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Structure of 7-Phenyl-*s*-triazolo[1,5-*b*]pyridazine-8-carbonitrile

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Abstract. $C_{12}H_7N_5$, $M_r = 221{\cdot}2$, orthorhombic, $P2_12_12_1$, $a = 3{\cdot}867\,(2)$, $b = 14{\cdot}302\,(3)$, $c = 18{\cdot}469\,(3)$ Å, $V = 1021{\cdot}4\,(9)$ Å^3, $Z = 4$, $D_m = 1{\cdot}42\,(4)$, $D_x = 1{\cdot}438$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}02$ cm^{-1}, $F(000) = 456$, $T = 293\,(1)$ K, final $R = 0{\cdot}047$ for 621 observed reflexions. The *s*-triazolo[1,5-*b*]pyridazine part of the molecule is essentially planar, with the phenyl ring twisted about the bond C(7)—C(9) [torsion angles C(6)—C(7)—C(9)—C(14) 43·2 (8), C(8)—C(7)—C(9)—C(10) 42·2 (8)°]. Bond lengths and angles agree with expected values.

Introduction. The crystal structure of 7-phenyl-*s*-triazolo[1,5-*b*]pyridazine-8-carbonitrile was determined as part of a study of bicyclic heterocyclic systems. In the same series of compounds the crystal structures of 6-hydroxy-*s*-triazolo[4,3-*b*]pyridazine (Golič, Leban, Stanovnik & Tišler, 1977), *s*-triazolo[4,3-*b*]pyridazine, *s*-triazolo[1,5-*b*]pyridazine and tetrazolo[1,5-*b*]pyridazine (Golič, Leban, Stanovnik & Tišler, 1978) have been determined. *N*-Heteroaryl-*O*-acetylformamide oximes usually cyclize into *s*-triazolo[1,5-*x*]azines (Verček, Stanovnik, Tišler & Zrimšek, 1978). When 3-acetoxyiminomethyleneamino-4-cyano-5-phenylpyridazine was heated in acetic acid a compound with molecular formula $C_{12}H_7N_5$, m.p. 398 K, was obtained (Stanovnik, Stibilj, Tišler, Leban & Golič, 1986). Since the band at 2150 cm^{-1}, characteristic of a cyano group, was absent in the IR spectrum, one could assume that the 4-cyano group might be involved in a cyclization reaction. This seems to be highly improbable on the basis of general knowledge about this type of compound [see Stanovnik (1987) for a review].

The present X-ray investigation was undertaken in order to resolve this ambiguity and to find a possible correlation between the structure and chemical reactivity. The crystals of the compound were kindly supplied by Mg B. Huč, Department of Chemistry and Chemical Technology of E. Kardelj University.

Experimental. Density measured by flotation in chlorobenzene/CCl_4; colourless prisms, $0{\cdot}25 \times 0{\cdot}25 \times 0{\cdot}40$ mm; Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation (graphite monochromator), lattice parameters by least-squares fit to angular settings of 25 well centered reflexions ($6 < \theta < 11°$); $\omega/2\theta$ scans, variable scan rate (min. 1·55, max. 6·72° min^{-1}), max. scan time 60 s, scan width (2θ) $(0{\cdot}8 + 0{\cdot}3\tan\theta)°$, aperture $(2{\cdot}5 + 9\tan\theta)$ mm, background measured for 0·25 of scan time at each of the scan limits, $[(\sin\theta)/\lambda]_{\max}$ in intensity measurements 0·70 Å^{-1}. Three reflexions monitored at regular intervals for intensity change, three reflexions regularly measured for change of orientation, no significant intensity decline (~0·7%); data corrected for intensity variation and Lp effects, but absorption ignored; 3539 ($+h$, $-k$, $\pm l$) measured reflexions, 1558 unique [$R_{\text{int}}(I) = 0{\cdot}023$ for 3439 contributing reflexions], 621 observed (h 0/5, k 0/18, l 0/22) with $I > 1{\cdot}5\sigma(I)$, $\sigma(I)$ based on counting statistics. Structure solution by direct methods with *SHELXS*84 (Sheldrick, 1985), full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ with *SHELX*76 (Sheldrick, 1976); final R and wR values: 0·047 and 0·046 with $w = 0{\cdot}540/[\sigma^2(F_o) + 0{\cdot}001F_o^2]$; H atoms found from a difference synthesis and included in the refinement at calculated positions $d(\text{C—H}) = 1{\cdot}08$ Å, a common isotropic temperature factor U for H atoms was fixed to 0·12 Å^2. $\Delta\rho$ within 0·20 and −0·20 e Å^{-3} in final difference map. At convergence max. and mean values of Δ/σ: 0·059 and 0·011. Scattering factors for N and C with 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. *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used for data reduction and interpretation.

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. Bond

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* Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms, selected torsion angles and mean-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43982 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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lengths and angles in the *s*-triazolo part of the molecule agree well with those found in *s*-triazolo[1,5-*b*]pyridazine (Golič *et al.*, 1978). The bond lengths of type $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ are in the range from 1·331 (7) to 1·371 (7) Å, with corresponding valency angles from 100·9 (5) to 117·1 (5)°. This part of the molecule is planar [the largest deviation from the mean plane through atoms N(1), C(2), N(3), N(4), C(8*A*) is 0·007 (6) Å for C(8*A*)] and it could therefore be considered as an aromatic heterocyclic system. The pyridazine part of the molecule deviates from planarity. This effect was expected because the phenyl and cyano groups are attached to C(7) and C(8). Accordingly, the displacements from the mean plane through the atoms N(4), N(5), C(6), C(7), C(8), C(8*A*) for atoms C(7) and C(8) are 0·019 (6) and −0·018 (6) Å respectively.

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

	x	*y*	*z*	U_{eq}
N	−5360 (17)	8498 (4)	6793 (3)	62 (4)
N(1)	−1173 (16)	8082 (3)	8559 (2)	50 (3)
N(3)	1259 (17)	6865 (4)	9198 (3)	58 (3)
N(4)	291 (15)	6583 (3)	8525 (2)	48 (3)
N(5)	743 (16)	5697 (3)	8295 (2)	52 (3)
C(2)	318 (18)	7765 (5)	9181 (3)	57 (4)
C(6)	−260 (19)	5569 (4)	7623 (3)	46 (4)
C(7)	−1700 (17)	6262 (4)	7149 (3)	36 (4)
C(8)	−2209 (17)	7135 (4)	7432 (3)	37 (3)
C(8*A*)	−1115 (17)	7317 (4)	8149 (3)	39 (3)
C(9)	−2403 (17)	6013 (4)	6383 (3)	37 (3)
C(10)	−1438 (17)	6634 (4)	5833 (3)	42 (3)
C(11)	−1992 (20)	6389 (4)	5114 (3)	48 (4)
C(12)	−3559 (19)	5550 (5)	4940 (3)	56 (4)
C(13)	−4547 (19)	4940 (4)	5483 (3)	53 (4)
C(14)	−3936 (18)	5154 (4)	6205 (3)	50 (4)
C(15)	−3924 (18)	7893 (4)	7053 (3)	42 (4)

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

N–C(15)	1·135 (8)	C(7)–C(9)	1·484 (8)
N(1)–C(2)	1·363 (7)	C(8)–C(8*A*)	1·414 (8)
N(1)–C(8*A*)	1·331 (7)	C(8)–C(15)	1·451 (8)
N(3)–N(4)	1·359 (7)	C(9)–C(10)	1·400 (8)
C(2)–N(3)	1·338 (9)	C(9)–C(14)	1·403 (8)
N(4)–N(5)	1·348 (6)	C(10)–C(11)	1·390 (8)
N(4)–C(8*A*)	1·371 (7)	C(11)–C(12)	1·382 (9)
N(5)–C(6)	1·313 (7)	C(12)–C(13)	1·383 (9)
C(6)–C(7)	1·435 (8)	C(13)–C(14)	1·388 (8)
C(7)–C(8)	1·368 (8)		

C(2)–N(1)–C(8*A*)	101·5 (5)	C(8*A*)–C(8)–C(15)	116·8 (5)
C(2)–N(3)–N(4)	100·9 (5)	N(1)–C(8*A*)–N(4)	110·4 (5)
N(3)–N(4)–N(5)	122·1 (5)	N(1)–C(8*A*)–C(8)	132·8 (5)
N(3)–N(4)–C(8*A*)	110·2 (5)	N(4)–C(8*A*)–C(8)	116·9 (5)
N(5)–N(4)–C(8*A*)	127·7 (5)	C(7)–C(9)–C(10)	119·4 (5)
N(4)–N(5)–C(6)	113·0 (5)	C(7)–C(9)–C(14)	120·7 (5)
N(1)–C(2)–N(3)	117·1 (5)	C(10)–C(9)–C(14)	119·9 (5)
N(5)–C(6)–C(7)	126·5 (5)	C(9)–C(10)–C(11)	119·5 (5)
C(6)–C(7)–C(8)	117·0 (5)	C(10)–C(11)–C(12)	120·6 (5)
C(6)–C(7)–C(9)	119·1 (5)	C(11)–C(12)–C(13)	120·0 (5)
C(8)–C(7)–C(9)	123·8 (5)	C(12)–C(13)–C(14)	120·7 (6)
C(7)–C(8)–C(8*A*)	118·9 (5)	C(9)–C(14)–C(13)	119·3 (5)
C(7)–C(8)–C(15)	124·3 (5)	N–C(15)–C(8)	176·0 (6)

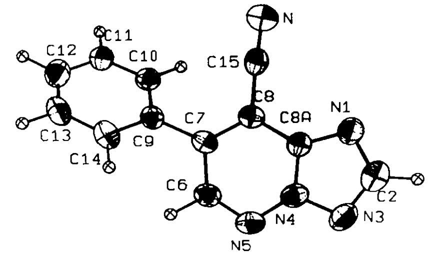

Fig. 1. *ORTEP* (Johnson, 1965) view of the molecule. The atoms are represented by thermal ellipsoids at the 50% probability level.

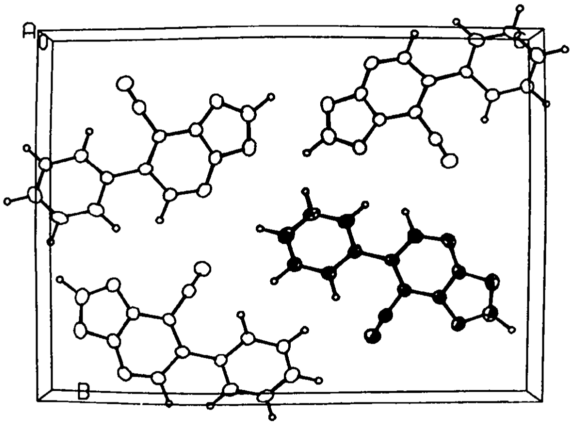

Fig. 2. View of the molecular packing.

The phenyl ring is planar to within 0·011 (7) Å, with the bond lengths ranging from 1·382 (9) to 1·403 (8) Å and the angles from 119·3 (5) to 120·7 (5)°. The bond length C(15)–N is typical for the cyano group at 1·135 (8) Å. The phenyl group is twisted about the bond C(7)–C(9), with torsion angles C(6)–C(7)–C(9)–C(14) and C(8)–C(7)–C(9)–C(10) of 43·2 (8) and 42·2 (8)°. Because of the rather short *a* parameter of the unit cell [3·867 (2) Å] the molecules are stacked in columns parallel to the [100] direction. Similar packing was also observed in *s*-triazolo[1,5-*b*]pyridazine (Golič *et al.*, 1978). There are no abnormally short intermolecular contacts.

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

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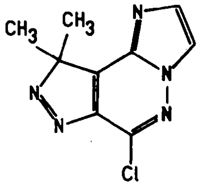
Abstract. $C_9H_8ClN_5$, $M_r = 221{\cdot}6$, triclinic, $P\bar{1}$, $a = 5{\cdot}569\,(2)$, $b = 5{\cdot}712\,(2)$, $c = 16{\cdot}208\,(3)$ Å, $\alpha = 89{\cdot}95\,(2)$, $\beta = 93{\cdot}73\,(2)$, $\gamma = 106{\cdot}09\,(2)^\circ$, $V = 494{\cdot}3$ Å^3, $Z = 2$, $D_m = 1{\cdot}50\,(5)$, $D_x = 1{\cdot}489$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ 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, $0{\cdot}53 \times 0{\cdot}46 \times 0{\cdot}29$ 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 ($7 < \theta < 11^\circ$); $\omega/2\theta$ scans, variable scan rate (min. 1·8, max. 20·1° min^{-1}), max. scan time 40 s, scan width (2θ) $(0{\cdot}8 + 0{\cdot}2\tan\theta)^\circ$, 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 [$R_{\text{int}}(I) = 0{\cdot}040$ 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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