Crystal structure of *rac-cis-N*-(2,4-dinitrophenyl)-3,4-diphenyl-5*H*-1,2-oxathiol-5-amine 2-oxide, C₂₁H₁₅N₃O₆S, *sultim* and *sultam* structures – part 4

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Abstract

C₂₁H₁₅N₃O₆S, monoclinic, *P*12₁/*c*1 (no. 14), *a* = 9.624(3) Å, *b* = 8.446(3) Å, *c* = 23.756(8) Å, β = 93.998(7)°, *V* = 1926.3 Å³, *Z* = 4, *R*_{gt}(*F*) = 0.080, *wR*_{ref}(*F*²) = 0.228, *T* = 213 K.

Source of material

The title compound was prepared by oxidation of 2-(2,4-dinitrophenyl)-4,5-diphenylisothiazolium perchlorate with H₂O₂ in acetic acid at room temperature for 25 minutes (m.p. 419–423 K). Crystals were obtained from acetone.

Experimental details

The high *R* values are caused by the poor quality of the crystals which is reflected in asymmetric reflection profiles and confirmed by two further data collections.

Discussion

The oxidation of monocyclic and bicyclic isothiazolium salts has been researched intensively since the last years [1–7] and can be classified in two principle oxidation methods. At first, the salts

can be oxidized with H₂O₂ in acetic acid to yield 3-hydroperoxy-sultims *rac-cis/trans*, sultams and 3-oxosultams [1–5]. Furthermore, the isothiazolium salts reacted with magnesium monoperoxyphthalate (MMPP) in water or alcohol to obtain the 3-hydroxy-sultims *rac-cis/trans*, sultams or 3-alkoxysultams [6,7].

The *rac-cis-N*-(2,4-dinitrophenyl)-3,4-diphenyl-5*H*-1,2-oxathiol-5-amine 2-oxide was obtained unexpectedly after oxidation of the isothiazolium salt to 3-hydroxysultim, ring cleavage between the sulfur and nitrogen atoms, rearrangement and cyclization. The molecular structure is characterized by a strong intramolecular hydrogen bond (N1–H1N···O2). The bond parameters are *d*(N1–H1N) = 0.76(5) Å, *d*(H1N···O2) = 2.09(5) Å, *d*(N1···O2) = 2.643(5) Å and $\angle$ N1–H1N···O2 = 130(4)°. The 1,2-oxathiole ring is nearly planar with an averaged deviation of 0.063 Å. The O6 and S1 atoms are deviated from the plane by –0.0928 Å and 0.0834 Å, respectively. The two phenyl rings (C4–C9 and C10–C15) are not coplanar with the 1,2-oxathiole ring. The dihedral angles are 36.1° for the phenyl ring C4–C9 and 36.3° for C10–C15. The C1=C2 bond distance of 1.327(5) Å has the typical value for a C=C double bond.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.20 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.15 cm ^{–1}
Diffraction, scan mode:	Siemens SMART CCD, ω
$2\theta_{\max}$:	52.76°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	8480, 3721
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 3015
<i>N</i> (<i>param</i>) _{refined} :	340
Programs:	SHELXS-97 [8], SHELXL-97 [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1N)	4e	0.197(5)	0.128(6)	0.190(2)	0.03(1)
H(3)	4e	0.079(4)	–0.138(5)	0.197(2)	0.022(9)
H(5)	4e	0.245(4)	0.014(5)	0.415(2)	0.03(1)
H(6)	4e	0.375(5)	–0.081(6)	0.490(2)	0.04(1)
H(7)	4e	0.512(5)	–0.289(5)	0.487(2)	0.04(1)
H(8)	4e	0.510(5)	–0.431(7)	0.398(2)	0.05(1)
H(9)	4e	0.382(5)	–0.335(6)	0.322(2)	0.04(1)
H(12)	4e	0.500(5)	–0.056(6)	0.279(2)	0.04(1)
H(13)	4e	0.700(5)	–0.112(6)	0.235(2)	0.05(1)
H(14)	4e	0.664(5)	–0.271(6)	0.153(2)	0.04(1)
H(15)	4e	0.448(5)	–0.332(6)	0.112(2)	0.05(1)
H(16)	4e	0.253(5)	–0.262(5)	0.160(2)	0.03(1)
H(17)	4e	–0.089(5)	–0.060(6)	0.139(2)	0.05(1)
H(18)	4e	–0.211(5)	–0.031(5)	0.056(2)	0.03(1)
H(20)	4e	0.054(6)	0.336(7)	0.021(2)	0.06(2)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	4e	0.2132(4)	−0.0958(4)	0.3084(1)	0.033(2)	0.017(2)	0.029(2)	−0.002(1)	0.009(1)	−0.000(1)
C(2)	4e	0.2322(4)	−0.1026(4)	0.2536(1)	0.033(2)	0.017(2)	0.027(2)	−0.002(1)	0.001(1)	0.002(1)
C(3)	4e	0.1067(4)	−0.0527(5)	0.2162(2)	0.033(2)	0.027(2)	0.034(2)	−0.001(2)	0.006(2)	−0.000(2)
C(4)	4e	0.2992(4)	−0.1491(4)	0.3587(1)	0.033(2)	0.024(2)	0.022(2)	−0.006(1)	0.009(1)	0.002(1)
C(5)	4e	0.2971(4)	−0.0713(5)	0.4106(2)	0.044(2)	0.028(2)	0.028(2)	−0.004(2)	0.013(2)	−0.003(1)
C(6)	4e	0.3758(5)	−0.1267(6)	0.4573(2)	0.054(3)	0.048(3)	0.024(2)	−0.018(2)	0.008(2)	−0.002(2)
C(7)	4e	0.4578(5)	−0.2598(6)	0.4535(2)	0.046(3)	0.061(3)	0.028(2)	−0.009(2)	−0.003(2)	0.011(2)
C(8)	4e	0.4592(5)	−0.3381(5)	0.4029(2)	0.040(2)	0.037(2)	0.041(2)	0.002(2)	0.005(2)	0.010(2)
C(9)	4e	0.3806(4)	−0.2847(5)	0.3558(2)	0.042(2)	0.027(2)	0.028(2)	0.000(2)	0.009(2)	−0.001(1)
C(10)	4e	0.3570(4)	−0.1499(4)	0.2253(1)	0.038(2)	0.022(2)	0.019(2)	0.001(2)	0.004(1)	0.002(1)
C(11)	4e	0.4890(4)	−0.1080(5)	0.2467(2)	0.037(2)	0.028(2)	0.027(2)	−0.000(2)	0.006(2)	−0.002(1)
C(12)	4e	0.6052(4)	−0.1486(5)	0.2189(2)	0.035(2)	0.030(2)	0.040(2)	0.000(2)	0.009(2)	0.006(2)
C(13)	4e	0.5891(5)	−0.2347(5)	0.1689(2)	0.049(3)	0.032(2)	0.034(2)	0.012(2)	0.018(2)	0.004(2)
C(14)	4e	0.4590(5)	−0.2794(5)	0.1473(2)	0.059(3)	0.038(2)	0.023(2)	0.010(2)	0.009(2)	−0.003(2)
C(15)	4e	0.3428(5)	−0.2371(5)	0.1750(2)	0.045(2)	0.035(2)	0.024(2)	0.002(2)	−0.001(2)	−0.004(1)
C(16)	4e	0.0609(4)	0.1070(4)	0.1314(2)	0.031(2)	0.024(2)	0.030(2)	0.007(1)	0.006(1)	−0.006(1)
C(17)	4e	−0.0587(4)	0.0181(5)	0.1146(2)	0.035(2)	0.031(2)	0.038(2)	0.004(2)	0.002(2)	−0.004(2)
C(18)	4e	−0.1293(5)	0.0382(5)	0.0637(2)	0.043(2)	0.042(2)	0.038(2)	0.013(2)	−0.005(2)	−0.016(2)
C(19)	4e	−0.0866(5)	0.1515(6)	0.0266(2)	0.046(3)	0.055(3)	0.029(2)	0.027(2)	−0.000(2)	−0.010(2)
C(20)	4e	0.0266(5)	0.2445(5)	0.0412(2)	0.055(3)	0.039(2)	0.029(2)	0.025(2)	0.012(2)	−0.002(2)
C(21)	4e	0.0980(4)	0.2241(5)	0.0926(2)	0.037(2)	0.027(2)	0.032(2)	0.010(2)	0.010(2)	−0.002(1)
N(1)	4e	0.1326(4)	0.0782(4)	0.1815(1)	0.031(2)	0.028(2)	0.032(2)	−0.005(1)	−0.003(1)	0.002(1)
N(2)	4e	0.2170(4)	0.3273(4)	0.1051(2)	0.040(2)	0.029(2)	0.049(2)	0.007(2)	0.015(2)	0.012(2)
N(3)	4e	−0.1593(5)	0.1706(6)	−0.0289(2)	0.070(3)	0.079(3)	0.030(2)	0.042(3)	−0.004(2)	−0.015(2)
O(1)	4e	0.0746(3)	0.1573(4)	0.3347(1)	0.051(2)	0.033(2)	0.065(2)	0.017(1)	0.010(2)	−0.005(1)
O(2)	4e	0.2731(3)	0.3311(4)	0.1527(1)	0.043(2)	0.049(2)	0.049(2)	−0.010(1)	0.001(1)	0.008(1)
O(3)	4e	0.2579(4)	0.4084(5)	0.0668(2)	0.068(2)	0.065(3)	0.071(2)	−0.006(2)	0.019(2)	0.033(2)
O(4)	4e	−0.2522(5)	0.0750(6)	−0.0422(2)	0.078(3)	0.108(4)	0.042(2)	0.032(3)	−0.022(2)	−0.032(2)
O(5)	4e	−0.1234(5)	0.2787(6)	−0.0585(2)	0.116(4)	0.104(4)	0.034(2)	0.042(3)	−0.012(2)	0.008(2)
O(6)	4e	−0.0040(3)	−0.0198(4)	0.2539(1)	0.028(1)	0.050(2)	0.042(2)	0.004(1)	0.006(1)	0.007(1)
S(1)	4e	0.0476(1)	−0.0077(1)	0.31992(4)	0.0328(6)	0.0332(6)	0.0390(6)	0.0035(4)	0.0144(4)	0.0082(4)

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