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Spin Trapping by Use of Nitroso-Compounds. VII.[1)]β-Fluorine Splitting Constants in Nitroxides

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Hyperfine splitting constants of β-fluorine atoms in aryl perfluoroalkyl nitroxides, $\mathrm{ArN(R_f)O\cdot}$, where Ar= 2,4,6-tri-*t*-butylphenyl, phenyl, pentafluorophenyl, and 2,3,5,6-tetramethylphenyl and $\mathrm{R_f}$= trifluoromethyl, pentafluoroethyl, and heptafluoroisopropyl were explored. The temperature dependence of hyperfine splitting constants was studied in the cases of 2,4,6-tri-*t*-butylphenyl and pentafluorophenyl nitroxides. In the former nitroxides the conformation of β-fluorine atoms are rigid and dihedral angles between the C_β–F bonds and p_z orbitals are 30 and 0° when perfluoroalkyl groups are ethyl and isopropyl, respectively. The conformational dependence of β-fluorine splitting constants are discussed, and it is concluded that the $\cos^2\theta$ law, $a_\beta{}^F=(B_0+B\cos^2\theta)\rho^\pi$, is also applicable to β-fluorine splitting constants in a series of nitroxides. The values of B_0 and B seem significantly dependent on the compound.

The conformational dependence and the origin of β-hydrogen splitting constants have been well established.2,3) However, several different proposals4–13) have recently been advanced concerning those of the β-fluorine atom. It is desirable for the elucidation of the dependence of β-fluorine splitting constants on conformation to investigate the ESR spectra of radicals having β-fluorine atoms in known conformations. Such radicals may include those in single crystals and rigid cyclic radicals. A few studies9,13–16) along these lines have been reported, although in most of these cases the assumed conformations of the alkyl group containing the β-fluorine atoms have not always been unequivocal.

We have previously found during the spin trapping study17) of 2,4,6-tri-*t*-butylnitrosobenzene that the ethyl and isopropyl groups in these adducts have substantially rigid conformations wherein the dihedral angles between

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1) Part VI, S. Terabe, K. Kuruma, and R. Konaka, *J. C. S. Perkin II*, in press.

2) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

3) D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967).

4) See, *e.g.*, D. Holtz, *ibid.*, **8**, 1 (1971) and references cited therein.

5) E. T. Strom and A. L. Bluhm, *Chem. Commun.*, **1966**, 115.

6) W. R. Knolle and J. R. Bolton, *J. Amer. Chem. Soc.*, **93**, 3337 (1971) and references cited therein.

7) J. L. Gerlock, E. G. Janzen, and J. K. Ruff, *ibid.*, **92**, 2037 (1970) and references cited therein.

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9) D. Kosman and L. M. Stock, *ibid.*, **92**, 409 (1970).

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11) G. R. Underwood, V. L. Vogel, and I. Krefting, *ibid.*, **92**, 5019 (1970).

12) M. Iwasaki, *ibid.*, **92**, 6348 (1970); *Mol. Phys.*, **20**, 503 (1971).

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15) R. J. Rontz, *ibid.*, **45**, 1339 (1966).

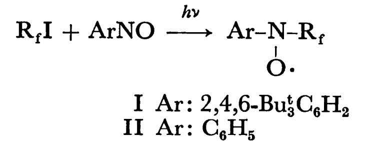
16) J. L. Gerlock and E. G. Janzen, *J. Phys. Chem.*, **72**, 1832 (1968).

17) S. Terabe and R. Konaka, *J. C. S. Perkin II*, in press; *J. Amer. Chem. Soc.*, **93**, 4306 (1971).

the C_β–H bonds and p_z orbitals containing the odd electron on the nitrogen atom are 30 and 0°, respectively. These conformational situations would be expected to remain unchanged if the *N*-alkyl groups are replaced by perfluoroalkyl groups. Hence perfluoroalkyl 2,4,6-tri-*t*-butylphenyl nitroxides were chosen to elucidate the dependence of β-fluorine splitting constants on conformation and a few other substituted phenyl perfluoroalkyl nitroxides were also prepared and studied for comparison.

Results

Substituted phenyl perfluoroalkyl nitroxides were produced by the photolysis of perfluoroalkyl iodides in the presence of substituted nitrosobenzenes.[10)]

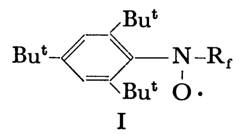


$$R_fI + ArNO \xrightarrow{h\nu} Ar\text{-}\underset{\underset{O\cdot}{|}}{N}\text{-}R_f$$

I Ar: $2,4,6\text{-}Bu^t_3C_6H_2$
II Ar: C_6H_5
III Ar: C_6F_5
IV Ar: $2,3,5,6\text{-}(CH_3)_4C_6H$

R_f: a) CF_3
b) CF_2CF_3
c) $CF(CF_3)_2$

TABLE 1. ESR TEMPERATURE STUDY OF 2,4,6-TRI-*t*-BUTYLPHENYL PERFLUOROALKYL NITROXIDES IN *n*-HEXANE

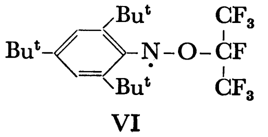


I

R_f	Temp. °C	*g* Value	Hyperfine splitting constants (G) $\lvert a^N \rvert$	$\lvert a_\beta{}^F \rvert$	$\lvert a_\gamma{}^F \rvert$	$\lvert a_m{}^H \rvert$
CF_3 (Ia)	60		9.44	9.44	—	0.70
	25	2.0066	9.44	9.44	—	0.70
	0		9.41	9.41	—	0.70
	−30		9.37	9.37	—	0.72
	−60		9.30	9.30	—	0.73
	−90		9.22	9.22	—	0.71
CF_2CF_3 (Ib)	60		9.64	27.02	0.68	0.68
	25	2.0065	9.63	27.21	0.69	0.69
	0		9.55	27.51	0.70	0.70
	−30		9.51	27.82	0.75	0.75
	−60		9.42	28.14	a)	a)
	−90		9.37	28.31	a)	a)
$CF(CF_3)_2$ (Ic)	25	2.0066	9.73	48.4	a)	a)

a) Hyperfine splittings were not resolved because of line broadening.

g Values and the temperature dependence of hyperfine splitting constants of the nitroxides Ia, Ib, and Ic are shown in Table 1. The photolysis of 2-iodoheptafluoropropane in the presence of 2,4,6-tri-*t*-butylnitrosobenzene produced *N*-perfluoroisopropoxy-2,4,6-tri-*t*-butylanilino radical (VI) as the major product whose spectra (g=2.0034) consisted of a triplet (a^N= 9.36 G) of multiplets having 0.30 G spacings (Fig. 1a) and the nitroxide Ic as minor ones together with other unknown radicals whose spectra could not be analyzed because of the superposition of the complex and strong spectrum of VI. However, since the anilino radical VI was less stable than the nitroxide Ic the former VI disappeared completely on standing in solution for a day and permitted the ESR spectra of minor radicals to be obtained (Fig. 1b), and it was inferred that at least three radicals existed in the solution. The main six lines shown in Fig. 1b are considered to be due to the nitroxide Ic because *g* value and the nitrogen splitting constant are very similar to those of Ia and Ib. Further standing of the solution for a total of three days gave the spectrum shown in Fig. 1c which



VI

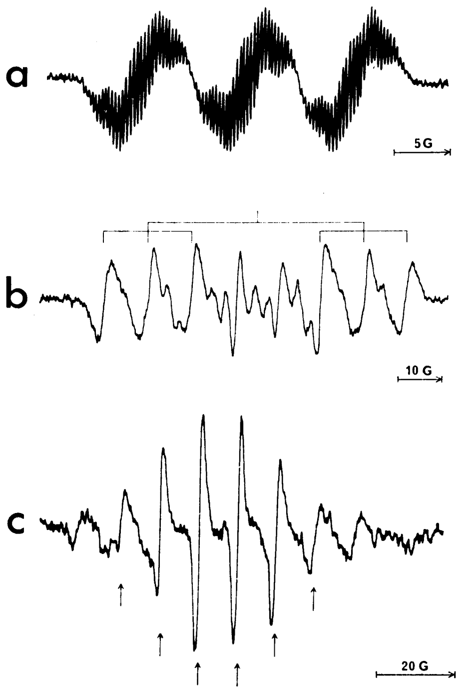


Fig. 1. ESR spectra obtained by the photolysis of 2-iodoheptafluoropropane in the presence of 2,4,6-tri-*t*-butylnitrosobenzene in *n*-hexane at 25°C. Intensities of these three spectra dose not show their relative concentrations because gains of the spectrometer were not equal in each measurement. In b and c, couplings of *meta*-hydrogens and γ-fluorines were not observed because of a high modulation amplitude.

a) Spectrum of *N*-heptafluoroisopropoxy-2,4,6-tri-*t*-butylanilino radical (VI).

b) Six lines indicated by the stick diagram demonstrate the absorption lines by 2,4,6-tri-*t*-butylphenyl heptafluoroisopropyl nitroxide (Ic). See text also.

c) Six lines indicated by arrows correspond to the absorption lines due to 2,4,6-tri-*t*-butylphenyl trifluoromethyl nitroxide (Ia). See text also.

TABLE 2. HYPERFINE SPLITTING CONSTANTS (G) AND *g* VALUES OF PHENYL PERFLUOROALKYL NITROXIDES IN BENZENE AT 25°C

R_f in $PhN(R_f)O\cdot$	*g* Value	$\lvert a^N \rvert$	$\lvert a_\beta{}^F \rvert$	$\lvert a_\gamma{}^F \rvert$	$\lvert a^H_{o,p} \rvert$	$\lvert a_m{}^H \rvert$
CF_3 (IIa)	2.0060	9.68	10.60	—	1.96	0.78
CF_2CF_3 (IIb)	2.0062	9.63	17.29	0.66	1.90	0.66
$CF(CF_3)_2$ (IIc)	2.0062	10.93	4.95	1.81	1.81	0.83

TABLE 3. ESR TEMPERATURE STUDY OF PENTAFLUOROPHENYL PERFLUOROALKYL NITROXIDES IN PERFLUORO(METHYLCYCLOHEXANE)

R_f in $C_6F_5N(R_f)O\cdot$	Temp. °C	g Value	Hyperfine splitting constants (G)				
			$\|a^N\|$	$\|a_\beta^F\|$	$\|a_\gamma^F\|$	$\|a^F_{o,p}\|$	$\|a_m^F\|$
CF_3 (IIIa)	40		9.41	7.78	—	a)	a)
	25	2.0068	9.52	7.75	—	0.96	0.30
	0		9.48	7.68	—	0.96	0.29
	−30		9.45	7.62	—	0.98	0.30
CF_2CF_3 (IIIb)	40		9.38	11.59	1.56	0.94	0.31
	25	2.0069	9.32	11.54	1.60	0.95	0.32
	0		9.30	11.39	1.63	0.97	0.32
	−30		9.16	11.29	1.72	1.00	0.33
$CF(CF_3)_2$ (IIIc)	40		10.10	4.71	1.67	1.03	0.32
	25	2.0068	10.09	4.53	1.64	1.01	0.32
	0		10.08	4.32	1.65	1.02	0.32
	−30		10.08	4.04	1.68	1.02	0.32

a) The nitroxide IIIa was unstable at this temperature, and small hyperfine splitting constants could not be determined.

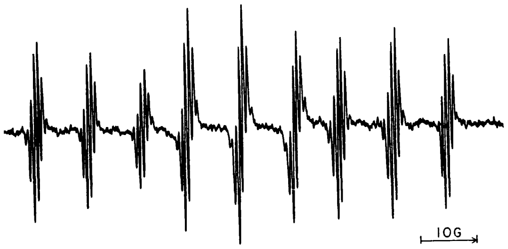


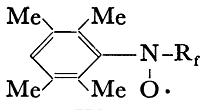
Fig. 2. ESR spectrum of 2,4,6-tri-*t*-butylphenyl pentafluoroethyl nitroxide (Ib) in *n*-hexane at 25°C.

indicated that trifluoromethyl nitroxide Ia was the major radical and Ic was the minor one. This result implies that a minor radical observed in Fig. 1b is Ia. The concentration of Ic was too low to observe *meta*-hydrogen and γ-fluorine splittings and to study the temperature dependence of β-fluorine splitting.

The ESR spectrum of the pentafluoroethyl nitroxide Ib is shown in Fig. 2. The rather low peak heights of the three central multiplets suggest that the two β-fluorine atoms are not completely equivalent, but they could not be distinguished within this experiment.

Spectral data at room temperature (25°C) of the nitroxides IIa, IIb, and IIc and those of the nitroxides IVa, IVb, and IVc are given in Tables 2 and 4, respectively. The temperature study of the nitroxides IIIa, IIIb, and IIIc and that of the 2,4,6-tri-*t*-butylphenyl alkyl nitroxides (V)[17] are summarized in Tables 3 and 5. The latter study was undertaken for the confirmation of the expected conformation of *N*-alkyl groups.

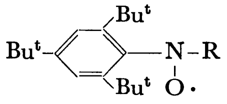
TABLE 4. HYPERFINE SPLITTING CONSTANTS (G) AND g VALUES OF 2,3,5,6-TETRAMETHYLPHENYL PERFLUOROALKYL NITROXIDES IN BENZENE AT 25°C



IV

R_f	g Value	$\|a^N\|$	$\|a_\beta^F\|$	$\|a_\gamma^F\|$
CF_3 (IVa)	2.0066	10.15	9.38	—
CF_2CF_3 (IVb)	2.0067	10.31	17.64	0.95
$CF(CF_3)_2$ (IVc)	2.0066	11.10	13.27	1.55

TABLE 5. ESR TEMPERATURE STUDY OF 2,4,6-TRI-*t*-BUTYLPHENYL ALKYL NITROXIDES IN *n*-HEXANE



V

R	Temp. °C	g Value	Hyperfine splitting constants (G)			
			$\|a^N\|$	$\|a_\beta^H\|$	$\|a_\gamma^H\|$	$\|a_m^H\|$
CH_3 (Va)	90		12.82	11.97	—	0.81
	65		12.81	12.01	—	0.81
	25	2.0061	12.78	12.04	—	0.78
	0		12.80	12.17	—	0.80
	−30		12.70	12.27	—	0.82
	−60		12.62	12.38	—	0.81
	−90		12.58	12.58	—	0.81
CH_2CH_3 (Vb)	90		13.34	17.03	a)	0.83
	65		13.30	17.22	a)	0.83
	25	2.0061	13.26	17.58	a)	0.81
	0		13.25	17.84	a)	0.80
	−30		13.20	18.11	a)	0.79
	−60		13.22	18.53	a)	0.82
	−90		13.17	18.88	a)	0.77
$CH(CH_3)_2$(Vc)	90		13.24	21.04	0.36	0.72
	65		13.16	21.33	0.38	0.75
	25	2.0061	13.07	21.68	0.38	0.76
	0		13.03	22.11	0.37	0.73
	−30		13.02	22.26	0.39	0.79
	−60		13.01	22.52	a)	b)

a) No splitting observed for γ-protons.
b) *meta*-Hydrogen splittings were not resolved because of line broadening.

The ESR spectrum of IIIb is shown in Fig. 3. Some other substituted phenyl perfluoroalkyl nitroxides have been described previously.[1]

Discussion

2,4,6-Tri-t-buthylphenyl Perfluoroalkyl Nitroxides. The nitrogen splitting constant of each 2,4,6-tri-*t*-butylphenyl alkyl nitroxide increases with increase in tem-

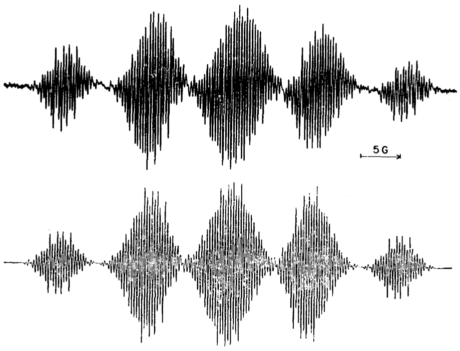


Fig. 3. ESR spectrum of pentafluorophenyl pentafluoroethyl nitroxide (IIIb) in perfluoro(methylcyclohexane) at 25°C. The upper spectrum is experimental and the lower is a simulation based on the splitting constants given in Table 3 and Lorentzian line shapes.

perature as shown in Table 5, and this observation is expected from the results of MO calculations[18] which have shown that the nitrogen splitting constant increases with the torsion of the nitroxide group. The decrease in the β-hydrogen splitting constant of the methyl nitroxide Va with temperature is also consistent with MO calculations[18] which have predicted that the β-hydrogen hyperfine splittings for free rotating hydrogens decrease as the out-of-plane torsion angle of the N–O bond increases. Slightly larger variations of β-hydrogen splitting constants in the nitroxides Vb and Vc with temperature than that in the nitroxide Va would mainly be attributable to the conformational changes of β-hydrogens.

The β-hydrogen splitting constants have been well known to obey the $\cos^2\theta$ law,[2,3,19]

$$a_\beta{}^{\mathrm{H}} = (B_0 + B\cos^2\theta)\rho^\pi \qquad (1)$$

where B_0 and B are constants, θ is the dihedral angle between the C_β–H bond and the p_z orbital containing an odd electron, and ρ^π is the π electron spin density. The value of B_0 is known to be small and is regarded to be zero in this consideration, and ρ^π is assumed to be constant among the nitroxides Va, Vb, and Vc, although the three nitroxides have slightly different values for nitrogen splitting constants. Then, Eq. (1) becomes

$$a_\beta{}^{\mathrm{H}} = B\cos^2\theta\rho^\pi{}_{\mathrm{N}} \qquad (2)$$

The methyl group on the nitrogen in Va is considered as freely rotating which leads to $\cos^2\theta = 1/2$. Taking $a_\beta{}^{\mathrm{H}} = 12.83$ G for Va at -60°C Eq. (2) gives $B\rho^\pi{}_{\mathrm{N}} = 24.76$ G. On substituting this value in turn into Eq. (2), dihedral angles at -60°C for Vb and Vc are found to be 30 and 17°, respectively. Examination of molecular models of Vb and Vc has predicted the angles are 30 and 0°, respectively, as described previously.[17] These values are in fair agreement with those obtained above. Although the value (17°) obtained by the above considerations for Vc seems large as compared with the predicted one from a molecular model, the difference between the magnitude of β-hydrogen splitting constants is only 1.4 G.

It will be reasonable to assume that the perfluoroalkyl groups in 2,4,6-tri-*t*-butylphenyl perfluoroalkyl nitroxides have the same conformations as the alkyl groups in 2,4,6-tri-*t*-butylphenyl alkyl nitroxides. A molecular model of the heptafluoroisopropyl nitroxide Ic indicates that steric repulsion between two *t*-butyl groups at the *ortho* positions and two trifluoromethyl groups in the heptafluoroisopropyl group is very large. This is probably the reason why the concentration of the nitroxide Ic formed was very low as mentioned above. The temperature effect on nitrogen splitting constants in the nitroxides Ia and Ib was similar to that in the corresponding alkyl nitroxides Va, Vb, and Vc in the direction and magnitude of variations. Changes of β-fluorine splitting constants with temperature were less than those of β-hydrogen splitting constants in the corresponding alkyl nitroxides.

The applicability of the $\cos^2\theta$ law (Eq. (3)) to the

$$a_\beta{}^{\mathrm{F}} = (B_0 + B\cos^2\theta)\rho^\pi{}_{\mathrm{N}} \qquad (3)$$

β-fluorine splitting constant is evaluated on the nitroxides shown in Table 1. Spin densities on nitrogens are assumed to be constant among the three nitroxides, although, in fact, nitrogen splitting constants differ slightly. We can take the values $a_\beta{}^{\mathrm{F}} = 9.44$ G (25°C) and $\cos^2\theta = 1/2$ for the nitroxide Ia, and $a_\beta{}^{\mathrm{F}} = 48.4$ G and $\theta = 0°$ for the nitroxide Ic. Hence, Eq. (3) gives $B_0\rho^\pi{}_{\mathrm{N}} = -29.52$ G and $B\rho^\pi{}_{\mathrm{N}} = 77.92$ G. On substituting these values and $\theta = 30°$ into Eq. (3), the β-fluorine splitting constant for Ib is found to be 28.92 G, which is close to the observed value (27.21 G). The assumed dihedral angle (0°) for Ic is chosen for convenience, but it must be near to zero-degrees. A change of even 10° does not affect the results seriously. The results obtained reveal that the Eq. (3) can relate β-fluorine splitting constants to dihedral angles at least in the series of nitroxides shown in Table 1. If we assume arbitrarily $\rho^\pi{}_{\mathrm{N}} = 0.30$, B_0 and B are found to be -98 G and 260 G, respectively. The negative value of B_0 is unequivocal so long as the β-fluorine splitting constant is taken to be positive. The negative value of B_0 has also been deduced by INDO calculations.[11] Large β-fluorine splitting constants have also been found in some other nitroxides where the dihedral angles are assumed to be small by Janzen and co-workers.[20,21]

Phenyl Perfluoroalkyl Nitroxides. Free rotation about the C_β–N bond is possible in the nitroxides shown in Table 2, so that the conformation of the β-fluorine atom is not definite. β-Hydrogen splitting constants decrease in the order methyl>ethyl>isopropyl in phenyl alkyl nitroxides.[19,22] This observation implies that the average dihedral angle θ increases reversely in that order. The conformational analogy between phenyl alkyl nitroxides and *t*-butyl alkyl nitroxides has been known.[19,22] In *t*-butyl perfluoroalkyl nitroxides, however, the conformational preference has been inferred to be somewhat different.[10,11] Trifluoromethyl and heptafluoroisopropyl groups are considered

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[18] J. Duady, Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, *Mol. Phys.*, **17**, 217 (1969).

[19] G. Chaplet-Letourneux, H. Lemaire, R. Lenk, M.-A. Maréchal, and A. Rassat, *Bull. Soc. Chim. Fr.*, **1968**, 3963.

[20] E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

[21] E. G. Janzen, private communication.

[22] E. G. Janzen, *Topics Stereochem.*, **6**, 177 (1971).

to have similar conformational preference to the corresponding alkyl groups in *t*-butyl nitroxide, but pentafluoroethyl group is assumed to lie in the averaged dihedral angle less than 45°.[10,11]

The conformational analogy between *t*-butyl perfluoroalkyl nitroxides and phenyl perfluoroalkyl nitroxides should be valid. We assume averaged dihedral angles of β-fluorine atoms in the nitroxides IIa, IIb, and IIc to be 45, 35, and 80°, respectively, though the choice of the latter two values is rather arbitrary. Spin densities on nitrogens are assumed constant among IIa, IIb, and IIc. Substitution of β-fluorine splitting constants and dihedral angles for IIa and IIc into Eq. (3) gives $B_0\rho^{\pi}_{N}=-5.95$ G and $B\rho^{\pi}_{N}=33.10$ G. These values and $\theta=35°$ are in turn substituted into Eq. (3) to give the β-fluorine splitting constant of 16.26 G, which is fairly close to the observed value for IIb. By taking ρ^{π}_{N} as 0.30, B_0 and B are found to be -25 and 110 G, respectively. In the above consideration the β-fluorine splitting constant of IIc is assumed to be negative. If we assume it to be positive, we cannot relate the observed results through Eq. (3). Evidently it is possible to apply Eq. (3) to phenyl perfluoroalkyl nitroxides, although the interpretation is not unequivocal.

Pentafluorophenyl Perfluoroalkyl Nitroxides. The temperature dependence of the hyperfine splitting constants shown in Table 3 is small. It will be reasonable to expect that preferred conformations of these nitroxides are similar to those of phenyl perfluoroalkyl nitroxides. Average dihedral angles of IIIa, IIIb, and IIIc are assumed to be the same as in the corresponding phenyl perfluoroalkyl nitroxides. The same treatment utilizing hyperfine splitting constants at -30°C as mentioned above gives $B_0\rho^{\pi}_{N}=-4.79$ G and $B\rho^{\pi}_{N}=24.82$ G, thus $a_{\beta}^{F}=11.86$ G for $\theta=35°$. The calculated value is close to observed value for IIIb. B_0 and B are found to be -19 and 100 G, respectively, if $\rho^{\pi}_{N}=0.25$. The β-fluorine splitting constant of IIIc is assumed similarly to be negative.

2,3,5,6-Tetramethylphenyl Perfluoroalkyl Nitroxides. β-Hydrogen splitting constants of corresponding methyl, ethyl, and isopropyl nitroxides are 12.17, 10.97, and 6.92 G, respectively.[1] These values are similar in tendency to phenyl alkyl nitroxides but the magnitude of differences is not large. It is difficult to deduce suitable average dihedral angles for 2,3,5,6-tetramethylphenyl perfluoroalkyl nitroxides because the steric effect of two *ortho*-methyl groups on *N*-substituents is very subtle,[1] so that the validity of Eq. (3) cannot be tested

Conclusion

The conformations of β-fluorine atoms in Ib and Ic are rigid, and related to β-fluorine splitting constants through Eq. (3), where a negative value of B_0 is essential. For phenyl and pentafluorophenyl perfluoroalkyl nitroxides the application of Eq. (3) is possible although some ambiguity exists. Three series of perfluoroalkyl nitroxides studied give different values of B_0 and B. The validity of Eq. (3) is also confirmed concerning *t*-butyl perfluoroalkyl nitroxides[10,11] though the agreement between the calculated and observed values is not so good as in examples described above. The dihedral angle of 90° in perfluoro-2-azopropane radical anion[7] which shows very large β-fluorine splitting constant seems questionable because second order splittings will possibly be observed even at $\theta=0°$.[23] If this interpretation is correct β-fluorine splitting constants in perfluoroazoalkane radical anions can be successfully related to dihedral angles through Eq. (3) to give $B_0\rho^{\pi}_{N}=-26.93$ G and $B\rho^{\pi}_{N}=88.38$ G.

The results concerning B are consistent with SCF-MO calculations by Morokuma[8] which show that B depends on the particular molecule but that B_0 is near zero. Chachaty and co-workers[13] have proposed the values of B_0 and B to be ~-20 and -80 G, respectively for some perfluoroalkyl radicals. The meaning of B_0 is obscure at present.

Experimental

Trifluoromethyl iodide, pentafluoroethyl iodide, and heptafluoroisopropyl iodide were purchased from PCR, Incorp., and used without further purifications. Preparation of nitroso-compounds have been described previously.[1,17] For the preparation of perfluoroalkyl nitroxides,[10] 0.005—0.01 M deoxygenated solution of a nitroso-compound containing a suitable amount of a perfluoroalkyl iodide was irradiated by the light from a high pressure mercury lamp in the cavity of a spectrometer until an appropriate concentration of the nitroxide was attained. All spectra were recorded on a Varian V-4502-15 X-band spectrometer with 100 kHz magnetic field modulation. Temperature study was achieved with a Varian V-4557 variable temperature accessory in a 3 mm o.d. quartz cell, and temperature was calibrated by a thermometer. Hyperfine splitting constants and *g* values listed in Tables are the average values of at least three measurements. Measurements of magnetic field and microwave frequency, and ESR simulation have been given previously.[24]

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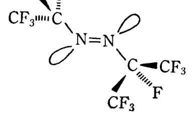
[23] Dr. K. Nishikida suggested that two β-fluorine atoms will be almost completely equivalent in the conformation shown below,



where perfluoro-2-azopropane radical anion shows possibly second order splittings.

[24] S. Terabe and R. Konaka, *J. C. S. Perkin II*, **1972**, 2163.