

Low-Temperature Crystal and Molecular Structure of 3-Phenyltetrazolo- [4,5-*a*]pyridinium Tetrafluoroborate, $C_{11}H_9N_4 \cdot BF_4$

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Abstract

$C_{11}H_9N_4 \cdot BF_4$ crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 13.712$ (4), $b = 6.196$ (2), $c = 14.175$ (3) Å and $\beta = 89.28$ (2)° (at a temperature of about 123 K). The structure was solved by direct methods and refined by a least-squares procedure to a final $R = 0.041$ for 2755 independent reflections. The geometry of the tetrazolopyridinium cation indicates limited aromaticity of the six-membered ring. Quantum-chemical calculations supplement the structural information obtained from the X-ray analysis. While from room-temperature diffraction data an ill-defined BF_4^- tetrahedron was obtained, the low-temperature data resulted in a quite regular tetrahedron.

Introduction

The reactivity of tetrazolopyridinium salts can easily be studied (Messmer & Gelléri, 1965). Independently of solvents they react at C(5) with such nucleophiles as BH_4^- , CN^- and amines, while phenolates and thio-phenolates attack at C(8a). Subsequently it is hoped to clarify the stereospecificity of the reactions by studying both the X-ray structure of the title compound and other relevant information.

Experimental

Crystals of the title compound were obtained by slow evaporation of its saturated acetonitrile solution. Diffractometer data were collected at room tem-

perature as well as at low temperature (about 123 K) on a Syntex $P2_1$ automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell parameters and their e.s.d.'s were calculated from the diffractometer data using the least-squares technique. Data collection was performed first at room temperature, which resulted in 1250 independent reflections. The crystal data at room temperature are: $a = 13.592$ (2), $b = 6.295$ (1), $c = 14.325$ (2) Å and $\beta = 90.53$ (2)°, $V = 1225.62$ Å³, $C_{11}H_9N_4 \cdot BF_4$, $M_r = 284.023$, $D_x = 1.539$, $D_m = 1.53$ Mg m⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $\mu = 15.4$ mm⁻¹, space group $P2_1/c$, $Z = 4$. During the structure determination, however, it was found that because of very high thermal vibration the BF_4^- tetrahedron was distorted; therefore reflection data were re-collected at low temperature. In this way 2755 independent reflections were obtained from which 511 were taken as unobserved [$I \leq 2\sigma(I)$]. Low-temperature cell parameters are: $a = 13.712$ (4), $b = 6.196$ (2), $c = 14.175$ (3) Å and $\beta = 89.28$ (2)°, $V = 1204.21$ Å³, $D_x = 1.566$ Mg m⁻³. No absorption correction was made.

Determination and refinement of the structure

The absolute scale and approximate temperature factor ($B = 1.51$ Å²) for the room-temperature data were obtained from a Wilson plot using all reflections.

The phase problem was solved by the direct method using the *MULTAN* program (Germain, Main & Woolfson, 1971) with 185 normalized structure factors ($E \geq 1.40$). The phase set of the highest combined FOM revealed 16 out of 20 non-hydrogen atoms in the E map. Positions of the rest were taken from a subsequent electron-density calculation. Positional and

anisotropic thermal parameters of the non-hydrogen atoms were refined by the least-squares technique using the weighting scheme of Hughes. With the room-temperature data the refinement resulted in an *R* of only 0.12, the e.s.d.'s were very high, the BF₄⁻ tetrahedron was extremely distorted and the thermal parameters of the F atoms were as high as 20 Å². Therefore the low-temperature reflection data were used for the final refinement of the structure. The H atoms were located in a difference Fourier map and refined isotropically. The final structure factor calculation gave *R* = 0.041 for all reflections. From a difference Fourier map no sign of disorder of the BF₄⁻ ion could be detected. The final atomic coordinates are listed in Tables 1 and 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34491 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates ($\times 10^4$) for the non-hydrogen atoms

Estimated standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	3419 (2)	499 (4)	2049 (1)
N(2)	2474 (2)	752 (3)	1967 (1)
N(3)	2294 (1)	2667 (3)	1575 (1)
N(4)	3154 (1)	3687 (3)	1394 (1)
C(5)	3325 (2)	5658 (4)	976 (2)
C(6)	4281 (2)	6259 (4)	904 (2)
C(7)	5043 (2)	4907 (4)	1230 (2)
C(8)	4847 (2)	2930 (4)	1621 (2)
C(8a)	3860 (2)	2314 (4)	1701 (2)
C(9)	1332 (2)	3509 (4)	1425 (2)
C(10)	1093 (2)	5550 (4)	1766 (2)
C(11)	137 (2)	6264 (5)	1653 (2)
C(12)	-550 (2)	4928 (5)	1240 (2)
C(13)	-293 (2)	2886 (5)	918 (2)
C(14)	665 (2)	2162 (5)	996 (2)
F(1)	3922 (1)	4373 (3)	4616 (1)
F(2)	2985 (1)	4935 (3)	3328 (1)
F(3)	2640 (1)	2166 (3)	4339 (1)
F(4)	2381 (1)	5637 (3)	4809 (1)
B	2974 (2)	4283 (5)	4261 (2)

Table 2. Final fractional coordinates ($\times 10^3$) of the hydrogen atoms

Estimated standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
H(5)	270 (2)	649 (5)	76 (2)
H(6)	440 (2)	761 (5)	64 (2)
H(7)	571 (2)	542 (5)	114 (2)
H(8)	533 (2)	204 (5)	179 (2)
H(10)	151 (2)	639 (5)	205 (2)
H(11)	-6 (2)	766 (5)	186 (2)
H(12)	-116 (2)	540 (5)	118 (2)
H(13)	-72 (2)	203 (5)	69 (2)
H(14)	84 (2)	78 (5)	81 (2)

Discussion

A view of the molecule with the atomic numbering is shown in Fig. 1. Bond lengths and angles are given in Tables 3 and 4. The pyridinium-ring dimensions in this case differ from many of those found previously, e.g. in the iodide, chloride and picrate salts of 1-methyl-nicotinamide (Freeman & Bugg, 1974), in 1-[2-(3-indolyl)ethyl]-3-carbamoylpyridinium chloride (Herriott, Camerman & Deranleau, 1974), and in *N*-[3-(9-adenyl)propyl]-3-carbamoylpyridinium bromide trihydrate (Johnson, Maier & Paul, 1973; Johnson, Frank & Paul, 1973). In all these cases the bond lengths are similar to each other and the bond angles are close to 120°, indicating the aromatic character of the pyridinium rings in these compounds. In the title molecule the geometry of the six-membered ring deviates not only from those cited above but also from that of the 1-(2,6-dichlorobenzyl)-2-ethoxypyridinium cation (Wheeler & Ammon, 1974). This deviation is greatest for the ring angles at C(5) and N(4).

Table 3. Bond lengths (Å) with their estimated standard deviations in parentheses

N(1)–N(2)	1.312 (3)	C(9)–C(10)	1.392 (4)
N(1)–C(8a)	1.366 (3)	C(9)–C(11)	1.384 (4)
N(2)–N(3)	1.335 (3)	C(10)–C(11)	1.395 (4)
N(3)–N(4)	1.360 (3)	C(11)–C(12)	1.389 (4)
N(3)–C(9)	1.437 (3)	C(12)–C(13)	1.389 (4)
N(4)–C(5)	1.376 (3)	C(13)–C(14)	1.393 (4)
N(4)–C(8a)	1.364 (3)	B–F(1)	1.401 (3)
C(5)–C(6)	1.365 (4)	B–F(2)	1.382 (3)
C(6)–C(7)	1.422 (4)	B–F(3)	1.393 (3)
C(7)–C(8)	1.370 (4)	B–F(4)	1.397 (3)
C(8)–C(8a)	1.409 (3)		

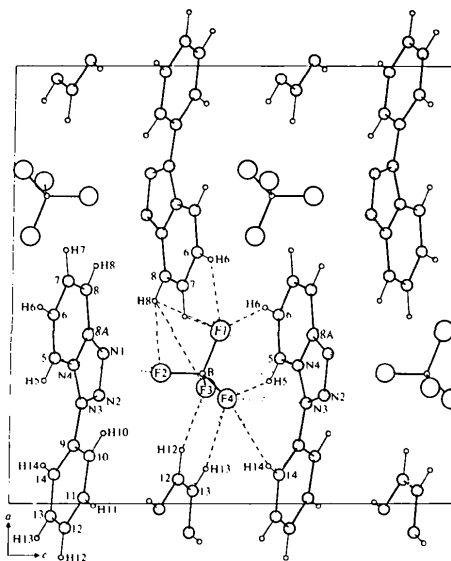


Fig. 1. Orthogonal projection of the unit cell on the plane (010). Short intermolecular contacts are indicated by broken (F–H) and by dotted lines (F–N and F–C).

A possible criterion for establishing the relative degree of delocalization of bond lengths has been proposed by Julg & Francois (1967) and Julg (1971). It is expressed by an aromaticity index A in the form

$$A = 1 - \frac{225}{n} \sum_{i=1}^n (1 - d_i/\bar{d})^2,$$

where \bar{d} is the average length of n bonds. The mean aromatic C—C and C—N distances are 1.395 and 1.340 Å (Wheeler & Ammon, 1974) which take into account differences in the types of atoms and charges. On this scale a normal aromatic pyridine ring has $A = 1.0$; in close agreement with this are the A indices for the compounds cited above which are in the range 0.95–0.99. Thus the decreased aromaticity of the pyridinium ring in the title compound is expressed also by the relatively low A index of 0.91. Similar low indices (0.89, 0.85, 0.72) can be derived for the 2-pyridone moieties in 2-pyridone:6-chloro-2-hydroxypyridine (Almlöf, Kvik & Olovsson, 1971), 5-chloro-2-pyridone (Kvik & Booles, 1972) and 1-(2,6-dichlorobenzyl)-2-pyridone (Wheeler & Ammon, 1974).

A simple quantum-chemical model was invoked to find an explanation for variations in the bond lengths. It is supposed that differing bond distances are due to two principal factors: the localizability of π orbitals and electrostatic effects. The higher the localizability is of a π orbital to two neighbouring atoms (*i.e.* the double-bond character) the shorter the bond is. Delocalization of double bonds and lone pairs to neighbouring atoms also leads to shortening of the corresponding bond.

Localized molecular orbitals were obtained from CNDO/2 calculations (Pople & Beveridge, 1970) coupled with a localization procedure (Trindle & Sinanoğlu, 1968). π -Orbital localizabilities (Diner, Malrieu, Jordan & Claverie, 1970) in per cent values were calculated according to Náray-Szabó & Horváth (1977). Calculations were based on the X-ray geometry with the modification that the 3-phenyl group was

omitted and instead of it a H atom was geometrically positioned. Some results of the calculations are summarized in Fig. 2. The localizability of the N(3) lone pair is 83.7%, while that of the N(4) lone pair is 64.7%. Lone pairs at N(1) and N(2) are of σ symmetry, thus lying in the molecular plane, and therefore they do not mix with the π orbitals. Bond lengths are also influenced by delocalization. For example, amounts of delocalization of the N(1)—N(2) π orbital to N(3) and the lone pair at N(3) to N(2) are 0.0% and 9.2%, respectively. Experimental bond lengths are in agreement with the parameters of Fig. 2. In all cases theory and experiment coincide. It is the localizability situation which primarily determines bond lengths. For N(4)—C(8a) and N(1)—C(8a), however, electrostatic effects are opposite, elongating the former and shortening the latter bond. As a result both distances are about the same.

The aromaticity index (A), calculated as proposed by Náray-Szabó & Horváth (1977) with respect to the structure as depicted in Fig. 2, is 17.8%. This value indicates a medium aromaticity, in accordance with Julg's index. [$A = 26.6\%$ for benzene, 26.8% for pyridine and 11.1% for 2-pyridone (Náray-Szabó & Horváth, 1977).] Nevertheless, we do not claim that this simple approximation, which is primarily aimed at explaining bond lengths, can explain all the properties of the title compound.

Bonds in the tetrazolo moiety show certain variations with respect to the values found in 5-amino-2-methyltetrazole and in the hydrazine salt of 5-amino-tetrazole (Bryden, 1956, 1958). The double bond is about the same length but its position is moved from the corresponding N(2)—N(3) site to N(1)—N(2).

The average bond-length value of 1.391 Å in the phenyl ring is close to the expected aromatic value

Table 4. Bond angles ($^\circ$) with their estimated standard deviations in parentheses

N(2)—N(1)—C(8a)	107.6 (2)	N(3)—C(9)—C(10)	119.4 (2)
N(1)—N(2)—N(3)	109.4 (2)	N(3)—C(9)—C(14)	117.3 (2)
N(2)—N(3)—N(4)	109.1 (2)	C(10)—C(9)—C(11)	123.2 (2)
N(2)—N(3)—C(9)	124.0 (2)	C(9)—C(10)—C(11)	117.8 (2)
N(4)—N(3)—C(9)	126.8 (2)	C(10)—C(11)—C(12)	120.2 (3)
N(3)—N(4)—C(5)	129.5 (2)	C(11)—C(12)—C(13)	120.7 (3)
N(3)—N(4)—C(8a)	105.5 (2)	C(12)—C(13)—C(14)	120.2 (3)
C(5)—N(4)—C(8a)	125.0 (2)	C(13)—C(14)—C(9)	118.0 (2)
N(4)—C(5)—C(6)	115.6 (2)	F(1)—B—F(2)	109.4 (2)
C(5)—C(6)—C(7)	121.6 (2)	F(1)—B—F(3)	108.3 (2)
C(6)—C(7)—C(8)	121.1 (2)	F(1)—B—F(4)	108.2 (2)
C(7)—C(8)—C(8a)	117.3 (2)	F(2)—B—F(3)	110.6 (2)
C(8)—C(8a)—N(1)	132.2 (2)	F(2)—B—F(4)	110.9 (2)
C(8)—C(8a)—N(4)	119.3 (2)	F(3)—B—F(4)	109.4 (2)
N(1)—C(8a)—N(4)	108.5 (2)		

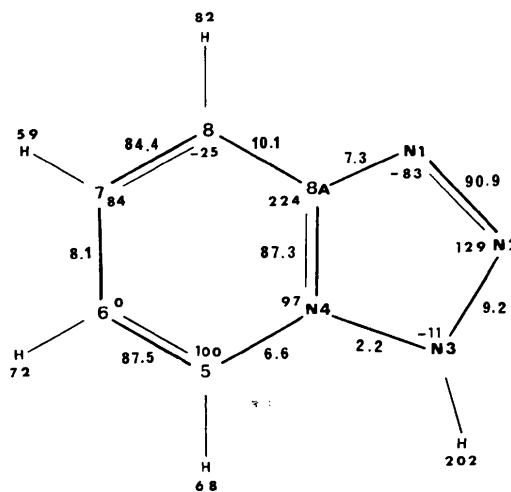


Fig. 2. Double-bond localizabilities (written on the double lines) and delocalization of bonds (written on the single lines) to neighbouring atoms. Net charges (in millielectrons) are assigned to the atoms.

(1.395 Å) and the N(3)–C(9) length (1.437 Å) indicates only a weak interaction between the π system of the phenyl ring and that of the tetrazolopyridinium moiety. This is also expected on the basis of their dihedral angle (49.2°). The tetrazolo ring is almost planar ($\Delta_{\max} = 0.003$ Å) but the other two rings show deviations from planarity (Table 5) with $\Delta_{\max} = 0.013$ Å.

The BF₄⁻ tetrahedron has been found to be quite regular at low temperature. The mean value of the F–B–F angles is 109.5° (mean deviation 0.9°). The mean value of the B–F bond lengths is 1.393 Å (maximum deviation 0.011 Å) in agreement with earlier reported values (1.40 Å) in NaBF₄, KBF₄ and NH₄BF₄ (Bellanca, 1948; Bellanca & Sgarlata, 1951; Pendred & Richards, 1955). The F–F distances vary between 2.265 and 2.289 Å.

The form of the BF₄⁻ tetrahedron determined from the room-temperature reflection data was very much distorted regarding the B–F lengths as well as the F–B–F angles. A similar phenomenon was observed in three recently published structures which were determined at room temperature. In 3-ethyl-2-methylbenzothiazolium tetrafluoroborate, C₁₀H₁₂NS·BF₄ (Srenger, 1974) and {Ni[SO₂(OC₂H₅)]N[C₂H₄-P(C₆H₅)₂]₃}·BF₄·½C₂H₅OH·½H₂O (Ghilardi, Midallini & Sacconi, 1977) only a distortion of the BF₄⁻ tetrahedron was found. However, in 3-ethyl-2-methyl-6-nitrobenzothiazolium tetrafluoroborate, C₁₀H₁₁N₂O₂S·BF₄ (Srenger & Robert, 1978), besides distortion of the tetrahedron, two positions for one of the F atoms were found statistically. These results illustrate the effect of thermal vibration at room temperature. When, however, observations are made at low temperature and thus the thermal motion is reduced, the weak ionic and van der Waals forces overcome the thermal effects and keep the BF₄⁻ ion in a fixed position.

Table 5. Atomic least-squares planes of the molecule with deviations (Å) from planes of atoms forming the plane

The plane constants ($Ax + By + Cz = D$) are referred to orthogonal axes and coordinates are in Å. The mean e.s.d. for the deviations is 0.005 Å.

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	
P1	-0.0440	0.4199	0.9065	2.6115	
P2	-0.0573	0.4274	0.9022	2.5482	
P3	-0.2348	-0.3885	0.8911	0.5479	
P1	N(1),N(2),N(3),N(4), C(8a)	-0.002 0.003	0.001	0.001	-0.003
P2	N(4),C(5),C(6),C(7), C(8),C(8a)	0.012 -0.007	-0.009 -0.004	-0.001	0.009
P3	C(9),C(10),C(11), C(12),C(13),C(14)	0.001 -0.002	0.009 0.013	-0.009 -0.012	

The dihedral angle P1–P3 is 49.2°.

Table 6. Short intermolecular atomic distances (Å)

The symmetry-related positions (*International Tables for X-ray Crystallography*, 1969) of the second atoms are denoted by Roman numbers and their shifts parallel to the crystallographic axes are denoted by the letters *a*, *b* and *c* with the corresponding signs in parentheses.

From atom at <i>x, y, z</i>	To atom	At position	Distance
F(1)	H(6)	IV(<i>b</i>)	2.46 (3)
	H(6)	III(<i>a</i> , - <i>b</i>)	2.57 (3)
	H(7)	III(<i>a</i> , - <i>b</i>)	2.72 (3)
	H(8)	III(<i>a</i>)	2.78 (3)
	C(6)	III(<i>a</i> , - <i>b</i>)	3.208 (3)
	C(6)	IV(<i>b</i>)	3.305 (3)
	C(7)	III(<i>a</i> , - <i>b</i>)	3.327 (3)
	C(8)	III(<i>a</i>)	3.272 (3)
	C(8a)	IV	3.135 (3)
	N(4)	IV	3.315 (2)
F(2)	H(8)	III(<i>a</i>)	2.66 (3)
	C(5)	I	3.390 (3)
	C(8a)	I	3.054 (3)
	N(1)	I	3.342 (3)
	N(2)	I	3.311 (3)
	N(3)	I	3.018 (2)
	N(4)	I	2.855 (2)
	H(7)	III(<i>a</i> , - <i>b</i>)	2.59 (3)
F(3)	H(12)	III(- <i>b</i>)	2.43 (3)
	C(5)	IV	3.063 (3)
	C(12)	III(- <i>b</i>)	3.297 (3)
	N(3)	IV	3.201 (2)
	N(4)	IV	3.052 (2)
	H(5)	IV(<i>b</i>)	2.28 (3)
	H(13)	III(- <i>b</i>)	2.54 (2)
F(4)	H(14)	IV	2.68 (3)
	C(5)	IV(<i>b</i>)	3.120 (3)
	C(13)	III	3.358 (3)
	C(14)	IV	3.358 (3)
	N(2)	IV	3.182 (3)
	N(3)	IV	3.235 (2)

The arrangement of the molecules in the crystal lattice conforms to molecular close packing (Fig. 1). The symmetry-related molecules surround the BF₄⁻ ion at F···H van der Waals separations (2.55 Å). The F atoms have a number of neighbouring N and C atoms also close to van der Waals distances, of which those shorter than 3.40 Å are summarized in Table 6. The F(2)···N(4) contact is the shortest (2.855 Å), all others are greater than 3.02 Å. Although F(2) and N(4) are at the van der Waals distance, their contact may be taken as a weak ionic bond which is elongated by the numerous F···H van der Waals contacts hindering closer packing.

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The Crystal and Molecular Structures of 2,2,7,7-Tetramethyl-1,4-diaza-5-cycloheptanone (2,2,7,7-Tetramethyl-5-homopiperazinone) and the Corresponding Seven-Membered-Ring Nitroxide

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Abstract

The title compounds are, respectively, monoclinic, space group $P2_1/c$ [$a = 11.722$ (2), $b = 7.777$ (1), $c = 11.534$ (2) Å, $\beta = 109.88$ (1)°] and orthorhombic, space group $P2_12_12_1$ [$a = 8.123$ (1), $b = 10.858$ (2), $c = 11.561$ (1) Å]. The two molecules [(1) and (2) respectively] have flattened chair conformations. By hydrogen bonding, they are arranged in pairs in (1) and chains in (2). The geometrical parameters of the nitroxide group in (2) are compared with those reported earlier for five- and six-membered-ring nitroxides.

Much structural information about pyrrolidinoxyl (five-membered-ring) and piperidinoxyl (six-membered-ring) free radicals is available. However, no structural study has been reported on seven-membered-ring nitroxides. Since the reactivity and physical properties

of cyclic nitroxides, as in the corresponding cyclic amines, depend upon ring size, it is unfortunate that nothing is known about the structure and conformation of these free radicals.

The most common method used in the determination of molecular conformation is NMR spectroscopy which, however, gives rather qualitative data for molecules in solution and does not always lead to unequivocal answers. Furthermore, for paramagnetic species, it is often difficult to assign a resonance signal to the right proton group without selective deuterium labeling which requires much synthetic work. A quantitative determination of the shape of molecules in the solid state is possible by diffraction methods.

The simplest representative of seven-membered-ring nitroxides described up to now is 2,2,7,7-tetramethyl-5-oxohomopiperazin-1-oxyl (2), the synthesis of which was reported several years ago (Rozantsev & Papko, 1962, 1963). This compound is interesting, not only because of the oxyl group, but also because of its parent amine (1), both of which give general information on the 1,4-diazacycloheptane system.

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