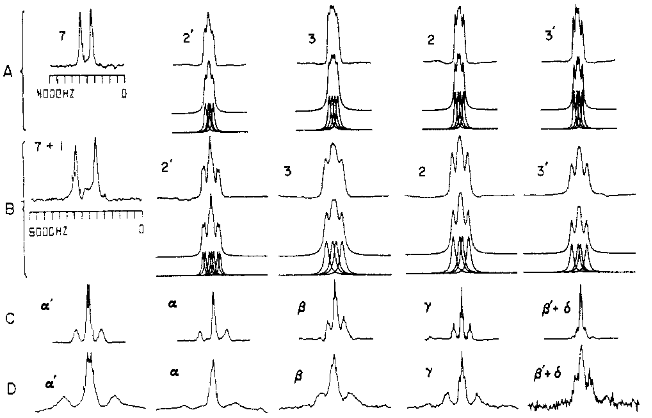

**Figure 2.** Carbon-13 spectra of EBBA at 75.4 MHz and 54 °C. The spectra were obtained by using the 2-D method of separated local field spectroscopy and show proton–carbon splittings of individual carbons in the $\omega_1$ dimension. (A) The aldehyde carbon and protonated aromatic carbons. The calculated spectra and their components are shown under the experimental spectra. The spectra of the quarternary carbons are not shown because no splittings were observed. The angle of the spinning axis ($\theta$) was 49.6°. (B) Same as A, except $\theta$ = 44.6°. (C) Aliphatic carbons; $\theta$ = 49.6°. (D) Aliphatic carbons; $\theta$ = 44.6°.

hanced (Figure 1C). The splitting between adjacent peaks in a multiplet is then

$$\Delta\nu = f\cdot[(3\cos^2\theta - 1)D + J] \qquad (1)$$

where $f$ is a scaling factor characteristic of the decoupling sequence, $D$ is the proton–carbon dipolar coupling constant, and $J$ is the scalar coupling constant. We used the BLEW-48 sequence[11b] for decoupling, because it is very effective for moderate decoupling power. The validity of applying the BLEW-48 sequence to study liquid crystals is discussed elsewhere.[13] Experimentally, it was implemented with hardware control in our spectrometer.[14] The spinning angle $\theta$ was accurately determined by measuring the proton doublet of $CH_2Cl_2$ dissolved in ZLI 1167 with and without sample spinning. Care was taken to maintain a constant temperature by using the same air flow.

Some of the carbon peaks in Figure 1C overlap with each other, and the overlapping becomes more serious when $\theta$ is moved further away from the magic angle. A 2-D technique can be used to solve this problem.[2,3] With this method, the $\omega_2$ dimension gives carbon-13 chemical shifts and the $\omega_1$ dimension gives proton–carbon splittings of individual carbon peaks. Figure 2 shows the spectra of EBBA in the $\omega_1$ dimension at two different angles. They were obtained by using a "double-window" sequence[15] with BLEW-48 decoupling[11b] in the evolution period. The spectral resolutions in Figure 2 are much better than those obtained for *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) with off-resonance CW decoupling and without sample spinning.[2] The peaks for the protonated aromatic carbons are not entirely resolved. Nevertheless, the splittings can be obtained readily with errors of 1% or less by fitting the spectra to sums of Lorentzian pairs. Spectra calculated from the results of least-squares fits are shown in Figure 2 for comparison with the experimental spectra.

The dipolar splittings increase with a decrease of $\theta$ for $\theta < 54.7°$. As a result, long-range couplings are resolved for some peaks but they only contribute to line broadening for some others. For example, at $\theta$ = 44.6°, the peak of carbon 2' can be resolved into four doublets due to one-, two-, and three-bond couplings (Figure 2B; the two central peaks differ by only 14 Hz and appear superimposed). On the other hand, the resolutions of most other peaks diminish due to unresolved long-range couplings.

Values of proton–carbon dipolar couplings can be readily calculated from eq 1 by using the spectra obtained at several angles. They can then be used to determine the order parameters of EBBA. Since the alkyl chains are very flexible and can adopt many conformations, statistical methods have to be applied for data analysis.[16,17] This subject will be discussed separately.

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## Tetrakis(pentafluorosulfanyl)hydrazine and Bis(pentafluorosulfanyl)aminyl Radical

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The first examples of compounds containing two pentafluorosulfanyl ($SF_5$) groups attached to the same nitrogen were prepared only a short time ago by Waterfeld and Mews.[1] On the basis of the structures of $(SF_5)_2NH$ and $(SF_5)_2NF$ (large SNS angles of 134.8° and 138.3°, respectively)[1] and the reaction shown in eq 1,[2] it was postulated that there would not be sufficient space

$$\begin{aligned}(CF_3)_2CN_2 + ClN(SF_5)_2 &\nrightarrow Cl(CF_3)_2CN(SF_5)_2 + N_2\\ &\rightarrow (CF_3)_2C{=}NSF_5 + SF_5Cl + N_2\end{aligned} \qquad (1)$$

around nitrogen for three $SF_5$ groups. The subsequent preparations of $CF_3N(TeF_5)_2$[3,4] and $CF_3N(SF_5)TeF_5$[4] show that these spatial concerns may be unwarranted. In an attempt to prepare tris(pentafluorosulfanyl)amine by the route shown in eq 2, we have

$$SF_5NCl_2 \xrightarrow[-Cl_2]{h\nu,\ SF_5Cl} (SF_5)_2NCl \xrightarrow[-Cl_2]{h\nu,\ SF_5Cl} (SF_5)_3N \quad ?? \qquad (2)$$

obtained instead the previously unreported tetrakis(pentafluorosulfanyl)hydrazine. The two possible pathways which could have resulted in the formation of $(SF_5)_2NN(SF_5)_2$ are shown in eq 3.

$$2(SF_5)_2NCl \xrightarrow[-Cl_2]{h\nu} (SF_5)_2NN(SF_2)_2$$

$$2(SF_5)_3N \xrightarrow[-S_2F_{10}]{h\nu} (SF_5)_2NN(SF_2)_2 \qquad (3)$$

The second route is supported by the synthesis of tetrakis((trifluoromethyl)thio)hydrazine form the photolysis of tris((trifluoromethyl)thio)amine,[5] although this hydrazine has never been obtained in the isolated state.

In a typical reaction, $SF_5NCl_2$ (43.9 mmol) and $SF_5Cl$ (150.0 mmol) were loaded into a 5-L Pyrex flask to give a pressure of about 1 atm at room temperature. This mixture was then irradiated for 4$^1/_2$ to 5 h with an internal medium-pressure mercury lamp. Repeated trap-to-trap distillation of the volatile products gave $(SF_5)_2NN(SF_5)_2$ (2.3 g, 4.3 mmol) in 20% yield in the −30 °C trap. Other products included $S_2F_{10}$, $Cl_2$, $N_2$, and $(SF_5)_2NCl$. Up to 10% yield of the chloroamine has been obtained in reactions where the initial quantity of $SF_5Cl$ (85.0 mmol) was less.

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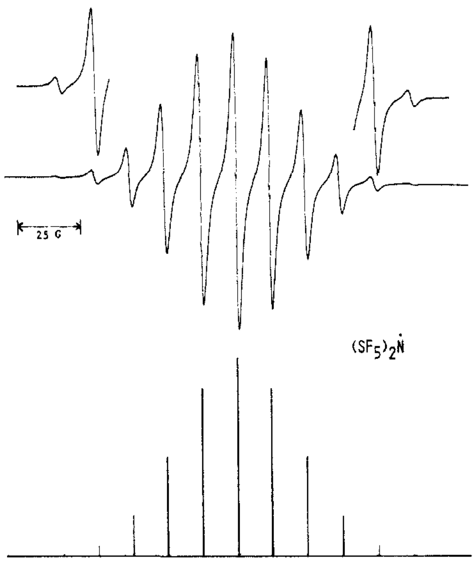

**Figure 1.** ESR spectrum of a $10^{-2}$ M solution of $(SF_5)_2NN(SF_5)_2$ in $CCl_3F$ at 298 K.

Tetrakis(pentafluorosulfanyl)hydrazine is a colorless, sublimable, crystalline solid which melts at 44.5–46.0 °C without decomposition. The infrared spectrum of the gas[6] shows intense bands in the region of 1000–500 cm$^{-1}$ characteristic of the pentafluorosulfanyl group. The $^{19}F$ NMR spectrum is minimally an $AB_4B'_4A'$ pattern[1] and is conceivably much more complex since all of the $SF_5$ groups could couple with one another.[7] Approximate values for the chemical shifts and the $J_{AB}$ coupling are $\delta_A$ 69.6, $\delta_B$ 88.5, and $J_{AB}$ = 145 Hz. The NMR spectra had to be obtained in $CCl_3F$ solution as rapid decomposition to $S_2F_{10}$ and other products was observed in nonperhalogenated solvents such as $CDCl_3$. Neither the electron impact nor the chemical ionization mass spectrum[6] of $(SF_5)_2NN(SF_5)_2$ exhibited a molecular ion. The highest mass fragment observed in the EI spectrum was at $m/z$ 127 for $SF_5^+$. The intense ion at $m/z$ 269 $[(SF_5)_2NH^+]$ in the CI spectrum is consistent with homolytic N–N bond cleavage followed by chemical ionization. Anal. $(N_2S_4F_{20})$ N, S.

**Table I.** ESR Parameters for Aminyl Radicals

| radical | $a(^{14}N)$/G | $a(^{19}F)$/G | $g$ | ref |
|---|---|---|---|---|
| $(SF_5)_2\dot{N}$ | 13.5 | 13.5 | 2.0033 | this work |
| $(FSO_2)_2\dot{N}$ | 8.4 | 8.0 | 2.0063 | 11 |
| $(CF_3S)_2\dot{N}$ | 13.20 | 1.95 | 2.00652 | 5 |
| $F_2\dot{N}$ | 16 | 56 | 2.009 | 9 |

The identity of the hydrazine is further supported by the ESR spectrum obtained on a $10^{-2}$ M solution of the material in $CCl_3F$ at 273–313 K. The spectrum of the radical (Figure 1) is clearly attributable to $(SF_5)_2\dot{N}$. It consists of an 11-line pattern (overlapping triplet to nonets; $a(^{14}N)$ = 13.5 G, $a(^{19}F)$ = 13.5 G) with an intensity ratio of 1:9:37:92:154:182:154:92:37:9:1, thus indicating eight equivalent (basal) fluorines. No hyperfine interaction is observed for the axial fluorine atoms as is also the case with the $SF_5$ radical.[8] The proportional increase and decrease in signal intensity with change in temperature indicates a homolysis/dimerization equilibrium[5,9] in this system. The appearance of the spectrum remained unchanged over a period of several hours; no other radicals were observed including $\dot{S}F_5$. The ESR parameters of $(SF_5)_2\dot{N}$, which are shown in Table I with those of related aminyl radicals, are consistent with a $\pi$-electron configuration.[10]

The X-ray crystal structure, N–N bond homolysis, and chemistry of $(SF_5)_2NN(SF_5)_2$ are under active investigation and will be reported separately. Further attempts are being made to discern whether or not $(SF_5)_3N$ can be prepared by the reaction reported herein.

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(6) IR (gas): 991 (vs), 968 (vs), 935 (m), 910 (w), 892 (w), 787 (vs), 719 (s), 617 (w), 589 (m) 556 (s) cm$^{-1}$; mass spectrum (20 eV), $m/z$ 127 ($SF_5^+$, 100%), 108 (1%), 104 (4%), 103 (3%), 89 ($SF_3^+$, 37%), 70 (1%), 65 (1%); chemical ionization mass spectrum (methane) major, $m/z$ 282 [$(SF_5)_2N_2^+$, 5%], 269 [$(SF_5)_2NH^+$, 43%], 250 ($SF_5NHSF_4^+$, 33%), 249 ($SF_5NSF_4^+$, 20%), 230 ($SF_5NSF_3^+$, 53%), 127 (100%), 108 (13%), 104 (43%), 103 (4%), 89 (100%), 70 (8%).

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