Intermolecular Proton Transfers in the Solid State. Conversion of the Hydroxyazo into the Quinone Hydrazone Tautomer of 2-Amino-3-hydroxy-6-phenylazopyridine. X-Ray Crystal Structures of the Two Forms

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The thermal transformation of the low (1a) to the high temperature (1b) form of 2-amino-3-hydroxy-6-phenylazopyridine has been studied by differential scanning calorimetry and variable temperature i.r. spectroscopy. Form (1a) is converted into (1b) through two intermediate phases and the i.r. spectra show changes in the $>C=C<$ and $-N=N-$ stretches. X-Ray crystal structures of (1a and b) have been determined. The red crystals of (1a) are orthorhombic, $a = 10.026(7)$, $b = 20.452(9)$, $c = 10.111(9)$ Å; the space group is $Pbca$ and the structure has been refined to R 0.080 for 443 non-zero reflections. The blue crystals of (1b) are monoclinic, $a = 22.666(6)$, $b = 3.886(4)$, $c = 11.373(7)$ Å, $\beta = 91.82(3)°$; the space group is $P2_1/c$ and the structure has been refined to R 0.048 for 607 non-zero reflections. The bond lengths in (1a and b) are in accord with a hydroxyazo and a quinone hydrazone structure, respectively. The hydrogen bonding in each form can only be explained if (1a) is the azo and (1b) the hydrazone tautomer. In the crystal structure of (1a), the hydroxy-group is close to an azo-group of an adjacent molecule and the solid state tautomerization can be accounted for by an intermolecular co-operative shift of protons across the various hydrogen bonds in structure (1a).

There are several interesting reactions of organic compounds in the solid state where the only significant change is a rearrangement of one or more labile protons with only small perturbations in the non-hydrogen atom positions. Hydrogen transfer has been invoked to explain such varied phenomena as the loss of information in the biological code of the DNA molecule and the conductivity of ice.[1] When the hydrogen transfers in the solid state are reversible one has, in principle, a chemical memory device since there are two chemically distinct states of a system that can be switched thermally or photochemically by the transfer.[2] Hence these reactions are also of practical importance.

The thermochromism and photochromism of salicyclidene-aniline derivatives are classical examples of reversible intramolecular proton transfers between two states of a system which are tautomerically related.[3] In this case, the proton shift is obviously intramolecular but one could also have co-operative intermolecular proton shifts between the tautomeric forms of a compound. Such changes should be highly dependent on the crystal structure.

The present investigation of such a solid state process was prompted by the observation that 2-amino-3-hydroxy-6-phenylazopyridine (1) crystallizes both as a red low temperature form and a blue high temperature form with i.r. spectra strongly suggestive of a tautomeric relationship between the two forms. In this paper the solid state transformation between the forms and their X-ray crystal structures are described. In addition, some possible reaction pathways are postulated on the basis of these crystal structures.

Experimental

M.p.s were measured on a Büchi apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer model 580 spectrometer. The differential scanning calorimetry (d.s.c.) studies were done using a Perkin-Elmer DSC-2 instrument. [1]H N.m.r. spectra were recorded on a JEOL FX-100 Fourier transform instrument. Computations were carried out at the Computer Maintenance Corporation, Hyderabad, on a Robotron Computer and at the School of Chemical Sciences,

(1)
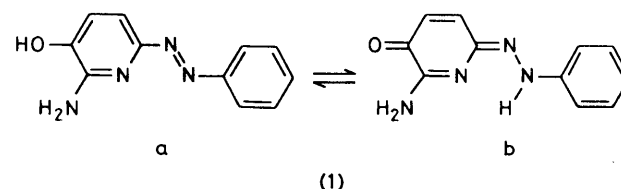
University of Illinois, Urbana, Illinois, on a Vax/VMS computer.

2-Amino-3-hydroxy-6-phenylazopyridine (1).—This was prepared in nearly quantitative yield by coupling benzene-diazonium chloride [from aniline (2.1 g)] with 2-amino-3-hydroxypyridine (2.35 g; Aldrich) in 10% NaOH solution (25 ml). The crude solid melted at 175 °C, δ 6.5 (1 H, d, J_{AB} 9 Hz) and 6.8—7.7 (9 H, m). Recrystallization from EtOH gave both the low (1a) and the high (1b) temperature forms, m.p. 181—182 °C. Form (1a) was obtained from concentrated solutions as irregularly shaped red flakes which appeared red when viewed by transmitted light. The other form crystallized as lustrous needles with a strong blue reflex. The relative amounts of the two forms varied considerably from batch to batch. Form (1b) was always obtained; the amount of (1a) obtained depended on the concentration and temperature of recrystallization. Both forms were highly coloured and crystals of each form were separated manually from the recrystallized material.

D.s.c. Studies.—Several runs using ground (1a and b) were made. Form (1a) did not change directly to (1b) but two intervening forms, hereinafter referred to as X and Y, were detected. The changes (1a) ⟶ X ⟶ Y ⟶ (1b) were accompanied by small exotherms and had extrapolated onsets (uncorrected) as given in Table 1. The melting endotherm had an extrapolated onset at 182 °C. The d.s.c. run of (1b) showed no peaks before the melting endotherm at 182 °C. The enthalpy changes were calculated from the known enthalpy change for a standard indium sample.

Table 1. D.s.c. results for the (1a) ⟶ (1b) transformation

Transformation	Temperature (°C)	Transition enthalpy (kJ mol⁻¹)
(1a) ⟶ X	120	−1.32
X ⟶ Y	169	−0.49
Y ⟶ (1b)	176	−3.97
(1b) ⟶ melt	182	27.60

Variable Temperature I.r. Studies.—A small sample of (1a) was mulled in Fluorolube and scanned in the range 1 350—1 800 cm⁻¹. Spectra were recorded between 25 and 125 °C. The major changes in the spectra were seen in the range 100—115 °C. The spectrum of (1b) was recorded independently and showed no change with temperature.

Choice of Crystals for X-Ray Work.—Crystals of both forms were extremely small, thin, and irregularly shaped. It was therefore difficult to find crystals completely suitable for *X*-ray studies. However, as the knowledge of the crystal structures of the two forms (1a and b) was deemed to be crucial towards any understanding of the thermal rearrangement, it was decided finally to use the largest single crystals that were available.

X-Ray Structure Determination of the High Temperature Form (1b) of 2-Amino-3-hydroxy-6-phenylazopyridine.—Crystal data. $C_{11}H_{10}N_4O$, $M = 214.23$, monoclinic, $a = 22.666(6)$, $b = 3.886(4)$, $c = 11.373(7)$ Å, $\beta = 91.82(3)°$, $V = 1\,001 \times 10^{-24}$ cm³, $F(000) = 448$, $\mu = 0.91$ cm⁻¹ (Mo-K_α), $\rho_{calc} = 1.42$, $Z = 4$; systematic absences, $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$, lead unambiguously to the space group $P2_1/c$ (no. 14), (Mo-K_α, $\lambda = 0.710\,69$ Å). Unit cell parameters were determined by a least-squares fit to the settings for 15 accurately centred high order reflections. Intensity data were collected on a computer-controlled Enraf-Nonius CAD-4 diffractometer on a small crystal $0.17 \times 0.02 \times 0.04$ mm. A total of 607 reflections was considered non-zero at the 2.0σ significance level out of 1 314 possible reflections in the 2θ range 3—45°. No absorption or extinction were applied and there was no evidence for crystal decomposition. The weights were taken as $0.5799\{[\sigma(F_0)]^2 + (0.04F_0)^2\}$ where $\sigma(F_0)$ is the standard deviation based on counting statistics. The scattering factors were taken from the expression in ref. 4.

The structure was solved using the MULTAN 78 program.[5] Least-squares refinement incorporating positional and anisotropic temperature parameters for the non-hydrogen atoms gave R 0.08. An electron density difference map at this stage, revealed the position of all ten hydrogen atoms, including the hydrazone hydrogen atom bonded to N(2) (see Figure 2).* Since the quantity of data did not justify varying the hydrogen positional and thermal parameters, each hydrogen atom was excluded in turn and allowed to emerge in successive difference maps, each following a cycle of least squares refinement, until all the hydrogen–heavy atom bond lengths and angles appeared reasonable and the positions of the heavy atoms showed no discernible change (shift/e.s.d. <0.005). Refinement incorporating positional and anisotropic temperature parameters for the 16 non-hydrogen atoms and fixed positions and

* All refinements were carried out using the program SHELX-76 written by G. M. Sheldrick; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w|F_o| - |F_c||^2/\Sigma w|F_o|^2]$; goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$; $m =$ number of observations, $n =$ number of variables.

Table 2. Atomic co-ordinates in fractional crystal co-ordinates for the two structures [a],[b]

	Molecule (1a)		
Atom	x	y	z
C(1)	0.308 6(12)	0.476 4(6)	0.423 2(11)
C(12)	0.376 4(14)	0.466 2(6)	0.294 8(11)
C(3)	0.491 0(12)	0.426 8(6)	0.294 3(10)
C(4)	0.530 2(12)	0.396 2(6)	0.411 0(12)
C(5)	0.459 3(13)	0.407 3(5)	0.528 8(11)
C(6)	0.479 5(13)	0.348 7(6)	0.859 1(11)
C(7)	0.613 6(12)	0.338 5(6)	0.880 1(12)
C(8)	0.651 7(13)	0.308 5(6)	1.001 6(13)
C(9)	0.555 9(16)	0.289 1(6)	1.090 5(13)
C(10)	0.422 1(15)	0.300 6(7)	1.064 6(12)
C(11)	0.380 9(14)	0.331 7(6)	0.948 6(12)
N(1)	0.507 1(10)	0.374 1(4)	0.643 3(9)
N(2)	0.429 6(10)	0.381 6(4)	0.743 3(10)
N(3)	0.352 5(10)	0.445 9(4)	0.533 6(9)
N(4)	0.201 4(10)	0.512 9(5)	0.432 1(8)
O(1)	0.332 8(8)	0.499 3(4)	0.196 0(8)
	Molecule (1b)		
Atom	x	y	z
C(1)	0.890 9(3)	−0.147(2)	0.649 6(5)
C(2)	0.901 6(3)	−0.050(2)	0.776 3(5)
C(3)	0.854 6(3)	0.127(2)	0.830 6(5)
C(4)	0.803 1(3)	0.165(2)	0.769 0(5)
C(5)	0.796 3(3)	0.042(2)	0.651 5(5)
C(6)	0.673 7(3)	−0.027(2)	0.450 1(5)
C(7)	0.661 7(3)	−0.161(2)	0.338 4(5)
C(8)	0.604 4(3)	−0.130(2)	0.290 6(5)
C(9)	0.560 5(3)	0.023(2)	0.350 9(6)
C(10)	0.573 8(3)	0.154(2)	0.461 3(6)
C(11)	0.629 8(3)	0.133(2)	0.512 9(5)
N(1)	0.742 2(2)	0.074(1)	0.607 8(4)
N(2)	0.730 3(2)	−0.056(1)	0.501 6(4)
N(3)	0.839 9(2)	−0.111(1)	0.591 8(4)
N(4)	0.937 6(2)	−0.277(2)	0.596 1(4)
O(1)	0.949 3(2)	−0.120(1)	0.825 8(3)

[a] Estimated standard deviations are given in parentheses. [b] For labelling of atoms, see Figures 2 and 3.

thermal parameters ($U = 0.06$) for the hydrogen atoms gave a final R of 0.048 and an R_w of 0.055. Six reflections of moderately low intensity had F_c values that were very small and were excluded from the refinements. The 'goodness of fit' between the calculated and observed models was 0.85. The final electron density difference map did not reveal any significant electron density above 0.1 e Å⁻³. The final atomic co-ordinates for (1b) are listed in Table 2. The values of the thermal parameters, the hydrogen atom positions, and of the structure factors are in Supplementary Publication No. SUP 23600 (24 pp.).†

Structure Determination of the Low Temperature Form (1a) of 2-Amino-3-hydroxy-6-phenylazopyridine.—Crystal data. $C_{11}H_{10}N_4O$, $M = 214.23$, orthorhombic, $a = 10.026(7)$, $b = 20.452(9)$, $c = 10.111(9)$ Å, $V = 2073 \times 10^{-24}$ cm³, $F(000) = 869$, $\mu = 0.88$ cm⁻¹ (Mo-K_x), $\rho_{calc} = 1.37$, $Z = 8$; systematic absences, $0kl, k = 2n + 1$; $h0l, l = 2n + 1$; $hk0, h = 2n + 1$, lead unambiguously to the space group $Pbca$ (no. 61) (Mo-K_α, $\lambda = 0.710\,69$ Å).

The procedures for the determination of cell parameters, data collection, and the scattering curves used were as for (1b). The weights were taken as $0.784\{[\sigma(F_0)^2] + (0.044F_0)^2\}$. A small crystal $0.03 \times 0.2 \times 0.08$ mm was used for the data

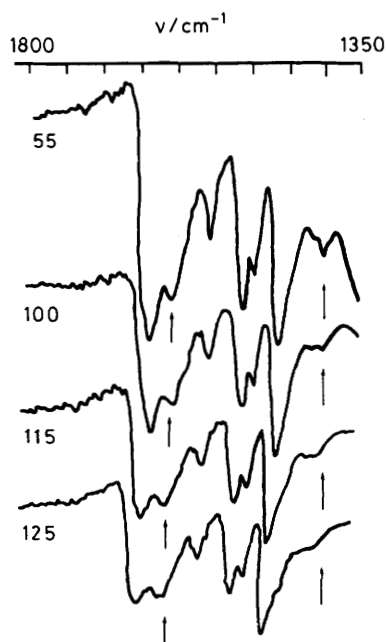† Details are in *J. Chem. Soc., Perkin Trans. 2*, 1983, Issue 1.

Figure 1. I.r. spectra of azo-dye (1) at 55, 100, 115, and 125 °C. The azo and olefin stretches are indicated by arrows. The horizontal scale is in cm⁻¹

collection. A total of 443 reflections was considered to be non-zero at the 1.5σ significance level out of 1 361 possible reflections in the 2θ range 3—45°.

The structure was solved using the MULTAN 78 program.[5] Least-squares refinement incorporating positional and isotropic thermal parameters gave R 0.151. The positional and anisotropic temperature factors were then varied separately in turn. The R obtained was 0.110 and all the hydrogen atoms except the phenolic hydrogen atom were revealed in a difference electron density map; these atoms were placed according to the difference map. The phenolic hydrogen atom was put in the calculated position. Further refinement with positional and anisotropic temperature factors varied separately in turn gave R 0.080 with R_w 0.080. This rather high value of R is an unavoidable consequence of using data at the 1.5σ level. The 'goodness of fit' between the calculated and observed models was 0.98. A final electron density difference map did not reveal any significant electron density above 0.34 e Å⁻³. The final atomic co-ordinates for (1a) are listed in Table 2. The values of the thermal parameters and the structure factors are in SUP 23600.

Results and Discussion

Studies of the Rearrangement.—Crystals of both the low (1a) and high (1b) temperature modifications of the azo-dye (1) were obtained from ethanol, the form being determined by the recrystallization conditions. Form (1a) was transformed to (1b) through two intermediate phases X and Y. All attempts to grow single crystals of X and Y proved unsuccessful. Judging from the small enthalpy changes involved and also drawing upon other recent examples of organic solid state transformations,[6,7] it seems reasonable to assume that the changes (1a) $\longrightarrow$ X $\longrightarrow$ Y $\longrightarrow$ (1b) are more or less continuous.

The thermal transformation of (1a) was studied by using several batches of crystals in a hot stage m.p. apparatus under
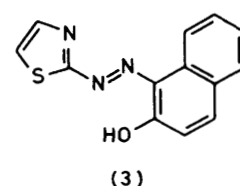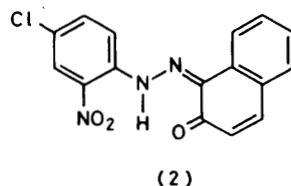
a microscope. Although the temperature of transformation varied, it was never very far from 120 °C. When viewed under the microscope, crystals of (1a) started reacting at several nuclei over the entire crystal surface and the reaction spread out from these nuclei, with no clear frontal migration, until the entire crystal was opaque and microcrystalline and would no longer extinguish plane polarized light. Such single crystal to microcrystalline transformations at several nucleation sites are characteristic of a 'heterogeneous' mechanism[8] and seem to be the rule rather than the exception for organic solid state thermal processes.

Spectroscopic Changes during the Transformation.—The transformation (1a) $\longrightarrow$ (1b) was monitored by variable temperature i.r. spectroscopy. One major change was seen across the transition; the intensity of the $-N=N-$ stretch at 1 400 cm⁻¹ disappeared (Figure 1). The spectrum obtained at 125 °C is very similar (if not virtually identical) to the spectrum of (1b) and suggests that X, Y, and (1b) are all very similar chemically. We infer then that the changes X $\longrightarrow$ Y and Y $\longrightarrow$ (1b) largely involve crystal structure (packing) changes rather than any variations at the molecular level.

The changes in the i.r. spectrum of (1) at *ca.* 125 °C suggest very strongly that a hydroxyazo–quinone hydrazone tautomerism is involved. The carbonyl absorption at 1 628 cm⁻¹ in the low temperature spectrum probably originates from some hydrazone impurity which could not be avoided in the manual separation of crystals of (1a and b) or else the low temperature form itself contains a small amount of the hydrazone form, possibly as a solid solution. This point is discussed later.

The tautomerism of hydroxyazo-compounds in solution has been studied extensively using a variety of chemical and spectroscopic techniques.[9] It has been found generally that the hydroxyazo-form predominates for azophenols and that azonaphthols exist primarily as quinone hydrazones, especially in polar solvents. On the other hand there have been only a few crystallographic studies of these compounds. An even smaller number have a precision that would enable any firm conclusions to be drawn.[10–12] Guggenberger *et al.* have shown,[11] by location of the hydrazone hydrogen atom, that 2'-nitro-4'-chlorophenylazo-2-naphthol (Parachlor Red) (2) is correctly represented as the 1,2-naphthoquinone (2-nitro-4-chlorophenylhydrazone) while Kurahashi has suggested that 1-(2-thiazolylazo)-2-naphthol (3) seems to exist in the solid as a tautomeric mixture with possibly the larger contribution from the azo-form.[12]

However, not much is known about azaquinones, *i.e.*, quinone equivalents of 3-hydroxypyridine. One paper refers to 'hydroxylated derivatives which can exist in several tautomeric forms' and the fact that 'no evidence has been presented which unambiguously establishes which isomer or isomers predominate'.[13] A recent monograph notes that for such tautomers 'proton transfer may occur in the crystal' but that 'no well authenticated case is known for heteroaromatic compounds'.[14]

Crystal structure determinations of (1a and b) were undertaken to not only ascertain the tautomeric relationship between the two forms but, more fundamentally, to find the structural basis for the (1a) $\longrightarrow$ (1b) transformations.
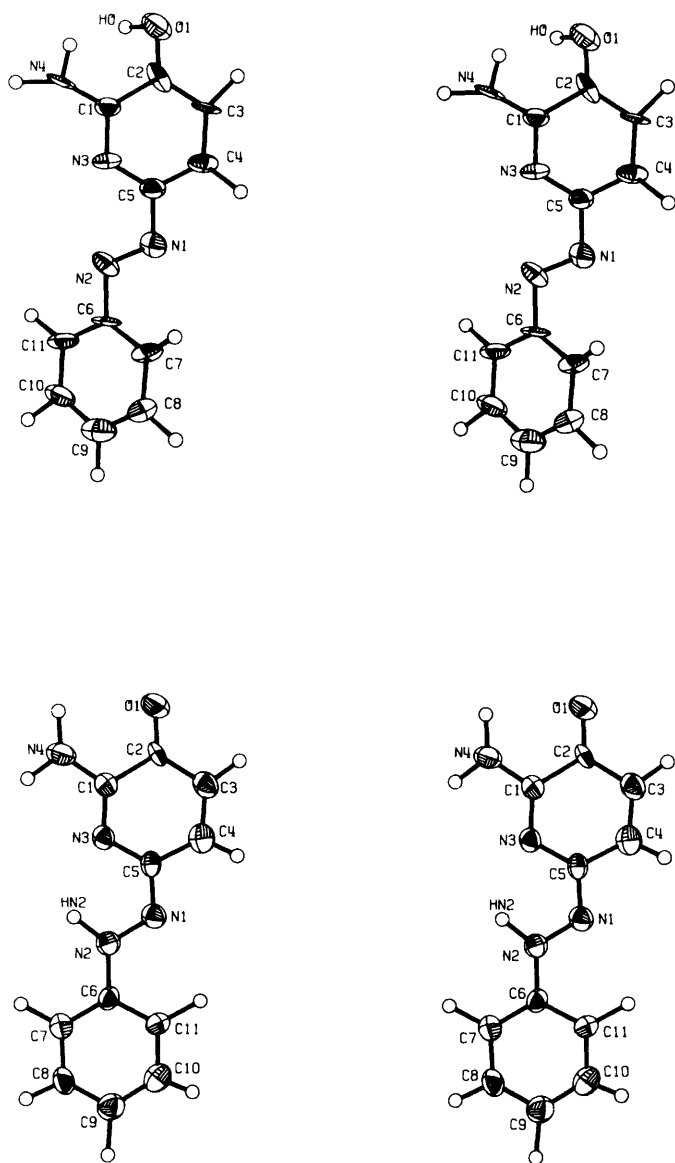
Figure 2. Stereodrawings of a single molecule of (1a and b)

Figure 3. Bond lengths and angles (with e.s.d.s) for (1a and b)

Molecular Changes in the Transformation.—Stereodrawings of a single molecule of (1a and b) are shown in Figure 2 while the bond lengths and angles (with e.s.d.s) are given in Figure 3. The molecule of (1b) is quite planar and the planes of the heterocyclic ring and the phenyl ring make angles of 6° with each other and angles of 6 and 1° with the plane formed by the four central atoms C(5), N(1), N(2), and C(6). In (1a), however, the two rings are at an angle of 34° to each other and inclined 6 and 28° to the central plane as defined above. We note that the bond lengths in (1b) are in good accord with an azaquinone hydrazone structure for this form. Not only is the C(2)−O(1) distance [1.233(7) Å] typical of a carbonyl group [1.248(7) Å in Parachlor Red] but N(1)−N(2) [1.330(7) Å] is almost the same as in Parachlor Red and approximately half-way between the values of the single bond distance between sp^2 nitrogens in benzaldehyde azine [1.412 (10) Å] [15] and the double bond distance in several azobenzenes (1.24 Å). [16] There is also a concomitant elongation and contraction of the bonds in the heterocyclic ring, consistent with quinonoid character. The significant difference between the lengths of C(5)−N(1), 1.315(7) Å, and C(6)−N(2), 1.396(7) Å, is also a sensitive indicator of the extent of quinonoid character in (1b).
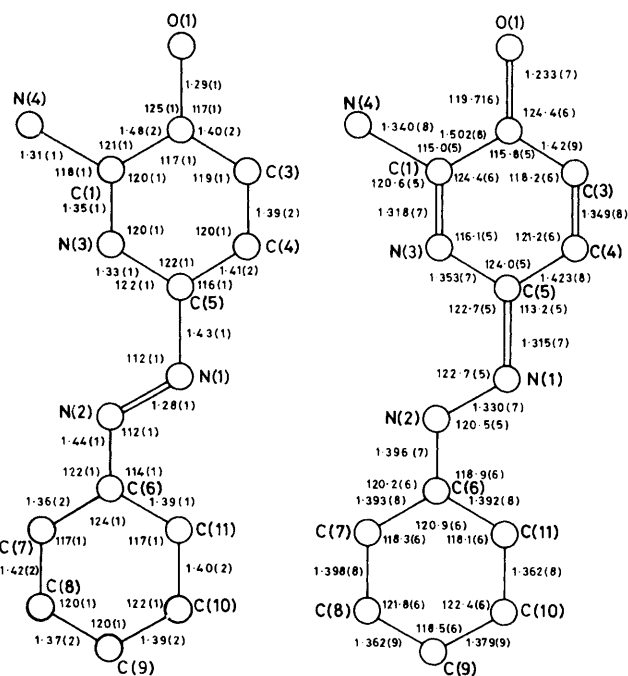
Clear evidence that (1b) is an azaquinone hydrazone was obtained from the unambiguous location of the hydrazone hydrogen H(N2) in a difference Fourier synthesis during the structure determination. The lengths of N(2)−H(N2) and N(3)−H(N2) are 1.08 and 2.13 Å with N(2) ··· N(3) being 2.667(6) Å. These distances indicate a moderately strong intramolecular hydrogen bond between the hydrazone hydrogen and the heterocyclic nitrogen. The formation of the five-membered ring may, in part, account for the contraction of the C(5)−N(3) bond to 1.353(7) Å (see Figure 3).

The molecular dimensions of (1a), in contrast, are more suggestive of a hydroxyazopyridine structure. Even though the precision of this structure is less than that for (1b), most of the significant lengths are clearly different and more than 3σ from the corresponding distances in (1b). The lengths around the heterocyclic ring are much closer to each other and parallel those in 6-bromo-2-hydroxypyridine which has been shown to be a pyridin-2-ol rather than a 2-pyridone in the solid state. [17] Appropriately, the N(1)−N(2) distance is 1.28(1) Å which is closer to the value for an azo double bond (1.24 Å) than is the corresponding distance in (1b).

It might also be suggested that (1a) is not exclusively an azo tautomer but that it contains some amount of the hydrazone form perhaps as a solid solution. We note that the i.r. spectrum of (1a) does indeed show a carbonyl stretch [though not as pronounced as in (1b)]. Though the e.s.d.s are large, the trends in the bond lengths also point in the same direction; the C(2)−O(1) distance, 1.29(1) Å, is slightly less than the 1.33 Å of 6-bromo-2-hydroxypyridine while N(1)−N(2) is 1.28(1) Å rather than the 1.24 Å of azobenzene.

Structural Changes in the Transformation.—More conclusive evidence that (1a and b) are the azo and hydrazone tautomers, respectively, of (1) can be obtained indirectly from the crystal structures and especially the hydrogen bonding arrangement in the two forms. Both forms are extensively hydrogen bonded but the nature and disposition of these bonds are remarkably different in the two structures. In (1b) the hydrogen bonding is of two types: an intramolecular bond
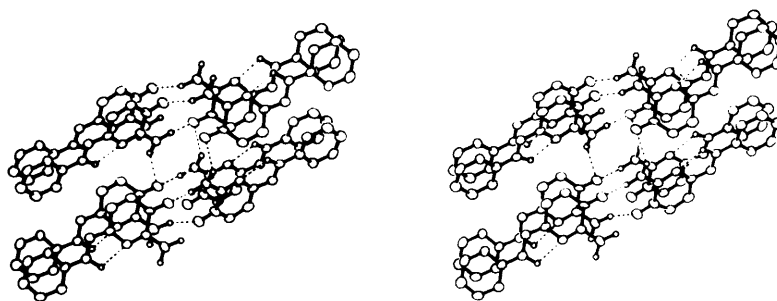
Figure 4. Stereodrawing of packing of (1b) down [011]. The reference molecule is at the bottom left corner. The *a* direction is along the horizontal. Hydrogen bonds are shown as dotted lines
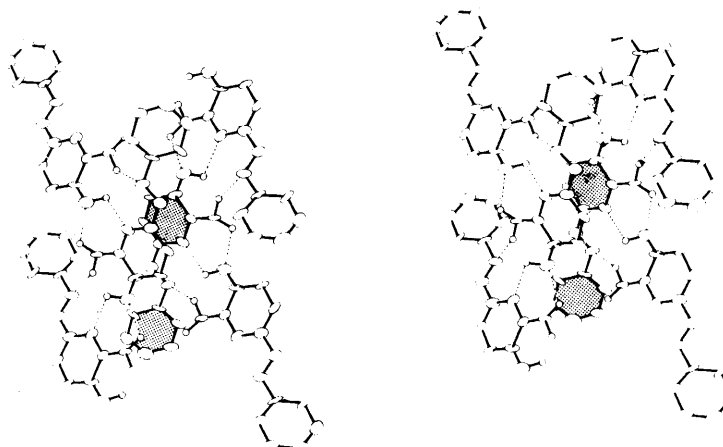

Figure 5. Stereodrawing of the packing of (1a) down [010]. The vertical direction is *c* and the horizontal direction *a*. Hydrogen bonds are shown as dotted lines. The reference molecule is shaded. Also shown is the molecule $(1 - x, 1 - y, 1 - z)$. Four other molecules related to these two by a 2_1 axis along *c* complete the Figure

between the hydrazone hydrogen H(N2) and the heterocyclic nitrogen N(3) and an intermolecular helical network around the two-fold screw axis that involves the amino-group of the reference molecule and a carbonyl group of a screw-related neighbour (Figure 4). Each amino-group is, in turn, bonded to an oxygen atom of a glide related molecule through its second hydrogen atom so that the helices are, in effect, themselves hydrogen bonded along the *c* direction. Alternatively each oxygen atom can be considered as being hydrogen bonded to two amino-hydrogens from two adjacent molecules with distances $O(x,y,z)^-N(4)$ $(2 - x, 1/2 + y, 1\frac{1}{2} - z)$ of 2.995(7) and $O(x,y,z)^-N(4)$ $(x, -1/2 - y, 1/2 + z)$ of 3.120(6) Å. The implication is, of course, that such an oxygen atom must be a carbonyl oxygen since this hydrogen bonding geometry would clearly be most unusual if the oxygen were to bear a phenolic hydrogen atom. A final feature of interest in structure (1b) is the very short repeat distance (3.886 Å) along the *b* direction, which is the direction of the hydrogen bonded helix. Every third molecule in the helix is a repeat of the first, every fourth of the second, and so on. This highly overlapped arrangement along *b* may be the reason for the lustrous, almost metallic appearance of crystals of (1b).

In contrast, the structure of (1a) displays a more open hydrogen bonding arrangement. It will be seen that this arrangement is consistent with a hydroxyazo structure. The packing down [010] is shown in Figure 5 while a schematic projection onto (101) showing hydrogen bond distances is given in Figure 6. Each amino-group is hydrogen bonded to an azo-nitrogen atom N(2) of a screw related molecule; N(4)-$(x,y,z)^-N(2)$ $(1/2 - x, 1 - y, -1/2 + z)$ is 3.17(1) Å. It is also hydrogen bonded to an oxygen atom of another screw
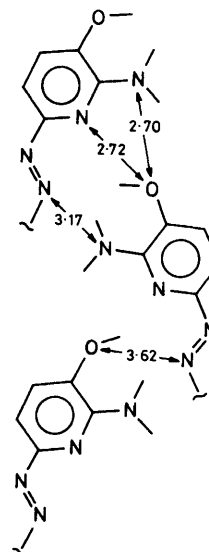

Figure 6. Schematic diagram of (1a) down [010] showing hydrogen bonds. The e.s.d.s are 0.01 Å in all cases

related molecule; N(4) $(x,y,z)^-O(1)$ $(1/2 - x, 1 - y, 1/2 + z)$ is 2.70(1) Å. Each oxygen atom is, in turn, hydrogen bonded to not only an amino-group as described above but also to a pyridyl nitrogen atom such that O(1) $(x,y,z)^-N(3)$ $(1/2 - x, 1 - y, -1/2 + z)$ is 2.72(1) Å. This hydrogen bonding arrangement is a strong indication that a proton is located on the oxygen atom and that there is no proton in the N(2)
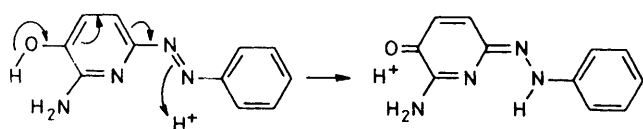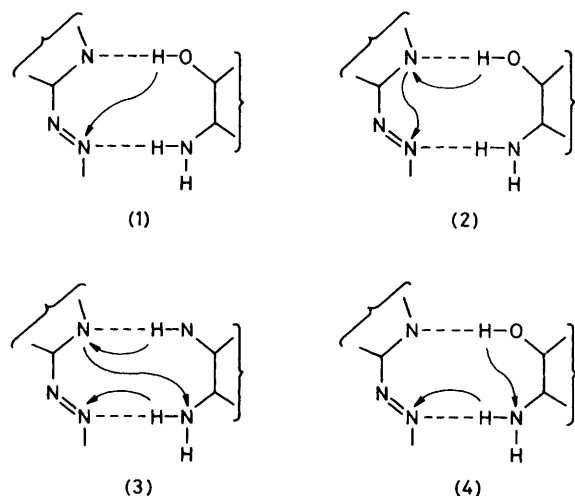
Scheme.

Figure 7. Possibilities (1)—(4) for intermolecular proton transfer in the solid state for the (1a) ⟶ (1b) transformation. The arrowheads represent the direction of proton movement

nitrogen atom; therefore (1a) is truly a hydroxyazo-tautomer. The distance to the oxygen atom to the nearest azo nitrogen N(2) is too long to be a hydrogen bond [3.62(1) Å].

Since the results of the crystal structure analyses and i.r. spectroscopy clearly indicate a tautomeric rearrangement of mobile protons in the solid state, the structure of (1a) should provide clues as to how such a proton shift could occur in the change. Clearly, such a tautomeric shift cannot be intramolecular in the solid state; the distances involved would be too great. Further the hydrogen shifts must be co-operative; while a phenolic hydrogen is lost to a neighbouring molecule, a similar proton from an adjacent site bonds to a hydrazone N(2) atom, so that the overall change is migration of a proton from oxygen to nitrogen (Scheme).

The structure of (1a) shows extensive hydrogen bonding across short distances and several processes can be formulated for the proton shifts. Four possibilities (1)—(4) will be mentioned here and are illustrated in Figure 7 but in the absence of further experimental evidence, it is not possible to define the ' correct ' mechanism for proton transfer. The factors taken into account in the formulation of these alternatives are: (a) minimum motion of heavy atoms, (b) relative basicities of the phenolic oxygen and of the amino, azo and pyridyl nitrogens in (1a), and (c) the lesser likelihood of charge separated canonical forms as intermediates.

The problem, in essence, is to determine the fate of a labile proton with respect to four basic sites, all within reasonable distance of each other. It must be noted that possibility (1) envisages a relatively large proton jump of 3.61 Å. The second possibility involves proton tunnelling across the hydrogen bonds O(1) ⋯ N(3) and N(3) ⋯ N(2) both relatively short distances. If the amino group, also highly basic, is taken into account, possibilities (3) and (4) have to be considered. Obviously more work, especially with related systems having slightly simpler hydrogen bond arrangements, is necessary before it is possible to draw firm conclusions.

Whatever the mechanism, however, the loss of the proton at oxygen is balanced by the acquisition of one at nitrogen in the same molecule by a similar process. Thus the overall effect is an intermolecular tautomeric proton shift.

Conclusions.—It has been shown that the forms (1a and b) of the azo-dye (1) are its hydroxyazo and quinone hydrazone tautomers and that the thermal rearrangement of (1a) to (1b) in the solid state involves intermolecular proton shifts from a phenolic oxygen in the azo-form to a hydrazone nitrogen in the quinonoid form.

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