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Identification of the *N*-Alkylation Product of 3-(2-Pyrrolyl)pyridazine

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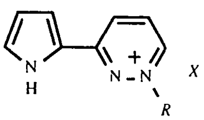
Abstract

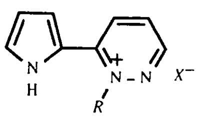
The title compound has been unequivocally identified as 1-ethyl-3-(2-pyrrolyl)pyridazinium tetrafluoroborate, $C_{10}H_{12}N_3^+.BF_4^-$.

Comment

3-(2-Pyrrolyl)pyridazine may be *N*-alkylated to yield either the 1- or the 2-alkylpyridazinium salt, (1) or (2), respectively. Molecular-orbital calculations (Domingo, 1993) indicate that conjugation of the pyridazine ring with the π-electron excessive pyrrole should enhance the nucleophilicity of N2, but the observed rates of alkylation of 2-(2-pyrrolyl)pyridine and 3-(2-pyrrolyl)-pyridine (Karatza, 1992) show that the 3-pyridyl system is considerably more reactive than the 2-pyridyl system. *N*-Alkylation of 3-(2-pyrrolyl)pyridazine with triethyloxonium tetrafluoroborate yields a single product, as confirmed by TLC analysis and by NMR spectroscopy, the structure of which could not be identified unambiguously from the ^{1}H or ^{13}C NMR spectroscopic data (Whitmore, 1994).



(1)



(2)

A projection of the crystal structure of the *N*-ethylated product (Fig. 1) shows unequivocally that it is the N1 atom of the pyridazine ring which is alkylated [(1), R = Et, X = BF_4]. The two rings are almost coplanar with an angle of only 5.4 (1)° between their mean planes. The C(1)—C(5) bond length [1.435 (3) Å] between the two rings indicates a high degree of conjugation between the π-electron excessive pyrrole ring and the π-electron deficient pyridazinium ring. The BF_4^- anions are linked to the cations by hydrogen-bonding interactions, the shortest of which are C9—H9$A\cdots$F1($1 - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$) [H$\cdots$F = 2.39 (4) Å] and N3—H3$A\cdots$F3($x - 1$, $\frac{1}{2} - y$, $\frac{1}{2} + z$) [H$\cdots$F = 2.16 (6) Å].

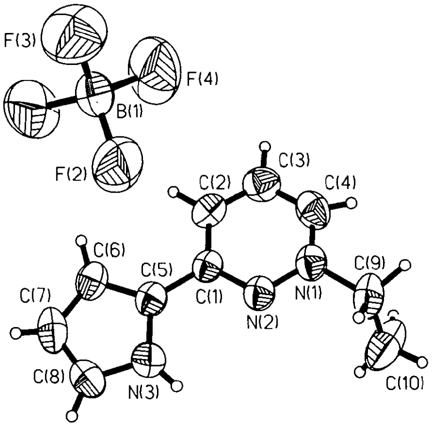


Fig. 1. *ORTEP*II (Johnson, 1976) view of the 1-ethyl-3-(2-pyrrolyl)-pyridazinium cation and the BF_4^- anion showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The *N*-alkylated product was obtained by the reaction of triethyloxonium tetrafluoroborate with 3-(2-pyrrolyl)-pyridazine in CH_2Cl_2 at room temperature. Recrystallization was from EtOH.

Crystal data

$C_{10}H_{12}N_3^+.BF_4^-$
M_r = 261.0
Monoclinic
$P2_1/c$
a = 8.232 (2) Å
b = 11.599 (3) Å
c = 12.996 (4) Å
β = 105.85 (2)°
V = 1193.8 Å^3
Z = 4
D_x = 1.452 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 5–15°
μ = 0.126 mm^{-1}
T = 295 K
Prism
0.70 × 0.50 × 0.30 mm
Yellow

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: none

$R_{\rm int}$ = 0.023
$\theta_{\rm max}$ = 25°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 14$

2392 measured reflections
2108 independent reflections
1615 observed reflections
[$F > 4\sigma(F)$]

2 standard reflections
monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.061$
$wR = 0.105$
$S = 1.17$
1615 reflections
199 parameters
H atoms located by difference synthesis and refined isotropically

$w = 1/[\sigma^2(F) + 0.0070F^2]$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	0.1739 (3)	0.0863 (2)	0.9600 (2)	0.046 (1)
C(2)	0.3011 (4)	0.0208 (3)	1.0287 (2)	0.057 (1)
C(3)	0.4164 (4)	0.0746 (3)	1.1074 (3)	0.066 (1)
C(4)	0.4056 (4)	0.1915 (3)	1.1164 (2)	0.066 (1)
C(5)	0.0467 (3)	0.0346 (2)	0.8742 (2)	0.049 (1)
C(6)	0.0305 (4)	−0.0777 (3)	0.8368 (2)	0.058 (1)
C(7)	−0.1139 (4)	−0.0826 (3)	0.7517 (3)	0.068 (1)
C(8)	−0.1823 (4)	0.0247 (3)	0.7374 (2)	0.066 (1)
C(9)	0.2628 (5)	0.3753 (3)	1.0589 (3)	0.070 (1)
C(10)	0.1409 (7)	0.4014 (3)	1.1183 (4)	0.105 (2)
N(1)	0.2828 (3)	0.2488 (2)	1.0498 (2)	0.054 (1)
N(2)	0.1647 (3)	0.2003 (2)	0.9710 (2)	0.049 (1)
N(3)	−0.0853 (3)	0.0954 (2)	0.8124 (2)	0.057 (1)
B(1)	0.6048 (4)	0.2063 (3)	0.4014 (3)	0.054 (1)
F(1)	0.5199 (3)	0.1057 (2)	0.3894 (2)	0.107 (1)
F(2)	0.4931 (3)	0.2943 (2)	0.3656 (2)	0.094 (1)
F(3)	0.7145 (3)	0.2028 (2)	0.3405 (2)	0.108 (1)
F(4)	0.6862 (4)	0.2260 (3)	0.5052 (2)	0.117 (1)

Table 2. *Selected geometric parameters (Å, °)*

C(1)—N(2)	1.335 (3)	C(7)—C(8)	1.358 (4)
N(1)—N(2)	1.330 (3)	C(8)—N(3)	1.355 (4)
N(1)—C(4)	1.318 (4)	N(3)—C(5)	1.359 (3)
C(4)—C(3)	1.366 (5)	N(1)—C(9)	1.484 (4)
C(3)—C(2)	1.345 (4)	C(9)—C(10)	1.456 (7)
C(2)—C(1)	1.400 (4)	B(1)—F(1)	1.347 (4)
C(1)—C(5)	1.435 (3)	B(1)—F(2)	1.368 (4)
C(5)—C(6)	1.385 (4)	B(1)—F(3)	1.354 (5)
C(6)—C(7)	1.386 (5)	B(1)—F(4)	1.352 (4)
C(1)—N(2)—N(1)	116.8 (2)	C(8)—N(3)—C(5)	109.3 (2)
N(2)—N(1)—C(4)	124.1 (2)	N(3)—C(5)—C(6)	107.2 (2)
N(1)—C(4)—C(3)	120.1 (3)	N(2)—N(1)—C(9)	114.0 (2)
C(4)—C(3)—C(2)	118.5 (3)	N(1)—C(9)—C(10)	110.8 (3)
C(3)—C(2)—C(1)	118.9 (3)	F(1)—B(1)—F(2)	109.1 (3)
C(2)—C(1)—N(2)	121.6 (2)	F(1)—B(1)—F(3)	108.4 (3)
N(2)—C(1)—C(5)	116.5 (2)	F(1)—B(1)—F(4)	111.2 (3)
C(1)—C(5)—C(6)	130.2 (2)	F(2)—B(1)—F(3)	108.5 (3)
C(5)—C(6)—C(7)	107.3 (3)	F(2)—B(1)—F(4)	108.4 (3)
C(6)—C(7)—C(8)	107.8 (3)	F(3)—B(1)—F(4)	111.1 (3)
C(7)—C(8)—N(3)	108.4 (2)		

Data collection: *P*3 (Siemens, 1989). Cell refinement: *P*3. Data reduction: *XPREP* in *SHELXTL-Plus* (Sheldrick, 1991). Structure solution: *XS* in *SHELXTL-Plus*. Structure refinement: *XLS* in *SHELXTL-Plus*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *SHELXTL-Plus*. Preparation of material for publication: *XPUB* in *SHELXTL-Plus*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1023). (00 pp.). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trichotomine Dimethyl Ester

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Abstract

The title compound, methyl 2-[6,11-dihydro-5-(methoxycarbonyl)-3-oxo-3*H*-indolizino[8,7-*b*]indol-2(5*H*)-ylidene]-2,5,6,11-tetrahydro-3-oxo-3*H*-indolizino[8,7-*b*]indole-5-carboxylate, $C_{32}H_{24}N_4O_6$, crystallized from *tert*-butanol as the disolvate. The compound has approximate C_2 symmetry. The two central five-membered rings are linked by a C═C double bond and are approximately coplanar. The two lateral indole rings are canted slightly out of this plane by 5 and 8°. The molecular skeleton is thus essentially planar, except for the methoxycarbonyl groups, which are nearly perpendicular to the rest of the molecule.

Comment

Trichotomine, isolated from *Clerodendron trichotomum Thunb*, has an H-type chromophore similar to that of indigo (Iwadera, Shizuri, Sasaki & Hirata, 1974). It is reported that indigo is planar, but *N*,*N*′-dimethylindigo

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