

SULFONE TRANSMITTED LONG RANGE COUPLING  
IN A 5-MEMBERED RING

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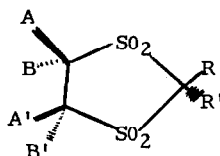
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The long range interproton coupling of protons separated by four single bonds is of particular interest in the study of saturated cyclic systems.<sup>1</sup> Although the spectrum of 4-phenyl-1,3-dioxane<sup>2a</sup> shows long range coupling through both four bonds ( $J_{2e6e} = 1.5$  Hz) and five bonds ( $J_{2e5e} = 0.9$  Hz), such coupling is generally restricted to fused ring or highly substituted systems. Only a few couplings of this type have been reported in saturated 5-membered rings<sup>2b,2c</sup> and in each case external substitution of the basic ring system removed in part its inherent flexibility.

We wish to report that when the sulfide linkages in 2-substituted-1,3-dithiolanes are oxidized with m-chloroperoxybenzoic acid to the corresponding 1,3-dithiolane 1,1,3,3-tetraoxides, long range interproton coupling through the sulfonyl function was observed (Table 1), a phenomenon not observed in the parent 1,3-dithiolanes<sup>3</sup>, or the isoelectronic 1,3-dioxolanes<sup>4</sup> and 1,3-oxathiolanes<sup>5</sup>.

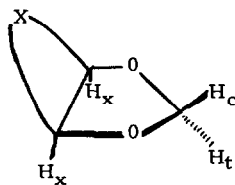
TABLE I

## Nmr Parameters of 1, 3-Dithiolane-1, 1, 3, 3-Tetraoxides



R	R'	Chemical shift (ppm)		Long-range coupling (Hz)
		H <sub>A</sub> , H <sub>A'</sub>	H <sub>B</sub> , H <sub>B'</sub>	
CH <sub>3</sub>	H	3.97	3.86	${}^4J_{R',A} = {}^4J_{R',A'}$ 0.68
Ph	H	4.20	4.10	0.48

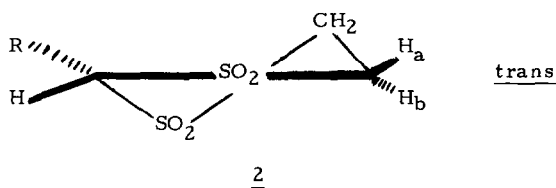
The long range coupling was observed only in the low field half of the AA'BB' multiplet arising from the C<sub>4,5</sub>-methylene protons. Chemical shift assignments for 1, 3-dithiolane-1, 1, 3, 3-tetraoxides can be made by analogy to those previously made for 1, 3-dioxolanes<sup>4</sup> and 1, 3-dithiolanes<sup>3</sup>. In these compounds, alkyl and aryl substituents at C<sub>(2)</sub> exert paramagnetic shifts on cis ring protons. Therefore, the downfield absorption arises from protons cis to the C<sub>(2)</sub> substituent and the long range coupling observed in the low field half of the AA'BB' multiplet is a trans coupling. Such results are supported by Anteonis<sup>6</sup> who has recently observed trans long-range couplings in a series of rigidly held bicyclic 1, 3-dioxolanes, 1.



$$J_{C, X} = 0.1 - 0.5 \text{ Hz.}$$

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The long range coupling observed in the 1,3-dithiolane disulfones could be due to the change in the hybridization of sulfur, whereby the sulfonyl function transmits couplings while divalent sulfur and oxygen do not. Furthermore, from space-filling models, it appears feasible that a non-bonding  $p$ -orbital on one of the sulfone oxygen atoms can function as an electron bridge facilitating coupling. Brink<sup>7</sup> has similarly observed long-range coupling through a sulfonyl function ( $^4J = 0.5$  Hz) in  $C_6H_5CH_2-SO_2-CH_2-COOCH_3$ . The observations of analogous couplings in rigid 1,3-dioxolanes suggests, however, long range coupling may be due to the external substitution of geminal oxygen atoms on the sulfurs which may introduce sufficient barriers to pseudorotation so that the population of some of the transiently present conformers required for optimal long range coupling (*i.e.* rotamers with maximal planar arrangements of trans protons, 2) are increased.



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