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### PMR Spectrum of Butadiene Sulphone Oriented in a Lyotropic Solvent

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## PMR SPECTRUM OF BUTADIENE SULPHONE ORIENTED IN A LYOTROPIC SOLVENT<sup>†</sup>

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Studies of the ring puckering vibrations in several 4 and 5 membered ring systems using the technique of NMR spectroscopy of oriented molecules have so far been undertaken in thermotropic solvents.<sup>1-10</sup> It has in general been found that whereas the four membered rings in systems like trimethylene sulphide and trimethylene oxide are puckered, the five membered ones (like in butadiene sulphone) are essentially planar with  $C_{2v}$ -symmetry. The influence of

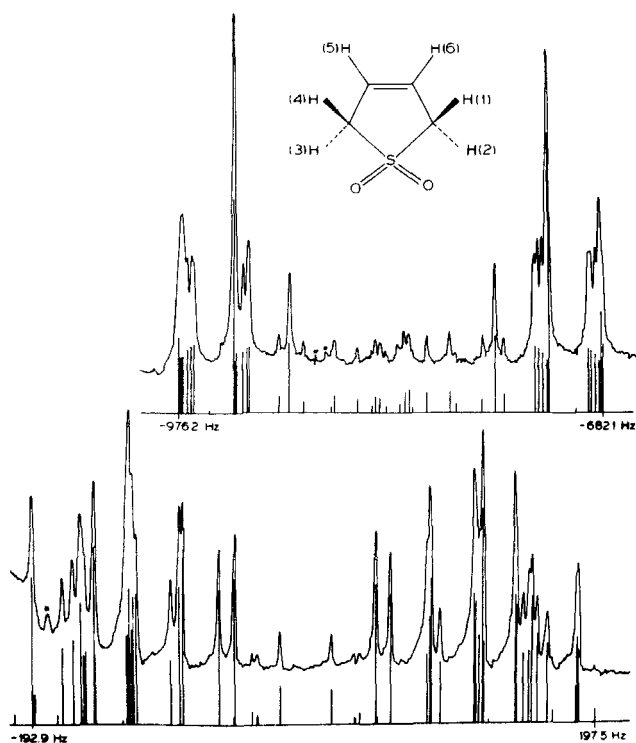
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solvents on the information thus derived has not been examined so far. An investigation on butadiene sulphone dissolved in a widely different phase formed by 43 per cent decylamine hydrochloride, 53 per cent heavy water, 1 per cent decanol and 3 per cent sodium sulphate (A) was undertaken in order to find out any solvent effect. The results are reported in the present communication.

The spectrum of 2.5 weight per cent solution of commercially available butadiene sulphone dissolved in the lyotropic phase (A) was recorded at 26°C on a Brüker FT-NMR spectrometer operating at 360 MHz. 100 transients were accumulated. The spectrum is shown in figure 1. The average line-width was 2.5 Hz.

The analysis was carried out using the LAOCOONOR programme<sup>11</sup> on an IBM-360/44 computer. The spectrum due to the olefinic protons appears nearly 825 Hz down field (upper trace in figure 1) compared to that due to aliphatic protons (lower trace in figure 1). Conditions of 'weak-couplings' for the dipolar couplings  $D_{15}$  and  $D_{16}$  are satisfied and hence the spectrum is sensitive to  $|J_{15} + 2D_{15}|$  and  $|J_{16} + 2D_{16}|$  rather than the individual coupling constants. In consistent with the results on the spectrum in the isotropic medium,<sup>1</sup> the indirect coupling constants  $J_{15}$  and  $J_{16}$  were neglected. All other parameters were iterated upon during analysis using the LAOCOONOR



Observed and calculated PMR spectra of butadiene sulphone oriented in the lyotropic solvent (A). The upper trace arises from the ethylenic protons whereas the lower one is due to aliphatic protons. The lines marked (\*) do not belong to butadiene sulphone.

program. The r.m.s. error between the observed and the calculated line positions was found to be 0.37 Hz when 76 observed lines were assigned. Values of the parameters derived are given in table 1. The signs of  $D_{15}$  and  $D_{16}$  (Table 1)

**Table 1.** Spectral and geometrical parameters for butadiene sulphone oriented in a lyotropic mesophase

Para- meter	Value	Para- meter	Value
$D_{12}$	$-79.64 \pm 0.02$ Hz ( $-79.65$ ) <sup>a</sup>	$J_{13}$	$1.75 \pm 0.06$ Hz ( $1.2 \pm 0.4$ ) <sup>c</sup>
$D_{13}$	$11.73 \pm 0.03$ Hz ( $11.47$ ) <sup>a</sup>	$J_{14}$	$1.16 \pm 0.06$ Hz ( $0.7 \pm 0.4$ ) <sup>c</sup>
$D_{14}$	$22.45 \pm 0.03$ Hz ( $22.50$ ) <sup>a</sup>	$J_{56}$	$8.7 \pm 0.07$ Hz ( $8.6 \pm 0.5$ ) <sup>c</sup>
$D_{15}$	$5.35 \pm 0.03$ Hz ( $5.15$ ) <sup>a</sup>	$r_{12}/r_{14}$	0.499 (0.474) <sup>c</sup>
$D_{16}$	$-24.45 \pm 0.03$ Hz ( $-24.42$ ) <sup>a</sup>	$r_{15}/r_{14}$	1.118 (1.085) <sup>c</sup>
$D_{56}$	$72.69 \pm 0.03$ Hz ( $72.70$ ) <sup>a</sup>	$r_{56}/r_{14}$	0.676 (0.672) <sup>c</sup>
$\Delta_{1-5}$	$824.2 \pm 0.1$ <sup>b</sup> Hz	$S_{11}$	$-0.00917$ <sup>d</sup> ( $-0.030$ ) <sup>c</sup>
$J_{12}$	$-0.14 \pm 0.15$ Hz	$S_{22}$	$0.00512$ <sup>d</sup> ( $0.081$ ) <sup>c</sup>

<sup>a</sup> 'Best-fit' values corresponding to geometrical and order parameters given in column 4

<sup>b</sup> at 360 MHz

<sup>c</sup> Values obtained from studies in a thermotropic phase<sup>1</sup>

<sup>d</sup>  $r_{12} = 1.827$  Å (assumed).

correspond to those which provide geometrical results consistent with studies in the thermotropic nematic phase.<sup>1</sup> Errors of the various parameters (table 1) correspond to the standard deviations of the LAOCOONOR programme. The results are consistent with the  $C_{2v}$ -symmetry of the ring skeleton like the X-ray data<sup>12</sup> in the solid state.

Values of the indirect spin-spin couplings determined from studies in a thermotropic solvent are included within parentheses in table 1. The two are in reasonable agreement with each other.

For the  $C_{2v}$ -symmetry of the ring skeleton of butadiene sulphone, three geometrical and two order parameters have to be derived from the 6 direct dipolar couplings. The 'least-square-fit' programme SHAPE<sup>13</sup> was used to derive the geometrical and the order parameters from the observed dipolar couplings and the values determined are included in table 1. The corresponding values obtained from studies in a thermotropic solvent are included within parentheses in table 1. The table shows that the geometrical parameters obtained from studies in the lyotropic phase are larger than those obtained in the nematic thermotropic solvent. There is an indication of a slight reduction of the distance between protons 1 and 4 in the lyotropic phase.

The signs of the various S-values are similar both in thermotropic and lyotropic solvents.

The largest positive S-value is along the  $C_2$ -axis of symmetry in both the cases.

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