ORGANIC COMPOUNDS

Acta Cryst. (1995). C**51**, 76–77

5,5′-Bithiazole and 2,5′-Bithiazole

NOURREDINE BENALI-CHERIF AND MARCEL PIERROT

Laboratoire de Bio-Inorganique Structurale, Faculté des Sciences et Techniques de Saint-Jerôme, Case C12, 13397 Marseille CEDEX 20, France

CHRISTOPHE BAUDRION AND JEAN PIERRE AUNE

ENSSPICAM, Faculté des Sciences et Techniques de Saint-Jerôme, Case C12, 13397 Marseille CEDEX 20, France

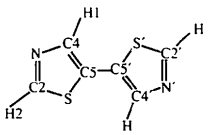
(*Received* 9 *August* 1993; *accepted* 16 *March* 1994)

Abstract

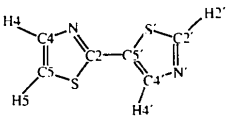
Bithiazoles are known to be potential antibacterial, antifungal and anti-inflammatory agents and their conformations are of particular interest. Of the six possible isomers only three structures have so far been studied: 2,2′-bithiazole [Bolognesi, Catellini, Destri & Porzio (1987). *Acta Cryst.* C**43**, 1171–1173], 4,4′-bithiazole [Ratzimbazafy (1987). Thèse de docteur es sciences, Univ. Aix-Marseille III, France] and 2,4′-bithiazole [Benali-Cherif, Pierrot, Baudrion & Aune (1995). *Acta Cryst.* C**51**, 72–75]. As a continuation of this series, we describe here the crystal structures of two other isomers, namely, 5,5′-bithiazole, $C_6H_4N_2S_2$, and 2,5′-bithiazole, $C_6H_4N_2S_2$. In both structures the bithiazole molecules are planar.

Comment

A comparison of the 5,5′-bithiazole (I) and 2,5′-bithiazole (II) with known bithiazoles does not reveal

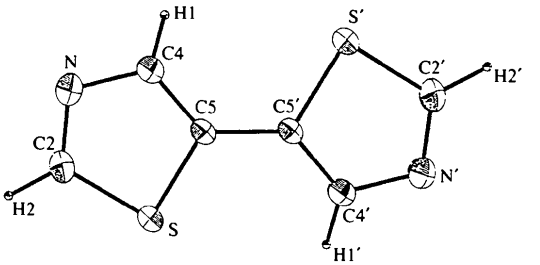


(I)

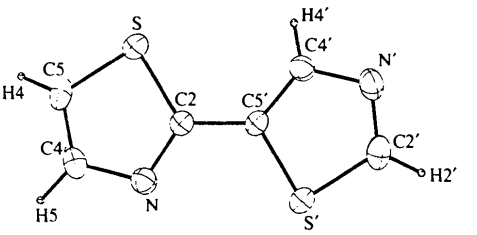


(II)

any differences either in bond distances or bond angles as shown in Table 2. Moreover, in both forms the thiazole rings are coplanar as has been found in the previously determined isomers (Graig, Goodwyn, Onggo & Rae, 1988; Bolognesi, Catellini, Destri & Porzio, 1987).



(*a*)



(*b*)

Fig. 1. *ORTEP* plots (Johnson, 1976) of the title compounds with the atomic numbering schemes: (*a*) (I) and (*b*) (II). Displacement ellipsoids are at the 50% probability level.

Experimental

5,5′-Bithiazole (I) was synthesized by the same method used to obtain 2,2′-bithiazole (Graig, Goodwyn, Onggo & Rae, 1988), a homocoupling reaction of 5-bromothiazole using nickel as catalyst. After liquid chromotographic purification the product was crystallized from an EtOH/H_2O solution over 2 weeks. 2,5′-Bithiazole (II) was synthesized by a cross-coupling reaction between 5-bromothiazole and 2-trimethyltinthiazole (Dondoni, Fogagnolo, Medici & Negrini, 1987). It was purified by liquid chromatography and crystallized after 1 year at 277 K in EtOH/H_2O solution.

5,5′-Bithiazole

Crystal data

$C_6H_4N_2S_2$
M_r = 168.24
Monoclinic
$P2_1/n$
a = 8.670 (3) Å
b = 3.902 (2) Å
c = 10.463 (1) Å
β = 95.32 (2)°
V = 352.5 (4) Å^3
Z = 2
D_x = 1.585 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 14–16°
μ = 0.641 mm^{-1}
T = 293 K
Rectangular
0.4 × 0.3 × 0.3 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
R_{int} = 0.024
θ_{max} = 24°

$\theta/2\theta$ scans
Absorption correction: none
1340 measured reflections
663 independent reflections
655 observed reflections [$I > 3\sigma(I)$]
$h = 0 \rightarrow 10$
$k = -4 \rightarrow 4$
$l = -12 \rightarrow 12$
2 standard reflections
frequency: 60 min
intensity variation: <1%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.038$
$S = 0.508$
655 reflections
54 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.259$ e Å^{-3}
$\Delta\rho_{min} = -0.272$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

2,5′-Bithiazole

Crystal data

$C_6H_4N_2S_2$
$M_r = 168.24$
Orthorhombic
$P2_12_12_1$
$a = 5.770$ (3) Å
$b = 5.923$ (2) Å
$c = 21.056$ (1) Å
$V = 719.6$ (3) Å^3
$Z = 4$
$D_x = 1.555$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 14$–$16°$
$\mu = 0.627$ mm^{-1}
$T = 293$ K
Prism
0.5 × 0.4 × 0.3 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
790 measured reflections
771 independent reflections
712 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 24°$
$h = 0 \rightarrow 6$
$k = -4 \rightarrow 7$
$l = -12 \rightarrow 25$
2 standard reflections
frequency: 60 min
intensity variation: <1%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.054$
$S = 2.3$
712 reflections
91 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
5,5′-Bithiazole				
S	0.65708 (8)	0.3036 (2)	0.86501 (6)	3.28 (1)
N	0.8262 (3)	0.2622 (8)	1.0773 (2)	4.16 (6)
C4	0.6848 (3)	0.3941 (9)	1.1031 (3)	3.49 (6)
C5	0.5785 (3)	0.4368 (7)	1.0022 (2)	2.37 (5)
C2	0.8271 (3)	0.2079 (9)	0.9550 (3)	3.69 (6)
2,5′-Bithiazole				
S	1.0429 (2)	0.5702 (2)	0.86101 (4)	4.05 (2)
S′	0.4611 (2)	0.1078 (2)	0.88846 (4)	3.85 (2)
N	0.6328 (4)	0.5300 (5)	0.8164 (1)	3.44 (5)
N′	0.7446 (6)	−0.0335 (5)	0.9727 (1)	4.12 (6)
C2	0.7754 (5)	0.4423 (5)	0.8581 (1)	2.71 (5)
C2′	0.5448 (7)	−0.0746 (5)	0.9475 (2)	4.20 (8)
C4	0.7376 (8)	0.7107 (6)	0.7861 (2)	3.84 (7)
C4′	0.8435 (5)	0.1508 (6)	0.9438 (2)	3.51 (7)
C5	0.9544 (7)	0.7551 (5)	0.8038 (2)	4.10 (7)
C5′	0.7179 (6)	0.2502 (5)	0.8975 (1)	2.80 (5)

Table 2. *Comparison of bond distances* (Å) *and angles* (°) *with 2,2′- and 4,4′-bithiazole*

	2,2′-Bithiazole*	4,4′-Bithiazole†	5,5′-Bithiazole	2,5′-Bithiazole‡
S—C2	1.717 (2)	1.710 (4)	1.715 (3)	1.716(3), 1.720(4)
S—C5	1.706 (2)	1.704 (4)	1.725 (3)	1.707(4), 1.716(3)
N—C2	1.306 (3)	1.300 (5)	1.297 (4)	1.310(4), 1.292(5)
N—C4	1.373 (3)	1.383 (3)	1.380 (4)	1.385(4), 1.374(5)
C4—C5	1.345 (4)	1.360 (5)	1.364 (4)	1.331(6), 1.349(4)
C—C′	1.449 (3)	1.469 (7)	1.445 (3)	1.448 (4)
S—C2—N	115.2 (2)	115.5 (3)	115.0 (3)	114.4(2), 115.5(3)
S—C5—C4	109.9 (2)	109.8 (3)	108.7 (2)	110.6(3), 109.3(2)
C2—N—C4	109.1 (2)	109.8 (3)	110.0 (2)	109.9(3), 109.8(3)
N—C4—C5	116.4 (2)	115.3 (3)	116.6 (2)	115.7(3), 116.3(3)
C2—S—C5	89.0 (1)	89.6 (2)	89.7 (1)	89.3(2), 89.2(2)

* Bolognesi, Catellini, Destri & Porzio (1987).
† Ratzimbazafy (1987).
‡ 2,5′-Bithiazole has no molecular symmetry. The two values are for corresponding but non-symmetrical distances and angles.

Absences for the $P2_1/n$ cell are $h0l$, $h + l$ odd, and $0k0$, k odd, and for the $P2_12_12_1$ cell are $h00$, h odd, $0k0$, k odd and $00l$, l odd. All non-H atoms were found by direct methods (Frenz, 1978) and the structures were refined successfully with a full-matrix least-squares procedure using anisotropic displacement parameters for the non-H atoms. For both compounds, H atoms were located on a difference Fourier synthesis and included in the refinement. The weighting scheme used was derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Benali-Cherif, N., Pierrot, M., Baudrion, C. & Aune, J. P. (1995). *Acta Cryst.* **C51**, 72–75.

Bolognesi, A., Catellini, M., Destri, S. & Porzio, W. (1987). *Acta Cryst.* **C43**, 1171–1173.

Dondoni, A., Fogagnolo, M., Medici, A. & Negrini, E. (1987). *Synthesis*, 185–186.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP - a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Graig, D. C., Goodwyn, H. A., Onggo, D. & Rae, A. D. (1988). *Aust. J. Chem.* **41**, 1625–1628.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Ratzimbazafy, A. (1987). Thèse de docteur es sciences, Univ. Aix-Marseille III, France.