

GEOMETRICAL ISOMERISM OF SULFUR DIIMIDES

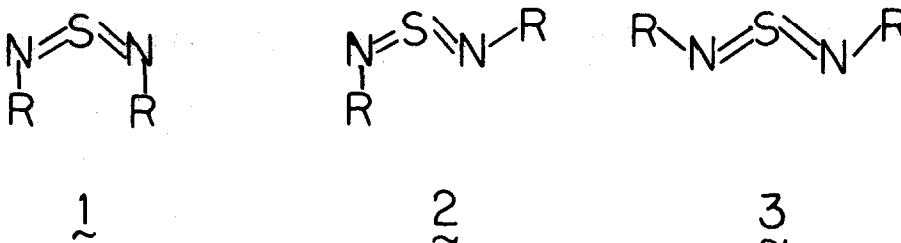
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The problem of geometrical isomerism in sulfur di-imides is indicated by previous results<sup>1-4</sup>. If nitrogen and sulfur are assumed  $sp^2$  hybridized, then three isomers - cis, cis (1), cis, trans (2), and trans, trans (3) - are possible. The nmr spectra of di-t-butylsulfur di-imide (4)



and dimethylsulfur di-imide (5) have been reported as a sharp single line at ambient ( $\sim 25^\circ$ ) temperature<sup>5,6</sup>. This observation is consistent with structures 1 and 3 unless the R groups exchange rapidly at ambient temperature by either inversion at nitrogen and/or rotation around the nitrogen sulfur bond. Our calculations on 5 show a small barrier ( $< 10$  kcal/m) for each of the exchange mechanisms<sup>1</sup>.

We wish to report the low temperature nmr spectra for 4 and 5. The spectra, which were run in chlorodifluoromethane as solvent and TMS as internal standard, are shown in fig. 1 and 2. The di-imides 4 and 5 were prepared by previously reported methods<sup>5,7</sup>.

As a sample of 4 is cooled the sharp resonance of the t-butyl protons broadens and at  $-29^\circ$  divides into two signals, which are completely separated into lines of equal intensity at  $-40^\circ$ .

At low temperatures the t-butyl groups are in two equally populated but magnetically nonequivalent magnetic environments, a result which is consistent for either the sole existence of isomer 2 or a fortuitous mixture of equal amounts of 1 and 3.

Cooling a sample of 5 causes the sharp line at 3.5  $\delta$  due to the methyl protons to broaden. At -20.5° the single resonance divides into two signals of unequal intensity. As the temperature is lowered further the two signals become equal in intensity and a third signal emerges downfield from the first two resonances. At -60° the lines of equal intensity are resolved into an  $A_3B_3$  pattern and the third line is a singlet. The  $A_3B_3$  pattern shows two quartets of coupling constant  $J = 1.5$  Hz which is consistent with long range coupling between two nonequivalent methyl groups. When the sample is allowed to warm up the three lines collapse to a single resonance.

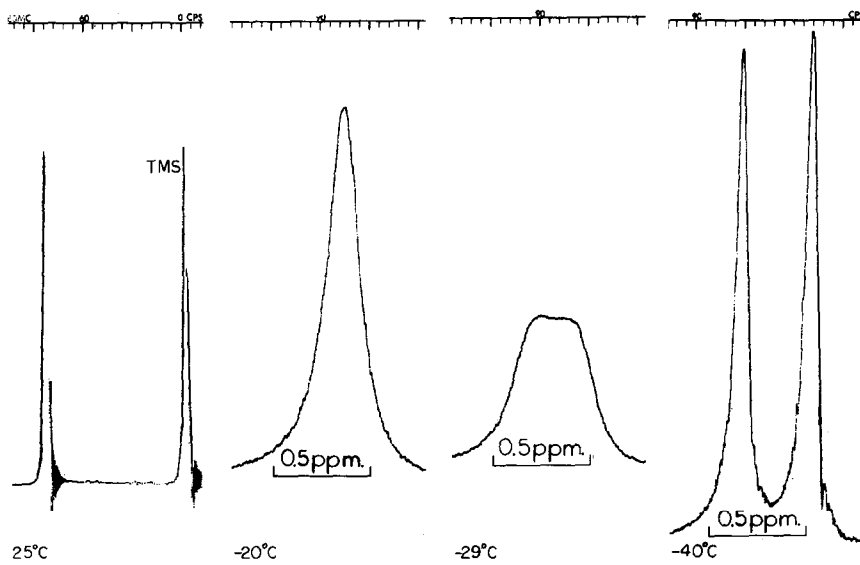
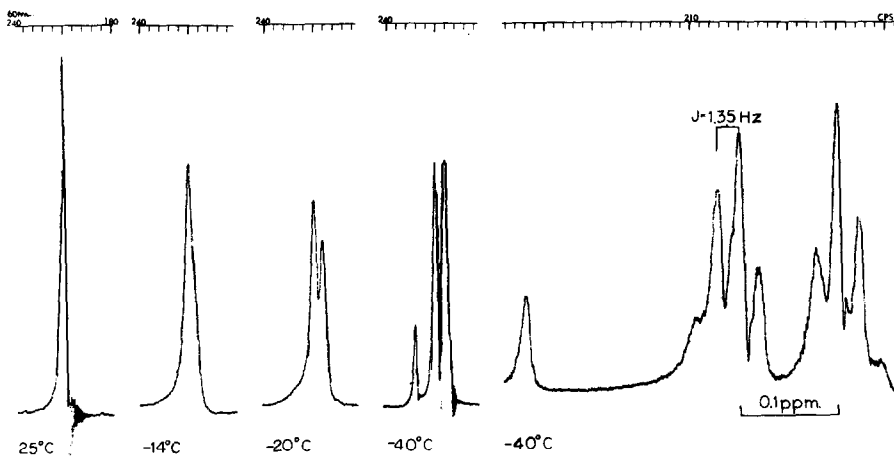
The coupled resonances are assigned to isomer 2 and the singlet resonance at 3.7 is one of the two symmetrical isomers 1 or 3, although based on our CNDO/2 calculations<sup>1</sup> and chemical intuition the resonance is due to 3, probably.

Clearly, the cis,trans isomer 2 is the most stable of the three possible geometrical isomers in solution for R equal to methyl and t-butyl. The same result was obtained for R equals 4-tolyl by others<sup>2</sup> using X-ray crystallography.

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#### References

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FIG.1  $(\text{CH}_3)_3\text{CN}=\text{S}=\text{NC}(\text{CH}_3)_3$ FIG.2  $\text{CH}_3\text{N}=\text{S}=\text{NCH}_3$