O21	0.3885 (2)	−0.2492 (4)	0.1908 (2)	0.0675 (11)
C22	0.4130 (4)	−0.2186 (6)	0.2694 (3)	0.0822 (21)
O23	0.3232 (2)	−0.3175 (3)	0.0510 (2)	0.0567 (11)
C24	0.2281 (4)	−0.3869 (5)	0.0754 (3)	0.0796 (21)
C25	0.0799 (4)	−0.5528 (6)	−0.1095 (3)	0.0863 (22)
C26	−0.0429 (4)	0.0199 (6)	−0.1211 (4)	0.1024 (27)

Table 2. *Geometric parameters* (Å, °)

N1—C2	1.324 (5)	C11—N12	1.404 (5)
N1—N5	1.370 (5)	N12—C13	1.364 (5)
C2—C3	1.386 (6)	C13—C14	1.502 (5)
C2—C25	1.490 (6)	C13—C18	1.335 (5)
C3—C4	1.355 (6)	C14—O15	1.195 (5)
C4—N5	1.346 (5)	C14—O16	1.335 (5)
C4—C26	1.489 (7)	O16—C17	1.441 (5)
N5—C6	1.425 (5)	C18—C19	1.460 (6)
C6—C7	1.370 (6)	C18—O23	1.385 (4)
C6—C11	1.396 (5)	C19—O20	1.210 (5)
C7—C8	1.389 (6)	C19—O21	1.338 (5)
C8—C9	1.372 (6)	O21—C22	1.447 (5)
C9—C10	1.375 (6)	O23—C24	1.419 (5)
C10—C11	1.389 (6)		
C2—N1—N5	104.9 (3)	C10—C11—N12	123.3 (3)
N1—C2—C25	121.0 (4)	C6—C11—N12	118.4 (3)
N1—C2—C3	110.4 (4)	C11—N12—C13	127.9 (3)
C3—C2—C25	128.6 (4)	N12—C13—C18	120.8 (3)
C2—C3—C4	107.0 (4)	N12—C13—C14	116.7 (3)
C3—C4—C26	131.9 (4)	C14—C13—C18	122.2 (3)
C3—C4—N5	106.2 (4)	C13—C14—O16	112.0 (3)
N5—C4—C26	122.0 (4)	C13—C14—O15	123.0 (3)
N1—N5—C4	111.5 (3)	O15—C14—O16	124.9 (3)
C4—N5—C6	128.8 (3)	C14—O16—C17	114.8 (3)
N1—N5—C6	119.1 (3)	C13—C18—O23	117.8 (3)
N5—C6—C11	118.8 (3)	C13—C18—C19	122.6 (3)
N5—C6—C7	120.6 (3)	C19—C18—O23	119.7 (3)
C7—C6—C11	120.6 (4)	C18—C19—O21	112.0 (3)
C6—C7—C8	120.6 (4)	C18—C19—O20	124.1 (4)
C7—C8—C9	118.9 (4)	O20—C19—O21	123.8 (4)
C8—C9—C10	120.9 (4)	C19—O21—C22	114.9 (3)
C9—C10—C11	120.6 (4)	C18—O23—C24	114.3 (3)
C6—C11—C10	118.3 (4)		

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71369 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1086]

References

Albini, A., Bettinetti, G. & Minoli, G. (1983). *J. Chem. Soc. Perkin Trans.* 1, pp. 2491-2494.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1-S19.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Keller, E. (1988). *SCHAKAL88. Fortran Program for the Graphical Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95-98.
Nardelli, M. (1992). *PARSTCIF. Program for the Creation of a CIF from the Output of PARST*. Univ. of Parma, Italy.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558-564.

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X-ray Crystallographic Analysis of 2-Acetylimino-3-isopropyl-5-methyl-4-phenyl-2,3-dihydro-1,3-thiazole

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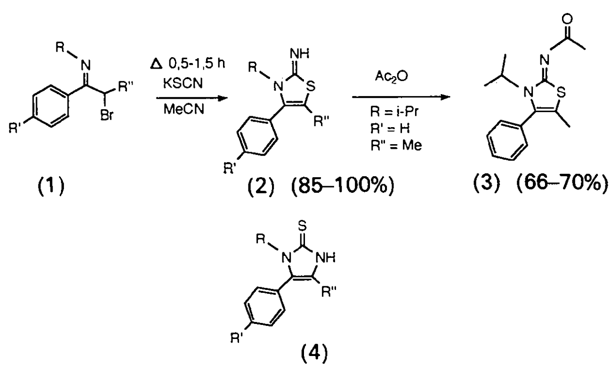
Abstract

The crystal structure determination of $C_{15}H_{18}N_2OS$ allows the unambiguous identification of the reaction product of an α-bromoketimine with potassium thiocyanate.

Comment

The reaction of α-bromoketimines (1) with potassium thiocyanate in acetonitrile under reflux afforded 3-alkyl-2-imino-4-aryl-2,3-dihydro-1,3-thiazoles (2) (De Kimpe, Boelens & Declercq, 1993). Since thiocyanate is an ambidentate nucleophile, capable of reacting *via* either the S or N terminus, care should be taken with respect to the structure of the resulting heterocycles. In order to distinguish unambiguously between the 2-imino-2,3-dihydro-1,3-thiazoles (2) and the isomeric 4-imidazoline-2-thiones (4), efforts were undertaken to prepare a crystalline derivative.



Acetylation of the heterocyclic compound, resulting from the reaction of *N*-(2-bromo-1-phenyl-1-propylidene)isopropylamine (1) (R = ^{i}Pr, R' = H, R'' = Me) and potassium thiocyanate under reflux, with excess acetic anhydride under reflux without any solvent, or with excess acetic anhydride in toluene at room temperature overnight, gave rise to 2-acetylimino-3-isopropyl-5-methyl-4-phenyl-2,3-dihydro-1,3-thiazole (3) in 66–70% yield. The structure of (3) was determined by X-ray crystallography, indicating that the reaction of α-bromoketimines with potassium thiocyanate leads to 3,5-dialkyl-2-imino-4-aryl-2,3-dihydro-1,3-thiazoles (2). The 2,3-dihydro-1,3-thiazol-2-imine ring and some of its substituents lie in a crystallographic mirror plane. The phenyl substituent at the 4 position is perpendicular to the 2,3-dihydro-1,3-thiazol-2-imine ring, while the *N*-acetyl group is coplanar with it.

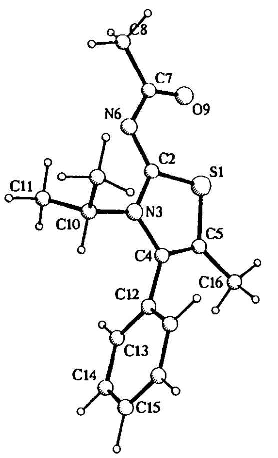


Fig. 1. View of the molecule and atom numbering.

Experimental

Crystal data

$C_{15}H_{18}N_2OS$
M_r = 274.4
Orthorhombic
Pnma
a = 13.454 (1) Å
b = 7.317 (1) Å
c = 15.181 (1) Å
V = 1494.5 (2) Å^3
Z = 4
D_x = 1.22 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 27 reflections
θ = 6–24°
μ = 1.82 mm^{-1}
T = 293 K
Parallelepiped
0.4 × 0.2 × 0.2 mm
Colourless

Data collection

Huber four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.55, T_{max} = 0.70
1620 measured reflections
1459 independent reflections
1314 observed reflections [$I > 2.5\sigma(I)$]

θ_{max} = 67.5°
h = 0 → 16
k = 0 → 8
l = 0 → 18
1 standard reflection monitored every 50 reflections
intensity variation: none

Refinement

Refinement on F
Final R = 0.054
wR = 0.072
S = 0.75
1314 reflections
107 parameters
Only H-atom U's refined; U common for all H atoms
$w = 1/[\sigma^2(F) + 0.021F^2]$

$(\Delta/\sigma)_{max}$ = 0.04
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Cell refinement, data collection and data reduction: local programs Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX-76* (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: local program.

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

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.04808 (6)	0.25	0.50453 (5)	0.0563 (4)
C2	−0.0797 (3)	0.25	0.4973 (2)	0.0513 (9)
N3	−0.1096 (2)	0.25	0.4119 (1)	0.0518 (7)
C4	−0.0305 (2)	0.25	0.3515 (2)	0.0499 (8)
C5	0.0587 (2)	0.25	0.3907 (2)	0.0550 (9)
N6	−0.1463 (2)	0.25	0.5628 (2)	0.0634 (9)
C7	−0.1089 (3)	0.25	0.6452 (2)	0.073 (1)
C8	−0.1847 (5)	0.25	0.7171 (3)	0.110 (2)
O9	−0.0183 (3)	0.25	0.6630 (2)	0.091 (1)
C10	−0.2159 (2)	0.25	0.3843 (2)	0.0623 (9)
C11	−0.2666 (2)	0.4253 (4)	0.4131 (2)	0.088 (1)
C12	−0.0495 (2)	0.25	0.2548 (2)	0.0529 (8)
C13	−0.0554 (2)	0.4132 (4)	0.2099 (1)	0.0697 (8)
C14	−0.0689 (2)	0.4122 (5)	0.1184 (2)	0.0797 (9)
C15	−0.0749 (3)	0.25	0.0735 (2)	0.082 (1)
C16	0.1597 (2)	0.25	0.3487 (3)	0.078 (1)

Table 2. *Selected geometric parameters* (Å, °)

C2—S1	1.722 (4)	C16—C5	1.500 (4)
C5—S1	1.734 (3)	C7—N6	1.348 (4)
N3—C2	1.356 (3)	C8—C7	1.493 (6)
N6—C2	1.340 (4)	O9—C7	1.248 (5)
C4—N3	1.405 (3)	C11—C10	1.517 (3)
C10—N3	1.490 (3)	C13—C12	1.378 (3)
C5—C4	1.340 (3)	C14—C13	1.400 (3)
C12—C4	1.489 (4)	C15—C14	1.371 (4)
C5—S1—C2	91.1 (1)	C16—C5—C4	128.4 (3)
N3—C2—S1	110.9 (2)	C7—N6—C2	116.1 (3)
N6—C2—S1	128.3 (2)	C8—C7—N6	115.0 (4)
N6—C2—N3	120.7 (3)	O9—C7—N6	124.4 (3)
C4—N3—C2	113.5 (2)	O9—C7—C8	120.6 (4)
C10—N3—C2	123.6 (2)	C11—C10—N3	110.6 (2)
C10—N3—C4	122.9 (2)	C11—C10—C11^i	115.4 (3)
C5—C4—N3	112.8 (2)	C13—C12—C4	119.9 (1)
C12—C4—N3	120.9 (2)	C14—C13—C12	119.6 (2)
C12—C4—C5	126.3 (3)	C13—C12—C13^i	120.2 (3)
C4—C5—S1	111.7 (2)	C15—C14—C13	120.4 (3)
C16—C5—S1	119.9 (2)	C14—C15—C14^i	119.9 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71377 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1085]

References

De Kimpe, N., Boelens, M. & Declercq, J.-P. (1993). *Tetrahedron*. In the press.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175-189. Oxford Univ. Press.

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Intramolecular Interactions in Dimethyl 2,2′-Bipyridine-3,3′-dicarboxylate

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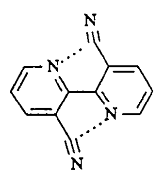
Abstract

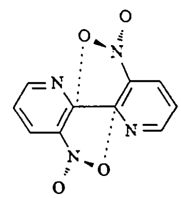
The title compound crystallizes from acetone with the pyridine rings arranged at 53° to each other in a *trans* conformation. There are intramolecular interactions between the alkoxy O atoms of the ester groups and the C2 atoms of the opposite rings, similar to those observed in the 3,3′-dinitro analogue. There are no significant intramolecular interactions between ring N atoms and ester carbonyl C atoms, although similar 1,5 interactions have been observed in other cases.

Comment

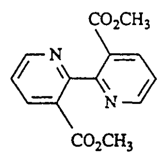
Intramolecular interactions in 3,3′-disubstituted 2,2′-bipyridines control the conformations observed in the solid state. In the dinitrile (1), attractive interactions between each pyridine N atom and the nitrile C atom of the opposite ring lead to the molecule adopting a *trans* conformation with an angle of only 23.6 (1)° between the best planes of the two heterocyclic rings. These short N···C contacts have been proposed as a model for an early stage in the addition of a nucleophile to a nitrile group. Indeed, the molecule shows in-plane distortions that widen the angle of approach of the nucleophilic centre to C≡N to 108° (Baxter, Connor, Povey & Wallis, 1991). In contrast, in the dinitro analogue (2), intramolecular interactions between the nitro O atoms and the electron-deficient C2 atoms of the opposite rings lead the molecule to deviate much further from a *trans* coplanar conformation. In this case, the inter-ring angle is 42.9 (1)° (Rice, Wallis & Povey, 1992). Although intramolecular interactions between the amino N-atom lone pairs and nitro groups have been observed in *peri*-substituted naphthalenes (Egli, Wallis & Dunitz, 1986), in (2) each pyridine N atom is only just in van der Waals contact with the nitro N atom attached to the opposite ring and, more significantly, the axes of the N-atom lone pairs are very poorly aligned for interaction with the nitro groups.



(1)



(2)



(3)

We have determined the X-ray crystal structure of the 3,3′-dicarboxylic ester (3) to investigate whether replacement of the nitro groups of (2) with more electrophilic ester groups induces a return to the type of interaction seen in (1). There are many examples of attractive interactions between electron-rich N atoms and carbonyl groups (Bürgi, Dunitz & Shefter, 1973; Schweizer, Procter, Kaftory & Dunitz, 1978).

The molecular conformation of (3) is illustrated in Figs. 1 and 2. Only half of the molecule is crystallographically unique; the two substituted pyridine rings are related by a twofold axis parallel to the *b* axis of the unit cell. The molecular conformation resembles that of the dinitro analogue (2) rather than the dinitrile (1). Thus, there are intramolecular interactions between the two halves of the molecule *via* ester O atoms and the ring C2 atoms, while the pyridine N atoms and carbonyl C atoms are only just in van der Waals contact.

The best planes through the two pyridine rings lie at 53.2 (1)° from the *trans* coplanar conformation. The rings are very slightly folded about the C3···C6 vector, but the maximum deviation of a ring atom from the best plane is very small [C6 = 0.009 (2) Å]. The ester groups lie at 39.7 (1)° to their respective pyridine rings, so that the alkoxy O atom of each

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