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Structure of 7-Amino-5-bromo-4-methyl-2-oxo-1,2,3,4-tetrahydro-1,6-naphthyridine-8-carbonitrile Monohydrate

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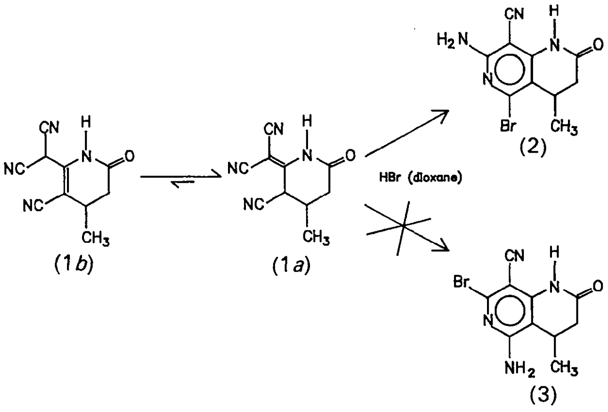
Abstract. $C_{10}H_9BrN_4O.H_2O$, $M_r = 299{\cdot}13$, monoclinic, $C2/c$, $a = 21{\cdot}938\,(2)$, $b = 16{\cdot}003\,(1)$, $c = 6{\cdot}847\,(1)$ Å, $\beta = 98{\cdot}32\,(1)°$, $V = 2378{\cdot}5$ Å^3, $Z = 8$, $D_m = 1{\cdot}71$, $D_x = 1{\cdot}670$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 33{\cdot}57$ cm^{-1}, $F(000) = 1200$, room temperature, $R = 0{\cdot}053$ for 1379 observed reflections. The X-ray diffraction study shows that the compound obtained in the cyclization of 5-cyano-6-(dicyanomethylene)-4-methyl-2-piperidone in HBr/dioxane is the title compound.

Introduction. 1,6-Naphthyridine systems are known (Reed, 1988; Vinick, 1989) but few structural data have been reported (Balogh, Hermecz, Naray-Szabo, Simon & Meszaros, 1986). As a part of a general study on cyclization of dinitriles (Victory, Nomen, Colomina, Garriga & Crespo, 1985) our group has designed a new synthesis of a great number of 1,2,3,4-tetrahydro-1,6-naphthyridines. The cyclization of (1*a*) in HBr/dioxane leads to one isomer in high yield (90%) (Victory & Teixidó, 1989) whose spectroscopic data (UV, IR, ^{1}H NMR, ^{13}C NMR, MS) do not allow unequivocal determination of bromo and amino positions: isomers (2) or (3).



Experimental. Colourless transparent needle crystals from ethyl acetate/hexane.§ Density measured by flotation. Crystal (0·6 × 0·3 × 0·1 mm) mounted on a newly upgraded Hilger & Watts four-circle diffractometer, filtered-monochromatized Mo $K\alpha$ radiation. Cell parameter standard deviations determined on an AFC5R diffractometer. 6575 reflections measured with an $\omega/2\theta$ scan to a maximum value of $\lambda/2\sin\theta = 0{\cdot}85$ Å. Ranges of hkl: $-24 \le h \le 24$, $0 \le k \le 17$, $0 \le l \le 7$. Three reflections, monitored every 100 measurements, showed no significant intensity

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§ Elemental analysis was consistent with the formula $C_{10}H_9BrN_4O.H_2O$: found C 40·3, H 3·6, N 18·2%; expected C 40·1, H 3·7, N 18·7%.

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Table 1. *Atomic fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *of the non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}
N1	0·3985 (3)	0·8063 (5)	−0·1286 (10)	0·041
C2	0·4096 (4)	0·7594 (5)	−0·2856 (11)	0·041
C3	0·3812 (4)	0·6746 (5)	−0·3007 (11)	0·045
C4	0·3777 (4)	0·6337 (5)	−0·1037 (11)	0·040
C5	0·3122 (3)	0·6764 (4)	0·1615 (10)	0·032
N6	0·2897 (3)	0·7281 (3)	0·2845 (9)	0·032
C7	0·3080 (3)	0·8080 (4)	0·2818 (10)	0·033
C8	0·3439 (3)	0·8369 (4)	0·1434 (10)	0·030
C9	0·3645 (3)	0·7811 (4)	0·0133 (10)	0·030
C10	0·3496 (3)	0·6960 (4)	0·0256 (10)	0·030
O11	0·4387 (3)	0·7870 (4)	−0·4085 (9)	0·065
C12	0·4403 (5)	0·6041 (7)	−0·0011 (15)	0·069
Br13	0·2875 (0)	0·5636 (0)	0·1896 (1)	0·049
N14	0·2863 (4)	0·8600 (5)	0·4150 (11)	0·047
C15	0·3560 (3)	0·9236 (4)	0·1345 (11)	0·035
N16	0·3634 (3)	0·9938 (5)	0·1302 (10)	0·052
O*W*	0·4945 (3)	0·9182 (4)	0·0452 (10)	0·056

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

C2—N1	1·362 (10)	C7—N6	1·341 (9)
C9—N1	1·368 (9)	C8—C7	1·396 (10)
C3—C2	1·491 (11)	N14—C7	1·369 (10)
C4—C3	1·511 (11)	C15—C8	1·416 (10)
C10—C4	1·522 (10)	C8—C9	1·383 (10)
C12—C4	1·524 (13)	C10—C9	1·405 (10)
N6—C5	1·326 (9)	C2—O11	1·211 (9)
C10—C5	1·364 (10)	N16—C15	1·136 (9)
Br13—C5	1·903 (6)		
C9—N1—C2	125·2 (7)	N14—C7—C8	122·4 (7)
C3—C2—N1	115·8 (7)	C9—C8—C7	119·5 (6)
O11—C2—N1	121·4 (7)	C15—C8—C9	121·7 (6)
O11—C2—C3	122·8 (7)	C10—C9—N1	119·0 (6)
C4—C3—C2	114·1 (6)	C15—C8—C7	118·7 (6)
C10—C4—C3	108·2 (6)	C10—C9—C8	119·1 (6)
C12—C4—C3	112·8 (7)	C5—C10—C4	125·5 (6)
C12—C4—C10	110·4 (7)	C9—C10—C4	118·8 (6)
C10—C5—N6	127·3 (7)	C9—C10—C5	115·6 (6)
C7—N6—C5	116·6 (6)	N16—C15—C8	177·2 (8)
C8—C7—N6	121·6 (7)	N1—C9—C8	121·9 (6)
N14—C7—N6	115·9 (6)		

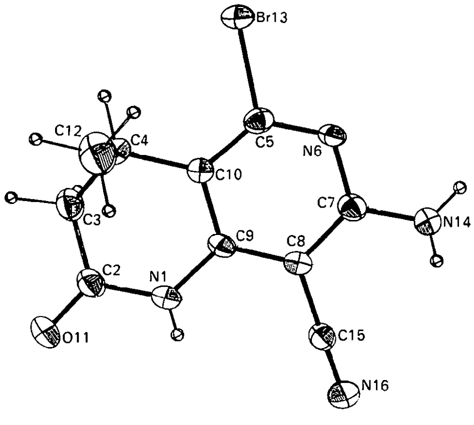

Fig. 1. A perspective drawing of the molecular structure showing the labelling of the atoms. The shape of the ellipsoids corresponds to 50% probability contours of atomic displacement (*ORTEP*; Johnson, 1965).

variation. Lorentz and polarization corrections but no absorption or extinction corrections were made. 1379 reflections with $I > 3\sigma(I)$ used in subsequent calculations.

The structure was solved by Patterson methods; a difference Fourier map based on the position of the Br atom showed the non-H atoms. The refinement was performed by full-matrix least squares on F using *SHELX76* (Sheldrick, 1976). H atoms on C3, C4 and C12 were placed in calculated positions; the others were located in difference maps and refined; isotropic temperature factors were refined for all H, those of H atoms on the same C or N were held equal. Final $R = 0{\cdot}054$, $wR = 0{\cdot}053$, $w^{-1} = [\sigma^2(F) + 3{\cdot}5 \times 10^{-4}F^2]$, 176 parameters, maximum shift/e.s.d. $= 0{\cdot}12$. Maximum and minimum heights in final difference Fourier synthesis 0·44 and $-0{\cdot}22$ e Å^{-3} near the Br atom. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The atomic parameters and geometrical data are given in Tables 1 and 2.* The molecular structure (Fig. 1) shows that the crystal studied corresponds to isomer (2). This fact suggests, according to the work of Victory & Garriga (1986), that the actual precursor of (2) is tautomer (1*b*) (even though it has not been detected) and not (1*a*) whose cyclization would lead to compound (3) (Johnson & Madroñero, 1966).

The C2—N1 distance [1·362 (10) Å] is longer than normal for a simple amide, suggesting less conjugation with the C=O bond.

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* Lists of structure amplitudes, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54365 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Two Cyclopropane Derivatives: *cis*- and *trans*-Caronic Acid

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Abstract. 3,3-Dimethylcyclopropane-1,2-dicarboxylic acid, $C_7H_{10}O_4$, $M_r = 158·2$, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·12\ \text{mm}^{-1}$, $T = 295$ K. *cis* isomer (I): monoclinic, $P2_1/c$, $a = 10·855\ (3)$, $b = 6·881\ (1)$, $c = 11·054\ (2)$ Å, $\beta = 109·23\ (1)°$, $V = 779·6\ (3)$ Å^3, $Z = 4$, $D_x = 1·347$ Mg m^{-3}, $F(000) = 336$, $wR = 0·042$, $R = 0·051$ for 1455 observed reflections. *trans* isomer (II): monoclinic, $C2/c$, $a = 12·516\ (6)$, $b = 6·122\ (2)$, $c = 10·950\ (2)$ Å, $\beta = 107·43\ (2)°$, $V = 800·5\ (5)$ Å^3, $Z = 4$, $D_x = 1·312$ Mg m^{-3}, $F(000) = 336$, $wR = 0·043$, $R = 0·050$ for 741 observed reflections. The intermolecular hydrogen bonds between the carboxylic groups form infinite layers in (I) and infinite chains in (II). Compound (II) has C_2 symmetry.

Introduction. As part of hydrogen-bond studies, the title compound (I) is of special interest as a potential precursor for compounds with intramolecular hydrogen bonds. An analysis of the dissociation constants of (I) suggests intramolecular hydrogen bonding to be present in the monodeprotonated anion in solution (Eberson & Wadsö, 1963; McCoy & Nachtigall, 1963; Haslam, Eyring, Epstein, Christiansen & Miles, 1965; Eyring & Haslam, 1966). Furthermore, a recent X-ray structure determination showed that *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid exhibits intramolecular hydrogen bonding (Weber, Hecker, Csöregh & Czugler, 1989), whereas the unsubstituted *cis*-cyclopropane-1,2-dicarboxylic acid does not (Schrumpf & Jones, 1987). In order to study the hydrogen bonding in the 3,3-dimethyl derivatives this X-ray structure analysis was undertaken.

Experimental. Compounds (I) and (II) were synthesized according to Fredga & Sikström (1955) and checked by IR spectroscopy.

(I): The crystal used for this study (mean diameter 0·3 mm) was obtained by evaporation of an aqueous solution at room temperature. Lattice parameters were refined using 30 diffractometer-measured reflections in the range $25 < 2\theta < 50°$. The intensities of 2567 reflections were collected on a Siemens–Stoe AED-2 diffractometer at 295 K by $\theta/2\theta$ scans in the 'learnt-profile' mode (Clegg, 1981). The range of 2θ was 4–60°; ranges of h, k, l were $-15/15$, $0/10$, $0/16$. Standard reflections 423, 131 and 308, monitored every hour, showed no significant variation over the data-collection period. The orientation matrix was also checked every 6 h. 1455 unique reflections with $I > 2\sigma(I)$ were used in the refinement ($R_{\text{int}} = 0·012$). No absorption correction was applied due to the small absorption coefficient in this compound. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986), which located the positions of all non-H atoms, and was refined (based on F) by *SHELX76* (Sheldrick, 1976). All H atoms were located in a difference Fourier synthesis. Final refinement yielded $wR = 0·042$, $R = 0·051$ (H atoms having isotropic, all other atoms having anisotropic displacement parameters; isotropic extinction correction; 142 parameters varied). Weights were calculated according to $w = 1/\sigma^2(F_o)$, maximum Δ/σ was 0·006. The isotropic extinction parameter g was $7·1\ (4) \times 10^{-7}$ [$F' = F(1 - gF^2/\sin\theta)$]. Maximum and minimum heights in the final difference Fourier synthesis map were 0·20 and $-0·19$ e Å^{-3}, respectively. Scattering factors for neutral atoms were taken from Cromer & Mann (1968). In addition, the programs *ORFFE* (Busing, Martin & Levy, 1964), *XANADU* (Roberts & Sheldrick, 1975) and *ORTEP*II (Johnson, 1976) were used. All calculations were carried out on a MicroVAX and on a PDP 10 at the

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