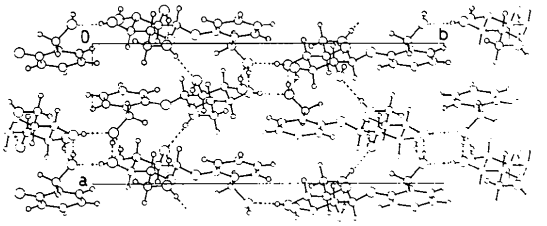

Fig. 2. The crystal structure viewed along the c axis. The hydrogen bonds are indicated by broken lines.

infinite strings along the twofold screw axes parallel to the a and c axes, respectively.

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2-Pyridine-*ONN*-azoxycyanide, $C_6H_4N_4O$: a Heterocyclic Analogue of Calvatic Acid

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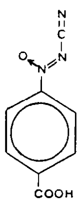
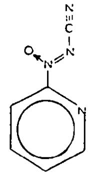
Abstract. $C_6H_4N_4O$, $M_r = 148{\cdot}1$, m.p. 347–348 K, triclinic, $P\bar{1}$, $a = 6{\cdot}368\,(2)$, $b = 7{\cdot}856\,(2)$, $c = 7{\cdot}902\,(2)$ Å, $\alpha = 115{\cdot}41\,(2)$, $\beta = 75{\cdot}32\,(2)$, $\gamma = 105{\cdot}42\,(2)^\circ$, $U = 339{\cdot}8\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}45$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}12$ mm^{-1}, $F(000) = 152$, room temperature, $R = 0{\cdot}052$ for 1173 reflexions. The O atom of the azoxy group is bonded to the N atom adjacent to the pyridine ring; the cyano and pyridine moieties are in *anti* orientation. The synthesis of the title compound has been confirmed to be regiospecific and also stereospecific.

Introduction. The structure and stereoisomerism of calvatic acid (1), *p*-carboxybenzeneazoxycyanide, an antibacterial and antifungal compound from *Calvatia lilacina* (Gasco, Serafino, Mortarini, Menziani, Bianco & Ceruti-Scurti, 1974), has been described by Viterbo, Gasco, Serafino & Mortarini (1975). As part of an extensive chemical and pharmaceutical investigation on *R*-*ONN*-azoxycyanides, a new direct synthesis to obtain alkyl, aryl and heteroaryl derivatives has recently been proposed (Fruttero, Mulatero, Calvino & Gasco, 1984). In the present article, as an example of the heteroaryl class, we describe the crystal and molecular structure of 2-pyridine-*ONN*-azoxycyanide (2), with the aim of confirming the regiospecificity and clarifying the stereospecificity of the above synthesis.



(1)



(2)

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Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq} or U
C(2)	−205 (3)	600 (2)	8077 (2)	49 (1)*
C(3)	1996 (3)	562 (3)	7857 (3)	63 (1)*
C(4)	2753 (3)	−1016 (4)	6399 (4)	75 (1)*
C(5)	1309 (4)	−2432 (3)	5267 (3)	71 (1)*
C(6)	−861 (4)	−2230 (3)	5646 (3)	66 (1)*
C(7)	−3806 (3)	3852 (3)	11197 (3)	66 (1)*
N(1)	−1661 (2)	−724 (2)	7040 (2)	56 (1)*
N(2)	−1092 (2)	2254 (2)	9620 (2)	52 (1)*
N(3)	−3115 (2)	2318 (2)	9706 (2)	64 (1)*
N(4)	−4628 (3)	5068 (3)	12391 (3)	85 (1)*
O	137 (2)	3470 (2)	10752 (2)	73 (1)*
H(3)	2906 (32)	1682 (25)	8641 (27)	83 (3)
H(4)	4329 (26)	−1088 (30)	6219 (29)	83 (3)
H(5)	1775 (34)	−3585 (26)	4213 (25)	83 (3)
H(6)	−2015 (30)	−3263 (27)	4940 (28)	83 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(2)–C(3)	1·375 (3)	C(2)–N(1)	1·324 (2)
C(2)–N(2)	1·475 (2)	C(3)–C(4)	1·381 (3)
C(4)–C(5)	1·379 (3)	C(5)–C(6)	1·375 (3)
C(6)–N(1)	1·338 (2)	C(7)–N(3)	1·355 (2)
C(7)–N(4)	1·148 (3)	N(2)–N(3)	1·286 (2)
N(2)–O	1·244 (2)		
C(3)–C(2)–N(1)	126·5 (1)	C(3)–C(2)–N(2)	118·3 (1)
N(1)–C(2)–N(2)	115·2 (1)	C(2)–C(3)–C(4)	116·3 (2)
C(3)–C(4)–C(5)	119·5 (2)	C(4)–C(5)–C(6)	118·5 (2)
C(5)–C(6)–N(1)	123·9 (2)	N(3)–C(7)–N(4)	172·0 (2)
C(2)–N(1)–C(6)	115·2 (2)	C(2)–N(2)–N(3)	116·9 (1)
C(2)–N(2)–O	118·6 (1)	N(3)–N(2)–O	124·6 (1)
C(7)–N(3)–N(2)	112·8 (1)		

Experimental. Nicolet *R*3 four-circle diffractometer, graphite-monochromatized Mo *K*α radiation, cell parameters from 21 reflexions, $22° \leq 2\theta \leq 35°$, $\theta/2\theta$ scan at variable speed, backgrounds measured in stationary mode for the same length of time of the peak scan; crystal (pale yellow, from diethyl ether) 0·35 × 0·40 × 0·45 mm; 2369 independent reflexions, $2\theta \leq 65°$, h −9 to 9, k −11 to 11, l 0 to 11, scan-speed range 5° min^{-1} for the weakest to 15° min^{-1} for the strongest reflexions, scan range 2°; 2% intensity variation in 2 standard reflexions; data reduction by means of Nicolet (1980) suite of programs; 1176 intensities with $I \geq 2\sigma(I)$ used in the refinement; direct methods. Attempts at solving the structure by both *SOLV* and *RANT* routines of *SHELXTL* (Sheldrick, 1981) system failed; structure solved by *SIR* (Burla, Camalli, Cascarano, Giacovazzo, Nunzi, Polidori, Spagna & Viterbo, 1983); 306 $|E|$'s $\geq$ 1·40, 20 one-phase seminvariants used only passively to compute a figure of merit, 113 two-phase seminvariants of which 17 actively used, 4000 triple-sign relations generated and estimated by the P_{10} formula (Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984), 2000 best positive estimates used actively, 132 negative estimates and 500 negative quartets employed to compute figures of merit; set with highest combined figure of merit gave an eight-atom fragment which was completed by weighted difference Fourier cycles but was shown to be displaced from the correct origin; Karle (1968) recycling in *P*1 gave fragment of second molecule and allowed location of the proper origin; for all subsequent computations *SHELXTL* (Sheldrick, 1981) was employed; least-squares refinement on *F*; all H atoms found on difference Fourier map at advanced stage of anisotropic refinement and refined under the constraint C—H = 0·98 ± 0·02 Å and a common isotropic thermal parameter which converged to 0·083 (3) Å^2; $w = 1/[\sigma^2(F_o) + GF_o^2]$, σ is standard deviation of the observed amplitude based on counting statistics; R = 0·052, wR = 0·054, G = 0·00071, goodness of fit = 1·504, 1173 reflexions, 113 parameters; three low-angle reflexions, measured with insertion of copper attenuator, discarded because of probable secondary-extinction effect; atomic scattering factors of *SHELXTL* used; highest and lowest residual peaks in the final difference Fourier map 0·15 and −0·20 e Å^{-3}, $(\Delta/\sigma)_{max} = |0·007|$. Table 1 gives the final coordinates, the equivalent isotropic thermal parameters for non-hydrogen atoms and the common isotropic parameter for the H atoms.*

Discussion. Table 2 lists the bond distances and angles and Fig. 1 is an *ORTEP*II drawing (Johnson, 1970) of the molecule together with the numbering scheme adopted. The X-ray analysis confirms the predictions of Fruttero *et al.* (1984) about the structure of 2-pyridine-*ONN*-azoxycyanide (2) obtained from 2-nitrosopyridine and cyanamide–(diacetoxyiodo)benzene. The position of the O atom, which is bonded to nitrogen N(2) adjacent to the pyridine ring (Fig. 1), confirms the regiospecific character of the synthesis. At

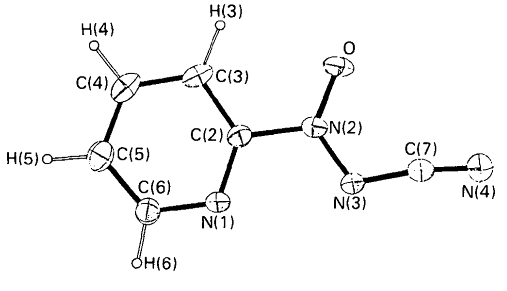

Fig. 1. *ORTEP*II drawing of the molecule of 2-pyridine-*ONN*-azoxycyanide, (2), with the thermal ellipsoids of the non-hydrogen atoms at the 20% probability level.

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39563 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the same time its stereospecificity is indicated by the *anti* orientation of the pyridine ring with respect to the cyano group (Fruttero *et al.*, 1984) the mutual orientation corresponding to that of calvatic acid (Viterbo *et al.*, 1975). The individual bond distances of the azoxycyano group are identical, within the standard deviations, in (1) and (2) excepting bond N(2)—O which is 1·244 (2) Å here and 1·218 (7) Å in (1). Also here its length remains shorter than in other azoxycyano compounds (range 1·26–1·30 Å; Hoesch & Weber, 1977; Cotrait, Marsau & Pasquer, 1979, and references therein; Lamotte, Dupont, Dideberg, Dive & Jamoulle, 1980). The —N(O)=N—C≡N moiety in (2) is not strictly planar: only the —N=N—C≡N group does not deviate significantly from planarity, with O(2) at 0·021 (2) Å out of the mean plane; instead, in calvatic acid (1) the whole azoxycyano group is planar (Viterbo *et al.*, 1975).

The pyridine ring is planar. The C—C distances are tightly distributed around their mean, 1·378 (2) Å, which is smaller than the value obtained for pyridine both by X-ray analysis, 1·392 (1) Å (Sörensen, Mahler & Rastrup-Andersen, 1974), and by microwave measurements, 1·3945 (2) Å (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). A similar trend was found in 3,5-dinitropyridine (Destro, Pilati & Simonetta, 1974), in picolinamide (Takano, Sasada & Kakudo, 1966) and in 2,5-pyridinedicarboxylic acid (Ito, Kashino & Haisa, 1976). The electron-withdrawing substituent at C(2), Fig. 1, also shortens bond N(1)—C(2) with respect to N(1)—C(6), Table 2, and induces a widening of the N(1)—C(2)—C(3) angle (Domenicano, Vaciago & Coulson, 1975). The dihedral angle between the planes through the pyridine and the azoxycyano groups is 5·8 (1)°, larger than in (1) [2·8 (1)°]. The preference, shown in the solid state, for the conformation with C(3)—H(3) on the same side of O, Fig. 1, is probably due to destabilization of the other conformer owing to repulsion between the lone pair of N(1) and the negatively charged O atom.

The packing of the molecules in the crystal reveals no intermolecular contacts shorter than the sums of the van der Waals radii.

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Polarized Twisted Ethylenes: Structure of 3-Dimethylamino-3-methylthio-2-phenylacrylonitrile, $C_{12}H_{14}N_2S$

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Abstract. $M_r = 218$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 8{\cdot}140$ (2), $b = 10{\cdot}434$ (2), $c = 14{\cdot}101$ (3) Å, $V = 1197{\cdot}6$ Å^3, $D_m = 1{\cdot}204$ (3) (by flotation method in KI solution), $D_x = 1{\cdot}209$ (3) g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) = $2{\cdot}29$ cm^{-1}, $F(000) = 464$, $T = 293$ K, $R = 3{\cdot}9\%$, 1169 significant reflections. The C—N(CH$_3$)$_2$

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