Experimental

Crystal data

$C_6H_{10}N_2S_2$
$M_r = 174.29$
Monoclinic
$A2/a$
$a = 10.653\ (1)$ Å
$b = 7.2936\ (6)$ Å
$c = 10.6398\ (9)$ Å
$\beta = 95.26\ (1)°$
$V = 823.2\ (1)$ Å^3
$Z = 4$

$D_x = 1.406$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 23 reflections
$\theta = 38–44°$
$\mu = 5.20$ mm^{-1}
$T = 293$ K
Needle shaped crystals
$0.25 \times 0.20 \times 0.13$ mm
Dark red

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1710 measured reflections
770 independent reflections
731 observed reflections $[I > 2.5\sigma(I)]$

$\theta_{max} = 69.71°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 12$
2 standard reflections
frequency: 66.67 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.037$
$wR = 0.07$
$S = 1.167$
714 reflections
67 parameters refined
$w = 1/[\sigma^2(F) + 0.0035F^2]$
$(\Delta/\sigma)_{max} = 0.783$
$\Delta\rho_{max} = 0.294$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Extinction correction: Zachariasen (1967)
Extinction coefficient: $g = 3.4\ (5) \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

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

The origin is located at a centre of symmetry on the glide plane *a*.
$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
S	0.11142 (4)	0.18040 (6)	0.05913 (4)	0.0460 (6)
C1	0.1977 (1)	0.3686 (3)	0.0442 (1)	0.0331 (9)
C2	0.2460 (3)	0.6922 (3)	0.0694 (3)	0.057 (1)
C3	0.0912 (2)	0.5405 (4)	0.2013 (2)	0.058 (1)
N	0.1807 (1)	0.5247 (2)	0.1041 (1)	0.0425 (9)

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

S—C1	1.668 (2)	C2—N	1.470 (3)
C1—N	1.325 (2)	C2—C2^{i}	1.487 (4)
C1—C1^{i}	1.523 (2)	C3—N	1.473 (3)
S—C1—N	124.1 (1)	C1—N—C2	120.3 (2)
S—C1—C1^{i}	120.0 (1)	C1—N—C3	122.0 (2)
N—C1—C1^{i}	115.9 (2)	C2—N—C3	117.6 (2)
N—C2—C2^{i}	108.7 (2)		

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

Crystals were prepared by Dr P. C. Servaas according to the literature procedure described by Isaksson, Liljefors & Sandström (1981). Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CELCON* program comparable to *Xtal LATCON* (Hall, Flack & Stewart, 1992). Data reduction: *Xtal ADDREF, SORTRF*. Structure solved by the heavy-atom method. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *Xtal BONDLA, CIFIO*.

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 71346 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1061]

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Acta Cryst. (1993). C49, 1976–1978

Structure of Dimethyl 2-[*o*-(3,5-Dimethyl-1-pyrazolyl)anilino]-3-methoxymaleate

NICOLA SARDONE AND ROBERTA OBERTI

CNR, Centro di Studio per la Cristallochimica e la Cristallografia, Via Bassi 4, I 27100 Pavia, Italy

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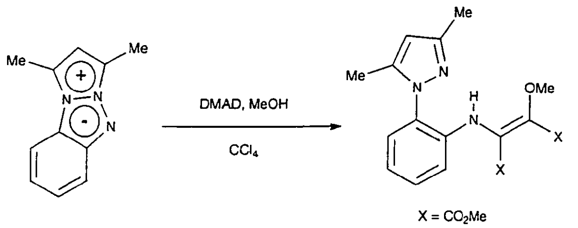
Abstract

In the title compound the pyrazole and benzene rings form a dihedral angle of 64.5 (1)°. Neither ring deviates significantly from planarity. There is an intramolecular hydrogen bond between atom N12 and atom O23 [N12···O23 2.682 (4) Å, N12—H12···O23 102.9 (2)°]; all other bond distances and angles are within the expected ranges.

Comment

This work is part of a more complex study on the chemistry of the Ramsden's Class *B* heteropentalenes. The title compound is formed by thermal addition from the reaction of heteropentalene (1) with an equimolar amount of dimethylacetylenedicarboxylate (DMAD) in the presence of methanol (5:1 molar ratio), which acts as a proton and methoxy source; the reaction proceeds directly to the stable enamine (2). The structural investigation was performed in order to identify the reaction product (2). Details on the chemical problem and the synthesis can be found in Albini, Bettinetti & Minoli (1983).



(1) (2)

All bond distances and angles are within the expected ranges (Allen *et al.*, 1987). The pyrazole and benzene rings form a dihedral angle of 64.5 (1)°. Neither ring deviates significantly from planarity. There is an intramolecular hydrogen bond between atom N12 and atom O23 [N12···O23 2.682 (4) Å, N12—H12···O23 102.9 (2)°], but no intermolecular hydrogen-bonding interactions are present.

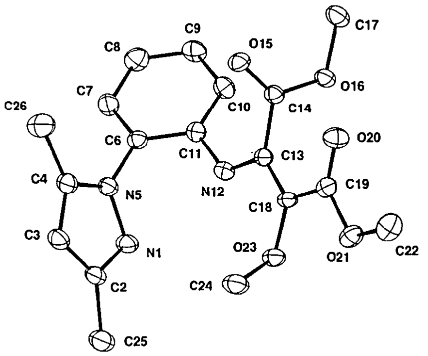


Fig. 1. Molecular structure and atomic numbering of (2). The thermal ellipsoids are drawn at 50% probability; H atoms are omitted.

Experimental

Crystal data

$C_{18}H_{21}N_3O_5$
$M_r = 359.38$
Monoclinic
$P2_1/c$
$a = 12.575\ (1)$ Å
$b = 8.489\ (1)$ Å
$c = 17.867\ (2)$ Å
$\beta = 92.76\ (1)°$
$V = 1905.1\ (3)$ Å^3
$Z = 4$
$D_x = 1.2530$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 35 reflections
$\theta = 3\text{–}22°$
$\mu = 0.087$ mm^{-1}
$T = 293$ K
Prism
0.06 × 0.05 × 0.05 mm
Yellow
Crystal source: slow evaporation of cyclohexane

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: spherical
$T_{\min} = 0.999$, $T_{\max} = 1.000$
1784 measured reflections
1784 independent reflections

1421 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 20°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 180 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.047$
$S = 0.9575$
1421 reflections
236 parameters
H-atom parameters not refined
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.22$
$\Delta\rho_{\max} = 0.317$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Extinction correction: Zachariasen (1967)
Extinction coefficient: 2268 (84)
Atomic scattering factors from *International Tables for X-ray Crystallography* [1974, Vol. IV, Tables 2.2A, 2.3.1 (N, C, O), 2.2C (H)]

The coordinates of the H atoms were calculated at convergance with *PARST* (Nardelli, 1983) and inserted with an overall $B = 5$ Å^2 but not allowed to vary in the subsequent least-squares cycles. Data collection: locally modifed Philips PW1100 software. Cell refinement: Philips *LAT* routine. Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: locally modifed *ORFLS* (Busing, Martin & Levy, 1962). Molecular graphics: *ORTEP*II (Johnson, 1976); *SCHAKAL* (Keller, 1988). Software used to prepare material for publication: *PARSTCIF* (Nardelli, 1992).

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

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

	x	y	z	$U_{\rm eq}$
N1	0.1516 (3)	−0.2953 (4)	−0.1434 (2)	0.0612 (15)
C2	0.0710 (3)	−0.3790 (5)	−0.1196 (2)	0.0570 (16)
C3	−0.0149 (3)	−0.2820 (5)	−0.1068 (3)	0.0662 (17)
C4	0.0144 (3)	−0.1333 (5)	−0.1243 (3)	0.0598 (16)
N5	0.1145 (2)	−0.1435 (4)	−0.1473 (2)	0.0510 (13)
C6	0.1861 (3)	−0.0198 (5)	−0.1640 (2)	0.0490 (14)
C7	0.1687 (3)	0.0714 (6)	−0.2266 (3)	0.0652 (18)
C8	0.2376 (4)	0.1935 (5)	−0.2423 (2)	0.0714 (18)
C9	0.3248 (3)	0.2196 (5)	−0.1949 (3)	0.0666 (19)
C10	0.3446 (3)	0.1265 (5)	−0.1328 (2)	0.0568 (17)
C11	0.2750 (3)	0.0061 (5)	−0.1157 (2)	0.0496 (15)
N12	0.2908 (2)	−0.0930 (4)	−0.0532 (2)	0.0530 (13)
C13	0.3234 (3)	−0.0521 (5)	0.0181 (2)	0.0438 (15)
C14	0.3338 (3)	0.1210 (5)	0.0344 (2)	0.0483 (15)
O15	0.2589 (2)	0.2072 (3)	0.0371 (2)	0.0651 (11)
O16	0.4355 (2)	0.1663 (3)	0.0412 (2)	0.0546 (10)
C17	0.4512 (4)	0.3321 (5)	0.0551 (3)	0.0717 (19)
C18	0.3367 (3)	−0.1612 (4)	0.0715 (2)	0.0469 (14)
C19	0.3642 (3)	−0.1214 (5)	0.1495 (2)	0.0523 (16)
O20	0.3667 (2)	0.0116 (3)	0.1740 (2)	0.0701 (12)

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]

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Acta Cryst. (1993). C**49**, 1978–1980

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

JEAN-PAUL DECLERCQ*

Université Catholique de Louvain, Laboratoire de Chimie Physique et de Cristallographie, 1 Place Louis Pasteur, B 1348 Louvain-la-Neuve, Belgium

NORBERT DE KIMPE AND MARC BOELENS

Department of Organic Chemistry, Faculty of Agricultural and Applied Biological Sciences, University of Gent, Coupure Links 653, B 9000 Gent, Belgium

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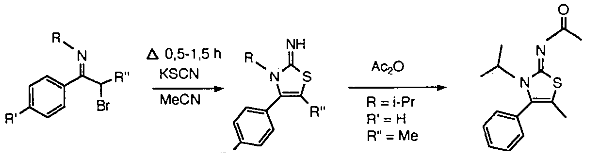
Abstract

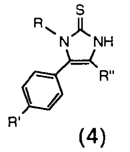
The crystal structure determination of $C_{15}H_{18}N_2OS$ allows the unambiguous identification of the reaction product of an α-bromoketimine with potassium thiocyanate.

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.



(1) (2) (85–100%) (3) (66–70%)



(4)

Acetylation of the heterocyclic compound, resulting from the reaction of *N*-(2-bromo-1-phenyl-1-propylid-