Crystal structure of dimethyl 1,4-dioxaspiro[4,5]dec-6-ene-(8*R*)-[(3,5-dinitrobenzoyl)oxa]-(2*R*,3*R*)-dicarboxylate, $C_{19}H_{18}N_2O_{12}$

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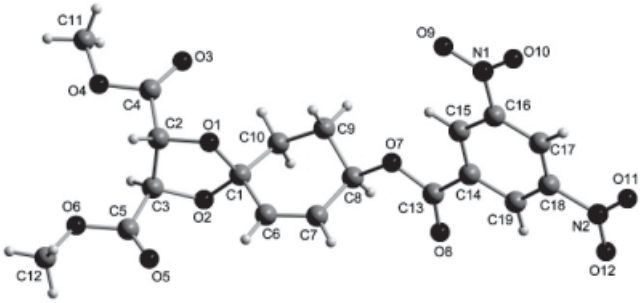

Abstract

$C_{19}H_{18}N_2O_{12}$, orthorhombic, $P2_12_12_1$ (no. 19), a = 6.2472(6) Å, b = 17.576(2) Å, c = 18.848(3) Å, V = 2069.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0393, $wR_{ref}(F^2)$ = 0.0694, T = 210 K.

Table 1. Data collection and handling.

Crystal:	colourless needles, size 0.06×0.06×1.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.27 cm^{-1}
Diffractometer, scan mode:	STOE IPDS 2, ω, 1.0°
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13358, 3655
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2332
$N(param)_{refined}$:	299
Programs:	SHELX [2], DIAMOND [3]

Source of material

The title compound was synthesized by treatment of dimethyl (8*R*)-hydroxy-1,4-dioxaspiro[4,5]-dec-6-ene-(2*R*,3*R*)-dicarboxylate with 3,5-dinitrobenzoyl chloride and two equivalents of diisopropylethylamine in dichloromethane. Colourless crystals were obtained by slow evaporation of the solvent from a solution in diethyl ether.

Experimental details

The hydrogen atoms were calculated in their expected positions and included in the refinement as riding atoms. The U_{iso}(H) values were constrained to be 1.2U_{eq}(C).

Discussion

During our work on auxiliary controlled singlet oxygen- ene reactions we were interested in enantiomerically pure ketals derived from cyclohexenones and various *L*-tartrates [1]. Thus, the ketalization of 2-cyclohexenone and dimethyl *L*-tartrate proceeded under migration of the double bond to afford dimethyl 1,4-dioxaspiro[4,5]dec-7-ene-(2*R*,3*R*)-dicarboxylate. After the singlet oxygen-ene reaction followed by reduction dimethyl 8-hydroxy-1,4-dioxaspiro[4,5]-dec-6-ene-(2*R*,3*R*)-dicarboxylate was obtained with a new stereogenic center at C8. For crystallization the two diastereomers were separated and converted into the corresponding 3,5-dinitrobenzoates. The title structure unequivocally proves the correct stereochemistry of the product. Beside the right-handed C2 and C3 atoms a new stereocenter at C8 is generated. The *R*-configuration corresponds to the minor diastereomer. Within the cyclohexene ring the geometrical parameters are as expected. The double bond is located between C6 and C7 (bond length: 1.340(4) Å). Five of the six carbon atoms are almost coplanar, with a maximal deviation from the best plane of 0.088(2) Å (C1). The carbon atom C9 is out of that plane by 0.687(4) Å. Therefore the C9 atom is not taken into account in the following dihedric calculations. The plane of the five-membered ring is nearly rectangular to the cyclohexene ring, characterized by an angle around the spiro atom C1 of 88.8(1)° formed by the C1/O1/O2 and C1/C6/C10 planes. The methyl carboxylate moieties point in the opposite direction but both facing away from the molecule. The oxygen atom O7 connecting the benzoyl moiety with the cyclohexene ring is in equatorial position as well as the hydrogen atoms on the sp^2 hybridized carbon atoms. The dinitrobenzoyloxy moiety is nearly planar and almost orthogonal to the cyclohexene ring, forming an dihedric angle of 80.2(1)°.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*a*	0.8555	0.6880	0.6337	0.045
H(3)	4*a*	0.6033	0.5729	0.6157	0.044
H(6)	4*a*	0.5926	0.6663	0.8211	0.049
H(7)	4*a*	0.6836	0.6406	0.9330	0.053
H(8)	4*a*	0.8508	0.5110	0.9331	0.047
H(9A)	4*a*	1.1526	0.5840	0.8425	0.056
H(9B)	4*a*	1.1585	0.4979	0.8652	0.056
H(10A)	4*a*	1.0158	0.5037	0.7510	0.052
H(10B)	4*a*	0.8326	0.4775	0.8026	0.052
H(11A)	4*a*	1.2444	0.5654	0.4999	0.070
H(11B)	4*a*	1.0578	0.5682	0.4443	0.070
H(11C)	4*a*	1.0683	0.5019	0.4998	0.070
H(12A)	4*a*	0.1641	0.7526	0.5985	0.085
H(12B)	4*a*	0.2814	0.7657	0.5260	0.085
H(12C)	4*a*	0.3732	0.8018	0.5957	0.085
H(15)	4*a*	1.3589	0.6582	1.0245	0.040
H(17)	4*a*	1.4948	0.7048	1.2296	0.048
H(19)	4*a*	0.9635	0.5859	1.1801	0.044

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*a*	0.7911(5)	0.5872(2)	0.7676(1)	0.035(2)	0.038(2)	0.031(1)	–0.004(2)	0.001(1)	–0.002(1)
C(2)	4*a*	0.8571(5)	0.6367(2)	0.6541(1)	0.043(2)	0.039(2)	0.031(1)	0.005(2)	0.001(1)	0.003(1)
C(3)	4*a*	0.6294(5)	0.6059(2)	0.6567(1)	0.042(2)	0.040(2)	0.028(1)	–0.001(2)	–0.004(1)	0.003(1)
C(4)	4*a*	1.0073(5)	0.5861(2)	0.6105(1)	0.041(2)	0.038(2)	0.035(2)	0.003(2)	0.002(1)	–0.003(1)
C(5)	4*a*	0.4727(5)	0.6717(2)	0.6563(2)	0.040(2)	0.051(2)	0.046(2)	–0.003(2)	0.001(2)	0.004(2)
C(6)	4*a*	0.6950(5)	0.6290(2)	0.8296(1)	0.041(2)	0.044(2)	0.038(2)	0.006(2)	0.002(1)	–0.001(1)
C(7)	4*a*	0.7521(5)	0.6142(2)	0.8968(1)	0.041(2)	0.057(2)	0.035(2)	0.005(2)	0.007(2)	–0.006(1)
C(8)	4*a*	0.9188(5)	0.5579(2)	0.9164(1)	0.041(2)	0.042(2)	0.033(1)	–0.003(2)	–0.004(2)	–0.006(1)
C(9)	4*a*	1.0648(5)	0.5401(2)	0.8536(1)	0.048(2)	0.055(2)	0.038(2)	0.015(2)	–0.004(2)	–0.007(1)
C(10)	4*a*	0.9256(5)	0.5196(2)	0.7902(1)	0.057(2)	0.043(2)	0.030(1)	0.012(2)	–0.002(2)	–0.006(1)
C(11)	4*a*	1.0954(7)	0.5550(2)	0.4922(1)	0.070(3)	0.070(3)	0.036(2)	0.011(2)	0.015(2)	–0.006(2)
C(12)	4*a*	0.3010(6)	0.7584(2)	0.5761(2)	0.068(3)	0.059(3)	0.086(2)	0.004(2)	–0.014(2)	0.025(2)
C(13)	4*a*	0.9834(6)	0.5830(2)	1.0407(1)	0.048(2)	0.038(2)	0.029(2)	0.005(2)	–0.003(2)	0.005(1)
C(14)	4*a*	1.1368(5)	0.6180(2)	1.0929(1)	0.043(2)	0.030(2)	0.025(1)	0.003(2)	–0.004(1)	0.001(1)
C(15)	4*a*	1.3230(5)	0.6547(2)	1.0723(1)	0.046(2)	0.027(2)	0.027(1)	0.005(2)	0.002(1)	0.000(1)
C(16)	4*a*	1.4551(5)	0.6862(2)	1.1236(1)	0.037(2)	0.028(2)	0.038(2)	0.006(2)	–0.002(1)	–0.001(1)
C(17)	4*a*	1.4069(6)	0.6826(2)	1.1956(1)	0.055(2)	0.036(2)	0.029(2)	0.002(2)	–0.007(2)	–0.001(1)
C(18)	4*a*	1.2243(5)	0.6448(2)	1.2137(1)	0.056(2)	0.033(2)	0.022(1)	0.002(2)	0.003(2)	–0.001(1)
C(19)	4*a*	1.0857(5)	0.6116(2)	1.1653(1)	0.045(2)	0.034(2)	0.031(2)	0.001(2)	0.004(2)	0.004(1)
N(1)	4*a*	1.6470(4)	0.7264(1)	1.1016(1)	0.041(2)	0.043(2)	0.047(2)	–0.001(2)	0.000(1)	–0.003(1)
N(2)	4*a*	1.1700(5)	0.6378(2)	1.2907(1)	0.081(2)	0.050(2)	0.024(1)	–0.008(2)	0.005(2)	–0.002(1)
O(1)	4*a*	0.9171(3)	0.6412(1)	0.72720(8)	0.042(1)	0.043(1)	0.033(1)	–0.007(1)	–0.0027(9)	–0.0051(9)
O(2)	4*a*	0.6235(3)	0.5622(1)	0.72022(8)	0.044(1)	0.044(1)	0.035(1)	–0.008(1)	–0.007(1)	0.0044(9)
O(3)	4*a*	1.1384(4)	0.5421(1)	0.6324(1)	0.054(2)	0.060(2)	0.042(1)	0.019(1)	–0.003(1)	–0.002(1)
O(4)	4*a*	0.9677(4)	0.5996(1)	0.54125(9)	0.060(2)	0.058(2)	0.031(1)	0.018(1)	0.005(1)	0.0022(9)
O(5)	4*a*	0.4072(4)	0.7067(1)	0.7062(1)	0.070(2)	0.074(2)	0.055(1)	0.027(2)	0.012(1)	0.000(1)
O(6)	4*a*	0.4285(4)	0.6907(1)	0.5881(1)	0.060(2)	0.063(2)	0.050(1)	0.006(1)	–0.011(1)	0.014(1)
O(7)	4*a*	1.0558(3)	0.5899(1)	0.97323(8)	0.049(1)	0.053(1)	0.026(1)	–0.008(1)	–0.0012(9)	–0.0033(8)
O(8)	4*a*	0.8174(4)	0.5534(1)	1.05651(9)	0.049(2)	0.062(2)	0.034(1)	–0.013(1)	–0.004(1)	0.006(1)
O(9)	4*a*	1.6925(4)	0.7279(1)	1.0379(1)	0.066(2)	0.062(2)	0.043(1)	–0.016(1)	0.010(1)	0.004(1)
O(10)	4*a*	1.7603(4)	0.7557(2)	1.1467(1)	0.060(2)	0.107(2)	0.059(1)	–0.034(2)	–0.005(1)	–0.020(1)
O(11)	4*a*	1.2947(4)	0.6667(1)	1.3334(1)	0.091(2)	0.072(2)	0.029(1)	–0.014(2)	–0.008(1)	–0.006(1)
O(12)	4*a*	1.0077(5)	0.6041(2)	1.3070(1)	0.100(2)	0.090(2)	0.034(1)	–0.041(2)	0.018(1)	–0.003(1)

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