radical is crucial for the success of this reaction.[7c,d,12] Direct dioxolane cleavage gave the previously prepared ketones **8x**/**8n**, however, in a reversed ratio of 2.5/1. As an added bonus, ketals **7x**/**7n** were readily separable by chromatography. Hydrolysis of the individual epimers produced pure **8x** and **8n**. Each of these ketones was then separately reduced to produce silphiperfol-6-ene (**1**) and 9-episilphiperfolene (**2**) in 66–80% yields. Synthetic **1** exhibited spectroscopic properties identical with those reported by Bohlmann.[3] Copies of spectra (^{1}H NMR, IR, MS) of synthetic silphiperfolene kindly provided by Processor Paquette were also identical.

In conclusion, the tandem radical cyclization approach to condensed cyclopentanoid natural products has now been extended to encompass angular triquinanes such as silphiperfolene.[13] With appropriate modifications, a variety of related angular triquinanes should also be readily accessible.[12]

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Supplementary Material Available: Spectra of compounds **2**, **4**, **5**, and **8x,n** (1 page). Ordering information is given on any current masthead page.

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Carbon-13 NMR of Liquid Crystals. Spinning near the Magic Angle with Proton–Proton Dipolar Decoupling

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Liquid crystals have orientational ordering and nonzero dipolar couplings. NMR spectra of small solute molecules often show well-resolved peaks which can be analyzed to determine order parameters and molecular structures.[1] On the other hand, molecules of the liquid crystal itself have extensive proton–proton couplings and show broad, overlapping proton NMR peaks. Fortunately, the carbon-13 spectra of liquid crystals are better resolved and proton–carbon dipolar couplings can be determined[2] by a 2-D method called separated local field spectroscopy.[3] We have found that the quality of the carbon-13 spectra can be greatly improved by using a combination of sample spinning near the magic-angle and proton–proton dipolar decoupling.

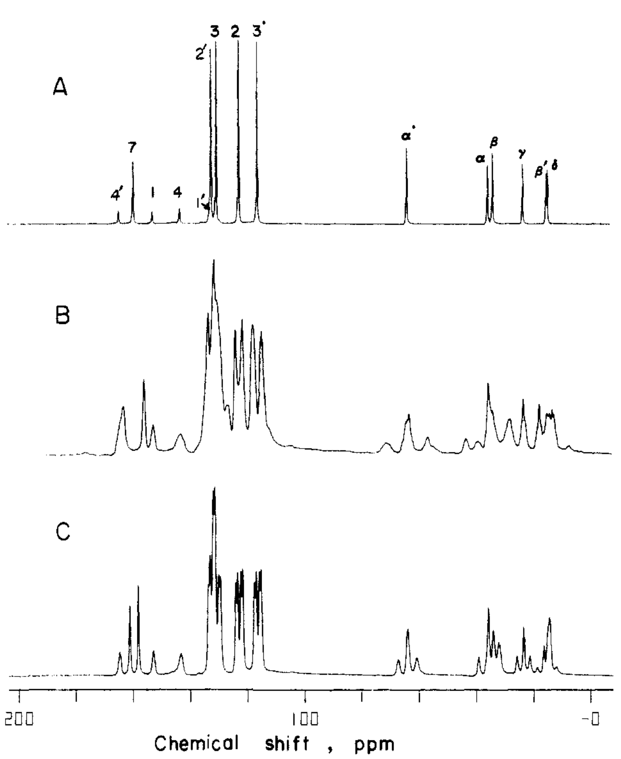
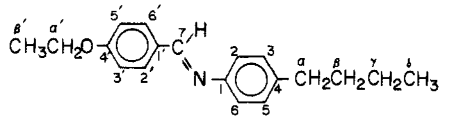


Figure 1. Carbon-13 spectra of EBBA at 75.4 MHz and 54 °C. The sample was spun at an angle of 52.8° with respect to B_0 at a rate of 1 kHz; $\gamma H_2/2\pi = 20$ kHz; 50% duty cycle: (A) with broad-band proton decoupling; (B) without decoupling; (C) with BLEW-48 decoupling. The accumulation time was 15 min for A and 1 h each for B and C. The scaling factor *f* for C is 0.420.[13]

When a nematic sample is spun rapidly (≳1 kHz at 7 T) at or near the magic angle, the long axes of the molecules can align along the spinning axis[4-6] and sharp carbon-13 peaks can be observed with only moderate proton decoupling power.[5,6] If the angle θ between the spinning axis and the magnetic field B_0 is equal to the magic angle (54.7°), the chemical shifts are essentially the same as those in the isotropic phase. They change with θ because of chemical shift anisotropies. The decoupled carbon-13 spectrum of *N*-(*p*-ethoxybenzylidene)*p*-*n*-butylaniline (EBBA) spun at θ



= 52.8° is shown in Figure 1A. Assignment of the peaks is given in the literature[7] and was checked by selective decoupling in an isotropic solution. At this angle, the signals of the 1'- and 2'-carbons overlap. For $\theta < 50°$, the signal of the 1'-carbon is resolved and appears at a lower field than that of the 2'-carbon, but the two methyl signals may overlap with each other. With rapid sample spinning at an angle θ, dipolar couplings are reduced by a factor of $(3 \cos^2 \theta - 1)/2$ and can be observed if proton decoupling is not used (Figure 1B). However, the carbon-13 spectrum is affected by both proton–proton and proton–carbon couplings. The peaks are rather broad and spectral analysis is not straightforward. This problem can be overcome by applying a pulse sequence which removes proton–proton dipolar couplings.[8-12] The spectrum is simplified and the resolution is en-

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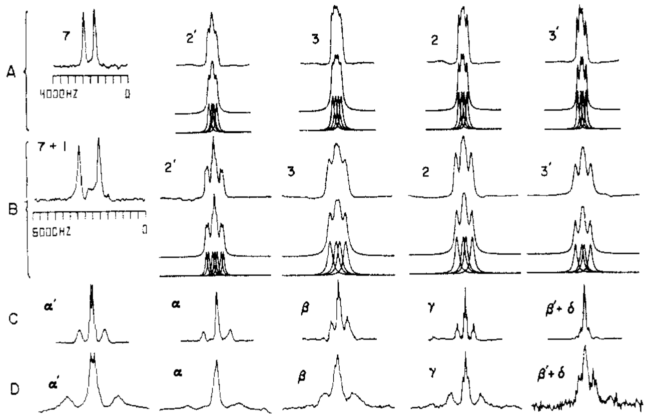

Figure 2. Carbon-13 spectra of EBBA at 75.4 MHz and 54 °C. The spectra were obtained by using the 2-D method of separated local field spectroscopy and show proton–carbon splittings of individual carbons in the ω_1 dimension. (A) The aldehyde carbon and protonated aromatic carbons. The calculated spectra 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 (θ) was 49.6°. (B) Same as A, except θ = 44.6°. (C) Aliphatic carbons; θ = 49.6°. (D) Aliphatic carbons; θ = 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 θ 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 θ 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 ω_2 dimension gives carbon-13 chemical shifts and the ω_1 dimension gives proton–carbon splittings of individual carbon peaks. Figure 2 shows the spectra of EBBA in the ω_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 θ 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 θ = 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

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

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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