Limiting indices	$-6 \leq h \leq 0$ $-12 \leq k \leq 12$ $-14 \leq l \leq 14$	$-5 \leq h \leq 5$ $-19 \leq k \leq 19$ $-25 \leq l \leq 25$
Reflections collected/unique	3257/2609 [$R_{\text{int}} = 0.0748$]	14271/2727 [$R_{\text{int}} = 0.12(8)$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2609/3/357	2727/0/423
Goodness-of-fit on F^2	1.066	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0378$, $wR_2 = 0.1041$	$R_1 = 0.0435$, [$N = 1993$]
R indices (all data)	$R_1 = 0.0440$, $wR_2 = 0.1082$	$R_1 = 0.0756$, $wR_2 = 0.0913$
Extinction coefficient	0.0120(14)	0.0053(6)
Largest diff. peak and hole (eÅ^3)	0.157 and −0.143	0.17 and −0.18

and bond angles are listed in Tables S3 and S4. The H atom fractional atomic coordinates, anisotropic atomic displacement parameters for non-hydrogen atoms and other supplementary crystallographic data for this paper have been deposited at the Cambridge Crystallographic Data Center.

Results and discussion

The perspective views[5] of the molecules are depicted in Fig. 1 and Fig. 2. The "absolute configuration" of the C-nucleoside was taken from the literature with C4 (sp^3) chiral center possessing the S configuration in both isomers because the Flack parameter[6] was inconclusive: 0.6(3) (for *E*) and. 0.3(21) (for *Z*).

Bond lengths agree well with corresponding data taken from the literature. The analysis of the molecular conformation, on the basis of the values of corresponding torsion angles O—C4—C3—C2 = 125.2(4)°(*E*), −134.8(4)° (*Z*); O—C7—C8—O8 = −173.0(2)° (*E*), 175.5(4)° (*Z*)−173.0(2)° (*E*), 175.5(4)° (*Z*) −173.0(2)° (*E*), 175.5(4)° (*Z*) −173.0(2)° (*E*), 175.5(4)° (*Z*) −173.0(2)° (*E*), 175.5(4)° (*Z*) confirmed that β bonding of C4 substituent occurs.

The analysis of the molecular geometry has indicated to the presence of a large number of C—H···O contacts within the molecule and between the symmetry related molecules within the crystal unit cell. C—H···A (A/the proton acceptor) system are usually classified as weak hydrogen bonds.[7] Systems with oxygen atom acceptors like in investigated structure are stronger than that with sulfur atom ones. This is confirmed not only by crystal structure results[7] but also by

Table S1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for *E*-isomer

Atom	x	y	z	U_{eq}
O	−3880(5)	3071(2)	−2428(2)	60(1)
O(1)	−4325(6)	732(3)	−5385(3)	84(1)
C(1)	−6012(8)	1543(4)	−5449(3)	61(1)
C(2)	−5960(7)	2623(4)	−4940(3)	59(1)
C(3)	−4213(7)	2720(3)	−4237(3)	55(1)
C(4)	−4151(6)	3732(3)	−3638(3)	47(1)
C(5)	−1903(6)	4611(3)	−3905(2)	40(1)
N(5)	−2270(5)	5657(2)	−4970(2)	44(1)
C(6)	−1648(6)	5014(3)	−2821(2)	43(1)
O(6)	−3471(4)	6075(2)	−2923(2)	50(1)
C(7)	−2368(7)	3787(3)	−1883(3)	48(1)
C(8)	−181(7)	2872(3)	−1308(3)	53(1)
O(8)	1182(5)	3509(2)	−642(2)	58(1)
O(9)	3095(7)	1623(3)	327(3)	88(1)
C(9)	2769(7)	2770(3)	155(3)	53(1)
C(10)	4083(7)	3540(3)	767(3)	51(1)
C(11)	5949(9)	2926(5)	1559(4)	72(1)
C(12)	7242(11)	3617(6)	2131(5)	97(2)
C(13)	6787(14)	4929(6)	1880(5)	105(2)
C(14)	4986(13)	5565(6)	1076(5)	97(2)
C(15)	3610(9)	4882(4)	522(4)	68(1)
C(16)	−3213(7)	6752(3)	−2155(3)	51(1)
O(16)	−1594(6)	6479(3)	−1434(2)	69(1)
C(17)	−5164(7)	7838(3)	−2323(3)	54(1)
C(18)	−7050(7)	8087(4)	−3145(3)	61(1)
C(19)	−8855(9)	9098(4)	−3238(4)	77(1)
C(20)	−8700(11)	9861(4)	−2508(5)	87(2)
C(21)	−6811(12)	9630(5)	−1700(4)	87(2)
C(22)	−5063(10)	8612(4)	−1598(4)	71(1)
C(23)	−330(6)	6257(3)	−5568(3)	43(1)
O(23)	1851(4)	5935(3)	−5235(2)	67(1)
C(24)	−946(6)	7294(3)	−6674(3)	42(1)
C(25)	719(9)	7463(5)	−7548(4)	90(2)
C(26)	207(12)	8377(7)	−8597(4)	111(2)
C(27)	−1935(9)	9149(4)	−8783(3)	72(1)
C(28)	−3555(10)	9025(4)	−7919(4)	81(1)
C(29)	−3099(9)	8100(4)	−6854(3)	72(1)
O(30)	−8209(6)	1556(3)	−5959(3)	80(1)
C(30)	−8577(10)	519(6)	−6450(5)	94(2)

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for *Z*-isomer

Atom	x	y	z	U_{eq}
O	1265(7)	6499(2)	9350(1)	31(1)
C(1)	2461(13)	6145(4)	10951(2)	43(2)
O(1)	2599(10)	5542(2)	10859(2)	65(2)
C(2)	614(13)	6627(3)	10707(2)	36(2)
C(3)	−136(12)	6601(3)	10224(3)	36(2)
C(4)	755(12)	6120(3)	9817(2)	25(2)
C(5)	−1393(11)	5608(3)	9662(2)	22(2)
N(5)	−1212(9)	4982(2)	9951(2)	24(1)
O(6)	797(7)	5021(2)	8969(1)	26(1)
C(6)	−1154(11)	5539(3)	9078(2)	23(1)
C(7)	−147(11)	6234(3)	8919(2)	27(2)
C(8)	−2307(12)	6730(3)	8779(2)	31(2)
O(8)	−3484(8)	6452(2)	8319(1)	33(1)
C(9)	−5351(12)	6826(3)	8095(2)	33(2)
O(9)	−6009(8)	7378(2)	8251(1)	42(1)
C(10)	−6504(12)	6468(3)	7643(2)	31(2)
C(11)	−8656(14)	6753(3)	7409(3)	44(2)
C(12)	−9807(14)	6452(5)	6986(3)	52(2)
C(13)	−8761(17)	5863(4)	6790(3)	55(2)
C(14)	−6621(16)	5579(4)	7026(3)	54(2)
C(15)	−5485(13)	5862(3)	7454(2)	39(2)
C(16)	863(12)	4798(3)	8471(2)	30(2)
O(16)	−529(8)	5008(2)	8138(1)	40(1)
C(17)	2912(12)	4272(3)	8399(2)	29(2)
C(18)	4628(12)	4100(3)	8790(2)	29(2)
C(19)	6529(13)	3622(3)	8709(3)	41(2)
C(20)	6699(16)	3305(3)	8246(3)	54(2)
C(21)	5000(15)	3448(3)	7858(3)	55(2)
C(22)	3074(13)	3949(3)	7925(2)	43(2)
C(23)	−3337(12)	4598(3)	10060(2)	23(2)
O(23)	−5523(7)	4784(2)	9920(1)	28(1)
C(24)	−2930(10)	3939(3)	10332(2)	17(1)
C(25)	−930(11)	3837(3)	10680(2)	24(2)
C(26)	−710(13)	3212(3)	10927(2)	35(2)
C(27)	−2466(12)	2704(3)	10819(2)	30(2)
C(28)	−4452(12)	2802(3)	10469(2)	30(2)
C(29)	−4689(11)	3426(3)	10227(2)	25(1)
C(30)	5816(13)	6029(3)	11563(2)	59(2)
O(30)	3902(9)	6451(2)	11309(2)	51(1)

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ab initio calculations.[8] The proton donating abilities of C—H bond depend on the following order $C(sp^3)$—$H<C(sp^2)$—$H<C(sp)$—H.[9,10]

The type and the length of the intramolecular contacts are given in the Table 2 and it can be seen that they are the same for both isomers except those related to the ester group CH—CH—CO_2Me in *Z*-isomer due to the formation of the relatively strong intramolecular hydrogen bond N5—H5···. O1: (N5—H5N = 0.895(46) Å, N5···O1 = 3.248(6) Å, H5N···O1 = 2.806(44) Å, ∠N5—H5N···O1 = 111.9(33)°) which is the consequence of the *cis* geometry.

The very different geometries of the *trans* and *cis* configurations about the C2—C3 double

Table S3. Selected Bond Lengths [Å] and Angles [°] for *E*-isomer

Bond lengths (Å)			
O−C(7)	1.434(4)	C(6)−C(7)	1.529(4)
O−C(4)	1.439(4)	O(6)−C(16)	1.362(4)
O(1)−C(1)	1.205(5)	C(7)−C(8)	1.511(5)
C(1)−O(30)	1.323(5)	C(8)−O(8)	1.431(4)
C(1)−C(2)	1.476(5)	O(8)−C(9)	1.326(4)
C(2)−C(3)	1.296(5)	O(9)−C(9)	1.191(4)
C(3)−C(4)	1.487(5)	C(9)−C(10)	1.473(5)
C(4)−C(5)	1.536(4)	C(16)−O(16)	1.193(4)
C(5)−N(5)	1.446(4)	C(16)−C(17)	1.488(5)
C(5)−C(6)	1.522(4)	C(23)−O(23)	1.227(4)
N(5)−C(23)	1.341(4)	C(23)−C(24)	1.494(4)
C(6)−O(6)	1.435(4)	O(30)−C(30)	1.438(5)
Bond angles (°)			
C(7)−O−C(4)	110.8(2)	C(8)−C(7)−C(6)	115.1(3)
O(1)−C(1)−O(30)	124.0(4)	O(8)−C(8)−C(7)	107.5(3)
O(1)−C(1)−C(2)	125.2(4)	C(9)−O(8)−C(8)	117.2(2)
O(30)−C(1)−C(2)	110.7(3)	O(9)−C(9)−O(8)	122.9(3)
C(3)−C(2)−C(1)	123.6(4)	O(9)−C(9)−C(10)	125.1(3)
C(2)−C(3)−C(4)	126.0(3)	O(8)−C(9)−C(10)	112.0(3)
O−C(4)−C(3)	107.7(3)	C(11)−C(10)−C(9)	118.9(3)
O−C(4)−C(5)	103.7(2)	C(15)−C(10)−C(9)	122.1(3)
C(3)−C(4)−C(5)	116.0(3)	O(16)−C(16)−O(6)	122.5(3)
N(5)−C(5)−C(6)	116.5(2)	O(16)−C(16)−C(17)	125.1(3)
N(5)−C(5)−C(4)	111.9(2)	O(6)−C(16)−C(17)	112.4(3)
C(6)−C(5)−C(4)	102.6(2)	C(18)−C(17)−C(16)	122.9(3)
C(23)−N(5)−C(5)	122.0(2)	C(22)−C(17)−C(16)	117.5(4)
O(6)−C(6)−C(5)	106.7(2)	O(23)−C(23)−N(5)	121.2(3)
O(6)−C(6)−C(7)	111.1(3)	O(23)−C(23)−C(24)	121.9(3)
C(5)−C(6)−C(7)	102.4(2)	N(5)−C(23)−C(24)	117.0(3)
C(16)−O(6)−C(6)	115.8(2)	C(25)−C(24)−C(23)	118.4(3)
O−C(7)−C(8)	106.5(3)	C(29)−C(24)−C(23)	123.4(3)
O−C(7)−C(6)	106.7(2)	C(1)−O(30)−C(30)	117.0(4)

Table S4. Selected Bond Lengths [Å] and Angles [°] for *Z*-isomer

Bond lengths (Å)			
O−C(7)	1.430(6)	O(6)−C(6)	1.455(6)
O−C(4)	1.443(6)	C(6)−C(7)	1.519(7)
C(1)−O(1)	1.213(7)	C(7)−C(8)	1.519(7)
C(1)−O(30)	1.329(7)	C(8)−O(8)	1.443(6)
C(1)−C(2)	1.482(9)	O(8)−C(9)	1.341(7)
C(2)−C(3)	1.309(8)	C(9)−O(9)	1.206(6)
C(3)−C(4)	1.487(8)	C(9)−C(10)	1.487(8)
C(4)−C(5)	1.546(8)	C(16)−O(16)	1.192(6)
C(5)−N(5)	1.443(6)	C(16)−C(17)	1.487(8)
C(5)−C(6)	1.522(7)	C(23)−O(23)	1.234(6)
N(5)−C(23)	1.356(7)	C(23)−C(24)	1.490(7)
O(6)−C(16)	1.362(6)	C(30)−O(30)	1.444(7)
Bond angles (°)			
C(7)−O−C(4)	111.9(4)	C(8)−C(7)−C(6)	113.2(5)
O(1)−C(1)−O(30)	123.3(6)	O(8)−C(8)−C(7)	104.9(5)
O(1)−C(1)−C(2)	125.4(6)	C(9)−O(8)−C(8)	116.6(5)
O(30)−C(1)−C(2)	111.3(6)	O(9)−C(9)−O(8)	123.3(6)
C(3)−C(2)−C(1)	124.7(6)	O(9)−C(9)−C(10)	125.3(6)
C(2)−C(3)−C(4)	127.7(6)	O(8)−C(9)−C(10)	111.4(6)
O−C(4)−C(3)	108.6(4)	C(15)−C(10)−C(9)	122.2(6)
O−C(4)−C(5)	104.4(4)	O(16)−C(16)−O(6)	123.7(5)
C(3)−C(4)−C(5)	112.3(5)	O(16)−C(16)−C(17)	125.1(5)
N(5)−C(5)−C(6)	115.7(5)	O(6)−C(16)−C(17)	111.2(5)
N(5)−C(5)−C(4)	112.0(5)	C(22)−C(17)−C(16)	118.2(6)
C(6)−C(5)−C(4)	105.0(4)	C(18)−C(17)−C(16)	121.9(5)
C(23)−N(5)−C(5)	122.1(5)	O(23)−C(23)−N(5)	120.3(5)
C(16)−O(6)−C(6)	115.3(4)	O(23)−C(23)−C(24)	121.6(5)
O(6)−C(6)−C(7)	110.1(4)	N(5)−C(23)−C(24)	118.1(5)
O(6)−C(6)−C(5)	108.1(4)	C(29)−C(24)−C(23)	116.8(5)
C(7)−C(6)−C(5)	102.5(4)	C(25)−C(24)−C(23)	122.7(5)
O−C(7)−C(8)	108.8(5)	C(1)−O(30)−C(30)	115.8(5)
O−C(7)−C(6)	106.8(4)		

bond (1.296(5) Å (*E*), 1.309(8) Å (*Z*) and torsion angle C1—C2—C3—C4 = $-175.6(4)^\circ$ (*E*), $-3.2(11)^\circ$ (*Z*)) cause the variation in intermolecular contacts and in packing of the molecules of *Z*-isomer with respect to *E*-isomer in the crystal unit cell. The geometry of C—H· · ·.O intermolecular contacts is given in the Table 3a and 3b. The contacts are grouped into those which bond the molecules parallel to each others

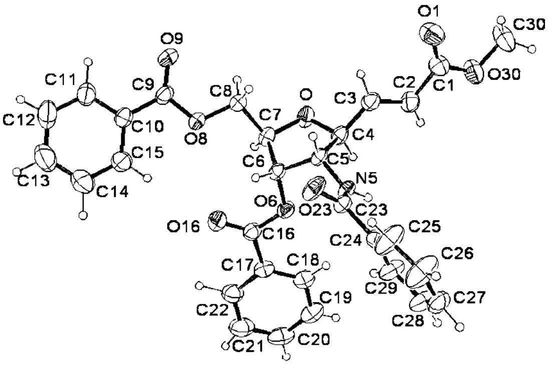


Fig. 1. ORTEP drawing of *E*-isomer with non-H labeling scheme. The displacement ellipsoids were drawn at 40% probability.

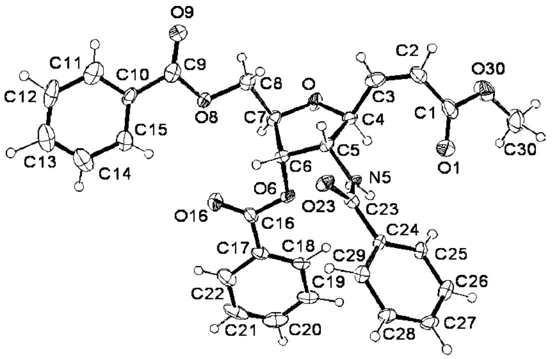


Fig. 2. ORTEP drawing of *Z*-isomer with non-H labeling scheme. The displacement ellipsoids were drawn at 40% probability.

Table 2. The Type and the Geometry of the Intramolecular C—H···O Contacts in *E*- and *Z*-Isomer of $C_{30}H_{27}NO_8$

N	D—H···A	Isomer	D—H (Å)	H···A (Å)	D···A (Å)	∠D—H···A (°)
1	C3—H3···O1	*E*(trans)	0.930	2.603	2.895(6)	98.8
	C4—H4···O1	*Z*(cis)	1.060(43)	2.528(42)	3.074(7)	111.1(28)
2	C30—H30C···O1	*E*(trans)	0.960	2.354	2.664(7)	98.1
		Z(cis)	0.980	2.464	2.639(8)	89.2
3	C4—H4···O6	*E*(trans)	0.980	2.794	2.945(5)	89.0
	C7—H7···O6	*Z*(cis)	0.975(45)	2.362(41)	2.438(6)	82.7(25)
4	C18—H18···O6	*E*(trans)	0.930	2.443	2.758(4)	99.8
		Z(cis)	1.021(48)	2.388(49)	2.713(7)	97.3(31)
5	C6—H6···O8	*E*(trans)	0.980	2.698	3.022(4)	99.7
		Z(cis)	1.035(44)	2.614(40)	2.916(6)	96.4(26)
6	C15—H15···O8	*E*(trans)	0.930	2.407	2.711(6)	98.9
		Z(cis)	0.909(52)	2.350(50)	2.721(7)	104.3(37)
7	C8—H81···O9	*E*(trans)	0.970	2.440	2.642(5)	91.0
		Z(cis)	0.985(44)	2.518(45)	2.665(7)	87.6(27)
8	C11—H11···O9	*E*(trans)	0.930	2.558	2.835(6)	97.6
		Z(cis)	0.892(51)	2.596(54)	2.846(8)	97.0(36)
9	C6—H6···O16	*E*(trans)	0.980	2.464	2.643(5)	89.4
		Z(cis)	1.035(44)	2.379(43)	2.664(6)	94.3(26)
10	C7—H7···O16	*E*(trans)	0.980	2.792	3.153(5)	102.6
		Z(cis)	0.975(45)	2.731(42)	3.151(7)	106.6(28)
11	C15—H15···O16	*E*(trans)	0.930	2.729	3.656(5)	174.6
		Z(cis)	0.909(52)	2.628(51)	3.524(8)	168.3(43)
12	C22—H22···O16	*E*(trans)	0.930	2.535	2.829(5)	98.6
		Z(cis)	0.950	2.572	2.839(7)	96.4
13	C5—H5···O23	*E*(trans)	0.980	2.488	2.747(4)	94.6
		Z(cis)	0.929(46)	2.471(45)	2.749(7)	97.4(32)
14	C25—H25···O23	*E*(trans)	0.930	2.590	2.855(5)	96.9
		Z (cis)	1.073(49)	2.523(46)	2.819(7)	94.6(28)

into stacks (Table 3a) and those which bond these stacks within **bc** plane (Table 3b and Figs. 3 and 4. The mark number of the contacts is the same in Table and Figure).

Intermolecular hydrogen bond N5—H5···O23 in both isomers (symmetry transformation $1 + x,\ y,\ z$) have the geometry: N5—H5N = 0.860 Å (*E*), 0.895(46) Å (*Z*);

Table 3a. The Geometry of C—H···O Intermolecular Contacts in *E*- and *Z*-isomer of $C_{30}H_{27}NO_8$ Which Are the Same or Similar in Both Isomers

N	D—H···A	Isomer	D—H (Å)	H···A (Å)	D.···(Å)	∠D—..A (°)
1	C4—H4···O23 (2)	*E* (trans)	0.980	2.415	3.262(4)	144.3
	C4—H4···O23 (1)	*Z* (cis)	1.060(43)	2.298(42)	3.258(7)	149.8(33)
2	C2—H2···O23 (2)	*E* (trans)	0.930	2.847	3.602(5)	139.1
	C18—H18···O23 (1)	*Z* (cis)	1.021(48)	2.199(48)	3.219(7)	176.1(39)
3	C30—H30B···O1 (2)	*E* (trans)	0.960	2.566	3.347(7)	138,6
	C7—H7···O8 (1)	*Z* (cis)	0.975(45)	2.952(47)	3.778(7)	143.1(35)
4	C8—H82···O (1)	*E* (trans)	0.970	2.877	3.612(5)	133.3
	C8—H82···O (2)	*Z* (cis)	0.994(44)	2.777(45)	3.641(7)	145.7(34)

Note. Equivalent positions: (1) $x + 1, +y, +z$ (2) $x - 1, +y, +z$.

Table 3b. The Geometry of C—H···O Intermolecular Contacts in the *E*- and *Z*-isomer of $C_{30}H_{27}NO_8$ Which Belong Only to the One Isomer

N	D—H···A	Isomer	D—H (Å)	H···A (Å)	D···A (Å)	∠D—H···A (°)
5	C12—H12···O30 (3)	*E*(trans)	0.930	2.630	3.542(6)	166.9
6	C21—H21···O9 (4)	*E*(trans)	0.930	2.810	3.736(7)	173.6
7	C28—H28···O9 (5)	*E*(trans)	0.930	2.648	3.384(5)	136.6
5	C21—H21···O9 (6)	*Z*(cis)	0.950	2.657	3.595(8)	169.2
6	C30—H30A···O9 (7)	*Z*(cis)	0.980	2.752	3.563(8)	140.5
7	C2—H2···O9 (8)	*Z*(cis)	0.968(43)	2.509(42)	3.434(7)	159.9(34)
8	C8—H8B···O30 (9)	*Z*(cis)	0.985(44)	2.702(44)	3.638(7)	158.9(34)
9	C13—H13···O1 (10)	*Z*(cis)	1.110(48)	2.969(47)	3.715(9)	124.7(30)

Note. Equivalent positions: (3) $x-2, +y, +z-1$; (4) $x+1, +y+1, +z$; (7) $x+1/2+1, -y+1/2+1, -z+2$; (8) $x+1/2, -y+1/2+1, -z+2$; (9) $x-1/2, -y+1/2+1, -z+2$; (10) $-x-1/2, -y+1, +z-1/2$; (5) $x+1, +y+1, +z+1$; (6) $-x, +y-1/2, -z+1/2+1$.

H5N···O23 = 2.323 Å (*E*), 2.117(47) Å (*Z*); N5···O23 = 3.133(3) Å (*E*), 2.945(6) Å (*Z*); ∠N5—H5N···O23 = 157.1° (*E*), 153.4(42)° (*Z*). The existence of these bond which are stronger than C—H···O hydrogen bond networks, determines the molecular packing in first step. Table 4 presents the analysis of the number of acceptor contacts realized by oxygen atoms in both isomers. The oxygen atoms O6 and O16 possess only intramolecular C—H···O contacts, which determine the conformation of the molecule, and these contacts are rather similar in both isomers. Oxygen atoms O1, O8, O9 and O23 realize several contacts of both inter- and intramolecular type. The contact that might be treated separately is the bond, which has a single acceptor in the C—H···O intermolecular contacts and satisfies the geometrical criteria of existence of the hydrogen bond. Such contacts are: the hydrogen bond C12(sp^2)—H···O30 in *E* isomer (C—O = 3.542(6) Å, H···O = 2.630 Å, ∠C—H···O = 166.86°) and C8(sp^3)—H···O30

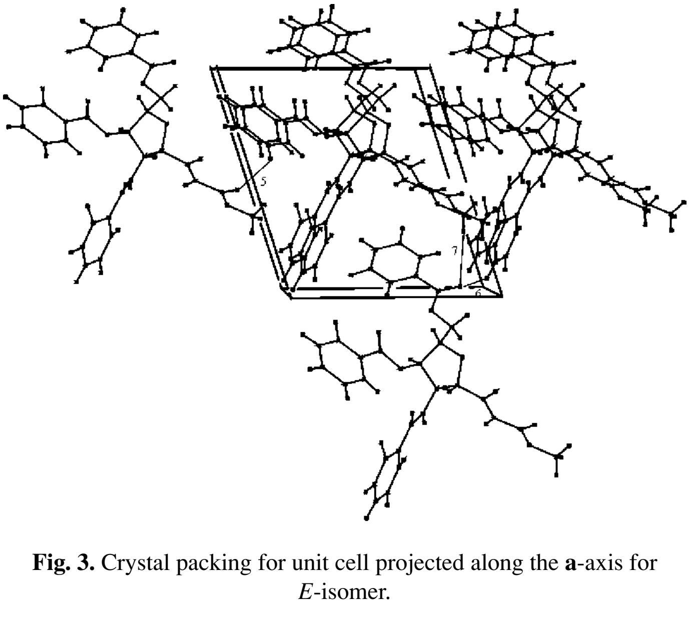


Fig. 3. Crystal packing for unit cell projected along the **a**-axis for *E*-isomer.

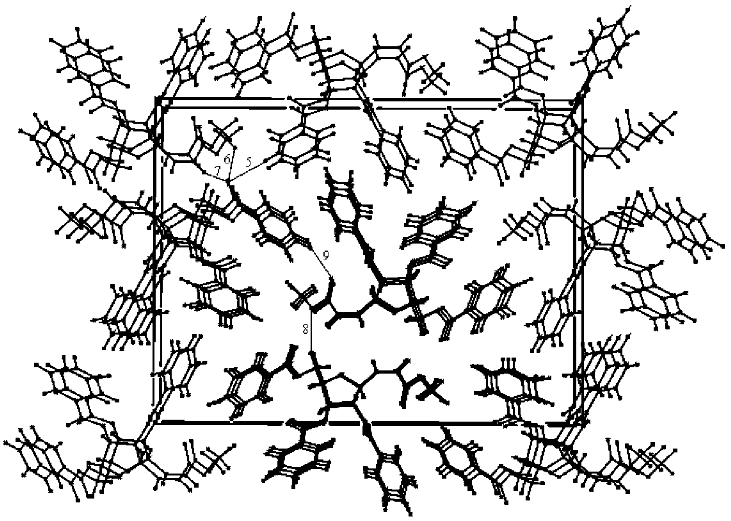


Fig. 4. Crystal packing for unit cell projected along the **a**-axis for *Z*-isomer.

in *Z* isomer (C—O = 3.638(7) Å, H· · ·O = 2.702(44) Å, ∠C—H· · ·O = 158.9(34)°) which is both with oxygen atom O30 from the side chain of esters group and also C8(sp^3)—H82· · ·O in both isomers (C8—O = 3.612(5) Å, (*E*), 3.641(7) Å (*Z*); H· · ·O = 2.877 Å (*E*), 2.777(45) Å (*Z*); ∠C8—H· · ·O = 133.3° (*E*), 145.7(34)° (*Z*)) where oxygen atom belongs to glycoside ring.

Table 4. Acceptors of C—H· · ·O Contacts in *E*- and *Z*-isomer of $C_{30}H_{27}NO_8$

Oxygen atoms	*E*-isomer	*Z*-isomer
O	1-inter* —	1-inter —
O1	1-inter 2-intra	1-inter 3-intra
O6	— 2-intra	— 2-intra *
O8	— 2-intra	1-inter 2-intra
O9	2-inter 2-intra	3-inter 2-intra
O16	— 4-intra	— 4-intra
O23	3-inter 2-intra	3-inter 2-intra
O30	1-inter * —	1-inter —

Conclusions

The analysis of the crystal and molecular structures of Methyl *E*(*Z*)- 4,7 anhydro-5-benzamido-6,8-di-*O*-benzoyl-2,3,5-trideoxy-D-allo-oct-2-enoate isomers shows that there is a large number of C—H· · ·O noncovalent contacts and possible week hydrogen bonds within the molecule and between the symmetry related molecules within the crystal unit cell. Packing of the molecules of *Z*- and *E*-isomer in the crystal unit cell was analyzed with respect to the type and the length of the possible intermolecular hydrogen bonds. The contacts that might induce the difference in melting point are the C—H· · ·O hydrogen bonds whose single acceptor in the intermolecular contacts is oxygen atom O30 from the side chain of esters group and O from glycoside ring and which do fulfill the geometrical criteria of existence of the hydrogen bond. These hydrogen bonds are shorter in *E* isomer than in *Z* isomer, since O30 is in contact with C12(sp^2)-H in *E* isomer and with C8(sp^3)-H in *Z* isomer that agrees with literature data.[9,10] The existence of shorter bond is correlated with higher bonding energy of the interaction between molecules in the crystal unit cell and maybe resulting also in higher melting point temperature, which is measured in the case of *E* isomer.

Supplementary Material CCDC 252512 & 252513. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Acknowledgments

This work was supported by a research grant from the Ministry of Science and Environmental Protection of the Republic of Serbia.

References

1. Popsavin, M.; Torović, L.j.; Spaić, S; Stankov, S.; Kapor, A.; Tomić, Z.; Popsavin, V. *Tetrahedron* **2002**, *58,* 569.
2. Sheldrick, G.M. *SHELXS86*, In *Crystallographic Computing 3;* Sheldrick, G.M.; Kruger, C.; Goddard, R., Eds; Oxford University Press, UK **1985**; pp. 175–189.
3. Sheldrick, G.M. *SHELXL93, Program for the Refinement of Crystal Structures;* University of Göttingen, Germany, **1993**.
4. Farrugia, L.J. *WinGX, J. Appl. Cryst.* **1999**, *32*, 837.
5. Farrugia, L.J. *ORTEP-3 for Windows, J. Appl. Cryst.* **1997**, *30,* 565.
6. Flack, H.D. *Acta Crystallogr.* **1983**, A*39,* 876.
7. Desiraju, G.R.; T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology;* Oxford University Press, New York, **1999**.
8. Novoa, J.J.; Planas, M.; Rovira, M.C. *Chem. Phys. Lett.* **1996**, *251,* 33.
9. Allerhand, A.; Schleyer, R. *J. Am. Chem. Soc.* **1963**, *85,* 1715.
10. Scheiner, S.; Grabowski, S.J.; Kar, T. *J. Phys. Chem. A* **2001**, *105,* 10607.