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NITROGEN INVERSION IN N-SUBSTITUTED 2,2-BIS(TRIFLUOROMETHYL)AZIRIDINES

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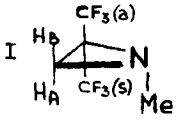
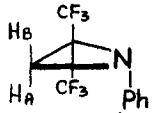
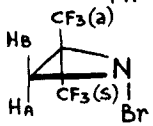
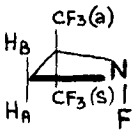
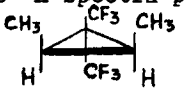
Surprising thermostability of N-halo-2,2-bis(trifluoromethyl)aziridines and high ν_{AB} magnitude of CF_3-groups in ^{19}F nmr spectra have enabled us to determine for the first time the nitrogen inversion barrier (E_a) of the N-halo - aziridine nitrogen atom (Table I, fig.1 and 2).

Substantial decrease of E_a of the 2,2-bis(trifluoromethyl)aziridines I - IV in comparison with the corresponding 2,2-dimethyl derivatives is apparently explained by steric effects [2,3,4].

Increase of the nitrogen inversion barrier in N-bromo-2,2-bis(trifluoromethyl)aziridine III in comparison with N-methyl-2,2-bis(trifluoromethyl)aziridine I, in which N-substituents' size is equal, is attributed to the lowering of the nitrogen lone pair p-character.The -I effect is especially significant in N-fluoro-2,2-bis(trifluoromethyl)aziridine IV.

TABLE I

Compounds	Solvent	^1H [a] δ ppm	^1H [a] J Hz	^{19}F [b] δ ppm [c]	^{19}F [b] J Hz	ν_{AB} Hz	T_c °C	E_a [d] kcal/mole	log A
I 	CH_2Cl_2 [e]	2.36 (A) 2.11 (B) 2.61 (Me)	2.7 (A-CF_3s) 2.0 (Me-CF_3s) [f]	+8.4 (a) -2.2 (s)	7.0 (as)	990	40	7.0 ± 2 [g]	6.1
II 	CCl_4	2.46 (CH_2)		+2.2			The signal has not been separated on cooling		
III 	CCl_4	2.56 (A) 2.50 (B) [h]	3.8 (AB) 2.2 (A-CF_3s) 0.6 (B-CF_3a)	+2.8 (a) -3.1 (s) (in $PhNO_2$)	7.5 (as) [i]	550	125	22.7 ± 2	13.0
IV 	$PhNO_2$	2.99 (A) 3.46 (B)	7.0 (AB) 2.4 (A-CF_3s) 0.8 (B-CF_3a) 29.0 (AF) 40.0 (BF)	+5.9 (a) -3.1 (s) +4.1 (NF)	7.0 (as) [i] 46 (CF_3s-FN) <6 (CF_3a-FN)	850	The spectrum has not been changed on heating up to 190°.		

[a] The spectra were recorded at 60 and 100 MHz. [b] At 94 MHz. [c] From $PhCF_3$ as an external standard. [d] Have been calculated as in ref.1. [e] At -40°. [f] A-CF_3a and B-CF_3s couplings have not been shown in the spectra of I - IV. [g] In $PhNO_2$. [h] The ^1H spectra parameters have been computed by the trial and error method. [i] $J_{CF_3-CF_3}$ is 8 Hz in  6.

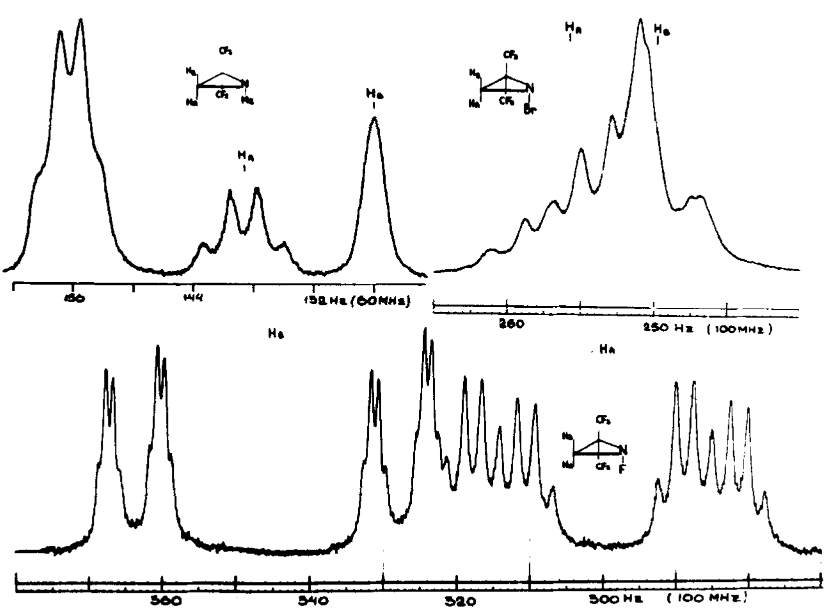

CF3
HB
HA
HB
HA
HB
CF3
HA
HB
CF3
CF3
N
Br
150
144
138 Hz (60 MHz)
260
250 Hz (100 MHz)
HB
HA
CF3
HB
HA
N
CF3
F
360
340
320
500 Hz
(100 MHz)

Fig. 1

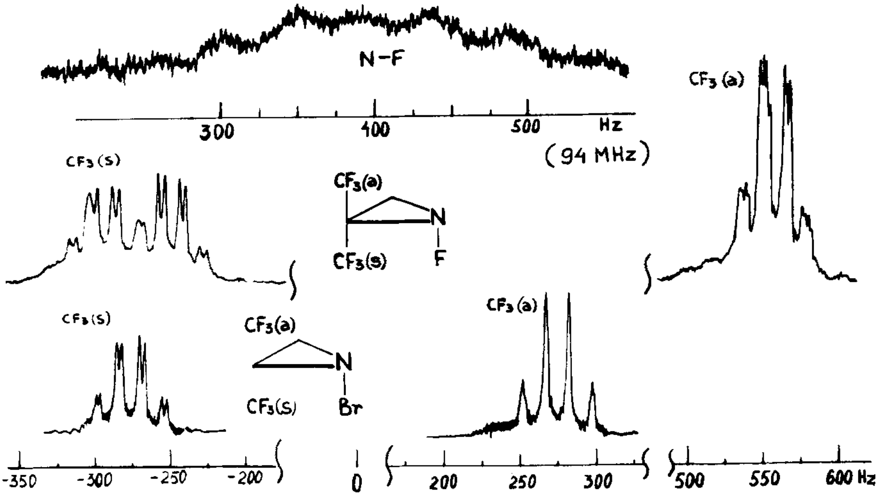
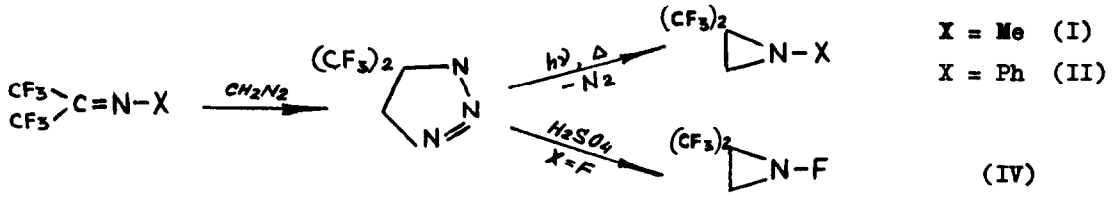

N-F
300
400
500
Hz
(94 MHz)
CF3 (a)
CF3 (S)
CF3(a)
N
CF3(S)
F
CF3(S)
CF3(a)
N
CF3(S)
Br
CF3 (a)
-350
-300
-250
-200
0
200
250
300
500
550
600 Hz

Fig. 2

The compounds I,II and IV have been prepared according to the scheme:



X = Me (I)
X = Ph (II)
(IV)

I: 23% yield; b.p.70-71°; n_D^{20} 1.3210; mass-spectrum,at 30 eV (relative abundance,%%): 193 (M^+,42); 178 (70); 128 (70); 69 (24); 33 (22); 28 (100).

II: 30% yield; b.p.30°(2 mm); n_D^{20} 1.4302; 255 (M^+,36); 186 (10); 104 (10); 91 (100); 77 (43); 51 (13).

IV: 38% yield (on $(CF_3)_2C{=}NF$); b.p.64-65°; n_D^{20} 1.2995; 197 (M^+,11); 178 (48); 159 (11); 128 (80); 109 (23); 78 (20); 69 (100); 33 (76); 28 (10).

III has been prepared in 52% yield by bromination of 2,2-bis(trifluoro - methyl)aziridine [5] by NaOBr in H_2O at 20°. B.p.93-94°; n_D^{20} 1.3685; 259 (M^+,11); 178 (100); 159 (30); 128 (63); 109 (30); 69 (68); 33 (37); 28 (5).

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