

## Direct Measurement of Chemical Shielding Anisotropies. Fluoranil

Sir:

Although the nuclear magnetic shielding coefficient  $\sigma$  is a tensor quantity, nearly all measurements of it have been confined to the mean shielding  $\sigma = \frac{1}{3} \text{Tr}(\sigma)$ , since all spectral information about its anisotropy is erased by rapid isotropic molecular tumbling in the usual liquid nmr sample. In solids, all information about  $\sigma$  is typically obscured by static dipolar broadening, although in a few favorable cases measurements of limited accuracy have been possible.<sup>1-10</sup> In recent years several rather precise measurements have been made on molecules aligned in liquid-crystal solvents.<sup>11-15</sup> These are complicated in the sense of requiring a rather elaborate analysis of dipolar and J-coupling effects and the manner in which they are averaged over an anisotropic molecular motion. And in general they yield only a linear combination of the three principal elements of  $\sigma$  rather than full knowledge of the tensor.

One of the principal promises of the multiple-pulse nmr coherent averaging technique<sup>16-18</sup> has been the full measurement of shielding anisotropies without the dipolar obscuration which beset direct measurements in solids and without the loss of information, due to motional averaging, which is inherent in the liquid crystal technique.

In this communication we illustrate the first experimental realization of this promise. Figure 1 shows the <sup>19</sup>F powder spectrum of solid fluoranil, C<sub>6</sub>F<sub>4</sub>O<sub>2</sub>,

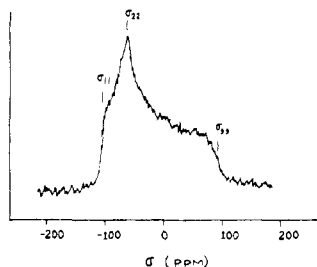


Figure 1. <sup>19</sup>F spectrum of powdered fluoranil at room temperature, obtained by the four-pulse dipolar narrowing technique. The zero of the horizontal scale refers to the resonance of an external liquid C<sub>6</sub>F<sub>6</sub> sample, also recorded using the four-pulse method.

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obtained at room temperature using a spectrometer<sup>19</sup> operating in the four-pulse mode<sup>16</sup> at 54.0 MHz. The spectrum remains unchanged down at least to  $-90^\circ$ , indicating that no motional averaging is present. The pattern obtained is typical of that expected for a chemical shift tensor all of whose principal values are different. These values, referred to an external reference of neat liquid C<sub>6</sub>F<sub>6</sub>, are

$$\sigma_{11} = -101 \pm 6 \text{ ppm}$$

$$\sigma_{22} = -62 \pm 6 \text{ ppm}$$

$$\sigma_{33} = 86 \pm 6 \text{ ppm}$$

defined in order of increasing magnitude.

We have made preliminary measurements of a similar sort in a number of other <sup>19</sup>F compounds. After completion and refinement they will be reported at length elsewhere, in conjunction with a discussion of the problem of referring  $\sigma$  to molecule-fixed axes  $x, y, z$ , the implications of the results in valence theory, their use to obtain new information about molecular geometry and molecular motion, and some possible large discrepancies with earlier results obtained by less direct means.

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## Electron Spin Resonance Evidence for the Pyramidal Structure of the Radical-Center Carbon Atom of 7-Oxabicyclo[2.2.1]hept-2-yl Radicals

Sir:

The structure around the radical-center carbon atom of free radicals of the 2-norbornyl type has been assumed essentially planar,<sup>1,2</sup> and the preference of free radicals of the 2-norbornyl type for reacting in atom-transfer reactions at the exo rather than the endo position has been explained as an effect of basically steric origin.<sup>1,2</sup> On the basis of extended Hückel calculations, Fujimoto and Fukui<sup>3</sup> proposed an idea that the radical-center carbon of 2-norbornyl radical may have a shallow pyramidal structure with the C<sub>2</sub>-H bond bent to the endo direction and that the stereoselectivity of this radical in transfer reactions is basically controlled by the frontier orbital.

Gloux, Guglielmi, and LeMaire<sup>4</sup> reported an esr study on 2-hydroxybicyclo[2.2.1]hept-2-yl radical. Their results show that the radical-center carbon of

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