form of an aziridinyl group, placing constraints on the sum of the angles about N. Clearly these compounds form a separate series from the remaining structures.

The relationship, which has been observed previously for select structures, between the P—N bond length and the sum of the interbond angles at N is apparently not a general trend, and no such relationship can be derived for 17 compounds reported to date.

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Structure of 3-Hydroxy-6-(4′-methyl)phenylazopyridine*

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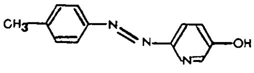
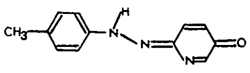
Abstract. $C_{12}H_{11}N_3O$, $M_r = 213\cdot24$, orthorhombic, $P2_12_12_1$, $a = 8\cdot2537\ (8)$, $b = 9\cdot3545\ (6)$, $c = 14\cdot6981\ (10)$ Å, $V = 1134\cdot8\ (4)$ Å^3, $Z = 4$, $D_m = 1\cdot22$, $D_x = 1\cdot25$ Mg m^{-3}, $F(000) = 448$, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot54178$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 5\cdot93$ mm^{-1}, $R = 0\cdot035$, $wR = 0\cdot034$ with 720 independent non-zero reflections. The molecule exists as the hydroxyazo tautomer, the angle between the phenyl and pyridyl rings is 26 (1)° and the hydroxyl group of one molecule is hydrogen-bonded to the heterocyclic N of the screw-related neighbour. This intermolecular hydrogen-bonding pattern is also a confirmation of the azo structure. The adoption of a non-centrosymmetric space group by the title compound is discussed.

Introduction. Several chemical and spectroscopic methods have been used to study the tautomerism of hydroxyazo compounds in solution (Zollinger, 1961; Morgan, 1961; Saeva, 1971). Generally, azophenols exist as the hydroxyazo tautomer while the quinone hydrazone form predominates for azonaphthols. Crystallographic results on such systems are, however, sparse (Pendergrass, Curtin & Paul, 1972; Guggenberger & Teufer, 1975; Kurahashi, 1976). Data on azopyridines are even more uncommon and this study follows from an earlier one (Desiraju, 1983) where the crystal structures of both azo and hydrazone forms of 2-amino-3-hydroxy-6-phenylazopyridine were reported. This paper is part of a systematic attempt to determine the effects of substituents on the stability of azopyridine tautomers in the solid state, especially in those cases where the solid-state behaviour differs from that in solution.



Hydroxyazo form



Quinone hydrazone form

Experimental. Dark-red needles, prepared by diazonium coupling of *p*-toluidine with 3-hydroxypyridine and recrystallization from EtOH, D_m by flotation in CCl_4— benzene, data collected on an Enraf–Nonius CAD-4 diffractometer, lattice parameters from 25 high-angle reflections (matrix check reflections 254 and $\bar{3}\bar{4}\bar{1}$), systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$, no absorption or extinction corrections applied, maximum $\sin\theta/\lambda = 0\cdot61$ Å^{-1}, ranges of h, k and l, 0 to 10, 0 to 10 and 0 to 17, standards ($\bar{1}\bar{4}\bar{3}$ and $1\bar{4}0$) did not vary more than 4%, 1183 reflections measured, 717 unique non-zero reflections at

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* IUPAC name: 5-hydroxypyridine-2-azo(4′-methylbenzene).

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Table 1. *Atomic coordinates in fractional crystal coordinates and equivalent isotropic values of the anisotropic thermal parameters for non-*H *atoms and isotropic thermal parameters for* H

Estimated standard deviations are given in parentheses. For labelling of atoms, see Fig. 1. $U_{eq} = \frac{1}{3}$ trace U.

	x	y	z	U(Å^2)
C(1)	1·2438 (5)	0·3053 (5)	0·0326 (3)	0·075 (2)
C(2)	1·3390 (5)	0·4261 (4)	0·0516 (3)	0·072 (2)
C(3)	1·2823 (6)	0·5198 (4)	0·1164 (3)	0·089 (3)
C(4)	1·1398 (6)	0·4939 (4)	0·1610 (3)	0·083 (2)
C(5)	1·0519 (5)	0·3718 (4)	0·1377 (3)	0·070 (2)
C(6)	0·6982 (5)	0·3679 (4)	0·2738 (3)	0·074 (2)
C(7)	0·6582 (7)	0·4185 (5)	0·3594 (4)	0·099 (3)
C(8)	0·5096 (7)	0·3884 (5)	0·3965 (3)	0·104 (3)
C(9)	0·3970 (6)	0·3069 (5)	0·3500 (3)	0·089 (2)
C(10)	0·4376 (6)	0·2582 (6)	0·2641 (3)	0·095 (3)
C(11)	0·5865 (6)	0·2872 (5)	0·2258 (3)	0·086 (3)
C(12)	0·2333 (10)	0·2696 (13)	0·3905 (7)	0·155 (6)
N(1)	0·8996 (5)	0·3318 (3)	0·1738 (2)	0·081 (2)
N(2)	0·8552 (5)	0·4038 (3)	0·2403 (2)	0·087 (2)
N(3)	1·1044 (4)	0·2804 (3)	0·0742 (2)	0·076 (2)
O(1)	1·4791 (4)	0·4517 (3)	0·0089 (2)	0·102 (2)
H(1)	1·278 (4)	0·238 (5)	−0·022 (3)	0·05 (1)
H(3)	1·354 (6)	0·590 (4)	0·137 (3)	0·08 (1)
H(4)	1·091 (5)	0·548 (4)	0·213 (2)	0·06 (1)
H(7)	0·749 (5)	0·461 (5)	0·398 (3)	0·07 (1)
H(8)	0·477 (5)	0·414 (4)	0·458 (2)	0·06 (1)
H(10)	0·351 (6)	0·208 (5)	0·223 (3)	0·08 (1)
H(11)	0·613 (5)	0·259 (4)	0·159 (2)	0·05 (1)
H(12*A*)	0·152 (14)	0·300 (11)	0·353 (5)	0·22 (5)
H(12*B*)	0·206 (12)	0·198 (9)	0·400 (6)	0·19 (5)
H(12*C*)	0·238 (8)	0·290 (8)	0·461 (5)	0·17 (3)
H(O)	1·009 (6)	0·109 (5)	0·032 (3)	0·07 (1)

the 3σ level, R_{int} after merging 0·068, 456 unobserved reflections; structure solution with *MULTAN*80 (Main, Woolfson, Lessinger, Germain & Declercq, 1980), least-squares refinement using F's, hydrogens located and refined isotropically, all other atoms refined anisotropically, $R = 0{\cdot}035$, $wR = 0{\cdot}034$, $w = 1{\cdot}00/\{[\sigma(F_o)]^2 + (0{\cdot}03F_o)^2\}$ where $\sigma(F_o)$ is the standard deviation based on counting statistics, maximum least-squares shift-to-error in final refinement cycle 0·98, maximum and minimum peak heights in final difference Fourier synthesis 0·10 and −0·14 e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974), refinements carried out with *SHELX*76 (Sheldrick, 1976).

Discussion. Since coupling into 3-hydroxypyridine may occur either at the 4 or 6 positions, the molecular structure of the title compound is confirmed. The atomic coordinates are reported in Table 1.* Fig. 1 shows the atom-numbering scheme and intramolecular bond lengths and angles. The phenyl and pyridyl rings are quite planar and make angles of 26 (1)° with each other and angles of 16 (1)° and 10 (1)° with the plane formed by the four central atoms C(5), N(1), N(2) and C(6). The bond lengths show that the compound definitely exists as the hydroxyazo tautomer. Not only is the N(1)—N(2) distance [1·242 (6) Å] typical of an azo group (1·24 Å in azobenzene) but the C(2)—O(1) distance [1·337 (7) Å] is indicative of a pyridinol. The fact that C(5)—N(1) [1·415 (7) Å] and C(6)—N(2) [1·426 (7) Å] are very similar is further confirmation of the hydroxyazo formulation. In the hydrazone form of 2-amino-3-hydroxy-6-phenylazopyridine, these corresponding distances are, respectively, N(1)—N(2), 1·330 (7) Å; C(2)—O(1), 1·233 (7) Å; C(5)—N(1), 1·315 (7) Å; C(6)—N(2), 1·396 (7) Å (Desiraju, 1983). We note that the difference between the C(5)—N(1) and C(6)—N(2) bond lengths is a sensitive indicator of the position of the tautomeric equilibrium.

Clear evidence that the title compound is a hydroxyazopyridine was also provided by the unambiguous location of the phenolic hydrogen H(O) in a difference Fourier synthesis and its successful refinement to give an O(1)—H(O) bond length of 0·86 (6) Å. Indirect evidence for the tautomeric preference may

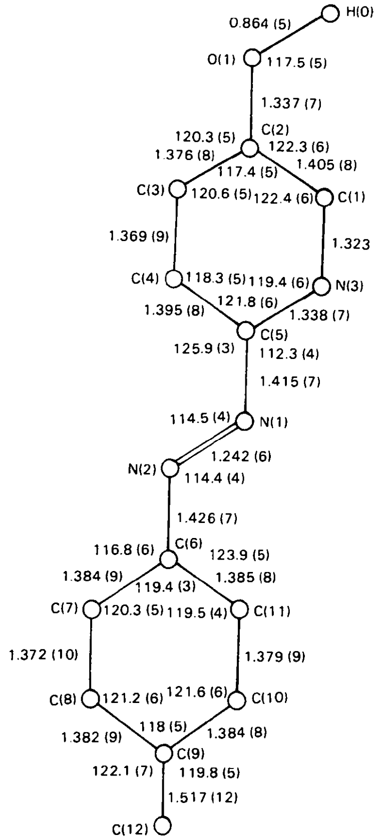

Fig. 1. Bond lengths (Å) and angles (°) and atom-numbering scheme for the title compound. Note the hydroxyazo formulation.

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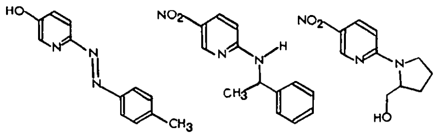
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42966 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

also be obtained from the intermolecular hydrogen-bonding arrangement (Fig. 2) where the phenolic O(1) of (x, y, z) is situated 2·693 Å from the heterocyclic N(3) of ($\frac{1}{2}+x, \frac{1}{2}-y, -z$). Such a hydrogen-bonding scheme is only consistent with the —O—H···N grouping, that is with the hydroxyazo tautomer.

An additional point of interest is the non-centrosymmetric space group of the title compound. Currently there is much interest in obtaining non-centrosymmetric molecular crystals since these may show appreciable second harmonic generation (SHG) or frequency doubling effects. A trivial means of ensuring adoption of such a space group is to use resolved materials but these are often difficult to obtain or very expensive. Much effort has been focused therefore on compounds which, though showing no optical activity in solution, resolve spontaneously on crystallization. The title compound belongs to this category.

In general, not much is known about molecular features which favour such spontaneous resolution. In this context, it is curious to note a certain similarity in the molecular framework of the title compound and the two others shown below:



These two other compounds are among those which show some of the largest SHG effects known today (Twieg & Jain, 1983).

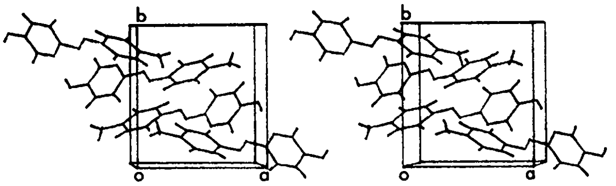


Fig. 2. Stereoscopic view of the crystal structure down the c axis.

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Absolute Conformation of 3-(*N*-Methyl-*N*-benzyl)carbamoyl-1,2,4-trimethylpyridinium Iodide (I) and Absolute Configuration of 3-[*N*-Methyl-*N*-(*R*)-α-methylbenzyl]carbamoyl-1,2,4-trimethylpyridinium Iodide (II)

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Abstract. (I): $C_{17}H_{21}N_2O^+.I^-$, $M_r = 396·27$, orthorhombic, $P2_12_12_1$, $a = 7·183$ (3), $b = 8·769$ (2), $c = 28·093$ (6) Å, $V = 1769·5$ (9) Å^3, $Z = 4$, $D_m = 1·47$ (1), $D_x = 1·487$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 16·73$ cm^{-1}, $F(000) = 792$, $T = 294$ K, final $R = 0·035$ for 2347 observed reflections. (II):

0108-2701/86/091248-04$01.50