

4-Dimethylaminopyridinium derivatives of 1,2-dibromo-1,1,2,2-tetrafluoroethane: molecular structure of 1-(4-dimethylaminopyridinium)-2-bromo-1,1,2,2-tetrafluoroethane bromide and 1-(4-dimethylamino-pyridinium)-1,1,2,2-tetrafluoroethane bromide ¹

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Abstract

The molecular structures of 1-(4-dimethylaminopyridinium)-2-bromo-1,1,2,2-tetrafluoroethane bromide (**1-Br**) (triclinic, $P\bar{1}$, $a = 538.80(10)$, $b = 916.6(3)$, $c = 1372.8(3)$ pm, $\alpha = 81.56(2)^\circ$, $\beta = 81.76(2)^\circ$, $\gamma = 82.53(2)^\circ$) and 1-(4-dimethylaminopyridinium)-1,1,2,2-tetrafluoroethane bromide (**2-Br**) (monoclinic, Cm , $a = 1159.6(2)$, $b = 2780.2(6)$, $c = 577.90(10)$ pm, $\beta = 95.78(3)^\circ$) were determined. The two bromides crystallize with one water molecule per formula unit. In cation **1** a hypervalent ion-pairing $\text{Br}^- \dots \text{BrCF}_2\text{CF}_2\text{N}$ (320.7 pm) was observed. A radical mechanism for the interaction of 4-dimethylaminopyridine with 1,2-dibromo-tetrafluoroethane is proposed. © 1997 Elsevier Science S.A.

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1. Introduction

Onio derivatives are accessible by 4-dimethylaminopyridinium and the appropriate carbon [1], silicon [2] and phosphorus [3] halides. Only recently, perhalogenated unsaturated fragments derived from tetrachlorocyclopropene [4], hexachlorocyclopentadiene [5], 1,2-dichlorotetrafluorocyclobutene [5] and hexafluorobenzene [1,5] were found to be bonded to the pyridinium nitrogen. From dibromodifluoromethane and 1,2-dibromotetrafluoroethane we could obtain the corresponding onio substituted alkanes, namely 4-dimethylaminopyridinium-bromodifluoromethane and 1-(4-dimethylaminopyridinium)-2-bromo-1,1,2,2-tetrafluoroethane [6], first examples of *N*-perhalogenoalkylated pyridine derivatives. Both compounds could be converted into the difluoromethane and tetrafluoroethane analogues using tri-*n*-butylstannane [6]. We describe here the molecular

structure of 1-(4-dimethylaminopyridinium)-2-bromo-1,1,2,2-tetrafluoroethane and 1-(4-dimethylamino-pyridinium)-1,1,2,2-tetrafluoroethane bromide, respectively.

2. Results and discussion

1,2-Dibromotetrafluoroethane and DMAP [6] reacted straightforwardly in polar, aprotic solvents, e.g. acetonitrile, to furnish 1-(4-dimethylaminopyridinium)-2-bromo-1,1,2,2-tetrafluoroethane bromide (**2-Br**) (Scheme 1) in the presence of catalytic amounts of activated copper or zinc almost quantitatively. Without a catalyst, on irradiation using UV light the yield decreased to 30%. If *p*-dinitrobenzene was added as a radical scavenger to the illuminated or catalyst-containing solution, compound **1** was not observed indicating a radical mechanism pathway [6]. In the presence of activated copper or zinc and stoichiometric amounts of *p*-dinitrobenzene, dibromodifluoromethane and DMAP reacted to give 4-dimethylaminopyridinium-bromodifluoromethane

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¹ Dedicated to Professor Alois Haas on the occasion of his 65th birthday.

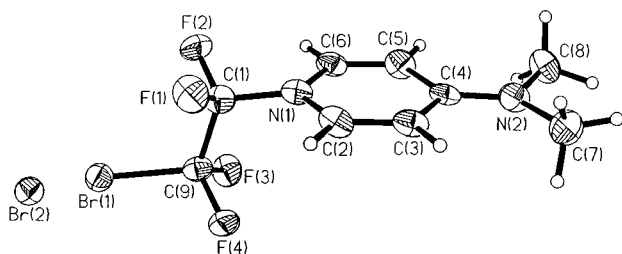
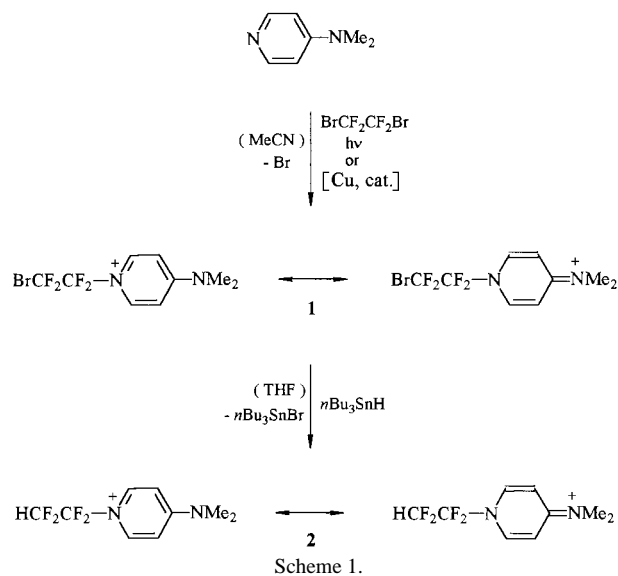


Fig. 1. Crystal structure of **1-Br** (thermal ellipsoids at 50% probability).

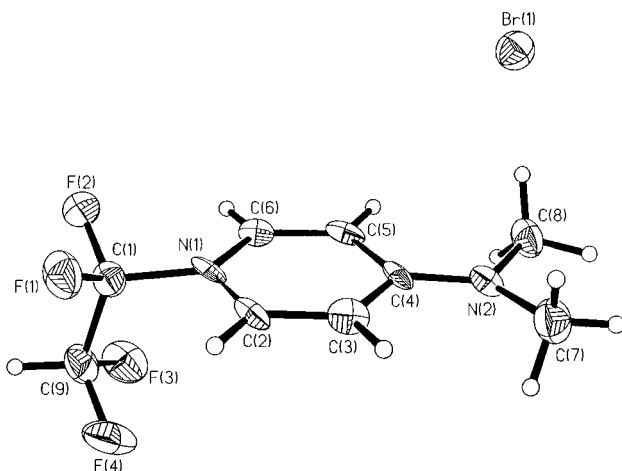


Fig. 2. Crystal structure of **2-Br** (thermal ellipsoids at 50% probability).

bromide in good yield owing to a difluorocarbene chain mechanism [6]. The 2-bromo-1,1,2,2-tetrafluoroethyl group bound to the pyridinium nitrogen was hydrogenated to yield the corresponding 1,1,2,2-tetrafluoroethyl moiety in compound **2-Br** (Scheme 1). The two pyridinium halides were colorless solids easily soluble in water and ethanol, less soluble in acetonitrile and methylene chloride.

Table 1

Selected bond distances (pm) and bond angles (deg) of cations **1** and **2**

	1	2
Br(1)–C(9)	191.6(5)	
C(1)–F(1)	134.0(5)	134.9(8)
C(1)–N(1)	146.0(6)	145.6(10)
C(1)–C(9)	152.8(7)	151.2(12)
C(2)–C(3)	135.8(7)	134.2(10)
C(2)–N(1)	136.9(6)	135.8(8)
C(3)–C(4)	142.3(6)	142.7(9)
C(4)–N(2)	130.9(6)	131.6(10)
C(4)–C(5)	143.5(6)	141.8(9)
C(5)–C(6)	134.4(7)	136.5(10)
C(7)–N(2)	146.3(6)	147.3(8)
N(1)–C(1)–C(9)	112.8(4)	114.7(6)
C(3)–C(2)–N(1)	121.4(4)	120.1(6)
C(3)–C(2)–C(4)	120.8(4)	121.7(6)
C(2)–N(1)–C(6)	119.5(4)	121.4(6)
C(3)–C(4)–C(5)	116.1(4)	116.0(7)
F(3)–C(9)–Br(1)	110.5(3)	
C(2)–N(1)–C(1)	119.9(4)	118.6(6)
C(6)–N(1)–C(1)	120.3(4)	119.4(6)
C(4)–N(2)–C(7)	122.0(4)	122.4(6)
C(4)–N(2)–C(8)	121.2(4)	120.3(6)
C(7)–N(2)–C(8)	116.4(4)	116.6(6)
F(3)–C(9)–F(4)	107.1(4)	108.2(6)

There was not much difference found in the carbon framework geometry of the molecular structures of **1-Br** and **2-Br** (see Figs. 1 and 2, Table 1). Both unit cells have one molecule of solvating water per molecule pyridinium salt. The unit cell of **2-Br**, however, contained two symmetrically independent cations not significantly different in their structural parameters. In one cation of **2-Br** with the least-squares plane through N(1), C(1), N(2), C(4), C(9) deviates from the respective ideal mirror plane by 0.23 pm (0.13 pm for **1**). The pyridinium moieties exhibit a substantial quinoidal character [1,6] as seen from the C(2)–C(3) and C(5)–C(6) distances (135.8 and 134.4 (**1**), 136.5 and 134.2 pm (**2**)) being significantly shorter than C(3)–C(4) (142.3 (**1**), 142.7 (**2**) pm). The bond lengths C(4)–N(2) (130.9 (**1**), 131.6 (**2**) pm) are very nearly a double bond [7]. There was not much evidence found for an sp³ lone pair, either at N(1) (sum of the angles 359.7° (**1**) and 359.4° (**2**)) or at N(2) (sum of the angles 359.6° (**1**) and 359.3° (**2**)). In the two molecular structures the anions were located in proximity to the respective dimethylamino nitrogen atom. In compound **2-Br** the Br[−]⋯BrCF₂CF₂N distance was observed to be 320.7 pm, much less than the sum of the Van der Waals radii (370 pm) accounting for a hypervalent ion-pairing [8] as in the case of 4-dimethylaminopyridinium-bromodifluoromethane bromide [6] (315.7 pm).

3. Experimental details

Compounds **1-Br** and **2-Br** were synthesized according to Ref. [6]. 4-Dimethylaminopyridine (1.44 g, 10 mmol) and

2.60 g (10 mmol) 1,2-dibromotetrafluoro-ethane in 10 ml acetonitrile were irradiated for 2 h using a mercury high pressure lamp (TQ 150 Hanau). The colorless solid formed was separated by filtration, washed twice with 3 ml methylene chloride and dried in vacuo yielding 1.20 g (30%) of **1-Br**. In the presence of 1.70 g (10 mmol) *p*-dinitrobenzene under the same reaction conditions no product was formed. 4-Dimethylaminopyridine (1.44 g, 10 mmol), 2.60 g (10 mmol) 1,2-dibromotetrafluoro-ethane, 1.70 g (10 mmol) *p*-dinitrobenzene and 3 μ g activated copper or zinc in 10 ml acetonitrile did not furnish compound **1-Br** at ambient temperature.

3.1. Crystal structure analyses of **1-Br** and **2-Br**

The structures [9] were analyzed using a Siemens P4 diffractometer (Mo K α , $\lambda = 71.073$ pm, highly oriented graphite crystal monochromator) at 173(2) K and were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL PLUS (VMS) and SHELXL 93. The main crystallographic data are listed in Table 2, the atomic coordinates in Tables 3 and 4.

Table 2
Crystal and data reduction parameters for compounds **1-Br** and **2-Br**

	1-Br	2-Br
Formula	C ₉ H ₁₀ Br ₂ F ₄ N ₂ * H ₂ O	C ₉ H ₁₁ BrF ₄ N ₂ * H ₂ O
Formula weight	400.03	321.12
Crystal size (mm)	0.6 × 0.4 × 0.3	0.6 × 0.5 × 0.3
$F(000)$	388	960
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	Cm
a (pm)	538.80(10)	1159.6(2)
b (pm)	916.6(3)	2780.2(6)
c (pm)	1372.8(3)	577.90(10)
α (°)	81.56(2)	90
β (°)	81.76(2)	95.78(3)
γ (°)	82.53(2)	90
V (nm ³)	0.6596(3)	1.8536(6)
Z	2	6
Absorption coefficient (mm ⁻¹)	6.182	3.363
D_{calc} (Mg m ⁻³)	2.014	1.726
Index ranges	$-1 \leq h \leq 6$ $-11 \leq k \leq 11$ $-17 \leq l \leq 17$	$-1 \leq h \leq 10$ $-1 \leq k \leq 36$ $-7 \leq l \leq 7$
θ range (°)	2.55–27.51	2.82–27.52
Reflections collected	4001	1998
Independent reflections	2990 ($R_{\text{int}} = 0.0349$)	1898 ($R_{\text{int}} = 0.0240$)
Absorption correction	DIFABS	
Data/restraints/parameters	2990/0/176	1898/2/258
Goodness-of-fit on F^2	1.007	1.023
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0442$, $wR_2 = 0.0977$	$R_1 = 0.0331$, $wR_2 = 0.0728$
R indices (all data)	$R_1 = 0.0667$, $wR_2 = 0.1069$	$R_1 = 0.0442$, $wR_2 = 0.0977$
Extinction coefficient	0.0045(14)	
Absolute structure parameter		0.00(2)
Largest diff. and hole (e nm ⁻³)	727 and -596	403 and -393

Table 3
Coordinates for non-hydrogen atoms ($\times 10^4$) and their equivalent isotropic temperature factors (pm² $\times 10^{-1}$) for **1-Br**

	x	y	z	$U(\text{eq})$
Br(1)	-1257(1)	2529(1)	1278(1)	31(1)
Br(2)	1988(1)	2612(1)	3050(1)	32(1)
C(1)	-1539(9)	2678(5)	-807(4)	33(1)
C(2)	-3163(9)	1258(5)	-1908(3)	31(1)
C(3)	-4690(10)	1134(5)	-2591(3)	32(1)
C(4)	-6143(9)	2405(5)	-3029(3)	26(1)
C(5)	-5809(10)	3800(5)	-2737(4)	33(1)
C(6)	-4280(9)	3867(5)	-2057(3)	30(1)
C(7)	-7931(11)	882(6)	-3993(4)	43(1)
C(8)	-9076(10)	3622(6)	-4153(4)	39(1)
C(9)	-3125(9)	2428(5)	207(3)	28(1)
F(1)	450(5)	1636(3)	-846(2)	45(1)
F(2)	-710(6)	4014(3)	-928(2)	43(1)
F(3)	-5144(5)	3455(3)	219(2)	38(1)
F(4)	-3985(6)	1100(3)	299(2)	39(1)
N(1)	-2946(8)	2604(4)	-1628(3)	29(1)
N(2)	-7698(8)	2297(4)	-3659(3)	33(1)
O(1) ^a	-3496(9)	2719(5)	4521(4)	51(1)

^aAtom of solvating H₂O molecule.

Table 4
Coordinates for non-hydrogen atoms ($\times 10^4$) and their equivalent isotropic temperature factors (pm² $\times 10^{-1}$) for **2-Br**

	x	y	z	$U(\text{eq})$
Br(1)	5156(1)	3285(1)	6292(1)	29(1)
C(1)	-376(7)	3441(3)	8664(11)	27(2)
F(1)	-258(4)	3081(2)	10231(7)	41(1)
F(2)	-222(4)	3859(1)	9879(7)	42(1)
N(1)	534(6)	3399(2)	7115(10)	23(1)
C(2)	828(7)	2953(2)	6408(12)	25(1)
C(3)	1558(7)	2904(2)	4765(12)	27(2)
C(4)	2024(7)	3310(2)	3675(13)	21(2)
C(5)	1706(7)	3767(2)	4500(12)	26(2)
C(6)	952(7)	3804(2)	6160(10)	22(2)
N(2)	2700(6)	3264(2)	1991(10)	25(1)
C(7)	3133(7)	2793(2)	1289(14)	37(2)
C(8)	3214(7)	3691(3)	1002(12)	33(2)
C(9)	-1595(7)	3434(3)	7459(14)	34(2)
F(3)	-1683(4)	3796(2)	5902(7)	45(1)
F(4)	-1722(4)	3016(2)	6288(9)	49(1)
Br(2)	2516(1)	0	2810(1)	29(1)
N(3)	2061(8)	0	2017(13)	26(2)
C(10)	2959(11)	0	491(19)	31(3)
F(5)	2857(4)	393(1)	-862(7)	40(1)
C(11)	1677(7)	423(2)	2888(12)	28(2)
C(12)	954(8)	441(3)	4505(12)	23(2)
C(13)	524(11)	0	5482(18)	22(3)
N(4)	-142(9)	0	7112(15)	21(2)
C(14)	-577(9)	-440(3)	8067(14)	32(2)
C(15)	4180(11)	0	1796(17)	32(3)
F(6)	4294(4)	391(1)	3137(8)	43(1)
O(1)	6598(6)	3407(3)	11510(11)	51(2)
O(2)	-2516(1)	0	2810(1)	29(1)

^aAtom of solvating H₂O molecule.

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