Z. Kristallogr. NCS **226** (2011) 597-598 / **DOI** 10.1524/ncrs.2011.0268

Crystal structure of methyl (5*R*,8*S*,10*S*,11*S*)-10,11-dihydroxy-1,3-dioxo-2-phenyl-2,3,5,8-tetrahydro-1*H*-5,8-ethano[1,2,4]-triazolo[1,2-*a*]pyridazine-5-carboxylate, $C_{16}H_{15}N_3O_6$

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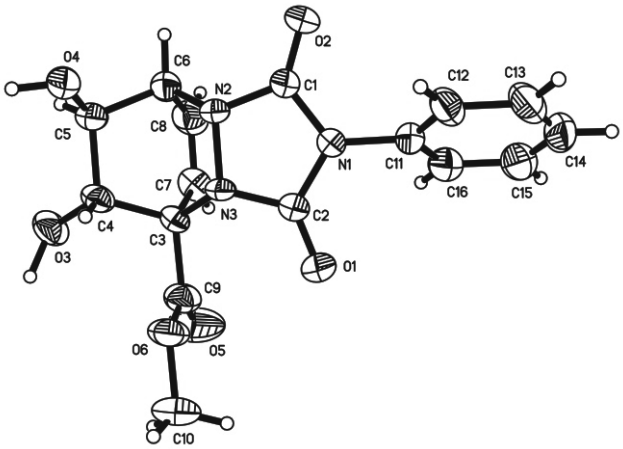
Received April 12, 2011, accepted and available on-line November 1, 2011; CCDC no. 1267/3522



Abstract

$C_{16}H_{15}N_3O_6$, monoclinic, $P2_1$ (no. 4), a = 8.156(4) Å, b = 10.396(1) Å, c = 9.865(1) Å, β = 111.89(1)°, V = 776.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.128, T = 293 K.

Source of material

Based on the literature procedure [1], a solution of freshly distilled 4-phenyl-1,2,4-triazole-3,5-dione (206 mg, 1.18 mmol) in dichloromethane (6.0 mL) was added dropwise to a solution of methyl (5*R*,6*R*)-5,6-dihydroxycyclohexa-1,3-dienecarboxylate (200 mg, 1.18 mmol) in dry dichloromethane (11.8 mL) at room temperature until the resulting suspension remained slightly pink. After 30 min stirring at room temperature, the resulting colourless precipitate was filtered and washed with cold dichloromethane. After recrystallization in acetone the title compound (398 mg, 1.15 mmol, 98 %) was obtained as colourless crystals (m. p. 121 °C, decomposition; $[\alpha]_D^{20}$ = +86, c = 0.9 in acetone).

Experimental details

H atoms were located on difference Fourier map, but refined with fixed individual displacement parameters, using a riding model with d(C—H) ranging from 0.93 to 0.98 Å. The hydrogen atoms of the hydroxy functions were refined freely, because of their relevance in hydrogen bond interactions. In addition, the methyl group was allowed to rotate but not to tip. The displacement parameters of C13, C14 and C15 of the phenyl moiety are slightly enlarged, which indicates an in-plane vibration of this ring system. The Flack parameter is 0.1(4), which is in accordance with the absolute configuration resulting from the synthetic pathway.

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Discussion

The double bond C7=C8 was clearly identified by the distance of 1.333(6) Å. The structure is stabilized by two intermolecular hydrogen bond interactions where the hydroxy functions work as donors in both cases. O3–H3A build up a hydrogen bond to the oxygen O4 of another hydroxy function as acceptor with d(H3A···O4) = 1.85(7) Å and ∠O3–H3A···O4 = 176(6)°. The oxygen O2 of the carbonyl function works as acceptor of the O4–H4A···O2 interaction with d(H4A—O2) = 1.90(8) Å, the relevant angle is 158(7)°. The angle between the best planes of the triazole moiety and the attached phenyl group is 63.9(2)°. The methylester function has a nearly perpendicular orientation to the diazine ring system (N2, N3, C3, C4, C5, C6). The angle between their best planes is 86.1(2)°. A view along [010] shows a layer-type orientation of the molecules. The layers are placed in the (100)-plane and stack along [100]. There is an alternate stacking of non-polar phenyl moieties and polar hydrogen bond interactions.

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.2 × 0.3 × 0.7 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	9.77 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	129.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2795, 2487
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2166
$N(param)_{refined}$:	236
Programs:	SHELXS-97, SHELXL-97, SHELXTL [2]

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

Atom	Site	x	y	z	U_{iso}
H(3A)	2*a*	–0.070(9)	0.314(7)	0.874(8)	0.11(2)
H(4A)	2*a*	–0.100(9)	0.620(8)	1.096(9)	0.12(3)
H(4)	2*a*	0.0735	0.4871	0.9648	0.046
H(5)	2*a*	–0.2476	0.6065	0.8586	0.049
H(6)	2*a*	–0.1533	0.8154	0.8097	0.051
H(7)	2*a*	–0.1029	0.5527	0.5285	0.055
H(8)	2*a*	–0.2475	0.7368	0.5668	0.064
H(10A)	2*a*	0.3062	0.2062	0.7799	0.105
H(10B)	2*a*	0.4562	0.2392	0.9301	0.105
H(10C)	2*a*	0.4613	0.2976	0.7852	0.105
H(12)	2*a*	0.5386	0.9854	0.9027	0.055
H(13)	2*a*	0.7172	1.1123	0.8164	0.070
H(14)	2*a*	0.7019	1.0864	0.5811	0.077
H(15)	2*a*	0.5048	0.9459	0.4253	0.075
H(16)	2*a*	0.3226	0.8225	0.5069	0.060

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}
O(1)	2*a*	0.4008(4)	0.6126(3)	0.7239(4)	0.063(2)	0.037(2)	0.086(2)	0.007(2)	0.051(2)	–0.001(2)
N(1)	2*a*	0.3045(4)	0.8149(3)	0.7629(4)	0.043(2)	0.026(2)	0.055(2)	0.001(1)	0.029(2)	0.002(2)
C(1)	2*a*	0.1681(5)	0.8607(4)	0.8015(4)	0.049(2)	0.028(2)	0.050(2)	0.000(2)	0.030(2)	–0.001(2)
O(2)	2*a*	0.1205(4)	0.9716(3)	0.7977(4)	0.070(2)	0.025(2)	0.081(2)	0.004(1)	0.048(2)	–0.002(1)
N(2)	2*a*	0.0996(4)	0.7549(3)	0.8490(3)	0.043(2)	0.024(1)	0.056(2)	0.004(2)	0.030(2)	–0.003(2)
C(2)	2*a*	0.3082(5)	0.6821(4)	0.7634(5)	0.043(2)	0.026(2)	0.050(2)	0.002(2)	0.024(2)	–0.000(2)
N(3)	2*a*	0.1896(4)	0.6422(3)	0.8262(4)	0.037(2)	0.020(2)	0.049(2)	0.004(1)	0.023(1)	–0.004(1)
O(3)	2*a*	–0.1378(4)	0.3996(3)	0.8277(3)	0.050(2)	0.032(2)	0.072(2)	–0.010(1)	0.021(1)	–0.001(1)
C(3)	2*a*	0.0601(5)	0.5373(4)	0.7571(4)	0.042(2)	0.021(2)	0.047(2)	–0.002(2)	0.021(2)	–0.002(2)
O(4)	2*a*	–0.0604(4)	0.6705(3)	1.0395(4)	0.071(2)	0.032(2)	0.060(2)	–0.001(1)	0.041(2)	–0.003(1)
C(4)	2*a*	–0.0217(5)	0.5071(3)	0.8715(4)	0.044(2)	0.023(2)	0.049(2)	–0.000(2)	0.018(2)	–0.002(2)
C(5)	2*a*	–0.1213(5)	0.6264(4)	0.8916(5)	0.044(2)	0.028(2)	0.056(2)	0.003(2)	0.026(2)	–0.001(2)
O(5)	2*a*	0.1124(6)	0.3670(4)	0.6148(4)	0.108(3)	0.068(2)	0.069(2)	0.025(2)	0.019(2)	–0.028(2)
O(6)	2*a*	0.2849(4)	0.3822(3)	0.8509(3)	0.061(2)	0.034(2)	0.059(2)	0.016(1)	0.025(2)	0.002(1)
C(6)	2*a*	–0.0939(5)	0.7366(4)	0.7982(5)	0.040(2)	0.035(2)	0.058(2)	0.007(2)	0.026(2)	0.010(2)
C(7)	2*a*	–0.0772(5)	0.5897(4)	0.6200(5)	0.051(2)	0.040(2)	0.043(2)	–0.002(2)	0.014(2)	0.001(2)
C(8)	2*a*	–0.1588(6)	0.6943(5)	0.6416(5)	0.048(2)	0.047(3)	0.061(3)	0.010(2)	0.016(2)	0.014(2)
C(9)	2*a*	0.1563(6)	0.4203(4)	0.7311(5)	0.057(2)	0.031(2)	0.051(2)	0.003(2)	0.022(2)	–0.007(2)
C(10)	2*a*	0.3857(7)	0.2719(5)	0.8352(7)	0.078(3)	0.042(3)	0.096(4)	0.026(3)	0.039(3)	0.003(3)
C(11)	2*a*	0.4156(5)	0.8932(4)	0.7116(4)	0.039(2)	0.033(2)	0.051(2)	0.002(2)	0.024(2)	0.005(2)
C(12)	2*a*	0.5316(5)	0.9780(4)	0.8067(5)	0.043(2)	0.035(2)	0.058(2)	–0.006(2)	0.016(2)	0.004(2)
C(13)	2*a*	0.6391(6)	1.0529(4)	0.7552(6)	0.045(2)	0.035(2)	0.089(4)	–0.003(2)	0.018(2)	0.012(2)
C(14)	2*a*	0.6283(7)	1.0381(5)	0.6142(7)	0.059(3)	0.049(3)	0.100(4)	0.009(2)	0.048(3)	0.028(3)
C(15)	2*a*	0.5114(7)	0.9538(5)	0.5211(6)	0.079(3)	0.051(3)	0.074(3)	0.011(3)	0.047(3)	0.017(2)
C(16)	2*a*	0.4028(6)	0.8800(4)	0.5695(5)	0.058(2)	0.042(2)	0.056(2)	0.002(2)	0.029(2)	0.000(2)

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