0.5-mm silica gel plate eluted with ethyl acetate afforded 17 mg of a mixture of **9c** and **10c** as a colorless oil (R_f 0.41) along with 8 mg of reduction product **10a** (R_f 0.15) and 8 mg of recovered ketone **8** (R_f 0.29). The mixture of **9c** and **10c** was rechromatographed on a 0.25-mm silica gel plate eluted twice with 3.5% methanol in methylene chloride. Two bands were extracted from the plate. The first (R_f 0.42) afforded 9 mg (20%) of **9c** as a colorless oil. The second band (R_f 0.30) afforded 3 mg (7%) of **10c** as a colorless oil. Potassium hydride (6 drops of a 25% oil dispersion) was added to a solution of **9c** (15 mg, 0.025 mmol) in 1 mL of dry THF. The mixture was stirred at room temperature for 15 min and then cooled to −78 °C. A solution of *tert*-butyllithium in pentane (0.15 mL of 2 M pentane solution, 0.30 mmol) was added and the yellow mixture was stirred at −78 °C for 2 h. Water (1 mL) was then added cautiously and the mixture was allowed to warm to ca. 5 °C. Ether (2 mL) was added and the layers were separated. The aqueous layer was extracted with ether (2 × 2 mL) and ethyl acetate (2 × 2 mL). The combined extracts were dried, filtered, and evaporated under vacuum. Preparative TLC of the oily residue on a 0.5-mm silica gel plate eluted with ethyl acetate afforded 9 mg (69%) of **11c** as a colorless oil (R_f 0.30). ^{1}H NMR data: δ 7.84 (1 H, br s, NH), 6.79 (1 H, d, J = 8 Hz, H_4), 6.66 (1 H, d, J = 8 Hz, H_5), 6.30 (1 H, d, J = 8 Hz, H_{24}), 4.87 (1 H, d, J = 8 Hz, H_{25}), 3.59 and 2.53 (2 × 1 H, 2 d, J = 11 Hz, H_{12}), 3.22–3.14 (1 H, m, H_{16b}), 3.03 (3 H, s, NCH_3), 3.00 (1 H, br dd, J = 10, 10 Hz, H_{20}), 2.68 and 1.85 (2 × 1 H, 2 d, J = 15 Hz, H_{10}), 2.59 (1 H, br s, OH), 2.30–2.15 (2 H, m, H_{15b} and H_{16}a), 1.92–1.70 (5 H, m, H_{15}a + H_{17} + H_{19}), 1.43 and 1.42 (2 × 3 H, 2 s, H_{27} and H_{28}), 1.08 and 0.83 (2 × 3 H, 2 s, H_{22} and H_{23}), 1.02 (3 H, t, J = 8 Hz, 17-CH_3). HRMS: m/z (M^+, $C_{29}H_{37}N_3O_5$) calcd 507.2733, obsd 507.2733. Application of the procedure described above to 5 mg of **10c** afforded a yellow oil, which was chromatographed on a 0.25-mm silica gel plate eluted with ethyl acetate to afford 3 mg (70%) of**12c** as a colorless oil (R_f 0.35). ^{1}H NMR data: δ 7.51 (1 H, br s, NH), 6.78 (1 H, d, J = 8 Hz, H_4), 6.66 (1 H, d, J = 8 Hz, H_5), 6.50 (1 H, br s, OH), 6.30 (1 H, d, J = 8 Hz, H_{24}), 4.87 (1 H, d, J = 8 Hz, H_{25}), 3.60 and 2.59 (2 × 1 H, 2 d, J = 11 Hz, H_{12}), 3.05–2.95 (2 H, m, H_{16b} and H_{20}), 3.08 (3 H, s, NCH_3), 2.68 and 1.85 (2 × 1 H, 2 d, J = 15 Hz, H_{10}), 2.50–2.40 and 2.22–2.10 (2 × 1 H, 2 m, H_{15b} and H_{16a}), 2.02–1.80 (3 H, m, H_{15a} and H_{19}), 1.74–1.54 (2 H, m, H_{17}), 1.43 and 1.42 (2 × 3 H, 3 s, H_{27} and H_{28}), 1.08 and 0.84 (2 × 3 H, 2 s, H_{22} and H_{23}), 1.02 (3 H, t, J = 8 Hz, 17-CH_3). HRMS: m/z (M^+, $C_{29}H_{37}N_3O_5$) calcd 507.2733, obsd 507.2733.

17-Norparaherquamide (11a) and 14-Epi-17-norparaherquamide (12a). A solution of 1 M lithium aluminum hydride in ether (0.14 mL, 0.14 mmol) was added to a cold (ice bath) solution of **8** (39 mg, 0.07 mmol) in 2 mL of dry THF. The mixture was stirred at 0 °C for 20 min and then water (1 mL) and ether (2 mL) were added and the layers separated. The aqueous layer was extracted with ether (2 × 2 mL) and ethyl acetate (2 × 2 mL). The combined extracts were dried, filtered, and evaporated under vacuum. Preparative TLC of the residue on a 0.5-mm silica gel plate eluted with 7% methanol in methylene chloride afforded 10 mg (26%) of **9a** as a colorless oil (R_f 0.20). A second band (R_f 0.36) afforded 15 mg (38%) of **10a** as a colorless oil. Application of the debromination procedure described above to 17 mg of **9a** and preparative TLC of the crude product on a 0.5-mm silica gel plate eluted with 7% methanol in methylene chloride afforded 4 mg (27%) of **11a** as a colorless oil (R_f 0.24). ^{1}H NMR data: δ 7.54 (1 H, br s, NH), 6.80 (1 H, d, J = 8 Hz, H_4), 6.66 (1 H, d, J = 8 Hz, H_5), 6.30 (1 H, d, J = 8 Hz, H_{24}), 4.88 (1 H, d, J = 8 Hz, H_{25}), 4.72 (1 H, br t, J = Hz, H_{14}), 3.63 and 2.61 (2 × 1 H, 2 d, J = 11 Hz, H_{12}), 3.18 (1 H, br t, J = 9 Hz, H_{16b}), 3.05 (1 H, br dd, J = 10, 10 Hz, H_{20}), 3.05 (3 H, s, NCH_3), 2.68 and 1.86 (2 × 1 H, 2 d, J = 15 Hz, H_{10}), 2.51–2.39 (1 H, m, H_{15b}), 2.22–2.10 (1 H, m, H_{16a}), 1.94–1.74 (4 H, m, H_{15a} + H_{19} + OH), 1.53 and 1.52 (2 × 3 H, 2 s, H_{27} and H_{28}), 1.11 and 0.85 (2 × 3 H, 2 s, H_{22} and H_{23}). HRMS: m/z (M^+, $C_{27}H_{33}N_3O_5$) calcd 479.2420, obsd 479.2420. Application of the debromination procedure described above to 21 mg of **10a** and preparative TLC of the crude product on a 0.5-mm silica gel plate eluted with 50% acetone in hexane afforded 9 mg (50%) of **12a** as a colorless oil (R_f 0.25). ^{1}H NMR data: δ 7.62 (1 H, br s, NH), 6.81 (1 H, d, J = 8 Hz, H_4), 6.68 (1 H, d, J = 8 Hz, H_5), 6.31 (1 H, d, J = 8 Hz, H_{24}), 5.53 (1 H, d, J = 11 Hz, OH), 4.90 (1 H, d, J = 8 Hz, H_{25}), 4.10–4.00 (1 H, m, H_{14}), 3.59 and 2.57 (2 × 1 H, 2 d, J = 11 Hz, H_{12}), 3.15–3.04 (2 H, m, H_{16b} and H_{20}), 3.09 (3 H, s, NCH_3), 2.69 and 1.87 (2 × 1 H, 2 d, J = 15 Hz, H_{10}), 2.48–2.32 (2 H, m, H_{15b} and H_{16a}), 2.21 (1 H, d, J = 11, 12 Hz, H_{19a}), 1.98–1.85 (1 H, m, H_{15a}), 1.52 (1 H, d, J = 11, 12 Hz, H_{19b}), 1.46 and 1.45 (2 × 3 H, 2 s, H_{27} and H_{28}), 1.11 and 0.88 (2 × 3 H, 2 s, H_{22} and H_{23}). HRMS: m/z (M^+, $C_{27}H_{33}N_3O_5$) calcd 479.2420, obsd 479.2420.

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Registry No. **1**, 77392-58-6; **2**, 125451-71-0; **3**, 125439-04-5; **4**, 125439-05-6; **7**, 125439-06-7; **8**, 125439-07-8; **9a**, 125515-20-0; **9b**, 120312-83-6; **9c**, 125439-09-0; **9d**, 125439-12-5; **10a**, 125439-08-9; **10b**, 125515-22-2; **10c**, 125515-18-6; **10d**, 125439-13-6; **11a**, 125439-11-4; **11c**, 125439-10-3; **11d**, 125439-14-7; **12a**, 125515-21-1; **12b**, 125515-23-3; **12c**, 125515-19-7; **12d**, 125439-15-8.

Supplementary Material Available: Experimental procedures for **11d**, **12b**, and **12d** and an alternative procedure for **4**; ^{1}H NMR spectra (300 MHz) of all title compounds and isolated intermediates; and ^{13}C NMR data for **2**, **3**, **8**, and **11d** (21 pages). Ordering information is given on any current masthead page.

Two Rings in One Step: A Novel 1,2,4-Triazolo[1,5-*a*]pyridone with an Unusual Crystal Structure

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Although the title molecules are reported to be useful compounds,[1] they are not easy to obtain.

The known methods for the synthesis of 1,2,4-triazolo[1,5-*a*]pyridines require several steps, with separate formation of each ring. The key step usually involves the construction of a triazole ring on a pyridine compound,[2-8] although syntheses starting from a triazole derivative have also been reported.[9] Triazolo[1,5-*a*]pyridines have also been prepared by ring transformation of isomeric triazolo[4,3-*a*]pyridines[10] and from 2-thioxopyrones.[11]

We report in this paper a one-step synthesis of a triazolo[1,5-*a*]pyridine, in anion form, involving the simultaneous generation of the two heterocyclic rings from acyclic starting materials.[12]

The reaction is very simple to carry out. It is performed in ethanol solution, using piperidine as the intended basic catalyst. A crystalline solid is thus obtained in moderate yield.

Structural assignment of this compound could not be unambiguously made from analytical and spectral data, showing the presence of a molecule of piperidine per molecule of each reactant, in disagreement with the mo-

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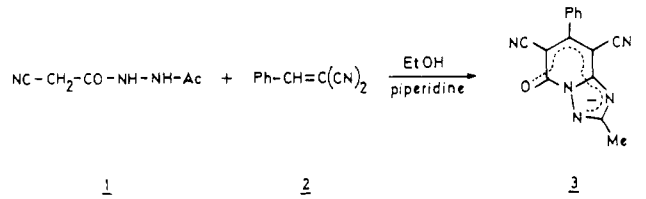
0022-3263/90/1955-2259$02.50/0

Scheme I



1 2 3

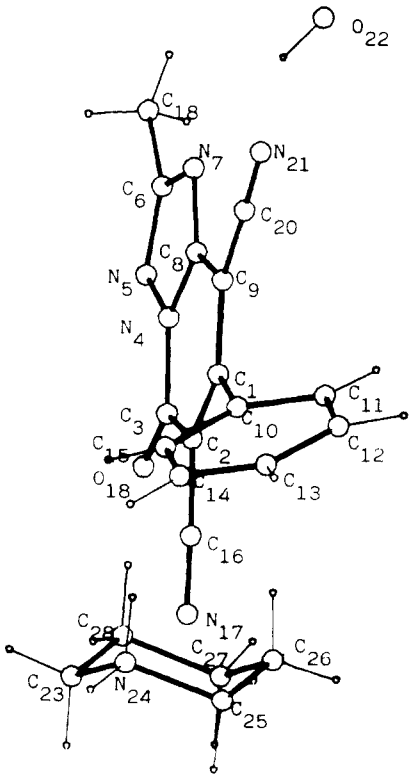


Figure 1. Perspective drawing of salt **3**, showing a unit of each component. The unseen water hydrogen is situated along a symmetry axis.

lecular mass given by the mass spectrum. Therefore, an X-ray crystallographic analysis was carried out. Compound **3** (Scheme I) was found to be a novel 1,2,4-triazolo[1,5-*a*]pyridone system as its piperidinium salt in a complex crystal structure including a water molecule. Figure 1 is a perspective drawing of **3** with the atomic labeling used in the crystallographic study. One triazolopyridine molecule, together with one piperidine and one water unit, are shown.

The 1,2,4-triazolo[1,5-*a*]pyridone rings are nearly planar, the phenyl group being the only substituent out of this plane. The piperidine ring is in a slightly distorted chair conformation.

The piperidine ring contains a quaternary nitrogen atom as a piperidinium cation. This positive charge is neutralized as a salt by a negative charge in the fused heterocyclic system, which exists as an anion with no ring hydrogens. The high acidity of the ring proton is due to the anion's stability, resulting from charge delocalization involving two triazole nitrogens. The pyridone oxygen extends delocalization to the six-membered ring (Scheme II). This bond delocalization is in agreement with the previously mentioned molecular planarity and the very small differences in interatomic distances within the rings (Table I).

The salt shows an unusual crystal packing, resulting from a complex hydrogen bonding network (Table II) involving two triazolopyridone units, two piperidine units, and one water molecule, which occupies a center of sym-

Scheme II

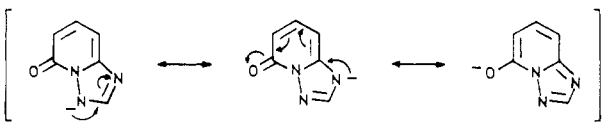


Table I. Bond Distances (Å)

C1–C2	1.412 (8)	C10–C11	1.395 (9)
C1–C9	1.397 (8)	C10–C15	1.395 (9)
C1–C10	1.492 (8)	C11–C12	1.406 (10)
C2–C3	1.429 (8)	C12–C13	1.374 (11)
C2–C16	1.425 (9)	C13–C14	1.377 (11)
C3–N4	1.405 (7)	C14–C15	1.381 (9)
C3–O18	1.231 (7)	C16–N17	1.139 (8)
N4–N5	1.380 (7)	C20–N21	1.145 (8)
N4–C8	1.369 (8)	C23–N24	1.507 (9)
N5–C6	1.323 (8)	C23–C28	1.501 (10)
C6–N7	1.366 (8)	N24–C25	1.506 (9)
C6–C19	1.491 (10)	C25–C26	1.512 (11)
N7–C8	1.334 (8)	C26–C27	1.508 (11)
C8–C9	1.417 (8)	C27–C28	1.531 (11)
C9–C20	1.423 (8)		

Table II. Hydrogen Bonds

donor-H	donor···acceptor[a]	H···acceptor[a]	donor-H···acceptor[a]
N24–H242	N24···O18 (0)	H242···O18 (0)	N24–H242···O18 (0)
0.945 (0.066)	2.862 (0.007)	1.918 (0.066)	176.80 (6.06)
O22–H22	O22···N7 (0)	H22···N7 (0)	O22–H22···N7 (0)
0.823 (0.061)	2.893 (0.003)	2.073 (0.061)	173.74 (6.00)
N24–H241	N24···O22 (1)	H241···O22 (1)	N24–H241···O22 (1)
0.957 (0.067)	2.898 (0.006)	1.989 (0.066)	158.15 (5.68)
N24–H241	N24···O22 (2)	H241···O22 (2)	N24–H241···O22 (2)
0.957 (0.067)	2.898 (0.006)	1.989 (0.066)	158.15 (5.68)

[a] (0) X, Y, Z; (1) $-X + {}^1/_2, Y - {}^1/_2, -Z + {}^1/_2$; (2) $X - {}^1/_2, Y - {}^1/_2, Z$.

(1) They are of interest as pharmaceuticals (immune adjuvants, stomach secretion inhibitors, antivirals, antihypertensives): Kyorin Pharmaceutical Co. French Patent 2450259, 1980; *Chem. Abstr.* **1982**, *97*, 72373*z*. Kuba, K.; et al. Yamamondu Pharmaceutical Co. Japanese Patent 7905996, 1979; *Chem. Abstr.* **1979**, *91*, 57007. Busseran, F.; Chermann, J. C.; De Clercq, E.; Hannoun, C.; *Ann. Virol.* **1983**, *134E*, 127. Carey, L.; et al. Eur. Pat. Appl. EP 48, 555, 1980; *Chem. Abstr.* **1982**, *97*, 55814*b*. As fluorescent brighteners for fabrics and fibers: Buell, B. G.; et al. American Cyanamid, U.S. Patent 3272831, 1966; *Chem. Abstr.* **1967**, *66*, 19832*g*. Weber, K. Ciba-Geigy Eur. Pat. Appl. E.P. 67792, 1982, *Chem. Abstr.* **1983**, *98*, 127689*k*. As complexing agents: Sanni, S. B.; et al. *J. Cryst. Spect. Res.* **1987**, *17*, 81.

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(11) Molina, P.; Alajarín, M.; Soler, A. *An. Quim., Ser. C*, **1980**, *76C*, 207.

(12) To tell the whole story, the original aim of this project was the synthesis of diazepinones by using $NCCONHAcNH_2$ as the reactant. However, the attempted synthesis of this compound, perhaps through an intramolecular transacetylation, yielded **1**, from which resulted the synthesis described in this paper.

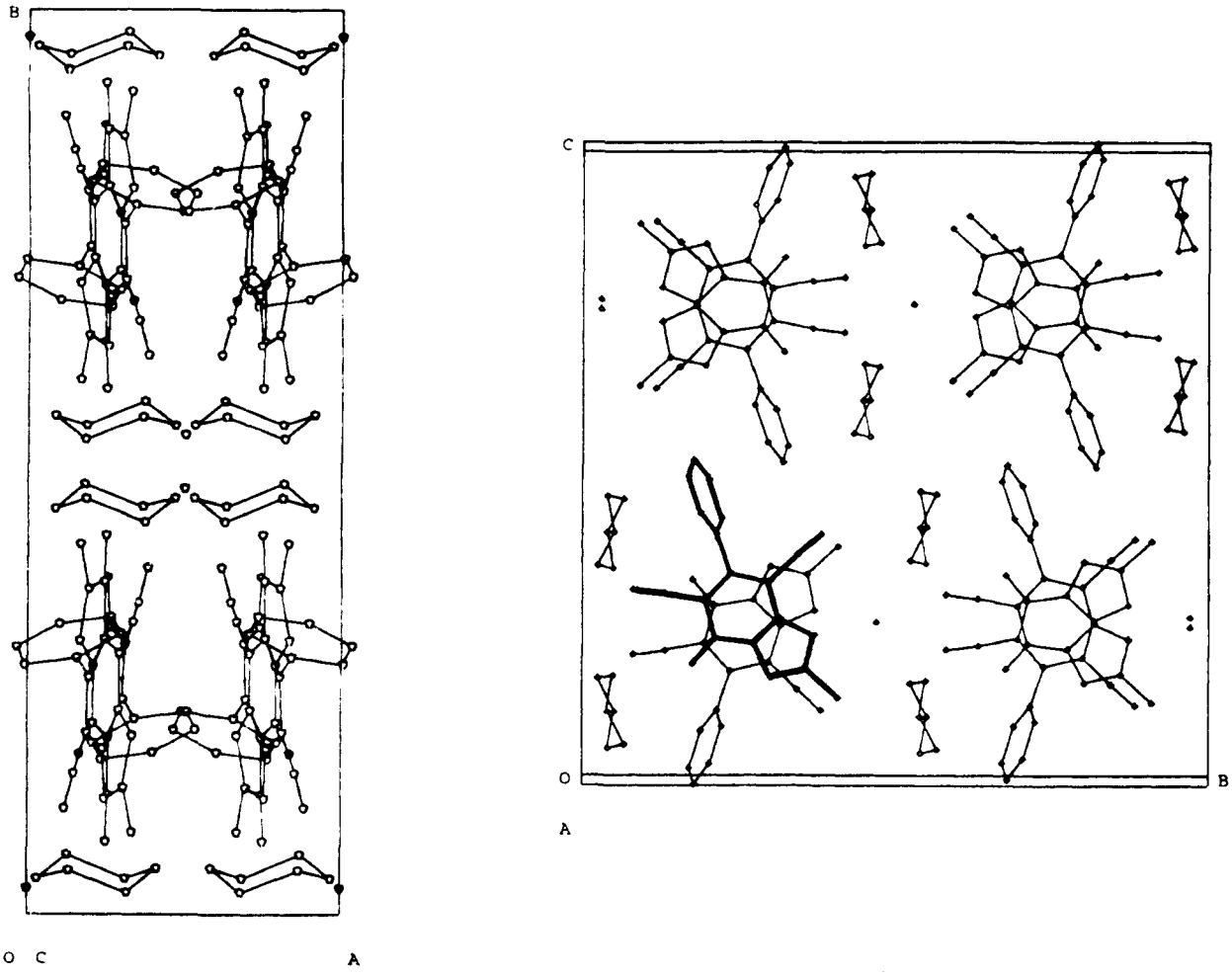

Figure 2. Crystal lattice of **3** along the *c* axis (left) and the *a* axis (right). The stoichiometry corresponds to a 2:1:2 ratio for the triazolopyridone/water/piperidinium units. In the view along the *a* axis, the water oxygen of the molecules above and below the projection plane appear duplicated in this representation (PLUTO78)[25] of the monoclinic crystal.

metry and is therefore disordered. The nitrogen protons of the piperidinium cation form two hydrogen bonds with ^{18}O and the water oxygen. In addition, the water oxygen bonds itself to another piperidinium ring and acts as a donor in its hydrogen bond with the heterocyclic N_7 atom. Thus, the water molecule is an acceptor in two hydrogen bonds and a donor in another two. This strong network of hydrogen bonding (Figure 2) contributes to the high stability of the system. In fact, the salt can be recrystallized without affecting the water contained in the crystal structure.

Formation of **3** can be rationalized as depicted in Scheme III. Base-catalyzed Michael addition of the acidic methylene group in **1** to the unsaturated nitrile **2** yields the open-chain intermediate **4**, which cyclizes to *N*-acetyl-1-aminopyridone **5**. The presence in intermediate **5** of an amino and acetylamino group next to one another allows the attack by the ring amino at the amide group, which behaves as a carbonyl group and leads to a dehydration. The nonisolable triazolopyridone **7** loses its acidic proton to a piperidine molecule, yielding salt **3**. The carbonyl group in the pyridine ring is responsible for this situation. In fact, triazolopyridines tend to behave only as bases, giving cations, sometimes as mesoionic compounds.[13-15] Simpler triazolopyridine systems are isolated as neutral compounds, and the molecules are held together only by van der Waals interactions.[16]

Experimental Section

Melting points were determined on a Büchi apparatus in capillary tubes and are uncorrected. Infrared spectra were obtained on Perkin-Elmer 257 and 781 spectrometers as KBr disks. The nuclear magnetic resonance spectrometers used were a Varian T 60A for the ^1H NMR spectra and a Varian FT-80A for the ^{13}C NMR spectra. Chemical shifts are given in ppm, downfield from internal tetramethylsilane. Reactions were monitored by TLC, using silica gel as the adsorbent and chloroform–methanol as the eluent. 2-Cyanoacetohydrazide and malononitrile were obtained from commercial sources and used without further purification.

X-ray Crystallographic Measurements. Crystal data: $C_{40}H_{42}N_{12}O_3$, M_r = 738.85, monoclinic, $C2/c$, a = 7.592 (2) Å, b = 22.093 (2) Å, c = 22.450 (2) Å, β = 92.66 (2), V = 3761 (1) Å^3, D = 1.3047 g/cm^3, z = 4, $F(000)$ = 1560, μ = 0.813 cm^{-1}. A suitable crystal of 0.30 × 0.30 × 0.35 mm was mounted on an automatic four-circle Enraf Nonius CAD-4 diffractometer with graphite-monochromated MoKα radiation. Refined cell parameters were obtained from setting angles of 45 reflections. The intensity data were collected using the $\omega/2\theta$ scan mode between $2 < \theta < 30°$; two standard reflections were measured every 100 reflections with no intensity variation. A total of 5484 reflections were measured and 1502 were considered as observed with the criterium $I > 3\sigma(I)$. R_{int} = 0.011. Index range h, 0/10; k, 0/30; l, −31/31. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using MULTAN80[17] and successive

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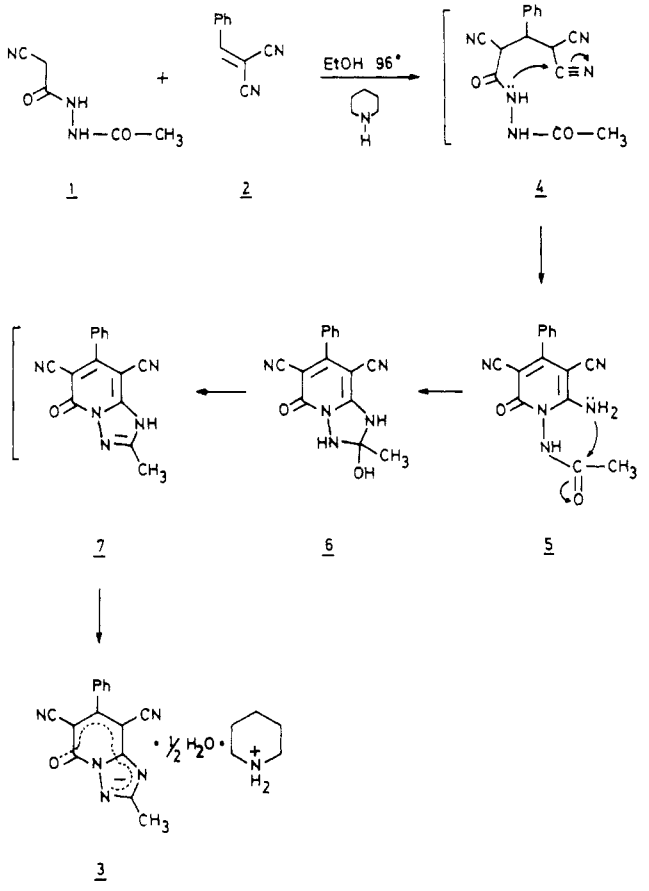
Scheme III



Fourier synthesis and shows the water oxygen in special position. The structure was refined with isotropic thermal parameters first, anisotropic later, for non-hydrogen atoms; H atoms included in mixed refinement with isotropic thermal parameters fixed. A convenient weighting scheme was applied to obtain flat dependence in $\langle w\Delta^2F\rangle$ vs $\langle F_o\rangle$ and vs $\langle \sin\theta/\lambda\rangle$.[18] Final R values: $R = 0.062$, $R_w = 0.052$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[19] Calculations were performed using XRAY76[20] and PARST.[21]

2′-Acetyl-2-cyanoacetohydrazide (1). A suspension of 20 mmol (2.0 g) of 2-cyanoacetohydrazide in 50 mL of acetic anhydride was kept at 60–70 °C for 10 h. After standing overnight, a white precipitate was formed. It was collected by filtration and washed with plenty of water to give 1.2 g (40% yield) of **1**: mp 176–178 °C (from ethyl acetate); IR (KBr) 3270 (NH), 3200 (NH), 2250 (CN), 1620 (CO) cm^{-1}; ^1H NMR (CD_3SOCD_3) δ 1.83 (s, 3 H, CH_3), 3.67 (s, 2 H, CH_2), 9.77 (br s, 1 H, NH), 9.97 (br s, 1 H, NH); ^{13}C NMR (CD_3SOCD_3) δ 20.5 (CH_3), 23.9 (CH_2), 115.8 (CN), 161.5 (CO), 168.3 (CO); mass spectrum, m/e 141 (M^+, 9), 102 (4), 101 (17), 100 (12), 99 (51), 70 (7). Anal. Calcd for $C_5H_7N_3O_2$: C, 42.55; H, 4.96; N, 29.79. Found: C, 42.70; H, 5.10; N, 29.80.

α-Cyanocinnamonitrile (2). This compound was prepared from malononitrile and freshly distilled benzaldehyde as previously reported.[22]

Piperidinium 6,8-Dicyano-2-methyl-5-oxo-7-phenyl-1,2,4-triazolo[1,5-*a*]pyridinide Hemihydrate (3). 2′-Acetyl-2-cyanoacetohydrazide (**1**) (0.5 g, 4 mmol) and α-cyanocinnamonitrile (**2**) (0.54 g, 4 mmol) were suspended in ca. 8 mL of ethanol containing a few drops of piperidine. The mixture was refluxed for 9 h, until TLC showed no starting materials left. The precipitate that separated was collected by filtration to give 0.38 g (37% yield) of **3**: mp 143–145 °C dec (from ethanol); IR (KBr) 3260, 3040, 2840, 2820, 2205, 1625, 1605, 1560, 1510 cm^{-1}; ^1H NMR (CD_3SOCD_3) δ 1.62 (b, 6 H, 3 CH_2 pip.), 2.38 (s, 3 H, CH_3), 3.05 (b, 4 H, 2 CH_2 pip.), 7.53 (s, 5 H, arom); ^{13}C NMR (CD_3SOCD_3) δ 14.19 (CH_3), 21.68 (γ-CH_2, piperidinium), 22.29 (β-CH_2, piperidinium), 43.98 (α-CH_2, piperidinium) (values in agreement with the literature[23]), 82.77, 90.94 (C_3, C_5 pyridone, see ref 24), 116.95, 118.42 (CN), 128.39, 128.67, 129.40 (C arom), 136.06 (C arom ipso), 153.10, 154.64, 156.46 (C_4, C_6 pyridone, C triazole), 162.24 (C=O); mass spectrum, m/e 275 (18), 274 (100), 273 (29), 247 (12), 86 (9), 85 (53), 84 (94). Anal. Calcd for $C_{40}H_{42}N_{12}O_3$: C, 65.04; H, 5.69; N, 22.76. Found: C, 65.34; H, 5.94; N, 22.73.

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Registry No. **1**, 55819-76-6; **2**, 2700-22-3; **3**·piperidine, 124443-25-0; **3**·piperidine hemihydrate, 124443-24-9; 2-cyanoacetohydrazide, 140-87-4.

Supplementary Material Available: Full X-ray data for compound **3** (4 pages). Ordering information is given on any current masthead page.

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