

latter case as compared with the strong complex formation in TCNE-DAP solutions may account for the different behavior observed in the  $I_2$ -surfactant concentration plots of these two surfactant (Figures 1-4). The strong interaction between TCNE and DAP leads to the observed more gradual change in the corresponding curves starting at lower surfactant concentrations whereas the non- or weakly interacting AOT causes no significant variation as compared with the neat results observed in the AOT-solvent systems.

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## Permutational Isomerization of Spirosulfuranes Derived from Catechols

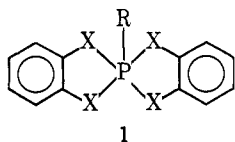
Benjamin A. Belkind,<sup>1a</sup> Donald B. Denney,\*<sup>1b</sup> Dorothy Z. Denney,<sup>1b</sup> Y. F. Hsu,<sup>1b</sup>  
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**Abstract:** The variable temperature <sup>13</sup>C NMR spectra of the sulfuranes **3**, **4a,b**, and **5** have been recorded as has the 220-MHz <sup>1</sup>H NMR of **4a,b** and **5**. The spectral data indicate that there is intramolecular ligand reorganization occurring in **3**, **4a,b**, and **5**. The data also show that **4a,b** and **5** do not interconvert at ambient temperature. It is concluded that these spirosulfuranes prefer structures that are trigonal bipyramidal or nearly so.

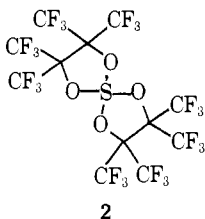
There has been considerable progress in recent years in the preparation and studies of the chemistry of sulfuranes and persulfuranes.<sup>2</sup> Even more progress has occurred in the related field of phosphorane chemistry.<sup>3</sup> Less progress has been made in studies of hexacoordinated phosphorus compounds which are analogues of the persulfuranes. Although it has been

generally recognized that phosphoranes can exist as trigonal bipyramids, TBP, or square pyramids, SP, it has only recently been shown that in the crystalline state there can be a gradual change in structure from TBP to SP within a series of compounds.<sup>4</sup> The series which has shown this change has the general structure **1**, where the X's are various heteroatoms. A



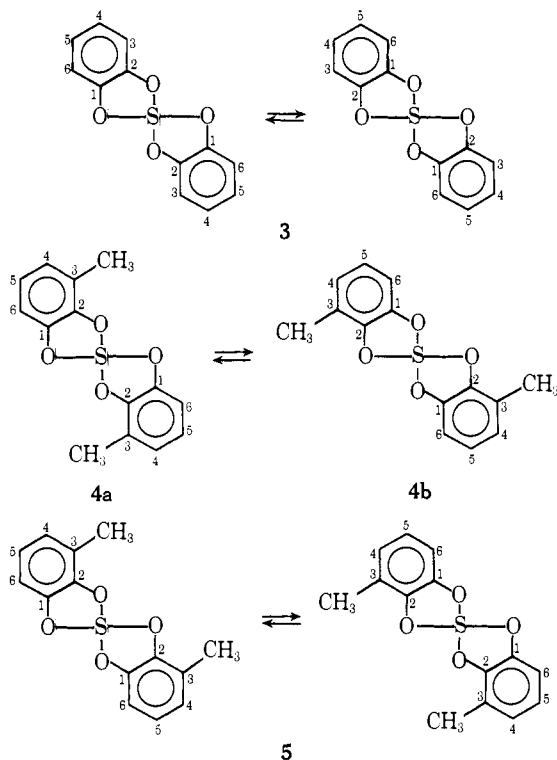
number of other phosphoranes have also been shown to have structures that are more nearly *SP* than *TBP*,<sup>5</sup>

The structures of sulfuranes are not nearly so well defined. Those that have been investigated by X-ray crystallography have been found to be *TBPs* or nearly so.<sup>2</sup> Astrologes and Martin<sup>6</sup> have investigated the variable temperature <sup>19</sup>F NMR spectra of **2** and have found that at  $-100\text{ }^\circ\text{C}$  it exists as a *TBP*



or near *TBP*. On warming an intramolecular ligand reorganization process occurs with  $\Delta G^\ddagger \approx 7.5\text{ kcal/mol}$ , which renders pairs of trifluoromethyl groups equivalent. Total equivalency is not achieved on heating to  $200\text{ }^\circ\text{C}$ .

More recently, Wilson and Belkind<sup>7</sup> have prepared the sulfurane **3** and the presumed mixture of sulfuranes **4a**, **4b**, and **5**.



The <sup>1</sup>H NMR spectrum at 220 MHz of **3** exhibits an *AA'BB'* pattern for the aromatic protons which is suggestive of rapid permutational isomerization in the NMR time frame. The complexity of the spectrum made it unattractive for deeper study.

The <sup>13</sup>C NMR spectrum of **3** at ambient temperature shows only three resonances at  $\delta$  144.2, 123.4, and 111.8 ppm relative to tetramethylsilane. These resonances are assigned to the (1,2), (4,5), and (3,6) pairs of carbons.<sup>8</sup> There are a number of ways in which these pairs of carbons can become equivalent, and the <sup>13</sup>C NMR data do not serve to distinguish between them.

The <sup>13</sup>C NMR spectrum of **3** at  $-90\text{ }^\circ\text{C}$  shows two reso-

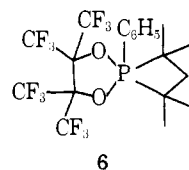
nances at  $\delta$  147.76 and 140.74 ppm. These are assigned to the 1 and 2 carbons. It is not possible to define which is which. Similarly, two resonances are found at  $\delta$  125.41 and 121.48. These are due to the 4 and 5 carbons. Once again an exact assignment cannot be made. The resonances for the 3 and 6 carbons are found as an apparent singlet at  $\delta$  111.91 ppm. The low-temperature <sup>13</sup>C NMR spectrum of **3** shows that the molecule prefers to adopt a *TBP* or near *TBP* structure.<sup>9</sup> The free energy of activation for the process which renders the pairs of carbons equivalent is ca. 9 kcal/mol.<sup>10</sup> This value was calculated from the coalescence temperature  $-80\text{ }^\circ\text{C}$  and  $\Delta\nu = 140\text{ Hz}$ .

The 220-MHz <sup>1</sup>H NMR spectrum of the presumed mixture of **4a**, **4b**, and **5** at  $18\text{ }^\circ\text{C}$  shows resonances for aromatic hydrogens centered at  $\delta$  6.82 ppm and a single resonance for hydrogens of methyl groups at  $\delta$  2.25 ppm. This resonance is well separated from the resonance of the hydrogens of the methyl group of 3-methylcatechol,  $\delta$  2.20 ppm, and the hydrogens of the methyl group of 3-methyl-*o*-phenylene sulfite,  $\delta$  2.34 ppm. These compounds are usually contaminants of the sulfuranes. Cooling a deuterated chloroform solution of the sulfuranes led to reversible splitting of the resonances of the hydrogens of the methyl groups into two resonances. A maximum separation of 4 Hz was found at  $-60\text{ }^\circ\text{C}$ . It was not possible to determine whether the intensities of the two resonances were the same or very nearly the same.

The <sup>13</sup>C NMR spectrum of an unusually pure sample of the methylcatechol sulfuranes in deuterated methylene chloride at ambient temperature has three resonances at  $\delta$  144.49, 144.05, and 143.64 which are assigned to carbons bonded to oxygen. These resonances are of unequal intensity with the resonance at  $\delta$  144.05 ppm being the largest. The best explanation for these findings is that there are four resonances, the  $\delta$  144.05 resonance arising from fortuitous overlap of two of them. Four resonances for carbons bonded to oxygen are predicted if **4a** and **4b** are interconverting and if **5** is exchanging *a-e* positions. In fact **5** could be rigid. In view of the findings with **3** and the need to postulate interconversion of **4a** and **4b**, it does not seem reasonable to expect **5** to be rigid. It is not unexpected that **4a** and **4b** do not interconvert into **5** and vice versa. Such a process has been observed in sulfurane chemistry<sup>11</sup> for a sulfurane containing two five-membered rings with each having a carbon and an oxygen bonded to sulfur. The activation energy,  $\Delta G^\ddagger$  ( $84\text{ }^\circ\text{C}$ ), for this process was found to be 30 kcal/mol.

The <sup>13</sup>C NMR spectrum of a solution of the sulfuranes **4a**, **4b** and **5** at  $-90\text{ }^\circ\text{C}$  is quite complex and it is that which would be expected if **4a** and **4b** are no longer interconverting. The resonances for the 1,2 carbons consisted of six lines two downfield of the other four by 140 Hz. These lines coalesced at  $-40\text{ }^\circ\text{C}$ . In principle eight lines should have been observed. The intensities of the downfield pair as compared to the upfield four suggest that there is an overlap in the downfield resonances. A  $\Delta G^\ddagger$  of ca. 11 kcal/mol was calculated using  $\Delta\nu = 140\text{ Hz}$  and  $-40\text{ }^\circ\text{C}$  for the coalescence temperature. The higher  $\Delta G^\ddagger$  for the ligand reorganization of the methyl-substituted sulfuranes as compared to the unsubstituted sulfurane is probably due to increased steric interactions during the interconversions.

The success of the measurements on catechol-derived sulfuranes prompted a similar investigation of **1**,  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{X} = \text{O}$ , and **6**. Both of these materials' crystal structures indicate



that they are SP or very nearly SP. The  $^{13}\text{C}$  NMR spectrum of **1**,  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{X} = \text{O}$ , down to  $-90^\circ\text{C}$  showed no change. All of the resonances remained remarkably sharp. Similarly the variable temperature  $^{19}\text{F}$  NMR spectra of **6** showed no change on cooling to  $-90^\circ\text{C}$ . These negative findings do not distinguish between interconverting TPs or a SP structure.

### Experimental Section

The variable temperature 220-MHz  $^1\text{H}$  NMR spectra were recorded on a  $\text{CDCl}_3$  solution of the methylcatechol sulfuranes. A maximum separation for the hydrogens of methyl groups was found to be 4 Hz at  $-60^\circ\text{C}$ . An apparent coalescence was found at  $-20^\circ\text{C}$ .

The  $^{13}\text{C}$  NMR spectra were recorded with a Varian FT-80 spectrometer operating at 20 MHz. Unless specifically stated all spectra were obtained under conditions of complete proton noise decoupling using a 2.0-kHz noise bandwidth.

The samples, ca. 100 mg, were dissolved in deuteriomethylene chloride which also served as the internal lock. The solutions were degassed by bubbling argon through them.

In a representative experiment, the sample was pulsed 2400 times, with a spectral width of 4000 Hz and using 16K data points and an acquisition time of 2.047 s. Normally a  $35^\circ$  flip angle was used which corresponds to a pulse width of 5  $\mu\text{s}$ . In the case of the mixture of methylcatechol sulfuranes at room temperature a flip angle of  $21^\circ$  was used which corresponds to a pulse width of 3  $\mu\text{s}$ . The reason for this change is that the carbons bonded to oxygen have long  $T_1$ 's and they were difficult to detect with the 5- $\mu\text{s}$  pulse.

At ambient temperature the  $^{13}\text{C}$  NMR spectrum of the mixture of methylcatechol sulfuranes had the following resonances, and a single off-resonance spectrum indicated that the carbons were coupled to the number of hydrogens indicated in the parentheses: 15.22 (3), 109.02 (1), 122.41 (0), 122.66 (1), 124.69 (0), 124.91 (1), 143.77 (0), 144.05 (0), 144.33 (0) ppm. At  $-90^\circ\text{C}$  the spectrum was quite complex. A resonance with a shoulder was found at 15.22 ppm as was one at 109.34 ppm. Broad resonances were found at 109.02, 126.37,

and 126.51 ppm. Relatively sharp resonances were found at 122.23, 122.68, 127.78, 122.96, 139.57, 139.66, 140.07, 140.17, 146.35, and 147.31 ppm.

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## Effect of Molecular Structure on Mesomorphism. 7.<sup>1</sup> Enhancement of Smectic-Isotropic Transition Temperatures in Binary Mixtures of a New Liquid Crystal Series: the 4-Nitrophenyl 4'-n-Alkoxybenzoates

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**Abstract:** The homologous series of 4-nitrophenyl 4'-n-alkoxybenzoates has been synthesized and transition temperatures have been determined. All members of this series with three carbons or more in the alkoxy chain exhibit liquid crystalline behavior. The familiar odd-even alternation in mesophase-isotropic temperatures was found. A method for determining mesophase-isotropic temperatures in strongly supercooled samples is described. This series of nitro esters exhibits marked nonlinear thermal behavior in selected binary mesophase systems. Maxima in mesophase-isotropic transition temperatures have been determined for mixtures of each of the 4-nitrophenyl 4'-alkoxybenzoates with 4-heptyloxybenzylidene-4'-butylaniline and with 4-octyloxybenzylidene-4'-butylaniline. These maxima occur at or very near 50:50 mole percent composition of the binary mixtures. A plot of the maxima vs. alkoxy chain length of the nitro esters exhibits an odd-even alternation. In mixtures of 4-substituted-phenyl 4'-decyloxybenzoates, enhanced  $S_A$  mesophases were found for the nitro ester when mixed with methyl and methoxy esters; linear, ideal mixture behavior was found for the nitro ester when mixed with trifluoromethyl and cyano esters. A  $\pi$  molecular complex is proposed to account for this nonideal solution behavior.

Liquid crystalline compounds and their mixtures offer unique opportunities to examine structure-property relationships in condensed phases. In general binary mixtures of

liquid crystalline materials exhibit eutectic behavior in their solid-mesophase transition temperatures, whereas their mesophase-isotropic transition temperatures vary linearly with