Table 3. *Bond distances* (Å) *and angles* (°) *in* (Hthiamin)Cl$(SO_4)_{0\cdot5}$.H_2O

S—C(2)	1·679 (4)	C(4′)—C(5′)	1·422 (4)
C(2)—N(3)	1·318 (4)	C(5′)—C(6′)	1·361 (4)
N(3)—C(4)	1·388 (4)	N(1′)—C(6′)	1·343 (4)
S—C(5)	1·723 (3)	N(1′)—C(2′)	1·345 (4)
C(4)—C(5)	1·358 (4)	C(2′)—N(3′)	1·317 (4)
C(5)—C(51)	1·500 (6)	N(3′)—C(4′)	1·355 (4)
C(51)—C)52)	1·535 (6)	C(2′)—C(21′)	1·485 (6)
C(52)—O(53)	1·405 (6)	C(4′)—N(41′)	1·328 (4)
C(4)—C(41)	1·484 (4)	S(1)—O(1)	1·454 (3)
N(3)—C(35′)	1·502 (4)	S(1)—O(2)	1·445 (4)
C(5′)—C(35′)	1·487 (4)		
C(5)—S—C(2)	91·4 (1)	C(4′)—C(5′)—C(35′)	122·7 (3)
N(3)—C(2)—S	111·9 (3)	C(4′)—C(5′)—C(6′)	116·3 (3)
C(4)—N(3)—C(2)	114·7 (3)	N(1′)—C(6′)—C(5′)	120·6 (3)
C(35′)—N(3)—C(2)	123·7 (3)	C(2′)—N(1′)—C(6′)	120·7 (3)
C(35′)—N(3)—C(4)	121·5 (3)	N(3′)—C(2′)—N(1′)	122·6 (3)
C(5)—C(4)—N(3)	111·4 (3)	C(21′)—C(2′)—N(1′)	117·9 (3)
C(41)—C(4)—N(3)	120·5 (3)	C(21′)—C(2′)—N(3′)	119·5 (3)
C(41)—C(4)—C(5)	128·1 (3)	C(4′)—N(3′)—C(2′)	118·0 (3)
C(4)—C(5)—S	110·6 (3)	N(3′)—C(4′)—C(5′)	121·8 (3)
C(51)—C(5)—S	122·2 (3)	N(41′)—C(4′)—C(5′)	122·1 (3)
C(51)—C(5)—C(4)	127·0 (3)	N(41′)—C(4′)—N(3′)	116·1 (3)
C(52)—C(51)—C(5)	111·9 (3)	O(2)—S(1)—O(1)	107·1 (2)
O(53)—C(52)—C(51)	112·9 (3)	O(1)—S(1)—O(1)	107·8 (2)
C(6′)—C(5′)—C(35′)	120·9 (3)	O(2)—S(1)—O(2)	111·9 (2)

pyrimidine moiety and electrostatic contacts with the thiazolium ring have been thought to constitute a determinant factor of the conformation of the molecule. In our case, the bridging interaction of this chloride results in torsion angles (Pletcher & Sax, 1972) $\varphi_T = 1{\cdot}30°$ and $\varphi_P = 76{\cdot}2°$, corresponding to the common *F* conformation (Shin, Pletcher, Blank & Sax, 1977).

Bond distances and bond angles (Table 3) within the thiamin unit are in accordance with those obtained in other thiamin structures in which the N(1′) position is protonated (Cramer, Maynard & Ibers, 1981). Both thiazolium and pyrimidine rings of the thiamin moiety are planar as shown by least-squares calculations (maximal deviations: 0·018 Å for the pyrimidine plane and 0·005 Å for the thiazolium plane). Bond distances and bond angles within the sulfate anion (Table 3) are comparable with those observed in other structures (Lanfredi, Pellinghelli & Tiripicchio, 1974; Weber, 1974). The slightly larger bond length obtained for S(1)—O(1) can be attributed to the strong O—N(1′) hydrogen bonds between this O and a neighboring pyrimidine. The geometry about the S atom is tetrahedral as indicated by the O—S—O angles which range from 107·1 (2) to 111·9 (2)°, similar to those reported previously (Lanfredi, Pellinghelli & Tiripicchio, 1974; Weber, 1974).

References

ARCHIBONG, E., ADEYEMO, A., AOKI, K. & YAMAZAKI, H. (1988). Private communication.

BRUCK, M. A. (1983). *PROCESS* program. Modified by M. J. CARRIE. Department of Chemistry, Univ. of Hawaii, USA.

CRAMER, R. E., KIRKUP, R. E. & CARRIE, M. J. (1988). *Inorg. Chem.* **27**, 123–130.

CRAMER, R. E., MAYNARD, R. B. & IBERS, J. A. (1981). *J. Am. Chem. Soc.* **103**, 76–81.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

LANFREDI, A. M. M., PELLINGHELLI, M. A. & TIRIPICCHIO, A. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 308–311.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PLETCHER, J. & SAX, M. (1972). *J. Am. Chem. Soc.* **94**, 3998–4005.

PLETCHER, J., SAX, M., YOO, C. S., CHU, J. & POWER, L. (1974). *Acta Cryst.* B**30**, 496–503.

PLETCHER, J., SAX, M., YOO, C. S., CHU, J. & WOOD, M. (1977). *J. Am. Chem. Soc.* **99**, 1396–1403.

PLETCHER, J., WOOD, M., BLANK, G., SHIN, W. & SAX, M. (1977). *Acta Cryst.* B**33**, 3349–3359.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHIN, W., PLETCHER, J., BLANK, G. & SAX, M. (1977). *J. Am. Chem. Soc.* **99**, 3491–3499.

WEBER, H. P. (1974). *Helv. Chim. Acta*, **57**(3), 623–630.

Acta Cryst. (1989). C**45**, 1902–1904

Structures of Aminopyrazole Derivatives

BY KENTARO YAMAGUCHI, AKIO OHSAWA, TERUMITSU KAIHOH, TAKASHI ITOH, MAMIKO OKADA, CHIKAKO KAWABATA AND HIROSHI IGETA

School of Pharmaceutical Sciences, Showa University 1-5-8, *Hatandai, Shinagawa-ku, Tokyo* 142, *Japan*

(*Received* 1 *February* 1989; *accepted* 29 *March* 1989)

Abstract. (I): 1-Amino-3-phenylpyrazole, $C_9H_9N_3$, $M_r = 159{\cdot}2$, monoclinic, $P2_1/n$, $a = 18{\cdot}729$ (1), $b = 5{\cdot}742$ (2), $c = 15{\cdot}807$ (2) Å, $\beta = 104{\cdot}39$ (1)°, $U = 1646{\cdot}7$ (7) Å^3, $Z = 8$, $D_x = 1{\cdot}285$ Mg m^{-3}, λ(Cu $K\alpha_1$) = 1·5405 Å, $\mu = 0{\cdot}658$ mm^{-1}, $F(000) = 672$, $T = 293$ K, final $R = 0{\cdot}053$ for 2715 observed reflexions.

0108-2701/89/121902-03$03.00

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

	x	y	z	B_{eq}
(I*A*)				
N(1*A*)	0·0775 (1)	0·2712 (2)	0·0451 (1)	3·59 (3)
N(2*A*)	0·0507 (1)	0·1642 (2)	0·1067 (1)	3·73 (3)
C(3*A*)	0·0531 (1)	0·3273 (2)	0·1678 (1)	3·43 (3)
C(4*A*)	0·0816 (1)	0·5357 (2)	0·1440 (1)	4·29 (4)
C(5*A*)	0·0962 (1)	0·4931 (2)	0·0651 (1)	4·17 (4)
N(6*A*)	0·0827 (1)	0·1589 (2)	−0·0315 (1)	4·24 (4)
C(7*A*)	0·0263 (1)	0·2773 (2)	0·2459 (1)	3·73 (4)
C(8*A*)	−0·0149 (1)	0·0794 (3)	0·2514 (1)	4·90 (5)
C(9*A*)	−0·0412 (1)	0·0383 (4)	0·3241 (1)	5·86 (6)
C(10*A*)	−0·0263 (1)	0·1924 (4)	0·3930 (1)	5·88 (6)
C(11*A*)	0·0147 (1)	0·3876 (4)	0·3887 (1)	5·80 (6)
C(12*A*)	0·0408 (1)	0·4305 (3)	0·3159 (1)	4·75 (4)
(I*B*)				
N(1*B*)	0·2000 (1)	0·6370 (2)	−0·1350 (1)	4·31 (3)
N(2*B*)	0·1976 (1)	0·7675 (2)	−0·0650 (1)	4·10 (3)
C(3*B*)	0·2566 (1)	0·9062 (2)	−0·0537 (1)	3·96 (4)
C(4*B*)	0·2952 (1)	0·8626 (3)	−0·1175 (1)	5·15 (5)
C(5*B*)	0·2573 (1)	0·6885 (3)	−0·1681 (1)	5·20 (3)
N(6*B*)	0·1474 (1)	0·4652 (3)	−0·1685 (1)	5·35 (4)
C(7*B*)	0·2743 (1)	1·0735 (2)	0·0183 (1)	5·35 (4)
C(8*B*)	0·2532 (1)	1·0363 (3)	0·0957 (1)	4·50 (4)
C(9*B*)	0·2707 (1)	1·1972 (3)	0·1627 (1)	5·34 (5)
C(10*B*)	0·3103 (1)	1·3940 (3)	0·1546 (1)	5·35 (5)
C(11*B*)	0·3316 (1)	1·4327 (3)	0·0789 (1)	5·22 (5)
C(12*B*)	0·3135 (1)	1·2750 (3)	0·0110 (1)	4·56 (4)
(II)				
N(1)	0·4342 (2)	0·0142 (1)	0·2356 (2)	3·54 (16)
N(2)	0·4582 (2)	−0·0463 (1)	0·2739 (2)	3·53 (16)
C(3)	0·3838 (2)	−0·0782 (1)	0·1666 (3)	3·31 (16)
C(4)	0·3149 (2)	−0·0375 (1)	0·0624 (3)	3·70 (16)
C(5)	0·3493 (2)	0·0214 (1)	0·1083 (3)	3·63 (16)
N(6)	0·4977 (2)	0·0628 (1)	0·3153 (3)	4·48 (17)
C(7)	0·3819 (2)	−0·1464 (1)	0·1672 (3)	3·43 (16)
C(8)	0·4730 (2)	−0·1810 (1)	0·2481 (3)	4·11 (16)
C(9)	0·4708 (3)	−0·2452 (1)	0·2439 (4)	4·74 (17)
C(10)	0·3773 (3)	−0·2762 (1)	0·1594 (4)	4·89 (17)
C(11)	0·2854 (3)	−0·2424 (1)	0·0814 (4)	5·06 (17)
C(12)	0·2874 (2)	−0·1784 (1)	0·0849 (4)	4·39 (17)
C(13)	0·3095 (3)	0·0832 (1)	0·0434 (5)	4·80 (17)

Table 2. *Bond lengths* (Å) *and angles* (°) *in the pyrazole rings*

	(I*A*)	(I*B*)	(II)
N(1)—C(5)	1·340 (2)	1·340 (3)	1·353 (4)
N(1)—N(2)	1·349 (2)	1·347 (2)	1·359 (3)
N(2)—C(3)	1·340 (2)	1·339 (2)	1·344 (3)
C(3)—C(4)	1·402 (2)	1·402 (2)	1·403 (4)
C(3)—C(7)	1·472 (2)	1·464 (2)	1·469 (4)
C(4)—C(5)	1·364 (3)	1·366 (3)	1·373 (4)
N(1)—N(6)	1·397 (2)	1·403 (2)	1·397 (4)
C(5)—C(13)			1·485 (5)
N(1)—N(2)—C(3)	104·5 (2)	104·3 (1)	103·9 (2)
N(2)—C(3)—C(4)	110·5 (1)	110·7 (1)	110·5 (2)
C(3)—C(4)—C(5)	105·5 (1)	105·5 (1)	106·5 (2)
C(4)—C(5)—N(1)	106·6 (1)	106·4 (1)	105·4 (2)
C(5)—N(1)—N(2)	112·7 (1)	113·0 (1)	113·4 (2)

(II): 1-Amino-5-methyl-3-phenylpyrazole, $C_{10}H_{11}N_3$, $M_r = 173{\cdot}2$, orthorhombic, *Pcab*, $a = 10{\cdot}945$ (2), $b = 21{\cdot}535$ (1), $c = 7{\cdot}619$ (1) Å, $U = 1795{\cdot}6$ (5) Å^3, $Z = 8$, $D_x = 1{\cdot}282$ Mg m^{-3}, λ(Cu $K\alpha_1$) = 1·5405 Å, $\mu = 0{\cdot}645$ mm^{-1}, $F(000) = 736$, $T = 293$ K, final $R = 0{\cdot}060$ for 1524 reflexions. N—NH$_2$ bond lengths are 1·397 (2), 1·403 (2) and 1·397 (4) Å for (I*A*), (I*B*) and (II), respectively. The amino nitrogen is indicated as having sp^3 character in both compounds.

Introduction. The title compounds were obtained from *N*-amination of the corresponding pyrazoles (Ohsawa, Kaihoh, Itoh, Okada, Kawabata, Yamaguchi & Igeta, 1988). The X-ray structure determination was undertaken to obtain general understanding of the structure of *N*-aminopyrazoles. It is interesting to investigate the nature of the N—NH$_2$ bond linkage because of the importance of the most characteristic property of azoles which is related to their *N*-substitution (Begtrup, Elguero, Faure, Camps, Estopá, Ilavský, Fruchier, Marzin & Mendoza, 1988).

Experimental. Intensity data collected from a crystal of dimensions 0·50 × 0·50 × 0·35 mm (I) and 0·50 × 0·40 × 0·20 mm (II). D_m not measured. Rigaku AFC5 four-circle diffractometer used with θ–2θ scan method, scan width (1·3 + 0·41tanθ)° and scan speed 16° min^{-1}. Lattice parameters obtained from least-squares analysis of 20 reflexions with 2θ values ranging from 54 to 60°. Out of 3291 (I) and 1823 (II) reflexions scanned within index range h −21–21, k 0–7, l 0–17 (I) and h 0–12, k 0–24, l 0–8 (II) up to $(\sin\theta)/\lambda \le 0{\cdot}59$ Å^{-1}, including 121 equivalent reflexions ($R_{\text{int}} = 0{\cdot}021$) in the case of (I), 2805 (I) and 1524 (II) unique reflexions classified as observed.

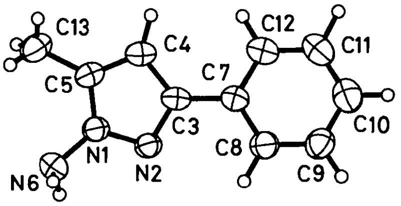

Fig. 1. *ORTEP* drawing (Johnson, 1965) of compound (II). Thermal ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

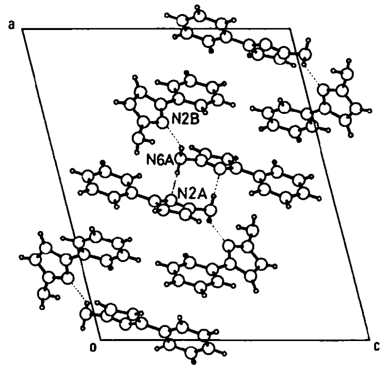

Fig. 2. Projection of the crystal structure of compound (I) along the *b* axis.

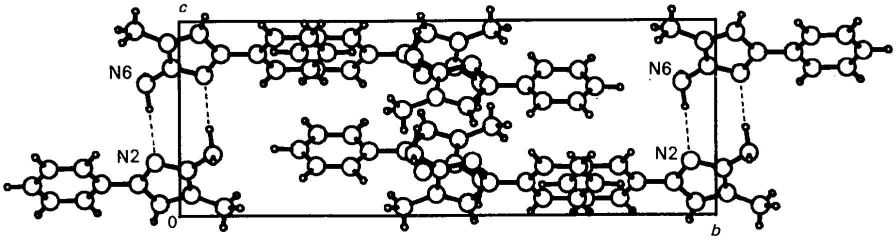

Fig. 3. Projection of the crystal structure of compound (II) along the *a* axis.

Three standard reflexions measured every 150 reflexions, no significant intensity variation. Intensities corrected for Lorentz and polarization factors, but absorption correction not applied.

Structure solved using program package *SAPI*85 (Yao, Zheng, Qian, Han, Gu & Fan, 1985) version of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms. The function minimized was $\sum w[|(|F_o|)^2 - (|F_c|)^2|]^2$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}02(F_o)^2]$, $\sigma(F_o)$ determined from counting statistics. All hydrogen atoms were located from the difference map and theoretical calculations. The initial thermal parameters were set at the equivalent isotropic thermal parameter of the bonded atoms. Final discrepancy indices $R = 0{\cdot}053$ (I) and 0·060 (II), $wR = 0{\cdot}064$ (I) and 0·068 (II), $\sum w\{[|(|F_o|)^2 - (|F_c|)^2|]^2/(N_r - N_v)\}^{1/2} = 1{\cdot}987$ (I) and 1·959 (II) for 2715 (I) and 1446 (II) reflexions with $F > \sigma(F)$. Maximum $\Delta/\sigma = 0{\cdot}36$ (I) and 0·56 (II) in the final least-squares cycle. Final difference Fourier map showed no residuals greater than 0·35 (I) and 0·42 (II) e Å^{-3}. All calculations performed using PANAFACOM computer with *RCRYSTAN* (Rigaku Corporation, 1985) X-ray analysis program system. The atomic scattering factors were those from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters for molecules (I*A*), (I*B*) and (II) are listed in Table 1 [two molecules are included in an asymmetric unit in the case of (I)].* The bond lengths and angles in the pyrazole rings are compared in Table 2. Fig. 1 shows the *ORTEP* drawing (Johnson, 1965) of compound (II) with atomic labeling. Figs. 2 and 3 are the *b*-axis (I) and *a*-axis (II) projections of the crystal structures. The bond lengths and angles in the pyrazole ring of these three molecules are almost consistent with each other. The rather long N(1)—N(6) distance of 1·397 (2) Å (I*A*), 1·403 (2) Å (I*B*) and 1·397 (4) Å (II) (*cf.* 1·35 Å for a single bond between an amino nitrogen and a 6-membered hetero aromatic carbon), and the definite sp^3-hybridized character of N(6) indicate the genuine single-bond nature of N(1)—N(6). The pyrazole rings are planar within experimental error for each compound indicating extensive electron delocalization. However, the C(4)—C(5) distances, 1·364 (3) Å (I*A*), 1·366 (3) Å (I*B*) and 1·373 (4) Å (II) indicate slightly localized electron density on this bond compared to the adjacent bond C(4)—C(3) [1·402 (2) Å (I*A*), (I*B*); 1·403 (4) Å (II)]. The torsion angles between the pyrazole and phenyl rings are 12·7° (I*A*), −27·3° (I*B*) and 14·6° (II). The hydrogen bonds N(2*A*)···N(6*A*) [3·105 (2) Å] and N(2*A*)···N(6*B*) [3·247 (2) Å] in compound (I) (Fig. 2), and N(2)···N(6) [3·190 (4) Å] in compound (II) (Fig. 3) are observed.

---

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52100 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

BEGTRUP, M., ELGUERO, J., FAURE, R., CAMPS, P., ESTOPÁ, C., ILAVSKÝ, D., FRUCHIER, A., MARZIN, C. & MENDOZA, J. (1988). *Magn. Reson. Chem.* **26** 134–151.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

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

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.

OHSAWA, A., KAIHOH, T., ITOH, T., OKADA, M., KAWABATA, C., YAMAGUCHI, K. & IGETA, H. (1988). *Chem. Pharm. Bull.* **36**(10), 3838–3848.

Rigaku Corporation (1985). *RCRYSTAN. X-ray Analysis Program System.* Rigaku Corporation, Tokyo, Japan.

YAO, J.-X., ZHENG, C.-D., QIAN, J.-Z., HAN, F.-S., GU, Y.-X. & FAN, H.-F. (1985). *SAPI85*. Program for the automatic solution of crystal structures from X-ray diffraction data. Institute of Physics, Academia Sinica, Beijing, People's Republic of China.