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CRYSTAL STRUCTURE INVESTIGATION OF (4*S*,5*S*)-4-[(DICHLOROACETOXY)METHYL]-5-(4-NITROPHENYL)-2-OXAZOLIDINONE

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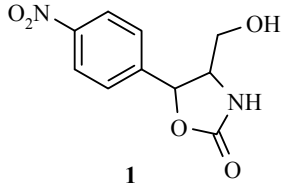
The structure of (4S,5S)-4-[(dichloroacetoxy)methyl]-5-(4-nitrophenyl)-2-oxazolidinone has been determined by crystal structure investigation.

Keywords: (4*S*,5*S*)-4-[(dichloroacetoxy)methyl]-5-(4-nitrophenyl)-2-oxazolidinone, (4*S*,5*S*)-4-hydroxymethyl-5-(4-nitrophenyl)-2-oxazolidinone, crystal structure investigation.

Earlier, we obtained a mixture of isomeric (4*S*,5*S*)-4-hydroxymethyl-5-(4-nitrophenyl)-2-oxazolidinone (**1**) and (1'*S*,4*S*)-4-[hydroxy(4-nitrophenyl)methyl]-2-oxazolidinone (**2**) by heterocyclization of (1*S*,2*S*)-2-amino-1-(4-nitrophenyl)-1,3-propanediol with ethyl chloroformate [1, 2].

The structure **1** has been attributed to a compound that possesses a lower chromatographic mobility (smaller R_f value), is more easily acylated, and has in the ^{1}H NMR spectrum a more simple signal of protons of group CH_2 [1, 2].

In the present work we present results of crystal structure investigations of (4*S*,5*S*)-4-[(dichloroacetoxy)methyl]-5-(4-nitrophenyl)-2-oxazolidinone (**3**), which has been prepared by the reaction of dichloroacetyl chloride with a compound to which earlier, on the basis of indirect data, the structure **1** was attributed.



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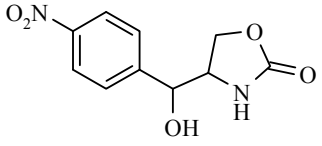

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Relevant crystal data are given in Table 1. An ORTEP-3 [3] drawing of the compound **3** together with the numbering of atoms is shown in Fig. 1. The bond lengths, valence angles, and torsion angles are listed in Tables 2–4. The basic geometric parameters of the molecule are normal [4]. The absolute configuration, determined using anomalous dispersion by chlorine atoms, confirms the *S*-configuration for both C(4) and C(5) atoms. The phenyl ring is planar, and r.m.s. deviation from the mean plane is ca. 0.007 Å.

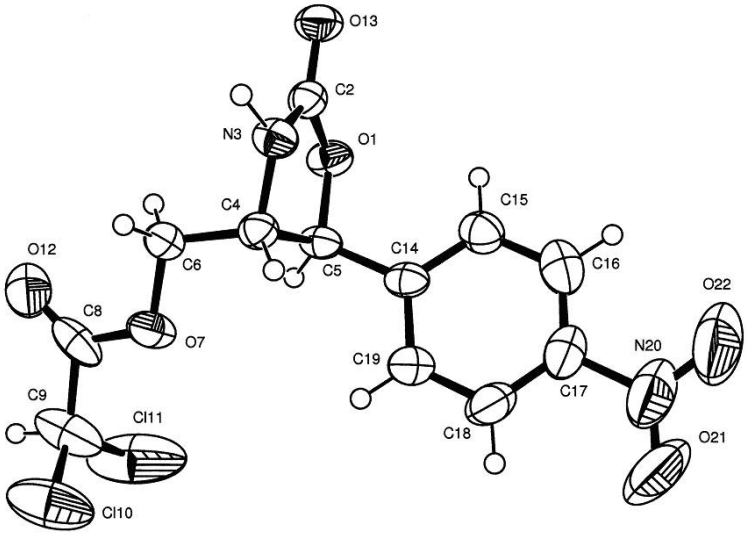

Fig. 1. ORTEP-3 drawing of the compound **3**, representing heavy atoms as 50% probability ellipsoids, and H atoms as spheres of arbitrary radius.

The oxazolidinone ring is in a twisted conformation relative to the C(4)–C(5) bond, with atoms C(4) 0.261(5) and C(5) 0.162(6) Å out of the O(1)/C(2)/N(3)/O(13) plane (r.m.s. deviation 0.004 Å). The (dichloroacetoxy)methyl and nitrophenyl groups adopt both axial positions while H(4) and H(5) adopt bisectional positions, and the H(3) substituent occupies an equatorial position. However, the nitrogen N(3) in the oxazolidinone ring has a slightly nonplanar environment: the sum of the bond angles at the N atom is equal to 350°.

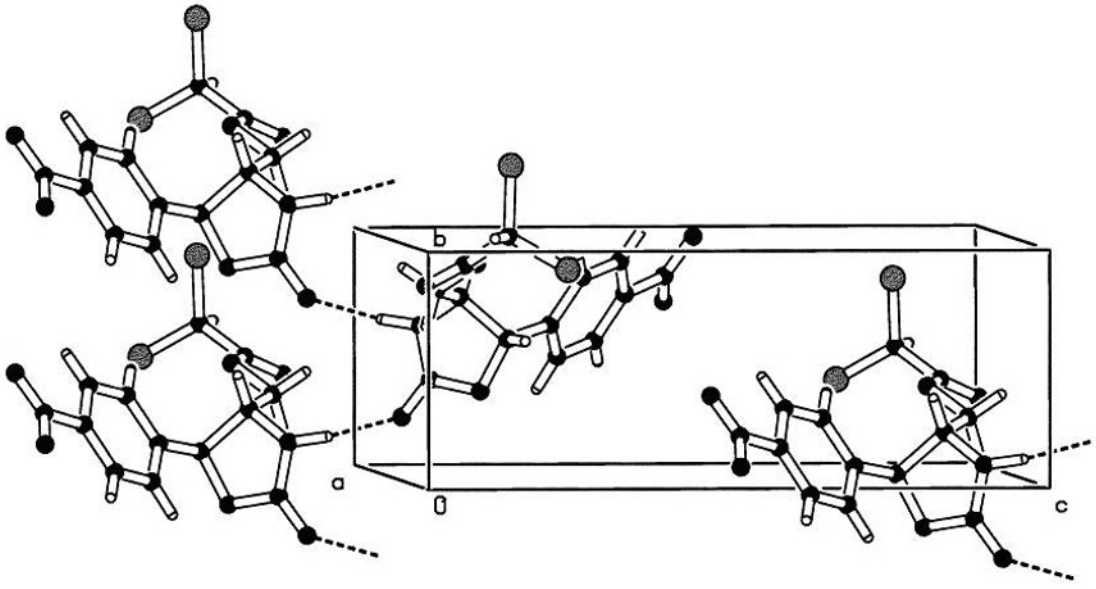

Fig. 2. Packing diagram of the compound **3** showing hydrogen bonds as dashed lines.

TABLE 1. X-ray Characteristics for Compound **3**

Empirical formula	$C_{12}H_{10}Cl_2N_2O_6$
Molecular weight	349.12
Crystal system	Monoclinic
Space group	$P2_1$ (N°4)
a, Å	8.6669(7)
b, Å	5.7294(3)
c, Å	15.0980(10)
β, °	101.425(3)
Unit cell volume, Å^3	734.85(9)
Z	2
d_{calc}, g · cm^{-3}	1.578
F(000)	356
μ(MoKα), mm^{-1}	0.47
Crystal parameters, mm	0.89 × 0.14 × 0.09
Temperature, K	293 (2)
Irradiation	MoKα radiation, λ = 0.71073 Å
Miller index range	$-10 \le h \le 10$; $-6 \le k \le 6$; $-18 \le l \le 18$
Reflections collected	6139
Independent reflections	2589 (R_{int} = 0.0239)
Number of observed reflections [$I \ge 2\sigma(I)$]	2141
θ_{min}, θ_{max}, °	1.38, 25.56
Absolute structure parameter	0.15(15)
Final number of parameters	203
R_1 [$I \ge 2\ \sigma(I)$]	5.31
$wR_2(F^2)$ [$I \ge 2\ \sigma(I)$]	15.69
Goodness of fit on F^2 ($GOOF$)	1.104
$w = 1/[\sigma^2(F_o^2) + (0.1223P)^2 + 0.3112P]$, where $P = (F_o^2 + 2F_c^2)/3$	
$\Delta\rho_{min}$, $\Delta\rho_{max}$, e · Å^{-3}	–0.45, 0.44

In the crystal structure, the molecules are stabilized by strong intermolecular NH···O hydrogen bonds, giving rise to an infinite chain along the *b* direction (Fig. 2). The parameters of the hydrogen bond are N(3)···O(13) 2.862(4), H(3)···O(13) 1.90(5) Å, and angle N(3)–H(3)···O(13) 173(5)°.

TABLE 2. Bond Lengths (*l*) for Compound **3**

Bond	*l*, Å	Bond	*l*, Å
O(1)–C(2)	1.363(4)	C(8)–C(9)	1.515(8)
O(1)–C(5)	1.442(5)	C(9)–Cl(11)	1.650(7)
C(2)–O(13)	1.219(5)	C(9)–Cl(10)	1.718(7)
C(2)–N(3)	1.332(6)	C(14)–C(15)	1.384(6)
N(3)–C(4)	1.455(5)	C(14)–C(19)	1.395(6)
N(3)–H(3)	0.96(5)	C(15)–C(16)	1.385(7)
C(4)–C(6)	1.505(6)	C(16)–C(17)	1.365(8)
C(4)–C(5)	1.544(5)	C(17)–C(18)	1.381(8)
C(5)–C(14)	1.515(6)	C(17)–N(20)	1.469(7)
C(6)–O(7)	1.449(5)	C(18)–C(19)	1.379(7)
O(7)–C(8)	1.372(7)	N(20)–O(21)	1.198(10)
C(8)–O(12)	1.161(7)	N(20)–O(22)	1.228(10)

TABLE 3. Valence Angles (ω) for Compound **3**

Angle	ω, deg	Angle	ω, deg
C(2)–O(1)–C(5)	108.7(3)	O(7)–C(8)–C(9)	110.1(6)
O(13)–C(2)–N(3)	129.0(4)	C(8)–C(9)–Cl(11)	114.3(4)
O(13)–C(2)–O(1)	120.7(4)	C(8)–C(9)–Cl(10)	112.9(4)
N(3)–C(2)–O(1)	110.3(3)	Cl(11)–C(9)–Cl(10)	117.5(5)
C(2)–N(3)–C(4)	111.0(3)	C(15)–C(14)–C(19)	119.2(4)
C(2)–N(3)–H(3)	109(3)	C(15)–C(14)–C(5)	121.8(4)
C(4)–N(3)–H(3)	130(3)	C(19)–C(14)–C(5)	119.0(4)
N(3)–C(4)–C(6)	109.1(3)	C(14)–C(15)–C(16)	120.5(5)
N(3)–C(4)–C(5)	99.9(3)	C(17)–C(16)–C(15)	118.5(5)
C(6)–C(4)–C(5)	112.9(3)	C(16)–C(17)–C(18)	122.9(4)
O(1)–C(5)–C(14)	111.3(3)	C(16)–C(17)–N(20)	119.8(6)
O(1)–C(5)–C(4)	103.4(3)	C(18)–C(17)–N(20)	117.3(6)
C(14)–C(5)–C(4)	112.6(3)	C(19)–C(18)–C(17)	117.9(5)
O(7)–C(6)–C(4)	108.2(3)	C(18)–C(19)–C(14)	120.9(5)
C(8)–O(7)–C(6)	113.6(4)	O(21)–N(20)–O(22)	122.9(6)
O(12)–C(8)–O(7)	125.8(5)	O(21)–N(20)–C(17)	120.2(7)
O(12)–C(8)–C(9)	124.1(6)	O(22)–N(20)–C(17)	116.8(7)

TABLE 4. Torsian Angles (φ) for Compound **3**

Angle	φ, deg	Angle	φ, deg
C(5)–O(1)–C(2)–O(13)	172.7(4)	O(7)–C(8)–C(9)–Cl(10)	67.7(6)
C(5)–O(1)–C(2)–N(3)	-6.0(4)	O(1)–C(5)–C(14)–C(15)	4.5(5)
O(13)–C(2)–N(3)–C(4)	169.6(4)	C(4)–C(5)–C(14)–C(15)	-111.1(4)
O(1)–C(2)–N(3)–C(4)	-11.9(5)	O(1)–C(5)–C(14)–C(19)	-177.0(4)
C(2)–N(3)–C(4)–C(6)	-95.8(4)	C(4)–C(5)–C(14)–C(19)	67.4(5)
C(2)–N(3)–C(4)–C(5)	22.8(4)	C(19)–C(14)–C(15)–C(16)	-2.0(6)
C(2)–O(1)–C(5)–C(14)	-101.3(3)	C(5)–C(14)–C(15)–C(16)	176.5(4)
C(2)–O(1)–C(5)–C(4)	19.8(4)	C(14)–C(15)–C(16)–C(17)	2.1(7)
N(3)–C(4)–C(5)–O(1)	-24.6(4)	C(15)–C(16)–C(17)–C(18)	-0.8(8)
C(6)–C(4)–C(5)–O(1)	91.1(4)	C(15)–C(16)–C(17)–N(20)	-179.7(5)
N(3)–C(4)–C(5)–C(14)	95.6(4)	C(16)–C(17)–C(18)–C(19)	-0.5(8)
C(6)–C(4)–C(5)–C(14)	-148.7(3)	N(20)–C(17)–C(18)–C(19)	178.3(5)
N(3)–C(4)–C(6)–O(7)	177.9(3)	C(17)–C(18)–C(19)–C(14)	0.7(7)
C(5)–C(4)–C(6)–O(7)	67.8(5)	C(15)–C(14)–C(19)–C(18)	0.6(7)
C(4)–C(6)–O(7)–C(8)	-168.0(4)	C(5)–C(14)–C(19)–C(18)	-178.0(4)
C(6)–O(7)–C(8)–O(12)	1.4(7)	C(16)–C(17)–N(20)–O(21)	-176.5(7)
C(6)–O(7)–C(8)–C(9)	-179.2(4)	C(18)–C(17)–N(20)–O(21)	4.6(9)
O(12)–C(8)–C(9)–Cl(11)	109.1(7)	C(16)–C(17)–N(20)–O(22)	7.8(9)
O(7)–C(8)–C(9)–Cl(11)	-70.3(6)	C(18)–C(17)–N(20)–O(22)	-171.2(7)
O(12)–C(8)–C(9)–Cl(10)	-112.9(7)		

EXPERIMENTAL

The (4*S*,5*S*)-4-[(dichloroacetoxy)methyl]-5-(4-nitrophenyl)-2-oxazolidinone (**3**) was crystallized from an ethanol solution at room temperature as colorless elongated prisms. A crystal 0.009×0.140×0.890 mm^3 in size was placed and optically centered on a Bruker KAPPA APEX II diffractometer equipped with MoKα radiation (λ = 0.71073 Å) at 293(2) K. The initial unit cell was indexed using the difference vectors method for a random set of reflections collected from three series of 0.5° wide omega-scans, 10 seconds per frame, and 12 frames per series that were well distributed in reciprocal space.

The crystal-to-detector distance was 35 mm. A total of 783 frames was collected to $\theta_{max} = 25.56°$ with 0.5° wide scans and an exposure time of 60 seconds per frame using the APEX2 software [5]. Unit cell refinement on all observed reflections and data reduction were performed using SAINT [6]. Scaling and a numerical absorption correction, based upon crystal size and face indexing, were done using SADABS [6]. The minimum and maximum transmission factors were 0.6782 and 0.9579, respectively.

Systematic absences and intensity statistics were consistent with the compound having crystallized in the noncentrosymmetric monoclinic space group $P2_1$ (No. 4). The observed mean $|E^2-1|$ value was 0.771 (versus the expectation values of 0.968 and 0.736 for centrosymmetric and noncentrosymmetric space groups, respectively). A total of 6139 reflections was collected, merged based upon identical indices yielding 2589 data ($R_{int} = 0.024$) of which 2141 had $I > 2\sigma(I)$.

The structure was determined by direct methods with the successful location of all non-hydrogen atoms of the unique molecule within the asymmetric unit using the program *SHELXS* [7]. The structure was refined with *SHELXL* [7]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions according to their geometry and refined riding on carbon atoms. The hydrogen atom bonded to the nitrogen atom N(3) was located from difference-Fourier maps and allowed to refine freely. The final structure was refined to convergence with *R(F)* = 5.31 % and *GOOF* = 1.104 for those 2141 data with $F_o > > 4\sigma(F_o)$ [*R(F)* = 6.96% and *GOOF* = 1.104 for all 2589 data]. Minimum and maximum residual peaks (–0.446 and 0.439 e · $Å^{-3}$ respectively) were observed in close proximity of the C(l) atoms (distances in 0.7 – 1.0 Å range) and have no chemical sense. An empirical correction for extinction was also attempted but found to be equal to zero within the error and therefore not applied.

CCDC 742486 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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