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Structure of 1-(5-Nitro-1,3-thiazol-2-yl)-2-imidazolidinone (Niridazole), $C_6H_6N_4O_3S$

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Abstract. $M_r = 214\cdot22$, orthorhombic, $Pc2_1n$, $a = 6\cdot467\,(1)$, $b = 6\cdot533\,(2)$, $c = 19\cdot701\,(4)$ Å, $V = 832\cdot4\,(3)$ Å^3, $Z = 4$, $D_m = 1\cdot69$, $D_x = 1\cdot710$ Mg m^{-3}, $\lambda(\text{Cu }K\alpha) = 1\cdot54178$ Å, $\mu(\text{Cu }K\alpha) = 3\cdot32$ mm^{-1}, $F(000) = 440$, room temperature, final $R = 0\cdot037$ for 701 observed reflections. The non-hydrogen atoms are nearly planar, with the carbonyl moiety *cis* to the S atom of the thiazolyl ring. The molecules are packed in parallel sheets perpendicular to the *b* axis and endless chains are formed in the **c** direction by a weak bifurcated hydrogen bond.

Introduction. Many nitro-substituted heterocyclic compounds, *e.g.* nitrothiazoles, nitroimidazoles and nitrofurans, have antibacterial and antiprotozoal properties. As part of an investigation on the structure–activity relationship of 5-nitro-substituted heterocyclic compounds the crystal structure of niridazole was determined.

Experimental. Crystals obtained at room temperature from a dimethylformamide/water solution. Density measured by flotation in *n*-heptane/bromoform, crystal ~0·6 × 0·6 × 0·4 mm, Hilger & Watts computer-controlled four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation, $\omega/2\theta$ scan technique ($2\theta_{\max} = 140°$, $0 \le h \le 8$, $0 \le k \le 8$, $-24 \le l \le 24$), cell dimensions by least-squares refinement of the setting angles of 16 reflections with $40° < 2\theta < 72°$; three standard reflections (008, 302, 040) measured after every 50 reflections showed a 0·92, 1·23 and 0·80% variation in intensity respectively (overall e.s.d.'s are 1·3, 1·3 and 1·1%); 1835 reflections measured, 848 unique reflections ($R_{\text{int}} = 0\cdot021$), 701 observed reflections with $[I > 3\sigma(I)]$, Lp corrections, absorption corrections by the method of North, Phillips & Mathews (1968) with values between 0·74 and 1·00, scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) (for H), scattering factor for S corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). Structure solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Refinement with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) by full-matrix least squares on *F*, first with isotropic temperature factors and then anisotropically. H atoms located in ΔF synthesis and refined with *B* equal to B_{overall}. Nine reflections suffering badly from extinction rejected. Because of the ambiguity in the space group, the structure was refined in both *Pcmn* and $Pc2_1n$. Final $R = 0\cdot045$ and $0\cdot037$ respectively. The differences in corresponding bond lengths and angles are smaller than the estimated standard deviations. An *R*-factor ratio test (Hamilton, 1965) with the hypothesis that the space group is *Pcmn* strongly indicates at the 0·5% significance level that this hypothesis should be rejected. The space group $Pc2_1n$ was therefore chosen as the correct one. Final $R = 0\cdot037$, $R_w = 0\cdot045$ and $S = 0\cdot61$, $w = 1$ for $F_o \le 20$ and $w = (20/F_o)^2$ for $F_o > 20$, $(\Delta/\sigma)_{\text{ave}} = 0\cdot21$, $(\Delta/\sigma)_{\max} = 1\cdot9$, $\Delta\rho$ in final difference map $= -0\cdot41 - 0\cdot23$ e Å^{-3} (rejection ratio = 0·3).

Discussion. The atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.† The structure with atomic numbering scheme is depicted in Fig. 1. Bond lengths and angles are listed in Tables 2 and 3. Compared to other thiazole derivatives (Caranoni & Reboul, 1982; Kurahashi, 1976) the most striking feature is the non-planarity of the thiazole ring. C(4) is displaced 0·12 (2) Å from the mean plane through S(1), C(2), N(3) and C(5). The C(2)—N(3), N(3)—C(4) and C(4)—C(5) distances of 1·319 (5), 1·355 (5) and 1·372 (6) Å respectively suggest a more delocalized system than in 2-amino-1,3-thiazole (Caranoni & Reboul, 1982). The bond angles are comparable with the literature values although the C(2)—S(1)—C(5) value of 86·4 (1)° is the lowest observed.

The bond lengths and angles of the nitro group appear normal and agree well with the values of the nitroimidazoles sulnidazole (Germain, Declercq, Van

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† Lists of structure factors and anisotropic thermal parameters and details of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39551 (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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Table 1. *Atomic coordinates* ($\times 10^4$; *for* H$\times 10^3$) *and equivalent isotropic thermal parameters with e.s.d.'s of the refined parameters in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
S(1)	7784 (1)	2500	1707 (1)	3·05 (2)
C(2)	10345 (5)	2404 (28)	1432 (2)	2·72 (10)
N(3)	11776 (4)	2454 (21)	1908 (1)	3·31 (10)
C(4)	10886 (7)	2319 (29)	2530 (2)	3·08 (15)
C(5)	8775 (6)	2522 (30)	2523 (1)	3·13 (10)
N(6)	7494 (5)	2460 (23)	3100 (1)	3·54 (10)
O(7)	5605 (4)	2462 (24)	3015 (1)	4·43 (9)
O(8)	8283 (5)	2480 (24)	3663 (1)	4·97 (10)
N(9)	10863 (4)	2427 (23)	768 (1)	2·92 (9)
C(10)	9450 (6)	2424 (27)	230 (2)	2·71 (9)
N(11)	10532 (5)	2427 (26)	−339 (1)	3·48 (10)
C(12)	12776 (6)	2537 (31)	−245 (2)	3·49 (11)
C(13)	13003 (6)	2404 (31)	531 (2)	3·59 (13)
O(14)	7586 (4)	2468 (21)	318 (1)	3·35 (7)
H(4)	1173 (6)	212 (10)	293 (2)	2·78
H(11)	993 (6)	207 (9)	−75 (2)	2·78
H(12*A*)	1334 (11)	135 (10)	−35 (3)	2·78
H(12*B*)	1340 (10)	362 (10)	−60 (2)	2·78
H(13*A*)	1357 (10)	87 (10)	68 (3)	2·78
H(13*B*)	1382 (9)	328 (9)	76 (3)	2·78

Table 2. *Bond lengths* (Å)

S(1)–C(2)	1·743 (4)	C(10)–N(11)	1·323 (5)
S(1)–C(5)	1·730 (3)	C(10)–O(14)	1·218 (4)
C(2)–N(3)	1·319 (5)	N(11)–C(12)	1·465 (6)
C(2)–N(9)	1·350 (5)	C(12)–C(13)	1·539 (7)
N(3)–C(4)	1·355 (5)	C(4)–H(4)	0·96 (4)
C(4)–C(5)	1·372 (6)	N(11)–H(11)	0·93 (5)
C(5)–N(6)	1·408 (5)	C(12)–H(12*A*)	0·88 (7)
N(6)–O(7)	1·233 (4)	C(12)–H(12*B*)	1·07 (6)
N(6)–O(8)	1·221 (4)	C(13)–H(13*A*)	1·11 (6)
N(9)–C(10)	1·400 (5)	C(13)–H(13*B*)	0·90 (6)
N(9)–C(13)	1·460 (5)		

Table 3. *Bond angles* (°)

C(2)–S(1)–C(5)	86·4 (1)	C(10)–N(11)–C(12)	114·6 (3)
S(1)–C(2)–N(3)	116·4 (3)	N(11)–C(12)–C(13)	102·6 (3)
S(1)–C(2)–N(9)	122·5 (2)	N(9)–C(13)–C(12)	103·2 (3)
N(3)–C(2)–N(9)	121·0 (3)	N(3)–C(4)–H(4)	120 (3)
C(2)–N(3)–C(4)	110·1 (3)	C(5)–C(4)–H(4)	126 (3)
N(3)–C(4)–C(5)	114·0 (4)	C(10)–N(11)–H(11)	121 (3)
S(1)–C(5)–C(4)	112·1 (3)	C(12)–N(11)–H(11)	123 (3)
S(1)–C(5)–N(6)	122·2 (3)	N(11)–C(12)–H(12*A*)	110 (5)
C(4)–C(5)–N(6)	125·1 (4)	N(11)–C(12)–H(12*B*)	109 (3)
C(5)–N(6)–O(7)	118·3 (3)	C(13)–C(12)–H(12*A*)	99 (4)
C(5)–N(6)–O(8)	119·2 (3)	C(13)–C(12)–H(12*B*)	130 (3)
O(7)–N(6)–O(8)	122·5 (3)	H(12*A*)–C(12)–H(12*B*)	106 (5)
C(2)–N(9)–C(10)	124·9 (2)	N(9)–C(13)–H(13*A*)	104 (3)
C(2)–N(9)–C(13)	123·1 (3)	N(9)–C(13)–H(13*B*)	113 (4)
C(10)–N(9)–C(13)	112·1 (3)	C(12)–C(13)–H(13*A*)	111 (3)
N(9)–C(10)–N(11)	107·3 (3)	C(12)–C(13)–H(13*B*)	122 (4)
N(9)–C(10)–O(14)	122·6 (3)	H(13*A*)–C(13)–H(13*B*)	104 (5)
N(11)–C(10)–O(14)	130·1 (3)		

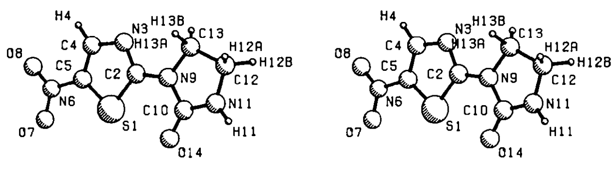

Fig. 1. Stereoscopic view (*PLUTO*78; Motherwell, 1978) with atomic numbering scheme.

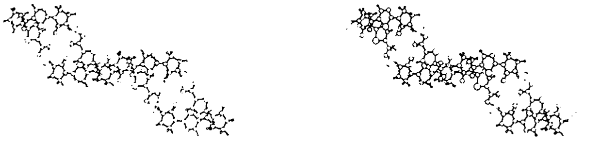

Fig. 2. Packing diagram (*PLUTO*78; Motherwell, 1978) with hydrogen bonds shown as broken lines.

Meerssche & Kock, 1977), carnidazole (Blaton, Peeters & De Ranter, 1979*a*) and metronidazole (Blaton, Peeters & De Ranter, 1979*b*). The angle between the plane through the nitro group and the plane through S(1), C(2), N(3) and C(5) is 1 (1)°.

The imidazolidine ring is a fairly flattened envelope with N(9), C(10), N(11) and C(13) planar to within ±0·004 Å, C(12) being 0·08 (2) Å from the plane. Bond distances and angles correspond to those reported for *trans*-1-carbamoyl-4,5-dihydroxy-2-imidazolidinone (Flippen, 1973). The dihedral angle between the least-squares planes through S(1), C(2), N(3) and C(5) and through N(9), C(10), N(11) and C(13) is 1·5 (9)°.

A packing diagram is shown in Fig. 2. The molecules pack in parallel sheets perpendicular to the b axis and endless chains are formed in the **c** direction by a weak bifurcated hydrogen bond N(11)–H(11)···O(7) and N(11)–H(11)···O(8) [N(11^{i})···O(7) = 3·320 (5), H(11^{i})···O(7) = 2·46 (4) Å, ∠N(11^{i})–H(11^{i})···O(7) = 153 (5)°; N(11^{i})···O(8) = 3·152 (5), H(11^{i})···O(8) = 2·39 (4) Å, ∠N(11^{i})–H(11^{i})···O(8) = 139 (4)°, symmetry code (i) $\frac{3}{2}-x, y, \frac{1}{2}+z$]. Potential-energy calculations with the program *EENY* (Motherwell, 1974) using empirical constants from Giglio (1969) revealed that the intermolecular energy in $Pc2_1n$ is 6·98 kJ less than that in space group *Pcmn*, where all atoms except the H atoms of C(12) and C(13) lie in the mirror plane with $y = 0{\cdot}25$. In the latter space group the close contacts between O(7) and H(4) and between O(14) and H(12*A*) and H(12*B*) are significantly shorter indeed than the sum of the van der Waals radii, while in space group $Pc2_1n$ only normal van der Waals contacts are observed. As a consequence the out-of-plane deviations of C(4) and C(12) are probably due to packing forces.

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Structure of the (1/1) Complex *cis*-3-(2,5-Dihydroxyphenyl)-5-hydroxy-3-methyl-2-(*N*-methylpropionamido)-2,3-dihydrobenzo[*b*]furan–($^2H_6$)Acetone, $C_{19}H_{21}NO_5.C_3D_6O$*

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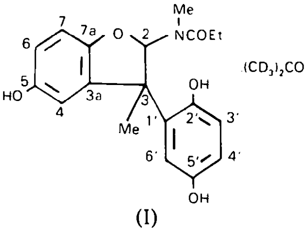
Abstract. $M_r = 407\cdot49$, triclinic, $P\bar{1}$, $a = 7\cdot263$ (3), $b = 15\cdot272$ (4), $c = 10\cdot051$ (3) Å, $\alpha = 103\cdot90$ (1), $\beta = 81\cdot23$ (1), $\gamma = 88\cdot53$ (1)°, $V = 1067\cdot3$ (6) Å^3, $Z = 2$, $D_x = 1\cdot268$ (1) g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 7\cdot11$ cm^{-1}, $F(000) = 428$, $T = 293$ K, final $R = 0\cdot045$ for 3039 independent observed reflections. The *N*-methylpropionamido and hydroquinone substituents situated at adjacent C atoms of the dihydrofuryl ring are almost eclipsed. The system of intermolecular hydrogen bonds in the crystal lattice consists of three types, two of which bond pairs of enantiomeric molecules into aggregates. The third type involves the acetone molecule. The aggregates form chains parallel to [011] in the crystal.

Introduction. Several dihydrobenzofuran as well as hydroquinone derivatives (MacNicol, McKendrick & Wilson, 1978; Helgeson, Lauer & Cram, 1983) are reported to have complexing properties for some organic molecules in the solid state. Similar properties were found recently (Kozerski, 1981) for some derivatives of 3-(2,5-dihydroxyphenyl)benzo[*b*]furan. They are chemically close to the dianine derivatives which in the solid state form hexahost cavities able to trap one or two simple guest molecules (MacNicol *et al.*, 1978). The title compound (I) is one of a series for which the complexing ratio of 1:1 was postulated on the basis of ^{1}H NMR spectra (Kozerski, 1981). The present X-ray structural investigation has been performed in order to elucidate the complexing mode of the solvent molecules which seems to be different from that of the dianine derivatives. A verification of NMR conclusions concerning the configuration of amide residues is also of interest.



(I)

Experimental. Crystal (0·2 × 0·2 × 0·3 mm) obtained from $(CD_3)_2CO$ solution from a ^{1}H NMR measurement. D_m not determined. Siemens AED automatic diffractometer, Cu $K\alpha$ radiation, $\omega/2\theta$ scan, $2\theta_{\max} = 108°$, $hkl_{\max} = 8$, 18, 12. Stability controlled with one reflection (430) at 50 reflection intervals (±4% intensity variation). 4018 unique reflections collected, 3049 with $I > 2\sigma_I$ regarded as observed. Cell constants refined against 28 reflections. Lorentz–polarization correction, no absorption correction. Space group $P\bar{1}$. Structure solved by direct methods (*SHELX76*, Sheldrick, 1976) followed by ρ maps. H and D atoms found from $\Delta\rho$ maps. Structure refined (F_{hkl}) by the full-matrix least-squares procedure (*XRAY70*, Stewart, Kundell &

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* Molecular Structures and Inclusion Properties of Some Benzofuran Derivatives. III. Part II: Urbańczyk-Lipkowska, Krajewski, Gluziński, Kozerski & Czugler (1982).

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