

Table 1
Crystallographic Data and Structural Refinement for Compound **1** and Its Hydroperchlorate **1a** [a]

		For 1	For 1a
Empirical formula		C ₁₀ H ₆ N ₂ S	C ₁₀ H ₇ ClN ₂ O ₄ S
Formula weight		186.23	286.69
Crystal appearance		colorless plate	yellow lath [b]
Crystal dimensions (mm)		0.50 × 0.29 × 0.015	0.065 × 0.19 × 0.57
Crystal system		orthorhombic	triclinic
Space group		Pna2 ₁	P(-1)
Unit cell dimensions (Å)	a	18.722 (4)	5.454 (1)
	b	3.877 (1)	8.095 (1)
	c	11.445 (1)	13.053 (2)
Unit cell angles (°)	α	90	101.65 (1)
	β	90	92.08 (1)
	γ	90	93.17 (1)
Unit cell volume (Å ³)		830.7 (2)	562.9 (2)
Z		4	2
Density (calculated) (g/cm ³)		1.489	1.691
Linear absorption coefficient (μ)		3.32 cm ⁻¹	5.32 cm ⁻¹
F (000)		384	292
Temperature (°C)		22	23
Maximum 2θ		54°	50°
Index ranges, <i>h</i> , <i>k</i> , <i>l</i>		0→23, 0→4, 0→14	0→6, -9→9, -15→15
Scan mode		ω-2θ	ω-2θ
Scan speed on ω (°/min)		3.3	4.1
Scan width (°)		0.95 + 0.35 tanθ	1.15 + 0.35 tanθ
Reference reflections			3, every 3600s exposure
Independent rflxns. scanned		943	1967
R _{int} (on F ²)		none measured	0.011
Absorption correction		none	azimuthal scans
Relative correction factors		-----	0.83-1.00
Secondary extinction parameter		fixed at zero	fixed at zero
Reflections in refinement (N)		943 (all data)	1645 [I≥σ(I)]
Number of parameters (V)		117	191
Function minimized		Σw(F _o - F _c) ²	Σw(F _o - F _c) ²
Weighting factor w		1/σ ² (F)	1/σ ² (F)
R(F), wR(F) [I≥σ(I)] [a]		-----	0.045, 0.051
R(F ²), wR(F ²) (all data) [a]		0.075, 0.088	-----
S [a]		1.15 (all data)	2.31 [I≥σ(I)]
Maximum Δ/σ, last cycle		0.01	0.01
Max., min. in final difference map (e/Å ³)		0.47, -0.55	0.45, -0.37

[a] For the diffractometer, radiation wavelength, and monochromator used, as well as the algebraic relationships for R(F), wR(F), wR(F²), and S, see references 13 and 14. [b] Analogously, colorless benzo[*h*]quinoline forms yellow salts with hydrogen chloride and with sulfuric acid. See J. Buckingham and S. M. Donaghy, eds, Dictionary of Organic Compounds, 5th Ed, Vol. 1, Chapman and Hall, New York, 1982, p 575.

Table 2 Bond Angles (°) for Compound 1 and Its Hydroperchlorate 1a		
Bond Angle	for 1 [a]	for 1a [b,c]
C9b-N1-C2	116.5 (4)	121.9 (3)
N1-C2-C3	123.7 (5)	120.7 (3)
C2-C3-C4	119.7 (5)	120.0 (4)
C3-C4-C4a	117.0 (5)	118.6 (3)
C4-C4a-C9b	120.7 (5)	120.7 (3)
C4a-C9b-N1	122.4 (5)	118.1 (3)
C4a-S5-C5a	91.0 (2)	90.6 (1)
S5-C5a-C9a	112.7 (3)	113.3 (2)
C5a-C9a-C9b	111.3 (4)	109.7 (3)
C9a-C9b-C4a	113.2 (5)	114.8 (3)
C9b-C4a-S5	111.9 (4)	111.4 (2)
C5a-N6-C7	113.3 (5)	115.7 (3)

Table 2 (continued)		
N6-C7-C8	125.8 (5)	124.7 (3)
C7-C8-C9	118.9 (6)	118.7 (4)
C8-C9-C9a	118.2 (5)	118.4 (3)
C9-C9a-C5a	117.5 (4)	118.0 (3)
C9a-C5a-N6	126.3 (5)	124.5 (3)

[a] Σ angles in ring A (of **1**) 720.0 ± 2.9°; ring B: 540.1 ± 1.8°; ring C: 720.0 ± 3.0°. [b] Σ angles in ring A (of **1a**): 720.0 ± 1.9°; ring B: 539.8 ± 1.1°; ring C: 720.0 ± 1.9°. [c] O-Cl-O angles vary from 107.4 ± 0.2° to 110.2 ± 0.2°.

are consistent only with exclusive protonation at N1 (see Experimental). Thus, there is no evidence of disorder in the crystalline structure. The seven hydrogen atoms in the

molecule all refine satisfactorily with isotropic thermal parameters without, at any stage, indicating the presence of residual electron density near N6 for location of a hydrogen atom there. Also, while N1 is within hydrogen-bonding distance of perchlorate oxygen atom O1, there are no contacts between N6 and any anionic oxygen of such nature.

Table 3

Bond Lengths (Å) for Compound 1 and Its Hydroperchlorate 1a		
Bond	for 1	for 1a [a]
N1-C2	1.335 (6)	1.332 (4)
C2-C3	1.391 (8)	1.363 (5)
C3-C4	1.373 (7)	1.387 (5)
C4-C4a	1.374 (7)	1.374 (5)
C4a-S5	1.745 (5)	1.743 (3)
S5-C5a	1.748 (5)	1.753 (3)
C5a-N6	1.341 (6)	1.327 (4)
N6-C7	1.333 (8)	1.323 (5)
C7-C8	1.388 (9)	1.403 (5)
C8-C9	1.372 (7)	1.368 (5)
C9-C9a	1.383 (6)	1.385 (5)
C9a-C9b	1.436 (6)	1.422 (4)
C9b-N1	1.345 (6)	1.364 (4)
C4a-C9b	1.392 (6)	1.395 (4)
C5a-C9a	1.398 (6)	1.412 (4)

[a] Also Cl-O bond lengths in the perchlorate ion: To O1, 1.431 (3); to O2, 1.419 (3); to O3, 1.413 (3); to O4, 1.424 (3). C-H bond lengths fall in the range of 0.88 (4) to 0.94 (3). The N1-H bond is 0.88 (3).

Therefore, we ascribe the aforementioned changes in ring C to secondary structural adjustments to protonation at N1.

A direct comparison of ^1H and ^{13}C nmr data for **1** and **1a** was not possible because of major differences in solubilities of these compounds. No common nmr solvent could be found. Compound **1** dissolves readily in deuteriochloroform which we used. A mixture of deuteriated methanol/deuterium oxide (2:1) was the only solvent we found for **1a**. It provided a suitable ^{13}C spectrum, but not a ^1H one since it led to partial H/D exchange. The signals for the alpha protons of **1** (in rings A and C) overlap downfield at δ 8.72 and the beta protons show identical double doublets at 7.46 and 7.39. Bay-region proton H-9 is shifted downfield to 8.67 (compared to 8.17 for H-4) [9].

The ^{13}C nmr signals for **1** and **1a** occur over the same ranges of 120-162 ppm. As expected, the spectrum of **1** shows four signals of low intensity (assigned to the four ring juncture carbon atoms) and six signals of greater intensity. Structural assignments of the signals for **1** are made by assuming that (a) there is a similar order of chemical shifts for the carbon atoms in ring A and those in the pyridine ring of **3** and (b) the same relationship occurs between carbon atoms in ring C and those in the pyridine ring of **2** [10]. In **1** the pairs of C2, C7; C4, C9; and C3, C8 show only slightly different chemical shifts. For **1a**, the preceding patterns are altered by the signal for C2, which is believed to be partially deuteriated. Since this should lower the intensity of the signal [11], it was not possible to clearly distinguish between resonances for C2 and C4a. Nonetheless, it appears that the C2 resonance in **1a** falls either 8 or 14 ppm upfield from that for C7. This upfield shift is probably the result of protonation at N1 [12].

EXPERIMENTAL

All nmr spectra were recorded on a Varian INOVA 300 MHz spectrometer. X-ray crystallographic studies of **1** and **1a** were

conducted with the apparatus and radiation as previously described [13,14]. A SIR92 E-map [15] showed all of the non-hydrogen atoms in each case. The identities of the nitrogen atoms were confirmed from their low thermal parameters when refined as carbon, and from bond lengths. The hydrogen atoms of **1** could not be clearly distinguished in a difference map following anisotropic refinement of the non-hydrogen atoms. They are shown (Figure 1) at positions recalculated after each cycle of refinement for $B(\text{H}) = 1.2B_{\text{eq}}(\text{C})$; and $d(\text{C-H}) = 0.95 \text{ \AA}$. On the other hand, all hydrogens of **1a** were located and refined isotropically (Figure 2). The final syntheses were featureless. The TeXsan program package [16], which incorporates complex atomic scattering factors, was used in all calculations (see Table 1). Bond angles are given in Table 2 and bond lengths in Table 3. N1 is hydrogen-bonded to O1 of the perchlorate ion with a distance of 3.038 Å [17] and an N-H...O angle of $177 \pm 3^\circ$.

Thieno[2,3-*b*:4,5-*b'*]dipyridine (**1**), mp 116-117° [1] is shown as ORTEP Figure 1; ^1H nmr (deuteriochloroform): δ 8.72 (two overlapping dd, 2H, H-2 and H-7), 8.67 (dd, $J_{7,9} = 1.8 \text{ Hz}$, 1H, H-9), 8.17 (dd, $J_{2,4} = 1.5 \text{ Hz}$, 1H, H-4), 7.46 and 7.39 (2 dd, $J_{2,3} = J_{7,8} = 4.7 \text{ Hz}$, $J_{3,4} = J_{8,9} = 7.9 \text{ Hz}$, 2H, H-3 and H-8); ^{13}C nmr: δ 161.9 (C-5a), 150.2 and 147.0 (C-2 and C-7), 149.5 (C-9b), 133.1 (C-4a), 130.8 and 130.5 (C-4 and C-9), 128.6 (C-9a), 121.7 and 120.1 (C-3 and C-8).

1 · Hydroperchlorate (**1a**), mp 198.5-200° [5] is shown as ORTEP Figure 2; ^{13}C nmr ($\text{CD}_3\text{OD}/\text{D}_2\text{O}$; 2:1 by volume): δ 162.1 (C-5a), 152.4 (C-7), 144.2 (C-2?), 144.9 (C-9b), 138.5 (C-4a?), 136.2 and 133.7 (C-4 and C-9), 126.2 (C-9a), 124.4 and 122.7 (C-3 and C-8) [18].

REFERENCES AND NOTES

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- [6] Although compounds **1** and **1a** have been available in our laboratory for more than 25 years, only recently have single crystal x-ray analyses become feasible for us. This now allows definitive investigation of the structural changes which occur on conversion of **1** into **1a**. Knowing the location of the proton on **1a** leads one to predict that ring C will undergo preferential electrophilic attack under strong Brønsted acidic conditions.
- [7] Similarly, a very small (but not quantitatively expressed) twist is reported for crystalline phenanthrene. See J. Trotter, *Acta Cryst.*, **16**, 605 (1963).
- [8] This possibility was suggested by a referee.
- [9] Analogous shifts are reported for the bay-region protons in benzo[*h*]quinoline (i.e. 1-azaphenanthrene) and phenanthrene itself. See J. D. Memory and N. K. Wilson, *nmr of Aromatic Compounds*, John Wiley and Sons, New York, 1982, pp. 43, 58.
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- [12] Compare an upfield shift of 7.8 ppm for the ^{13}C signal of C2

in pyridine on protonation at the nitrogen atom. See J. B. Stothers, *Carbon-13 nmr Spectroscopy*, Academic Press, New York, 1972, pp. 247-250.

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[18] Signals for C-2 and C-4a may be interchanged.