

Figure 1. Esr spectrum of  $\text{Ph}_2\text{SiMe}_2\cdot^-$  in THF,  $-80^\circ$ .

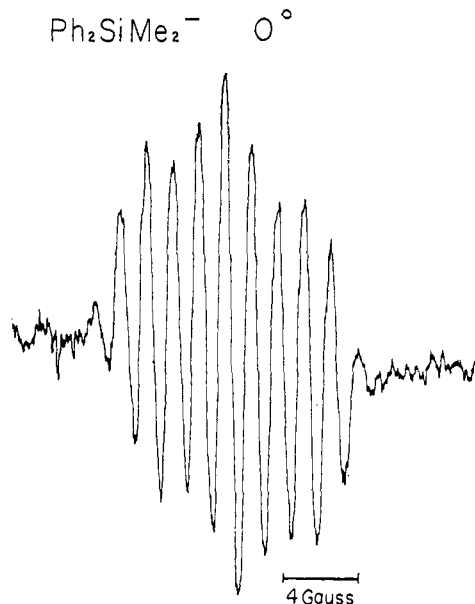


Figure 2. Esr spectrum of  $\text{Ph}_2\text{SiMe}_2\cdot^-$  in THF,  $0^\circ$ .

that the delocalized radical anion was not detected by these workers in view of the limited stability of the parent anion radical. Our studies indicate an approximate half-life for  $[\text{PhSiMe}_2\text{Ph}]\cdot^-$  of 50 min at  $-95^\circ$ . Even a moderate delay in obtaining high-temperature spectra would result in decomposition of this species.

If the number of silicon atoms bridging the two phenyl groups was greater than one, delocalization of the electron over two aromatic rings was not observed at any temperature.

The temperature-dependent behavior of diphenyldimethylsilane is in marked contrast to that of the related compound, diphenylmethane.<sup>4</sup> Even at low temperatures ( $T < -70^\circ$ ), the esr spectrum of chemically generated  $[\text{PhCH}_2\text{Ph}]\cdot^-$  consists of 11 equidistant lines which result from splitting by ten approximately equal ring hydrogens ( $A_H = 2.23$  G); the two methylene protons cause further splitting. Thus, even at low temperatures, the odd electron is delocalized over both phenyl rings. The next higher homolog,  $[\text{bibenzyl}]\cdot^-$ , is reported to show no delocalization of the unpaired electron at low temperatures.<sup>4,5</sup> Above  $-70^\circ$  the bibenzyl radical anion rapidly decays.<sup>6</sup>

In cases where the odd electron is localized on only one ring, the rate of electron transfer between rings,  $\nu_e$ , is slow compared to the esr hyperfine coupling constants ( $\nu_e < 10^8 \text{ sec}^{-1}$ ). If the electron is delocalized over both phenyl groups,  $\nu_e$  is fast compared to the hyperfine coupling constants ( $\nu_e > 10^8 \text{ sec}^{-1}$ ). McConnell<sup>6</sup> refers to these as "slow passage" or "fast passage" conditions, respectively. If, however,  $\nu_e$  is of the same order of magnitude as the hyperfine splittings ( $10^6 < \nu_e < 10^8 \text{ sec}^{-1}$ ), spectra with novel temperature effects are obtained.<sup>7,8</sup> Often the esr spectrum in this intermediate case assumes an S shape, with sharp components superimposed on the broad background. The line widths of the sharp components vary with temperature.

In  $[\text{PhSiMe}_2\text{Ph}]\cdot^-$ , where we observe both slow and

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fast passage extremes, we have been able to see spectra at temperatures between approximately  $-80$  and  $-40^\circ$  which indeed have a broad S shape and whose hyperfine structure line widths show anomalous temperature variation. The temperature interval for this intermediate range is extremely sensitive to variations in concentration, solvent, and method of preparation of the anion radical.

McConnell<sup>7</sup> and Harriman and Maki<sup>8</sup> have attempted to describe the factors controlling the rate of inter-ring intramolecular electron transfer in  $\alpha,\omega$ -diphenylalkanes and related compounds. Unfortunately, the expressions derived for  $\nu_e$  contain both implicit and explicit temperature-dependent variables in both exponential and preexponential factors. It is therefore impossible to use the theoretical expressions to explain the results for  $[\text{PhSiMe}_2\text{Ph}]\cdot^-$ . In particular, it is not at all clear why this anion radical, out of all the compounds studied to date, shows  $\nu_e$  to be significantly temperature dependent. At present, we can only state that our results are not inconsistent with the theoretical explanations that have been developed.

Studies on additional diphenyl silyl compounds are being undertaken to further elucidate the electron delocalization process.

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#### Molecular Conformation and Electronic Structure. The Solid State Spectrum of a Planar Anil

Sir:

Benzylideneaniline (BA), an isoelectronic analog of *trans*-azobenzene (A) and *trans*-stilbene (S), presents

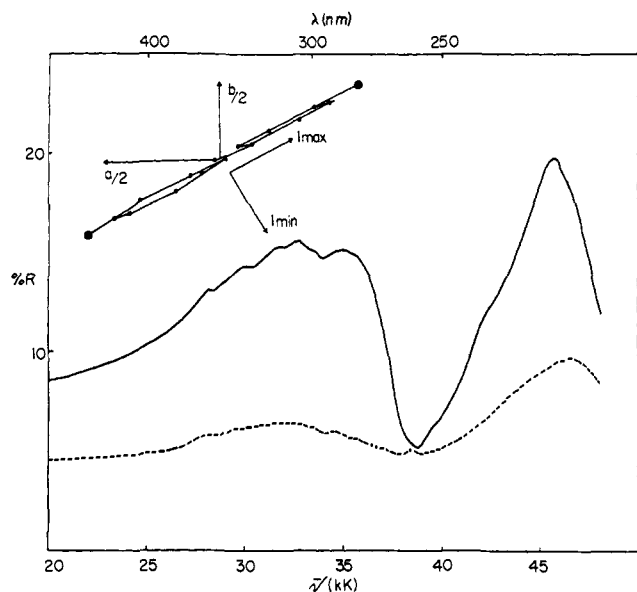


Figure 1. Reflection spectra at 298°K for light polarized parallel to the  $I_{\max}$  (—) and  $I_{\min}$  (----) extinction directions. Upper left: projection of the BACl molecule onto (001);  $I_{\max}$  and  $I_{\min}$  designate the principal vibration directions relative to the  $a$  and  $b$  crystallographic axes and the long and short axes of BACl.

an ideal system for the study of electronic structure as a function of molecular conformation. The A and S ultraviolet solution spectra<sup>1</sup> have intense bands ( $\epsilon \sim 25,000$ ) around 33 kK which show characteristic vibrational structure on the red side of the bands. The BA ultraviolet solution spectrum<sup>1</sup> shows a prominent shoulder ( $\epsilon \sim 10,000$ ) in this region of the spectrum with a more intense peak ( $\epsilon \sim 20,000$ ) occurring in the region of 37 kK. The marked difference between the ultraviolet solution spectrum of BA and those of A and S is thought<sup>1-7</sup> to be a manifestation of the nonplanarity of BA (primarily due to a rotation about the  $N$ -phenyl bond), while A and S are planar molecules in the solid<sup>8,9</sup> and are presumably so in solution. X-Ray crystallographic structure determinations of BA and three substituted benzylideneanilines<sup>10,11</sup> indicate that these molecules are nonplanar in the solid. For BA and two substituted benzylideneanilines, diffuse reflectance spectra<sup>12</sup> of the solid exhibit the general features of the corresponding solution spectra in accord with earlier spectroscopic arguments.

Recently reported calculations on BA indicate that for the free molecule the twisted form is favored over the planar form by about 2 kcal/mol.<sup>13</sup> Such a low-

energy barrier presents the possibility that under suitable conditions crystal packing forces may be sufficient to force the molecule into the planar conformation; if so, the electronic structure should be perturbed to the extent that the absorption spectrum resembles that of A and S. A direct test of the conclusions of the solution studies is thus provided.

The recently determined crystal structure of the metastable form of  $p$ -chlorobenzylidene- $p$ -chloroaniline<sup>14</sup> (BACl) shows that this molecule is planar in the solid. The addition of two chlorine substituents to the molecule does not significantly alter the solution absorption spectrum which, aside from a small blue shift, still exhibits the features characteristic of a benzylideneaniline spectrum indicating that BACl is nonplanar in solution. We herein report the crystal spectrum of BACl obtained by polarized specular reflection spectroscopy.

Single crystals of BACl suitable for spectroscopic studies are triclinic needles elongated along the crystallographic  $b$  axis.<sup>14</sup> The upper left of Figure 1 shows the projection of the single molecule in the unit cell onto the (001) face, together with the experimentally determined extinction directions.<sup>15</sup> When the electric vector of the exciting light is oriented parallel to  $I_{\max}$ , molecular excitation will be almost exclusively in the molecular plane and nearly along the projection of the longest axis of the molecule on (001). Orientation of the electric vector parallel to  $I_{\min}$  leads to excitation of out-of-plane molecular transitions. Disregarding the  $-\text{CH}=\text{N}-$  bridge, the molecular symmetry is essentially  $C_{2h}$ ; hence observed transitions will be polarized either out of plane or in plane with no symmetry restrictions on the direction of the latter since both in-plane molecular axes transform as the same irreducible representation. In A and S it has been shown that the polarization of at least the major portion of the intense, low-energy transition is very nearly parallel to the vector connecting the para and para' positions of the molecule.<sup>16-18</sup> On the basis of these geometric considerations, it is expected that for the low-energy transition in BACl, the band shape in the  $I_{\max}$  direction should closely resemble that of A and S.

Normal incidence specular reflection spectra were obtained with apparatus described previously.<sup>19,20</sup> Figure 1 shows these spectra for the incident light polarized along the two extinction directions of the (001) face. For  $I_{\max}$ , as expected for a planar analog of A and S, the low-energy band fails to show the prominent shoulder which is characteristic of the solution spectra of benzylideneanilines.<sup>21</sup> The low intensity in this band for  $I_{\min}$  indicates an in-plane long-axis polarization consistent with that of A and S.

There is significant vibrational structure on the red side of the low-energy band, similar to that observed in both A and S; such structure is not observed in

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