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Crystal structure of (4b*S*,9*S*)4b-hydroxy-11,13-dioxo-4b,7,8,9,10,11,12,13-octahydro-5*H*-6-thia-10,12a-diaza-cyclodeca[*a*]indene-9-carboxylic acid methyl ester, $C_{16}H_{18}N_2O_5S$, *with a remarkable short S···H contact of 2.61 Å*

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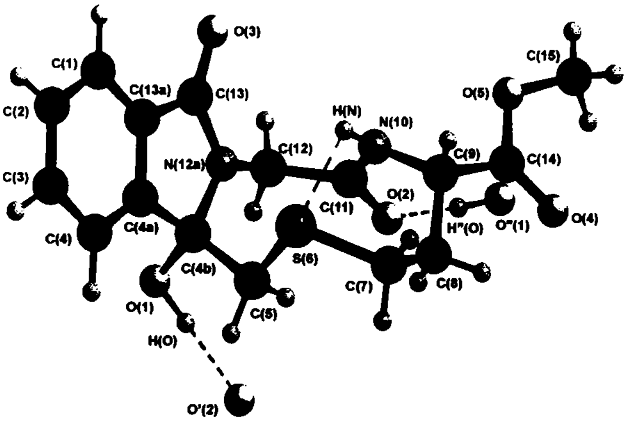

Abstract

$C_{16}H_{18}N_2O_5S$, monoclinic, $P2_1$ (No. 4), $a = 10.390(1)$ Å, $b = 7.105(1)$ Å, $c = 11.639(1)$ Å, $\beta = 109.95(1)°$, $V = 807.7$ Å^3, $Z = 2$, $R_{gt}(F) = 0.036$, $wR_{ref}(F^2) = 0.068$, $T = 293$ K.

Source of material

The title compound was prepared from the *N*-phthaloyl derivative of the dipeptide glycyl L-methionine by irradiation (300 nm wavelength, 27 hours, 2 mmol in 100 ml of acetone at room temperature). The crude product was purified by column chromatography on silica (methanol / methylene chloride 1:20) which yielded 54% of the diastereoisomerically pure *cis* compound. The resulting material was dissolved in acetone and after slow evaporation of the solvent, a colorless oil resulted from which tiny and air-sensitive colorless needles crystallized with mp of 468 K - 469 K (cf. 471 K - 473 K [1]).

Discussion

The reaction was performed in context with studies on intramolecular photoinduced electron transfer (PET) reactions of electron-donor substituted phthalimides. In earlier publications, the photocyclization of *N*-phthaloyl methionine [2] and the photoelimination of *N*-phthaloyl methionine sulfoxide methyl ester [3] were described. Recently, the PET-cyclization of MTM- and MTE-esters of phthalimido alkylcarboxylates was developed [4]. The presented reaction is analogous to the former transformations involving the single electron oxidation of the thioether sulfur and subsequent deprotonation/cyclization to give the title compound. The ten-membered central ring adopts a distorted chair conformation containing an *anti* orientated O=C–N–H group (torsion angle ∠O(2)–C11–N(10)–H(N) = –164.1°). This arrangement enables the C=O oxygen to take part in a hydrogen bond with the proton of the O–H group of the neighbouring molecule: *d*[O(2)···H"(O)] = 1.82 A, ∠O(2)–H"(O)–O"(2) = 173.7°); but most interestingly is the remarkable short contact of the hydrogen of the -N–H group to the sulfur in the opposite ring position *d*[H(N)···S(6)] = 2.61 Å!

Table 1. Data collection and handling.

Crystal:	colourless needle, size 0.15 × 0.15 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.30 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, 270 frames, $\Delta\varphi = 2°$, $\Delta\omega = 2°$
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4512, 2334
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1680
$N(param)_{refined}$:	291
Programs:	SHELXS-97 [5], SHELXL-97 [6], SCHAKAL 99 [7]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*a*	0.637(4)	1.185(6)	0.430(3)	0.07(1)
H(2)	2*a*	0.788(5)	0.938(7)	0.538(4)	0.11(2)
H(3)	2*a*	0.729(4)	0.622(5)	0.501(3)	0.06(1)
H(4)	2*a*	0.507(3)	0.539(4)	0.356(2)	0.024(8)
H(5A)	2*a*	0.215(4)	0.708(4)	0.040(3)	0.04(1)
H(5B)	2*a*	0.319(3)	0.554(5)	0.115(3)	0.05(1)
H(7A)	2*a*	0.429(4)	0.785(6)	–0.157(3)	0.07(1)
H(7B)	2*a*	0.354(4)	0.606(6)	–0.135(3)	0.07(1)
H(8A)	2*a*	0.148(4)	0.810(5)	–0.173(2)	0.03(1)
H(8B)	2*a*	0.200(3)	0.826(5)	–0.280(3)	0.043(9)
H(9)	2*a*	0.304(3)	1.106(4)	–0.182(2)	0.007(9)
H(N)	2*a*	0.302(4)	1.106(5)	–0.004(3)	0.04(1)
H(12A)	2*a*	0.131(3)	1.192(5)	0.138(3)	0.05(1)
H(12B)	2*a*	0.062(4)	0.990(5)	0.130(3)	0.04(1)
H(15A)	2*a*	0.024(5)	1.446(7)	–0.427(4)	0.10(2)
H(15B)	2*a*	–0.005(6)	1.558(8)	–0.341(5)	0.13(3)
H(15C)	2*a*	–0.084(5)	1.370(7)	–0.394(4)	0.09(2)
H(O)	2*a*	0.149(6)	0.649(9)	0.202(5)	0.13(2)

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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)	2*a*	0.6152(4)	1.0526(6)	0.4151(3)	0.049(4)	0.057(3)	0.042(2)	–0.020(2)	0.010(2)	–0.010(2)
C(2)	2*a*	0.7011(5)	0.9111(7)	0.4771(4)	0.038(4)	0.092(4)	0.042(2)	–0.012(3)	0.006(2)	–0.007(2)
C(3)	2*a*	0.6649(5)	0.7243(6)	0.4542(4)	0.041(4)	0.070(3)	0.045(2)	0.007(2)	0.004(2)	0.005(2)
C(4)	2*a*	0.5386(4)	0.6738(6)	0.3695(3)	0.041(3)	0.044(2)	0.051(2)	0.004(2)	0.012(2)	0.005(2)
C(4A)	2*a*	0.4525(3)	0.8151(5)	0.3081(3)	0.025(3)	0.037(2)	0.032(2)	–0.000(2)	0.007(2)	0.004(2)
C(4B)	2*a*	0.3108(3)	0.8022(5)	0.2138(3)	0.024(3)	0.029(2)	0.034(2)	–0.005(2)	0.008(2)	–0.001(2)
C(5)	2*a*	0.3086(4)	0.6980(5)	0.0980(3)	0.032(3)	0.032(2)	0.043(2)	–0.002(2)	0.004(2)	–0.005(2)
S(6)	2*a*	0.4349(1)	0.7884(1)	0.03787(8)	0.0346(8)	0.0510(5)	0.0463(5)	0.0052(5)	0.0125(4)	–0.0016(5)
C(7)	2*a*	0.3544(6)	0.7491(6)	–0.1264(3)	0.051(4)	0.062(3)	0.049(2)	0.018(2)	0.017(2)	–0.003(2)
C(8)	2*a*	0.2227(5)	0.8481(6)	–0.1931(4)	0.043(4)	0.061(3)	0.040(2)	–0.002(2)	0.015(2)	–0.009(2)
C(9)	2*a*	0.2201(5)	1.0588(5)	–0.1770(3)	0.029(4)	0.054(2)	0.033(2)	–0.006(2)	0.014(2)	–0.003(2)
N(10)	2*a*	0.2193(5)	1.1107(4)	–0.0565(3)	0.021(3)	0.050(2)	0.032(2)	0.001(2)	0.005(2)	0.003(1)
C(11)	2*a*	0.1142(6)	1.0713(5)	–0.0208(3)	0.028(4)	0.039(2)	0.041(2)	0.006(2)	0.009(2)	0.004(2)
C(12)	2*a*	0.1404(5)	1.0678(6)	0.1167(3)	0.037(4)	0.048(2)	0.039(2)	0.014(2)	0.016(2)	0.005(2)
N(12A)	2*a*	0.2753(3)	1.0039(3)	0.1898(2)	0.028(2)	0.032(2)	0.034(2)	0.005(1)	0.004(1)	–0.001(1)
C(13)	2*a*	0.3780(4)	1.1204(5)	0.2538(3)	0.045(3)	0.031(2)	0.034(2)	–0.002(2)	0.017(2)	–0.001(2)
C(13A)	2*a*	0.4909(4)	1.0011(5)	0.3303(3)	0.030(3)	0.041(2)	0.030(2)	–0.008(2)	0.010(2)	–0.002(2)
C(14)	2*a*	0.1060(4)	1.1538(5)	–0.2798(3)	0.036(3)	0.063(3)	0.031(2)	–0.004(2)	0.013(2)	–0.001(2)
C(15)	2*a*	–0.0003(7)	1.4412(9)	–0.3585(5)	0.077(5)	0.072(4)	0.044(3)	0.007(3)	0.004(3)	0.021(3)
O(1)	2*a*	0.2219(3)	0.7153(3)	0.2654(2)	0.034(2)	0.050(2)	0.046(1)	–0.010(1)	0.011(1)	0.004(1)
O(2)	2*a*	–0.0013(3)	1.0353(4)	–0.0922(2)	0.025(2)	0.079(2)	0.049(2)	0.003(2)	0.006(2)	0.004(2)
O(3)	2*a*	0.3731(3)	1.2930(4)	0.2465(2)	0.084(2)	0.032(1)	0.071(2)	–0.005(2)	0.017(2)	–0.001(2)
O(4)	2*a*	0.0412(3)	1.0757(4)	–0.3710(2)	0.063(2)	0.085(2)	0.037(2)	0.003(2)	–0.009(1)	–0.016(1)
O(5)	2*a*	0.0968(3)	1.3369(3)	–0.2579(2)	0.054(2)	0.060(2)	0.036(1)	0.000(1)	0.003(1)	0.008(1)

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