(Sheldrick, 1990). *SHELXL93* (Sheldrick, 1993) was used to refine the structure. Anisotropic displacement parameters were used for all non-H atoms. H atoms bonded to tertiary and aromatic C atoms were fixed in calculated positions, the H atoms in the hydroxy groups were located from a $\Delta\rho$ map and the remaining H atoms were refined with the restraint of a fixed angle and distance to the non-H atoms. The absolute configuration was chosen so as to be in agreement with the known absolute configuration of (*S*)-mandelic acid, the choice being supported by a Flack (1983) parameter of $\chi = -0.35\,(17)$. Although the compound contains both enantiomers of the 1-phenylethylammonium ion, it contains only the *S* form of the mandelate ion. Consequently the salt cannot crystallize in a centrosymmetric space group.

I am grateful to Mr Flemming Hansen for help with the experimental crystallographic work and Dr Sine Larsen for valuable discussions. Support from The Carlsberg Foundation is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AB1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
Brianso, M. C., Leclercq, M. & Jacques, F. (1979). *Acta Cryst.* B**35**, 2751–2753.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Johnson, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
Larsen, S. & Lopez de Diego, H. (1993). *Acta Cryst.* B**49**, 303–309.
Lopez de Diego, H. (1994). *Acta Chem. Scand.* **48**, 306–311.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

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Structures of Pyrazolo[1,5-*a*]pyridine Derivatives

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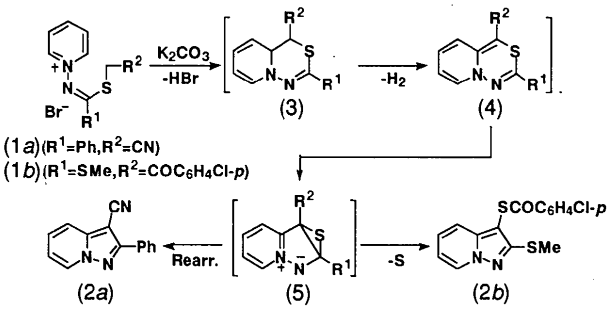
Abstract

The pyrazolo[1,5-*a*]pyridine skeletons of 2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile, $C_{14}H_9N_3$ (2*a*), and *S*-2-methylthiopyrazolo[1,5-*a*]pyridin-3-yl *p*-chlorothiobenzoate, $C_{15}H_{11}ClN_2OS_2$ (2*b*), are planar [maximum deviation 0.019 (3) Å for (2*a*) and 0.011 (5) Å for (2*b*)]. The pyrazolo[1,5-*a*]pyridine skeleton of compound (2*b*), in which the 2- and 3-substituents are bonded to the pyrazole ring by two long C—S bonds, shows no significant distortion, while in (2*a*), with the 2-phenyl and the 3-cyano groups, considerable changes are seen in the bond angles resulting from the severe steric interaction accompanied by the resonance effect between the pyrazolo[1,5-*a*]pyridine and the phenyl group.

Comment

The present study was undertaken to confirm the chemical structures of the title compounds, (2*a*) and (2*b*), and to determine their geometrical characteristics, which are undiscernible from their formation paths. Structural data for pyrazolo[1,5-*a*]pyridine derivatives are scarce.



The pyrazolo[1,5-*a*]pyridine rings in these molecules are almost planar [maximum deviation 0.019 (3) Å for (2*a*) and 0.011 (5) Å for (2*b*)] and constitute bicyclic 10π-electron aromatic systems. The bond distances and angles for (2*b*) are very similar to those of the INDO-optimized geometry for the parent pyrazolo[1,5-*a*]pyridine (Catalan *et al.*, 1988), except for the N(1)—N(2) bond length (1.3253 Å in the latter) and the N(1)—N(2)—C(1) angle (104.1° in the latter). Furthermore, the angle S(1)—C(1)—N(2) in (2*b*) is very similar to the angle S(1)—C(1)—C(2), and the angle S(2)—C(2)—C(1) is also very similar to the angle S(2)—C(2)—C(3), indicating the absence of any steric interaction between their substituents. The absence of such interaction must be caused by the two long C(1)—S(1) and C(2)—S(2) bonds. On the other hand, the geometry of the pyrazole moiety of (2*a*) is somewhat different from that of (2*b*). Owing to the extension of the conjugated system between the 2-phenyl group and the pyrazolo[1,5-*a*]pyridine ring [the dihedral angle is 6.3 (2)°] in (2*a*), a severe repulsion between the 2-phenyl and the 3-cyano groups is induced, as seen in the increase of the three bond angles C(2)—C(1)—C(8), C(1)—C(2)—C(14) and C(1)—C(8)—C(13), and in the deviation of the 2-cyano group from the plane of the ring.

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The geometry of the pyrazolo[1,5-*a*]pyridine skeleton in (2*b*) is also similar to that of 2-acetyl-3-amino-5-ethylthieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridine (Kakehi *et al.*, 1990).

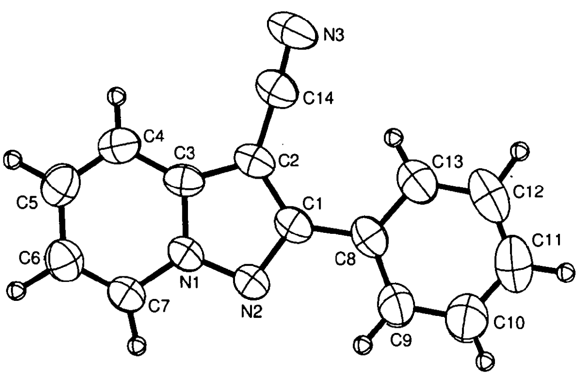

Fig. 1. An *ORTEP* (Johnson, 1965) view of compound (2*a*) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

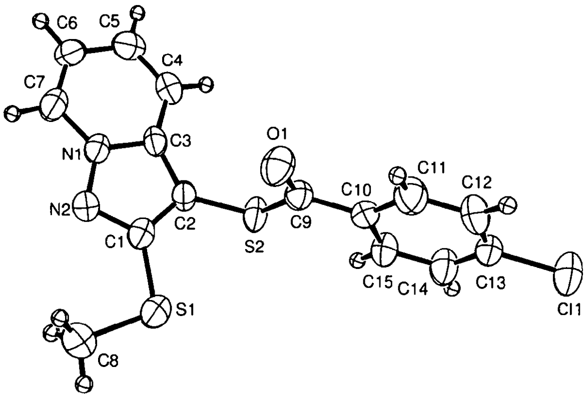

Fig. 2. An *ORTEP* (Johnson, 1965) view of compound (2*b*) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Chloroform solutions (40 ml) of 1-[2-(substituted methylthio)methyleneamino]pyridinium bromides [(1*a*) or (1*b*), 2 mmol], readily obtainable from the reactions of pyridinium thiobenzoylaminide with bromoacetonitrile or pyridinium (methylthio)thiocarbonylaminide with *p*-chlorophenacyl bromide, were treated with potassium carbonate (5 g) at room temperature for 1 d. After the removal of insoluble inorganic substances, each reaction solution was concentrated under reduced pressure and the residue was separated by column chromatography on alumina using hexane, ether and then chloroform. The concentration of the combined chloroform layers at reduced pressure provided (2*a*) (0.394 mg, 90%) (Kakehi, Ito, Nagata, Kinoshita & Kakinuma, 1987) or (2*b*) (582 mg, 87%) (Kakehi, Ito, Ito, Yotuya & Nagata, 1985). For X-ray analysis, compounds (2*a*) and (2*b*) were recrystallized from chloroform–ethanol to give colourless needles.

Compound (2*a*)

Crystal data

$C_{14}H_9N_3$
$M_r = 219.25$
Monoclinic
$P2_1/c$
$a = 5.506$ (1) Å
$b = 9.754$ (2) Å
$c = 20.339$ (2) Å
$\beta = 91.19$ (2)°
$V = 1092.1$ (3) Å^3
$Z = 4$
$D_x = 1.333$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 18.35$–19.78°
$\mu = 0.077$ mm^{-1}
$T = 295$ K
Needle
0.72 × 0.36 × 0.24 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: none
2931 measured reflections
2660 independent reflections
1262 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.038$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 12$
$l = -25 \rightarrow 26$
3 standard reflections monitored every 150 reflections
intensity variation: −0.5%

Refinement

Refinement on *F*
$R = 0.047$
$wR = 0.053$
$S = 1.57$
1262 reflections
191 parameters
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}

Extinction correction: analytical
Extinction coefficient: 0.10845×10^{-4}
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) *for* (2*a*)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$B_{\rm eq}$
N(1)	0.6807 (3)	0.1750 (2)	0.5045 (1)	3.5 (1)
N(2)	0.6798 (4)	0.0919 (2)	0.4508 (1)	3.8 (1)
N(3)	−0.0149 (4)	0.3791 (3)	0.4107 (1)	6.1 (1)
C(1)	0.4853 (4)	0.1323 (3)	0.4146 (1)	3.7 (1)
C(2)	0.3624 (4)	0.2403 (3)	0.4461 (1)	3.9 (1)
C(3)	0.4917 (4)	0.2674 (3)	0.5047 (1)	3.7 (1)
C(4)	0.4739 (5)	0.3576 (3)	0.5579 (2)	4.6 (1)
C(5)	0.6451 (6)	0.3529 (3)	0.6068 (2)	4.9 (2)
C(6)	0.8389 (5)	0.2586 (3)	0.6043 (2)	4.7 (1)
C(7)	0.8552 (5)	0.1701 (3)	0.5538 (1)	4.0 (1)
C(8)	0.4326 (5)	0.0633 (3)	0.3517 (1)	4.0 (1)
C(9)	0.5948 (6)	−0.0309 (4)	0.3280 (2)	5.8 (2)
C(10)	0.5479 (7)	−0.1010 (5)	0.2699 (3)	7.3 (2)
C(11)	0.3406 (7)	−0.0779 (4)	0.2338 (2)	6.6 (2)
C(12)	0.1783 (7)	0.0161 (4)	0.2561 (2)	6.4 (2)
C(13)	0.2215 (6)	0.0854 (4)	0.3149 (2)	5.5 (2)
C(14)	0.1512 (5)	0.3161 (3)	0.4253 (1)	4.5 (1)

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

N(1)—N(2)	1.360 (3)	C(3)—C(4)	1.400 (4)
N(1)—C(3)	1.377 (3)	C(4)—C(5)	1.358 (4)
N(1)—C(7)	1.375 (3)	C(5)—C(6)	1.410 (4)

N(2)—C(1)	1.347 (3)	C(6)—C(7)	1.346 (4)
C(1)—C(2)	1.414 (3)	C(1)—C(8)	1.468 (4)
C(2)—C(3)	1.401 (4)	C(2)—C(14)	1.434 (4)
N(2)—N(1)—C(3)	113.2 (2)	C(4)—C(5)—C(6)	120.6 (3)
N(2)—N(1)—C(7)	123.7 (2)	C(5)—C(6)—C(7)	120.6 (3)
C(3)—N(1)—C(7)	122.5 (2)	N(1)—C(7)—C(6)	118.5 (3)
N(1)—N(2)—C(1)	104.8 (2)	N(2)—C(1)—C(8)	118.9 (2)
N(2)—C(1)—C(2)	110.6 (2)	C(2)—C(1)—C(8)	130.4 (2)
C(1)—C(2)—C(3)	106.7 (2)	C(1)—C(2)—C(14)	130.1 (3)
N(1)—C(3)—C(2)	104.2 (2)	C(3)—C(2)—C(14)	123.2 (3)
N(1)—C(3)—C(4)	118.6 (2)	C(1)—C(8)—C(9)	119.6 (2)
C(2)—C(3)—C(4)	137.2 (2)	C(1)—C(8)—C(13)	123.2 (3)
C(3)—C(4)—C(5)	119.1 (3)		

Compound (2*b*)

Crystal data

$C_{15}H_{11}ClN_2OS_2$
$M_r = 334.84$
Monoclinic
$P2_1/c$
$a = 16.940$ (2) Å
$b = 5.680$ (1) Å
$c = 17.388$ (1) Å
$\beta = 115.880$ (6)°
$V = 1505.4$ (4) Å^3
$Z = 4$
$D_x = 1.477$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.02$–$17.92°$
$\mu = 0.517$ mm^{-1}
$T = 293$ K
Needle
0.54 × 0.20 × 0.16 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: none
3935 measured reflections
3810 independent reflections
1522 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.033$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 7$
$l = -22 \rightarrow 18$
3 standard reflections monitored every 150 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.043$
$wR = 0.046$
$S = 1.29$
1522 reflections
235 parameters
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Extinction correction: analytical
Extinction coefficient: 0.65716×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2*b*)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cl(1)	−0.04162 (9)	−0.3077 (3)	0.6241 (1)	6.54 (7)
S(1)	0.23187 (8)	0.5973 (3)	0.39629 (9)	4.96 (6)
S(2)	0.29709 (8)	0.1626 (2)	0.54622 (8)	3.91 (5)
O(1)	0.2612 (2)	0.4724 (6)	0.6397 (2)	4.7 (2)
N(1)	0.4683 (2)	0.6488 (6)	0.5680 (2)	3.2 (1)
N(2)	0.4006 (2)	0.7302 (6)	0.4943 (2)	3.4 (1)
C(1)	0.3360 (3)	0.5759 (8)	0.4817 (3)	3.3 (2)
C(2)	0.3601 (3)	0.4000 (8)	0.5431 (3)	3.4 (2)
C(3)	0.4475 (3)	0.4481 (8)	0.6002 (3)	3.8 (2)
C(4)	0.5119 (3)	0.3497 (9)	0.6751 (3)	3.8 (2)
C(5)	0.5920 (3)	0.4529 (10)	0.7136 (3)	4.2 (2)
C(6)	0.6108 (3)	0.6585 (10)	0.6790 (3)	4.0 (2)
C(7)	0.5494 (3)	0.7520 (9)	0.6063 (3)	3.9 (2)
C(8)	0.2426 (5)	0.8474 (13)	0.3387 (4)	5.5 (3)
C(9)	0.2423 (3)	0.2828 (8)	0.6046 (3)	3.4 (2)
C(10)	0.1730 (3)	0.1306 (8)	0.6093 (3)	3.2 (2)
C(11)	0.1333 (3)	0.1967 (11)	0.6602 (3)	4.7 (2)
C(12)	0.0676 (3)	0.0614 (11)	0.6652 (3)	4.9 (3)
C(13)	0.0421 (3)	−0.1398 (10)	0.6187 (3)	4.1 (2)
C(14)	0.0808 (3)	−0.2140 (10)	0.5681 (4)	4.6 (2)
C(15)	0.1457 (3)	−0.0780 (9)	0.5634 (3)	3.9 (2)

Table 4. *Selected geometric parameters* (Å, °) *for* (2*b*)

N(1)—N(2)	1.375 (5)	C(3)—C(4)	1.400 (6)
N(1)—C(3)	1.382 (5)	C(4)—C(5)	1.357 (6)
N(1)—C(7)	1.369 (5)	C(5)—C(6)	1.412 (7)
N(2)—C(1)	1.343 (5)	C(6)—C(7)	1.347 (7)
C(1)—C(2)	1.388 (6)	S(1)—C(1)	1.745 (4)
C(2)—C(3)	1.403 (6)	S(2)—C(2)	1.735 (4)
N(2)—N(1)—C(3)	113.5 (3)	C(3)—C(4)—C(5)	119.5 (5)
N(2)—N(1)—C(7)	124.2 (4)	C(4)—C(5)—C(6)	120.7 (5)
C(3)—N(1)—C(7)	122.3 (4)	C(5)—C(6)—C(7)	120.0 (5)
N(1)—N(2)—C(1)	102.8 (3)	N(1)—C(7)—C(6)	119.2 (5)
N(2)—C(1)—C(2)	113.5 (4)	S(1)—C(1)—N(2)	122.9 (3)
C(1)—C(2)—C(3)	105.6 (4)	S(1)—C(1)—C(2)	123.6 (3)
N(1)—C(3)—C(2)	104.5 (4)	S(2)—C(2)—C(1)	127.3 (3)
N(1)—C(3)—C(4)	118.2 (4)	S(2)—C(2)—C(3)	127.0 (3)
C(2)—C(3)—C(4)	137.2 (4)		

Azimuthal scans of several reflections indicated no need for an absorption correction. The H atoms were located from a difference Fourier map and refined isotropically. The structure was solved by direct methods (*SIR*88; Burla *et al.*, 1989) utilizing the *TEXSAN* package (Molecular Structure Corporation, 1985).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Catalan, J., de Paz, J. L. G., Yanez, M., Amat-Guerri, F., Houriet, R., Rolli, R., Zehringer, R., Oelhafen, P., Taft, R. W., Anvia, F. & Qian, J. H. (1988). *J. Am. Chem. Soc.* **110**, 2699–2705.

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

Kakehi, A., Ito, S., Ito, M., Yotuya, T. & Nagata, K. (1985). *Bull. Chem. Soc. Jpn*, **58**, 1432–1442.

Kakehi, A., Ito, S., Nagata, K., Kinoshita, N. & Kakinuma, N. (1987). *Chem. Pharm. Bull.* **35**, 156–169.

Kakehi, A., Ito, S., Sakurai, T., Urushido, K., Isawa, H. & Takashima, T. (1990). *Chem. Pharm. Bull.* **38**, 2667–2675.

Molecular Structure Corporation (1985). *TEXSAN*. *TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77831, USA.