

THE SIGN OF 4J IN THIETANE SULPHONES AND THEIR CORRELATION WITH STEREOCHEMISTRY

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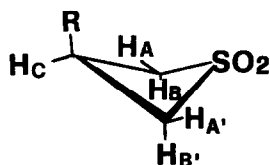
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Recently the sign of cross-ring 4J couplings was proposed as diagnostic for the stereochemistry of the interacting protons in cyclobutanes (1). In view of the interest in the chemical applications of this approach, and considering some discrepancies in sign observed in oxetane (2) and thietane derivatives (3), we have submitted some thietane sulphones to a complete n.m.r. analysis, in order to show if the presence of a heteroatom affects the signs of these coupling constants. Preliminary results of this investigation are reported here. The parameters in the Table were obtained by iterative analysis (4) of the AA'BB'C five-spin systems of 3-substituted thietane sulphones. Only the 3-acetoxy derivative gave a spectrum intermediate between AA'BB'C and AA'BB'M. In order to avoid possible alternative solutions of the same problem, not detected by the iterative procedure of analysis, the spectra were measured under the same conditions at 300 MHz. The analysis at this frequency (AA'MM'N or AA'MM'X spin systems) made the identification of chemical shift easier, and the parameters obtained gave an excellent fit with those at 100 MHz.

One pair of four-bond couplings (${}^4J_{AA'}$, and ${}^4J_{BB'}$) were found to be positive, and the other pair (${}^4J_{AB'}$, = ${}^4J_{A'B}$) negative in sign. The assignment of these couplings follows directly from the symmetry of the spectrum and holds whichever conformation the molecules adopt in solution. Thus $J_{AA'}$, and $J_{BB'}$, and $J_{AB'}$, = $J_{A'B}$ are cis, and trans interaction respectively. Consequently we can conclude that the correlation found in cyclobutanes between the sign of 4J and the orientation of the interacting protons is still valid in thietane sulphones, and seems to be a general property of the four-membered ring, independent of the presence of a heteroatom.

Another aspect of our investigation concerns the conformation of the thietane sulphone ring. If the molecule is flipping rapidly, we should expect an averaging of cis and trans couplings, with the correlation of signs still holding. The high value (~ 4 Hz) of one of the positive four-bond couplings (${}^4J_{AA'}$, , attributed to the interaction between the pseudoequatorial protons (6)) is in favor of the existence of a preferred conformation with a certain degree of puckering (6,7). Preliminary variable temperature experiments on 3 did not show significant changes in coupling constant values for a range of temperatures between 150° and -130°C.

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TABLE ^a

	Chemical shifts (Hz)			Coupling constants (Hz)					
	ν_A	ν_B	ν_C	$^4J_{AA'}$	$^4J_{BB'}$	$^4J_{AB'-A'B}$	$^3J_{AC=A'C}$	$^3J_{BC=B'C}$	$^2J_{AB=A'B'}$
<u>1</u> R=C1 RMS=0.025	431.122	485.101	491.702	3.875	2.484	-1.315	3.892	8.341	-14.558
<u>2</u> R=OH RMS=0.03	398.956	443.472	473.000	3.935	2.855	-1.183	3.504	7.525	-13.954
<u>3</u> R=OCOMe RMS=0.04	415.774	461.641	532.843	4.285	2.591	-1.246	3.206	7.793	-14.616

^a The spectra were measured with a Varian XL-100-15 Spectrometer in acetone-d₆, with TMS as internal standard. The calculated probable error for each of the parameters was ± 0.01 Hz, but we prefer to consider these data reliable to within ± 0.03 Hz in agreement with the suggestion of S.Castellano and A.A. Bothner-By (5).

An X-ray analysis (8) of 3 gave an angle of puckering of 18°, and pseudoaxial orientation of the substituent with dihedral angles $\nu_{AC} = 109^\circ$ (Heq,Heq) and $\nu_{BC} = 28^\circ$ (Hax,Heq). From 3J data (Table), and the reported values in other thietanes (9) and cyclobutanol (6), a predominant axial conformation of the substituents can be inferred for the liquid phase also. Taking into account the approximation in comparing data from the solid and the liquid phase, the dihedral angles of 109° and 28°, determined by X-ray analysis, are in agreement with a small ($^3J_{AC} \sim 3.5$ Hz) equatorial-equatorial and high ($^3J_{BC} \sim 8$ Hz) axial-equatorial three-bond couplings.

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