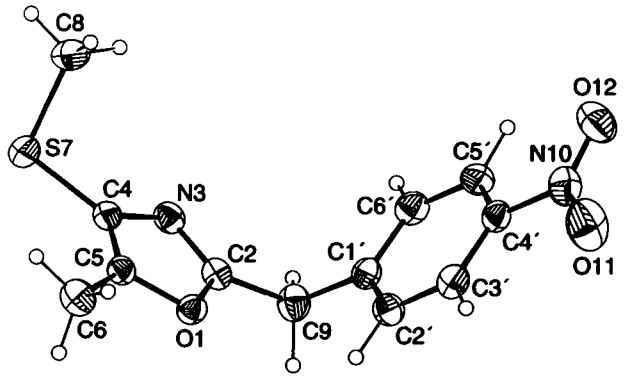
Crystal structure of 5-methyl-4-(methylthio)-2-(4-nitrobenzyl)oxazole, $C_{12}H_{12}N_2O_3S$

A. Herrera[I], R. Martínez-Álvarez*[,I], P. Ramiro[I] and M. Rosario Torres[II]

[I] Universidad Complutense, Facultad de Ciencias Químicas, Departamento de Química Orgánica, 28040 Madrid, Spain
[II] Universidad Complutense, Facultad de Ciencias Químicas, Laboratorio de Difracción de Rayos X, 28040 Madrid, Spain

Received March 17, 2005, accepted and available on-line April 7, 2005; CCDC no. 1267/1508



Abstract

$C_{12}H_{12}N_2O_3S$, triclinic, $P\bar{1}$ (no. 2), $a = 8.184(1)$ Å, $b = 8.355(1)$ Å, $c = 10.529(2)$ Å, $\alpha = 106.504(3)°$, $\beta = 97.948(3)°$, $\gamma = 110.631(3)°$, $V = 622.7$ Å^3, $Z = 2$, $R_{gt}(F) = 0.045$, $wR_{ref}(F^2) = 0.111$, $T = 293$ K.

Source of material

A solution of trifluoromethanesulfonic anhydride (5.34 g, 19.2 mmol; Tf_2O) in CH_2Cl_2 (20 mL) was added dropwise to a stirred and cooled (273 K) solution of α-(methylthio)acetone (2.00 g, 19.2 mmol) in CH_2Cl_2 (25 mL). After stirring the reaction mixture 1 h at 298 K, 25 mL of a solution containing 4-nitrophenylacetonitrile (1.55 g, 9.6 mmol) in CH_2Cl_2 were added. The reaction mixture was stirred during 3 days at 298 K. The course of the reaction can be monitored using TLC. The reaction mixture was hydrolyzed by careful addition of saturated aqueous solution of sodium hydrogen carbonate until it was basic. The organic layer was separated, washed with brine and the solvent removed under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate (95/5) as eluent. We obtained 1.58 g (62 %) of a yellow solid. The compound was recrystallized from boiling methanol (m.p. 92-94 °C).
Elemental analysis: found – C, 54.33 %; H, 4.25 %; N, 10.11 %; S, 11.98 %; calc. for $C_{12}H_{12}N_2O_3S$ – C, 54.53 %; H, 4.58 %; N, 10.60 %; S, 12.13 %. ^{1}H NMR, ^{13}C NMR, MS and IR data are available in the CIF file.

Discussion

The reaction between methylthioketones and nitriles affords unexpected products [1]. The obtained oxazole can be considered as the result of an addition of the carbon atom of the cyano group to the carbonylic oxygen while the nitrogen atom adds to the carbon supporting the methylthio group. The X-ray structure shows that the *p*-nitrobenzyl group is attached at the C2 position of the oxazole ring. The angle between both rings is 112.1(2)° near to the tetrahedral angle as expected. The thiomethyl group is attached at the C4 position, while the methyl group is bound to the C5.

Table 1. Data collection and handling.

Crystal:	yellow, prismatic, size 0.08 × 0.14 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.61 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	57.86°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4079, 2870
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1640
$N(param)_{refined}$:	163
Programs:	SHELXS-97 [2], SHELXL-97 [3]

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

Atom	Site	x	y	z	U_{iso}
H(2')	2*i*	0.2691	0.6535	0.6827	0.08
H(3')	2*i*	0.4815	0.6559	0.5563	0.08
H(5')	2*i*	0.2381	0.8495	0.2928	0.08
H(6')	2*i*	0.0226	0.8363	0.4229	0.08
H(6A)	2*i*	0.4142	1.2565	1.1695	0.08
H(6B)	2*i*	0.4780	1.1251	1.1018	0.08
H(6C)	2*i*	0.3235	1.0415	1.1617	0.08
H(8A)	2*i*	0.1835	1.4483	0.8264	0.08
H(8B)	2*i*	0.2413	1.6303	0.9638	0.08
H(8C)	2*i*	0.3828	1.5438	0.9388	0.08
H(9A)	2*i*	–0.1216	0.7658	0.5927	0.08
H(9B)	2*i*	–0.0437	0.6368	0.6741	0.08

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*i*	0.1870(2)	0.9161(2)	0.8789(1)	0.0456(8)	0.0419(9)	0.0437(8)	0.0211(7)	0.0102(7)	0.0158(7)
C(2)	2*i*	0.0660(3)	0.9149(3)	0.7750(2)	0.039(1)	0.049(1)	0.039(1)	0.017(1)	0.011(1)	0.016(1)
N(3)	2*i*	0.0367(2)	1.0609(3)	0.8034(2)	0.048(1)	0.055(1)	0.045(1)	0.025(1)	0.0145(9)	0.023(1)

* Correspondence author (e-mail: rma@quim.ucm.es)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(4)	2*i*	0.1459(3)	1.1692(3)	0.9371(2)	0.048(1)	0.043(1)	0.043(1)	0.022(1)	0.019(1)	0.019(1)
C(5)	2*i*	0.2367(3)	1.0825(3)	0.9824(2)	0.040(1)	0.041(1)	0.038(1)	0.015(1)	0.0136(9)	0.014(1)
C(6)	2*i*	0.3655(3)	1.1227(3)	1.1121(2)	0.051(1)	0.067(2)	0.049(1)	0.023(1)	0.005(1)	0.021(1)
C(8)	2*i*	0.2546(4)	1.5141(3)	0.9321(3)	0.083(2)	0.054(2)	0.085(2)	0.031(2)	0.036(2)	0.036(2)
C(9)	2*i*	−0.0111(3)	0.7504(3)	0.6457(2)	0.048(1)	0.056(2)	0.049(1)	0.015(1)	0.009(1)	0.010(1)
C(1′)	2*i*	0.1245(3)	0.7463(3)	0.5626(2)	0.046(1)	0.037(1)	0.038(1)	0.011(1)	0.005(1)	0.006(1)
C(2′)	2*i*	0.2610(3)	0.6925(3)	0.5992(2)	0.057(1)	0.051(1)	0.037(1)	0.021(1)	0.005(1)	0.016(1)
C(3′)	2*i*	0.3882(3)	0.6931(3)	0.5266(2)	0.050(1)	0.050(1)	0.045(1)	0.024(1)	0.003(1)	0.012(1)
C(4′)	2*i*	0.3777(3)	0.7479(3)	0.4147(2)	0.047(1)	0.040(1)	0.040(1)	0.015(1)	0.010(1)	0.008(1)
C(5′)	2*i*	0.2423(3)	0.7989(3)	0.3729(2)	0.061(1)	0.052(1)	0.046(1)	0.025(1)	0.012(1)	0.023(1)
C(6′)	2*i*	0.1163(3)	0.7982(3)	0.4478(2)	0.053(1)	0.053(1)	0.052(1)	0.027(1)	0.009(1)	0.019(1)
N(10)	2*i*	0.5142(3)	0.7501(3)	0.3382(2)	0.058(1)	0.065(1)	0.052(1)	0.022(1)	0.014(1)	0.013(1)
O(11)	2*i*	0.6204(3)	0.6843(3)	0.3658(2)	0.089(1)	0.142(2)	0.098(2)	0.080(2)	0.041(1)	0.048(2)
O(12)	2*i*	0.5186(2)	0.8205(3)	0.2509(2)	0.086(1)	0.096(2)	0.072(1)	0.032(1)	0.038(1)	0.040(1)
S(7)	2*i*	0.14820(9)	1.38079(9)	1.02759(7)	0.0926(5)	0.0499(4)	0.0707(4)	0.0400(4)	0.0445(4)	0.0269(3)

Acknowledgments. We gratefully acknowledge the Spanish Ministerio de Ciencia y Tecnologia (grant no. BQU 2004 00406). P. R. thanks the MEC (Spain) for a predoctoral fellowship.

References

1. Herrera, A.; Martínez-Álvarez, R.; Ramiro, P.: unpublished results.
2. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
3. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.