SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). *SHELXS84. Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

STANOVNIK, B. (1987). *New Approaches to the Synthesis of Bicyclic and Polycyclic Nitrogen-Containing Heterocycles*. Plenary Lecture, 6th International Conference on Organic Synthesis, Moscow, August 10–15 1986. IUPAC Special Publication. In the press.

STANOVNIK, B., STIBILJ, V., TIŠLER, M., LEBAN, I. & GOLIČ, L. (1986). Unpublished results.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VERČEK, B., STANOVNIK, B., TIŠLER, M. & ZRIMŠEK, Z. (1978). *Org. Prep. Proced. Int.* **10**, 293–295.

Acta Cryst. (1987). C**43**, 1814–1816

Structure of 6-Chloro-9,9-dimethyl-9*H*-imidazolo[1,2-*b*]pyrazolo[4,3-*d*]pyridazine

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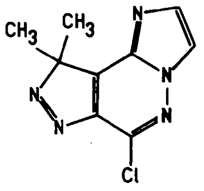
(*Received* 16 *March* 1987; *accepted* 21 *April* 1987)

Abstract. $C_9H_8ClN_5$, $M_r = 221{\cdot}6$, triclinic, $P\bar{1}$, $a = 5{\cdot}569\,(2)$, $b = 5{\cdot}712\,(2)$, $c = 16{\cdot}208\,(3)$ Å, $\alpha = 89{\cdot}95\,(2)$, $\beta = 93{\cdot}73\,(2)$, $\gamma = 106{\cdot}09\,(2)°$, $V = 494{\cdot}3$ Å^3, $Z = 2$, $D_m = 1{\cdot}50\,(5)$, $D_x = 1{\cdot}489$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}62$ cm^{-1}, $F(000) = 228$, $T = 293\,(1)$ K, final $R = 0{\cdot}044$ for 1298 reflexions. Bond lengths and angles lie within normal ranges. The imidazole ring is planar within experimental error, whereas the pyridazine and pyrazole rings deviate from planarity.

Introduction. The title compound (I) is obtained by a 1,3-diploar cycloaddition of 2-diazopropane to 6-chloroimidazo[1,2-*b*]pyridazine. The above reaction is highly regiospecific and proceeds as a cycloaddition across the C(7)—C(8) partially localized double bond of the pyridazine unit of the molecule. Since this is the first example of a new heterocyclic system, an X-ray analysis was undertaken in order to determine the orientation of the newly formed pyrazole moiety with respect to the imidazo[1,2-*b*]pyridazine system (Stanovnik, Kupper, Tišler, Leban & Golič, 1984).



(I)

Experimental. Density measured by flotation in chlorobenzene/CCl_4; colourless prisms, 0·53 × 0·46 × 0·29 mm; Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation (graphite monochromator), lattice parameters by a least-squares fit of θ values for 60 reflexions ($7 < \theta < 11°$); $\omega/2\theta$ scans, variable scan rate (min. 1·8, max. 20·1° min^{-1}), max. scan time 40 s, scan width (2θ) $(0{\cdot}8 + 0{\cdot}2\tan\theta)°$, aperture $(2{\cdot}5 + 0{\cdot}9\tan\theta)$ mm, background measured for 0·25 of scan time at each scan limit, $[\sin\theta/\lambda]_{\max}$ intensity measurements 0·64 Å^{-1}. Three reflexions monitored at intervals of 240 reflexions, no significant intensity decline (3·8%); data corrected for intensity variation and Lp effects, but absorption ignored; 4366 ($\pm h$, $\pm k$, $\pm l$) measured reflexions, 2049 unique [$R_{\rm int}(I) = 0{\cdot}040$ for 4365 contributing reflexions), 1298 observed (h −7/6, k −7/7, l 0/20) with $I > 3\sigma(I)$, $\sigma(I)$ based on counting statistics. Structure solution by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ with *SHELX76* (Sheldrick, 1976); final R and wR values: 0·044 and 0·057 with $w = 1{\cdot}04/[\sigma^2(F_o) + 0{\cdot}0008F_o^2]$; H atoms found from a difference synthesis and included in the constrained refinement, a common isotropic temperature factor U for H atoms refined to 0·063 (3) Å^2, $\Delta\rho$ within −0·13 and 0·13 e Å^{-3} in final difference map. At convergence max. and mean values of Δ/σ: 0·09 and 0·02. Scattering factors for Cl, N and C and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965). All calculations performed on the DEC 1091 computer at University Computer Centre, Ljubljana. *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used for data reduction and interpretation.

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Discussion. The final atomic parameters are in Table 1.* Bond lengths and angles are given in Table 2. Views of the molecule with the atomic numbering and of the molecular packing are presented in Figs. 1 and 2.

Table 1. *Fractional atomic coordinates* (×10^4 *for* Cl, N, C; ×10^3 *for* H) *and equivalent isotropic temperature factors* (Å^2 ×10^4) (*Hamilton*, 1959)

	x	*y*	*z*	U_{eq}
Cl	8125 (2)	5351 (2)	4236 (1)	647 (6)
N(1)	2258 (5)	10607 (5)	2367 (2)	448 (14)
C(2)	1588 (6)	11544 (6)	3063 (2)	502 (17)
C(3)	2599 (7)	10837 (6)	3764 (2)	525 (18)
N(4)	3974 (5)	9358 (5)	3514 (1)	410 (13)
N(5)	5315 (5)	8201 (5)	4015 (1)	461 (14)
C(6)	6436 (6)	6861 (6)	3625 (2)	420 (16)
C(6*A*)	6321 (6)	6620 (5)	2757 (2)	372 (15)
N(7)	7447 (5)	5201 (5)	2267 (2)	470 (14)
N(8)	6907 (5)	5495 (5)	1511 (2)	475 (15)
C(9)	5325 (6)	7218 (5)	1398 (2)	379 (15)
C(9*A*)	4997 (5)	7820 (5)	2271 (2)	345 (14)
C(9*B*)	3709 (6)	9267 (5)	2650 (2)	365 (15)
C(10)	6826 (7)	9415 (6)	0945 (2)	491 (18)
C(11)	2865 (7)	5878 (7)	0922 (2)	517 (18)
H(2)	62 (4)	1275 (3)	302 (2)	
H(3)	251 (4)	1111 (4)	433 (2)	
H(101)	839 (4)	1016 (4)	126 (2)	
H(102)	600 (4)	1068 (3)	93 (2)	
H(103)	715 (4)	895 (4)	39 (2)	
H(111)	201 (4)	442 (4)	122 (2)	
H(112)	184 (4)	704 (3)	89 (2)	
H(113)	320 (4)	538 (4)	40 (2)	

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cl—C(6)	1·714 (4)	C(9)—C(9*A*)	1·491 (5)
N(1)—C(2)	1·366 (5)	C(9)—C(10)	1·520 (4)
N(1)—C(9*B*)	1·320 (5)	C(9)—C(11)	1·530 (4)
C(2)—C(3)	1·347 (5)	C(9*A*)—C(9*B*)	1·401 (5)
C(3)—N(4)	1·365 (5)	C(2)—H(2)	0·99 (2)
N(4)—N(5)	1·359 (4)	C(3)—H(3)	0·93 (3)
N(4)—C(9*B*)	1·398 (4)	C(10)—H(101)	0·97 (2)
N(5)—C(6)	1·301 (5)	C(10)—H(102)	0·96 (2)
C(6)—C(6*A*)	1·409 (5)	C(10)—H(103)	0·97 (3)
C(6*A*)—N(7)	1·424 (5)	C(11)—H(111)	0·99 (2)
C(6*A*)—C(9*A*)	1·356 (5)	C(11)—H(112)	0·99 (2)
N(7)—N(8)	1·265 (5)	C(11)—H(113)	0·95 (3)
N(8)—C(9)	1·496 (5)		

C(2)—N(1)—C(9*B*)	104·2 (3)	N(7)—N(8)—C(9)	111·8 (3)
N(1)—C(2)—C(3)	112·9 (3)	N(8)—C(9)—C(9*A*)	101·7 (3)
C(2)—C(3)—N(4)	105·4 (3)	N(8)—C(9)—C(10)	107·4 (3)
C(3)—N(4)—N(5)	126·2 (2)	N(8)—C(9)—C(11)	108·4 (3)
C(3)—N(4)—C(9*B*)	106·5 (3)	C(9*A*)—C(9)—C(10)	112·3 (2)
N(5)--N(4)—C(9*B*)	127·3 (3)	C(9*A*)—C(9)—C(11)	113·2 (3)
N(4)—N(5)—C(6)	114·4 (2)	C(10)—C(9)—C(11)	113·0 (3)
Cl—C(6)—N(5)	115·8 (2)	C(6*A*)—C(9*A*)—C(9)	106·7 (3)
Cl—C(6)—C(6*A*)	120·4 (3)	C(6*A*)—C(9*A*)—C(9*B*)	118·6 (3)
N(5)—C(6)—C(6*A*)	123·8 (3)	C(9)—C(9*A*)—C(9*B*)	134·7 (3)
C(6)—C(6*A*)—N(7)	128·6 (3)	N(1)—C(9*B*)—N(4)	111·0 (3)
C(6)—C(6*A*)—C(9*A*)	120·6 (3)	N(1)—C(9*B*)—C(9*A*)	133·7 (3)
N(7)—C(6*A*)—C(9*A*)	110·7 (3)	N(4)—C(9*B*)—C(9*A*)	115·2 (3)
C(6*A*)—N(7)—N(8)	109·0 (3)		

The present study proves that the compound is a derivative of a novel heterocyclic system: 9*H*-imidazo[1,2-*b*]pyrazolo[4,3-*d*]pyridazine (Stanovnik, Kupper, Tišler, Leban & Golič, 1984). From an inspection of Table 2 it can be seen that the N(5)—C(6) [1·301 (5)] and N(7)—N(8) [1·265 (5) Å] bonds exhibit double-bond character, whereas the bond lengths in the imidazole part of the molecule suggest aromatic character. The bond lengths N(8)—C(9) [1·496 (5)] and C(9)—C(9*A*) [1·491 (5) Å] have single-bond character and are in the range of distances appropriate to N(sp^2)—C(sp^3) and C(sp^2)—C(sp^3). Furthermore, the imidazole ring is planar to within 0·003 (4) Å. The pyridazine ring deviates slightly from planarity; the largest deviations are 0·008 (3) Å for C(9*A*), and −0·005 (3) Å for C(9*B*). The pyrazole part of the molecule also deviates from planarity, owing mainly to the presence of two methyl groups C(10)H$_3$ and C(11)H$_3$ attached to C(9). The largest deviations are

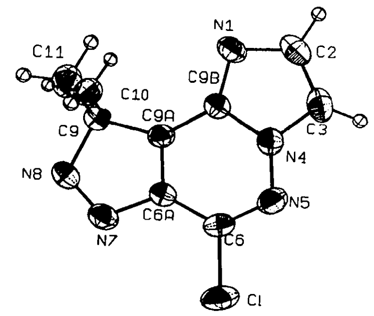

Fig. 1. *ORTEP* (Johnson, 1965) view of the molecule. The atoms are represented by thermal ellipsoids at the 50% probability level.

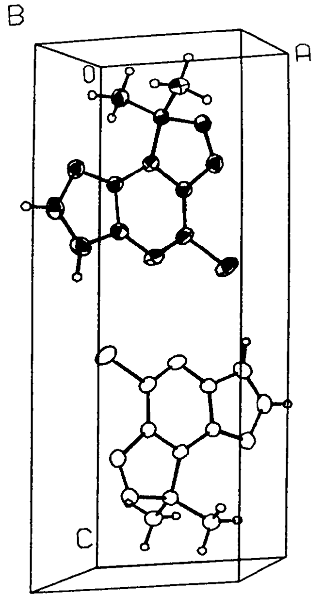

Fig. 2. View of the molecular packing.

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* Lists of structure factors, anisotropic thermal parameters, torsion angles and the results of mean-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43983 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0·011 (3) Å for C(9*A*) and −0·010 (3) Å for C(9). The remaining bond lengths and angles are within normal ranges for these types of heterocyclic systems. There are no noticeably short intermolecular contacts in the structure.

The financial support of the Research Community of Slovenia is gratefully acknowledged.

References

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, 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.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

STANOVNIK, B., KUPPER, M., TIŠLER, M., LEBAN, I. & GOLIČ, L. (1984). *J. Chem. Soc. Chem. Commun.* pp. 268–269.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1987). C**43**, 1816–1818

Structure of 7-(*p*-Tolyl)-2,3-dihydro-5*H*-thiazolo[4,3-*b*]thiazole-3,5-dione

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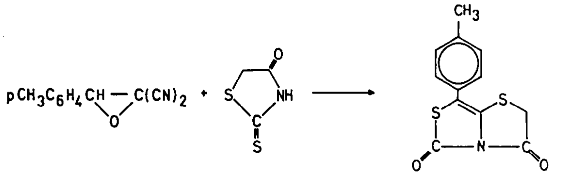
(*Received* 16 *March* 1987; *accepted* 21 *April* 1987)

Abstract. $C_{12}H_9NO_2S_2$, $M_r = 263·3$, monoclinic, $P2_1/c$, $a = 12·607$ (2), $b = 7·067$ (1), $c = 13·776$ (3) Å, $\beta = 112·40$ (1)°, $V = 1134·7$ (7) Å^3, $Z = 4$, $D_m = 1·53$ (5), $D_x = 1·540$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 4·46$ cm^{-1}, $F(000) = 544$, $T = 293$ (1) K, final $R = 0·040$ for 1552 observed reflexions. The two fused thiazole rings are coplanar [dihedral angle between ring planes: 0·7 (5)°]; the tolyl ring is twisted by 18·8 (6)° about the C(7)—C(8) bond.

Introduction. *gem*-Dicyanoepoxides normally react with *N*-monosubstituted thioamides to provide mesoionic thiazoles (Baudy & Robert, 1976, 1980). The reaction of the *gem*-dicyanoepoxide (I) and rhodanine (II) leads to the transposition product (III).



(I) (II) (III)

The epoxide and rhodanine were mixed in stoichiometric quantities and heated for 30 min at 423 K without solvent; compound (III) was isolated, purified and crystallized from benzene and acetone respectively.

Experimental. Density measured by flotation in chlorobenzene/CCl_4; colourless prisms, 0·38 × 0·28 × 0·41 mm; Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation (graphite monochromator), lattice parameters by least-squares fit to angular settings of 25 well centred reflexions ($6 < \theta < 11°$); $\omega/2\theta$ scans, variable scan rate (min. 1·10, max. 5·50° min^{-1}), max. scan time 60 s, scan width (2θ) ($0·7 + 0·3\tan\theta$)°, aperture ($2·5 + 0·9\tan\theta$) mm, background measured for 0·25 of scan time at each scan limit, $[(\sin\theta)/\lambda]_{\max}$ in intensity measurements 0·66 Å^{-1}. Three reflexions monitored at intervals of 300 reflexions, no significant intensity decline (0·6%); data corrected for intensity variation and Lp effects, but absorption ignored; 6244 ($\pm h$, $-k$, $\pm l$) measured reflexions, 2580 unique [$R_{\rm int}(I) = 0·028$ for 6219 contributing reflexions], 1552 observed (h −16/15, k 0/8, l 0/16) with $I > 2\sigma(I)$, $\sigma(I)$ based on counting statistics. Structure solution by

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