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The Structure of 9-Nitro-7-trifluoromethylpyrido[1,2-*a*]benzimidazole

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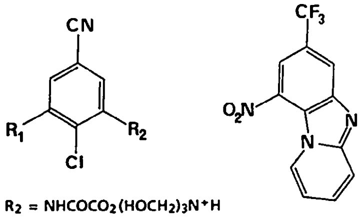
(*Received* 6 *December* 1985; *accepted* 28 *May* 1986)

Abstract. $C_{12}H_6F_3N_3O_2$, $M_r = 281{\cdot}2$, triclinic, $P\bar{1}$, $a = 4{\cdot}994\,(1)$, $b = 10{\cdot}713\,(1)$, $c = 11{\cdot}172\,(2)$ Å, $\alpha = 114{\cdot}31\,(1)$, $\beta = 92{\cdot}14\,(2)$, $\gamma = 95{\cdot}36\,(1)°$, $V = 540{\cdot}4\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}73$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 1{\cdot}2$ cm^{-1}, $F(000) = 284$, $T = 123$ K, $R = 0{\cdot}072$ for 1765 unique reflections. The structure has an exceptionally large number of close contacts. The close packing prevents rotation of the trifluoromethyl group, hence bond lengths are more accurate than those usually reported for this group. The close contacts have apparently caused this flat molecule to adopt a bowed conformation.

Introduction. The dioxamate (1) (lodoxamide) has been undergoing development in our corporate laboratories as an anti-asthmatic agent. As part of a program to study the metabolism of lodoxamide, an authentic sample of the diaminophenol [derived from (1)] was required. During the chemical synthesis of this potential metabolite, it was found that when the nitrohydroxylamine (2) was treated with acetic anhydride–pyridine in an attempt to acetylate it, the major product was instead a rearrangement which incorporated pyridine (Anderson & Taylor, 1986).



(1) $R_1 = R_2 = NHCOCO_2(HOCH_2)_3N^+H$
(2) $R_1 = NO_2$, $R_2 = NHOH$ (3)

We wished to determine the structure of this interesting rearrangement by X-ray analysis, and since crystals from this reaction were not very good, an analogous reaction was carried out on the nitrohydroxylamine with a trifluoromethyl group substituted for the cyano group. This reaction afforded crystals of the title compound (3), which were suitable for X-ray analysis.

Experimental. Clear prism $0{\cdot}08 \times 0{\cdot}13 \times 0{\cdot}30$ mm, Nicolet $P\bar{1}$ diffractometer controlled by Harris computer, graphite monochromator, Cu $K\alpha$, $2\theta_{\max} = 138°$, $h \pm 4$, $k \pm 12$, $l \pm 13$, all 1765 unique reflections measured, 1509 intensities $>2\sigma$, 2° min^{-1} $\theta/2\theta$ step-scans, scan widths $>3{\cdot}4°$, ten reflections periodically monitored showed no trend towards deterioration, $\sigma^2(I)$ was approximated by $\sigma^2(I)$ from counting statistics + $(0{\cdot}021I)^2$, where the coefficient of I was calculated from the variations in intensities of the monitored reflections, cell parameters by least-squares fit of Cu$K\alpha_1$ 2θ values [$\lambda(\mathrm{Cu}K\alpha_1 = 1{\cdot}5402$ Å)] for 29 high-2θ reflections (Duchamp, 1977), Lp correction appropriate for a monochromator with 50% perfect character, no absorption correction. A partial trial solution (8 atoms), obtained by direct methods, using *DIREC* (Duchamp, 1978), was extended using successive Fourier syntheses; hydrogens were found in difference maps very close to positions generated using planar or tetrahedral geometry, generated positions were used. Least-squares refinement included coordinates and anisotropic thermal parameters for non-hydrogen atoms; hydrogen parameters were included in the calculations but were not refined. The function minimized in the refinement was $\sum w(F_o^2 - F_c^2)^2$, where weights w were $1/\sigma^2(F_o^2)$.

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Atomic form factors were from Doyle & Turner (1968), and, for hydrogen, from Stewart, Davidson & Simpson (1965). In the final refinement cycle, all shifts were $<0{\cdot}05\sigma$. For all 1765 reflections, $R = 0{\cdot}072$ and $S = 2{\cdot}74$. $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2} = 0{\cdot}134$. Final difference Fourier peaks were $<0{\cdot}3$ e Å^{-3}, except those very close to known atoms. The *CRYM* system of computer programs was used (Duchamp, 1984).

Discussion. Atomic positions and equivalent isotropic temperature factors are listed in Table 1,* Fig. 1 shows numbering, and Table 2 gives bond lengths and angles and selected torsion angles. As torsion angles show, the nitro group is rotated about 11° out of the plane of the molecule. If this group were to be rotated about the N(9)—C(9) bond to be in the plane of the molecule, O(9*B*) would make a very close contact, 2·96 Å, with the same oxygen in the molecule related by $2-x$, $1-y$, $1-z$. Table 3 lists close contacts and gives the O(9*B*)—O(9*B*) distance as actually 3·076 Å, a figure which is in very good agreement with the revised van der Waals radii for oxygen, 1·54 Å, predicted by Nyburg & Faerman (1985). Other intermolecular contacts for nitro-group oxygens [O(9*A*)—F(2) = 2·99 Å and O(9*B*)—all five atoms of diazole ring: 3·12–3·19 Å] are all shorter than they would be if the nitro group were in the plane of the molecule. O(9*B*) is close to all five atoms of the diazole ring in the molecule translated by 1 in *x*. If the van der Waals radius for half an aromatic molecule is 1·7 Å (Pauling, 1960), the O(9*B*)—diazole ring contacts are either at or slightly less than the sum of the van der Waals radii, depending on whether the Pauling radius for oxygen, 1·4 Å, or the Nyburg & Faerman radius, 1·54 Å, is used. This close approach of O(9*B*) to the diazole ring evidently causes the slight bowing of the molecule apparent in an edge-on view. A plane calculation shows that atoms in the middle of the molecule, N(10) and C(9*A*), are displaced from the plane 0·03–0·04 Å in one direction, and atoms at the ends, C(7), C(8) and C(3), are

Table 1. *Fractional coordinates* (×10⁴) *and* B_{eq}(Å²) (*estimated standard deviations in parentheses*)

$$B_{\rm eq} = \tfrac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}).$$

	x	*y*	*z*	B_{eq}
C(1)	5689 (8)	3635 (4)	5401 (3)	2·58 (14)
C(2)	4586 (8)	2426 (4)	4463 (3)	2·84 (14)
C(3)	2287 (8)	1670 (3)	4678 (3)	2·75 (14)
C(4)	1237 (8)	2179 (4)	5867 (4)	2·76 (14)
C(4a)	2365 (7)	3444 (3)	6873 (3)	2·38 (13)
N(5)	1585 (6)	4106 (3)	8074 (3)	2·61 (11)
C(5a)	3328 (7)	5308 (3)	8635 (3)	2·30 (13)
C(6)	3207 (7)	6358 (3)	9880 (3)	2·42 (13)
C(7)	5042 (7)	7523 (3)	10268 (3)	2·38 (13)
C(7*F*)	4957 (8)	8720 (4)	11545 (4)	2·84 (14)
F(1)	3647 (5)	8370 (2)	12414 (2)	3·84 (9)
F(2)	7396 (4)	9324 (2)	12148 (2)	3·68 (9)
F(3)	3679 (5)	9716 (2)	11427 (2)	4·31 (10)
C(8)	7014 (7)	7638 (3)	9435 (3)	2·49 (13)
C(9)	7141 (7)	6587 (3)	8215 (3)	2·23 (12)
N(9)	9386 (6)	6823 (3)	7471 (3)	2·46 (11)
O(9*A*)	10632 (6)	7972 (3)	7891 (3)	3·53 (11)
O(9*B*)	9912 (5)	5844 (2)	6490 (2)	2·93 (10)
C(9a)	5272 (7)	5392 (3)	7763 (3)	2·15 (12)
N(10)	4641 (6)	4185 (3)	6628 (3)	2·29 (11)

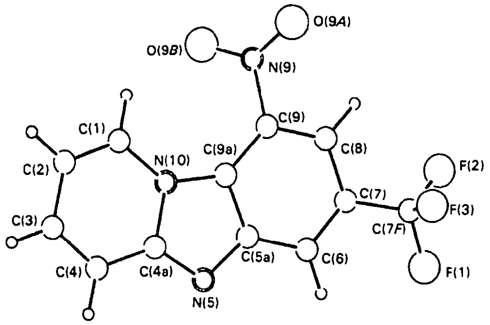

Fig. 1. View of the title compound showing atom numbering.

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsion angles* (°)

C(1)—C(2)	1·336 (4)	C(7)—C(7*F*)	1·480 (5)
C(1)—N(10)	1·395 (4)	C(7)—C(8)	1·411 (5)
C(2)—C(3)	1·428 (4)	C(7*F*)—F(1)	1·347 (4)
C(3)—C(4)	1·359 (5)	C(7*F*)—F(2)	1·338 (4)
C(4)—C(4a)	1·404 (4)	C(7*F*)—F(3)	1·341 (3)
C(4a)—N(5)	1·328 (4)	C(8)—C(9)	1·373 (5)
C(4a)—N(10)	1·424 (4)	C(9)—N(9)	1·484 (4)
N(5)—C(5a)	1·376 (4)	C(9)—C(9a)	1·405 (4)
C(5a)—C(6)	1·391 (4)	N(9)—O(9*A*)	1·217 (3)
C(5a)—C(9a)	1·423 (5)	N(9)—O(9*B*)	1·223 (3)
C(6)—C(7)	1·377 (4)	C(9a)—N(10)	1·387 (4)

C(2)—C(1)—N(10)	120·7 (3)	C(7)—C(7*F*)—F(3)	112·7 (3)
C(1)—C(2)—C(3)	121·2 (3)	F(1)—C(7*F*)—F(2)	105·6 (3)
C(2)—C(3)—C(4)	119·3 (3)	F(1)—C(7*F*)—F(3)	105·9 (3)
C(3)—C(4)—C(4a)	120·7 (3)	F(2)—C(7*F*)—F(3)	106·1 (2)
C(4)—C(4a)—N(5)	129·0 (3)	C(7)—C(8)—C(9)	120·5 (3)
C(4)—C(4a)—N(10)	118·9 (3)	C(8)—C(9)—N(9)	114·7 (2)
N(5)—C(4a)—N(10)	112·1 (2)	C(8)—C(9)—C(9a)	120·6 (3)
C(4a)—N(5)—C(5a)	105·1 (3)	N(9)—C(9)—C(9a)	124·7 (3)
N(5)—C(5a)—C(6)	125·5 (3)	C(9)—N(9)—O(9*A*)	118·0 (3)
N(5)—C(5a)—C(9a)	111·9 (3)	C(9)—N(9)—O(9*B*)	118·0 (2)
C(6)—C(5a)—C(9a)	122·6 (3)	O(9*A*)—N(9)—O(9*B*)	124·0 (3)
C(5a)—C(6)—C(7)	118·0 (3)	C(5a)—C(9a)—C(9)	117·3 (3)
C(6)—C(7)—C(7*F*)	121·5 (3)	C(5a)—C(9a)—N(10)	104·5 (2)
C(6)—C(7)—C(8)	121·0 (3)	C(9)—C(9a)—N(10)	138·2 (3)
C(7*F*)—C(7)—C(8)	117·5 (2)	C(1)—N(10)—C(4a)	119·2 (2)
C(7)—C(7*F*)—F(1)	112·2 (2)	C(1)—N(10)—C(9a)	134·3 (2)
C(7)—C(7*F*)—F(2)	113·7 (3)	C(4a)—N(10)—C(9a)	106·4 (3)

C(6)—C(7)—C(7*F*)—F(1)	21·8 (4)	C(8)—C(7)—C(7*F*)—F(3)	80·0 (4)
C(6)—C(7)—C(7*F*)—F(2)	141·6 (3)	C(8)—C(9)—N(9)—O(9*A*)	−11·0 (4)
C(6)—C(7)—C(7*F*)—F(3)	−97·6 (3)	C(8)—C(9)—N(9)—O(9*B*)	167·4 (2)
C(8)—C(7)—C(7*F*)—F(1)	−160·6 (3)	C(9a)—C(9)—N(9)—O(9*A*)	170·1 (3)
C(8)—C(7)—C(7*F*)—F(2)	−40·8 (3)	C(9a)—C(9)—N(9)—O(9*B*)	−11·4 (4)

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* Lists of structure factors, anisotropic thermal parameters, hydrogen coordinates, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43114 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Close intermolecular contacts between non-hydrogen atoms*

Symmetry operations listed were performed on the first atom. Distances are in Å.

F(3)···C(2)	$x, y-1, z-1$	3·416 (4)
C(1)···C(4)	$x-1, y, z$	3·427 (4)
F(2)···F(1)	$x-1, y, z$	3·414 (3)
F(2)···F(3)	$x-1, y, z$	3·300 (3)
N(9)···C(5a)	$x-1, y, z$	3·216 (3)
N(9)···C(6)	$x-1, y, z$	3·468 (4)
O(9*B*)···C(4a)	$x-1, y, z$	3·123 (3)
O(9*B*)···N(5)	$x-1, y, z$	3·192 (3)
O(9*B*)···C(5a)	$x-1, y, z$	3·161 (4)
O(9*B*)···C(9a)	$x-1, y, z$	3·155 (4)
O(9*B*)···N(10)	$x-1, y, z$	3·122 (3)
C(2)···N(9)	$1-x, 1-y, 1-z$	3·265 (4)
C(2)···O(9*A*)	$1-x, 1-y, 1-z$	3·499 (4)
C(2)···O(9*B*)	$1-x, 1-y, 1-z$	3·440 (3)
C(3)···O(9*A*)	$1-x, 1-y, 1-z$	3·348 (4)
C(1)···O(9*B*)	$2-x, 1-y, 1-z$	3·270 (4)
O(9*B*)···O(9*B*)	$2-x, 1-y, 1-z$	3·076 (2)
C(4)···F(1)	$-x, 1-y, 2-z$	3·315 (4)
N(5)···F(1)	$-x, 1-y, 2-z$	3·401 (3)
C(4)···F(1)	$1-x, 1-y, 2-z$	3·377 (4)
C(4)···F(2)	$1-x, 1-y, 2-z$	3·318 (3)
C(4a)···F(1)	$1-x, 1-y, 2-z$	3·202 (3)
C(5a)···C(6)	$1-x, 1-y, 2-z$	3·426 (4)
F(1)···N(10)	$1-x, 1-y, 2-z$	3·484 (2)
F(3)···C(8)	$1-x, 2-y, 2-z$	3·389 (2)
F(3)···O(9*A*)	$1-x, 2-y, 2-z$	3·304 (3)
F(2)···O(9*A*)	$2-x, 2-y, 2-z$	2·989 (2)
F(3)···O(9*A*)	$2-x, 2-y, 2-z$	3·429 (3)

displaced 0·05–0·06 Å in the opposite direction. If the molecules were not bowed, O(9*B*)–diazole ring contacts would be even shorter.

Fluorines of trifluoromethyl groups frequently have high thermal parameters (Chu & Napoleone, 1981; Allen, March & Nowell, 1984), and are sometimes disordered (Valle, Toniolo & Bonora, 1985). Consequently, the C—F bond distances reported are usually shorter than the distances reported here. In the packing environment for this molecule, the trifluoromethyl cannot rotate freely without incurring unfavorable short contacts with O(9*A*) (2·45 Å) and with C(2) (2·63 Å). The C—F distances of 1·34 Å for this structure are closer to the C—F single-bond length, 1·37 Å, calculated by Pauling (1960).

We gratefully acknowledge the expert technical assistance of Charlotte Waber.

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Acta Cryst. (1986). **C42**, 1771–1773

N-*n*-Butylpyridinium Chloride

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(*Received* 12 *March* 1986; *accepted* 25 *June* 1986)

Abstract. $C_9H_{14}N^+.Cl^-$, $M_r = 171·67$, orthorhombic, $P2_12_12_1$, $a = 8·095\,(3)$, $b = 10·621\,(4)$, $c = 11·419\,(5)$ Å, $V = 981·8\,(6)$ Å^3, $Z = 4$, $D_x = 1·16$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 3·3$ cm^{-1}, $F(000) = 368$, $T = 298\,(1)$ K, $R = 0·053$ for 1307 $[I > 3\sigma(I)]$ of 1676 unique reflections. *N*-*n*-butylpyridinium chloride (BPCl) was crystallized from a BPCl–$AlCl_3$ molten salt. The *n*-butyl chain of the cation is in extended staggered form and is approximately perpendicular to the plane of the pyridinium ring.

Introduction. Mixtures of *N*-*n*-butylpyridinium chloride (BPCl) and aluminium(III) chloride constitute an interesting continuum of ambient-temperature molten salt media which behave as somewhat unusual 'non-aqueous' solvents. These melts have been studied rather intensively by a number of investigators not only

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0108-2701/86/121771-03$01.50