Tetrahedron Letters No.23, pp. 2785-2788, 1968. Pergamon Press. Printed in Great Britain.

CONFORMATIONAL ANALYSIS IN MULTISULFUR HETEROCYCLES.

III. BIS-(TETRAMETHYLENE)-S-TETRATHIANE

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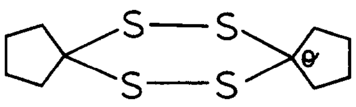
(Received in USA 1 February 1968; accepted for publication 12 March 1968)

The introduction of divalent sulfur into medium-sized ring systems can cause significant changes in the conformational dynamics of such heterocycles relative to the carbocyclic analogues.

Depending upon the substitution pattern, the barriers to conformational isomerism in multisulfur heterocycles can be raised (1,2,3) or lowered (4,5). In some instances, conformational preferences can be significantly altered by unique substitution of sulfur atoms in the ring (6,7). Recently, the unusual stability of the twist-boat conformer of tetramethyl-s-tetrathiane was observed (8).

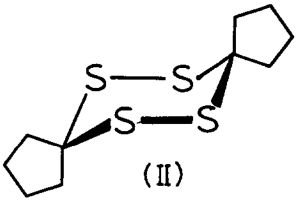
This report concerns a variable temperature study of the nuclear magnetic resonance (nmr) spectrum (9) of bis-(tetramethylene)-s-tetrathiane (I). The results indicate at least a strong preference for the chair conformation.



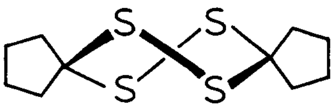
(I)

Examination of the nmr spectrum of I (10% by weight in $Cl_2C=C Cl_2$) at 37° reveals two broadened resonances of substantially different intensities centered at δ2.60 and 1.70 ppm (Figure 1). When the temperature was lowered to 0°, the two resonances sharpened in an expected manner to give a rough triplet at δ2.64 ppm and a large multiplet at δ1.70 ppm (Figure 1). The ratio of the areas of the low-field resonance to the high field resonance is 1:4 respectively at 0°. When the temperature was raised above 37°, further broadening of the two resonances was observed. The low-field peak began to coalesce with another resonance originally centered at low temperatures under the large multiplet at δ1.70 ppm (Figure 1). At 100°, these two signals had coalesced to a broad resonance centered at δ2.17 ppm and the peak at δ1.70 ppm showed substantial fine structure. The area ratio of the low-field to high field resonances at 100° is about 1.0:1.3. Upon lowering the temperature, an identical sequence of spectral events was observed.

The two resonances which coalesce with increasing temperature can be assigned to the equatorial and axial α-methylene groups of the chair conformer (II). If the diamagnetic anisotropy of the sulfur-sulfur bond is analogous to that proposed for the carbon-carbon bonds in cyclohexane (10), the signal at δ2.64 ppm observed at 0° may be assigned to the equatorial α-methylene group. If I existed exclusively as the chair conformer, the peak area ratios at 0° and 100° would be expected to be 1:3 and 1:1 respectively. The observed deviations (11) suggest the possibility of the presence of a certain amount of the twist-boat form (III). By analogy with the observed spectrum of the twist-boat conformer of tetramethyl-s-tetrathiane (8), it would not be expected that the α-methylene resonance of the twist-boat form (III) would be significantly temperature dependent.



(II)



(III)

The apparently more usual preference of I for the chair conformation as compared to the preference of tetramethyl-s-tetrathiane for the twist-boat form is intriguing. The variation of the geminal C-C-C bond angle (θ,I), the lack of free rotation about the axial and equatorial C-C bonds, and the possibility of $p_{\pi}d_{\pi}$ bonding between the two sulfur atoms may all play a role in determining the observed conformational preference.

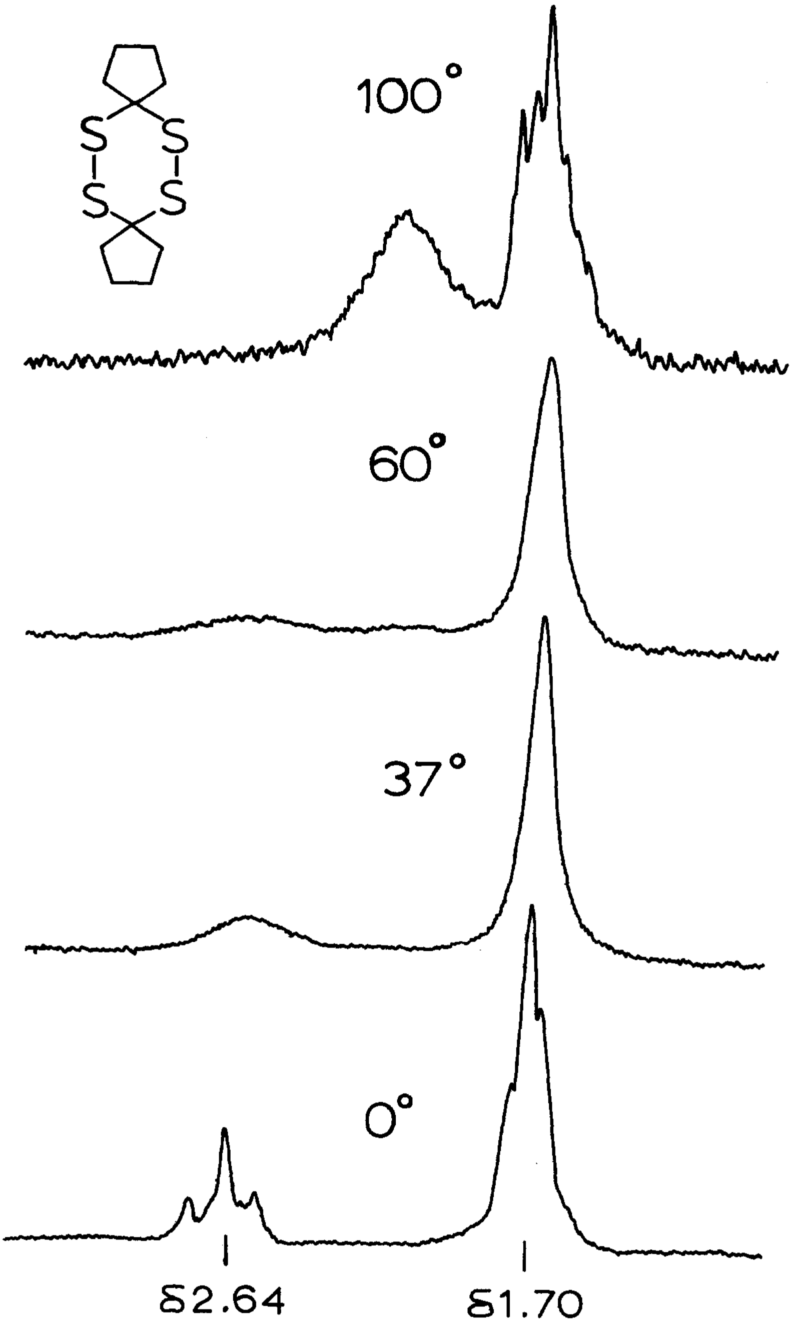


FIGURE 1

In order to more unequivocally identify the conformers present, the synthesis of appropriately deuteriated species is being pursued (12).

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9. The nmr spectra were recorded using a Varian Associates A-60 spectrometer. The temperature was measured using a methanol or ethylene glycol sample.
10. A. A. Bothner-By and C. Naar-Colin, Ann. New York Acad. Sci., **70**, 883 (1958).
11. The compound in question is apparently monomeric and pure by all the usual criteria.
12. A referee has suggested an alternative rationalization for the data presented in this report involving the existence of I exclusively as the twist-boat conformer (III) possessing a high barrier to pseudorotation. In such an instance, it is possible to envisage the non-equivalence of the two α-methylene protons of each α-methylene group due to diamagnetic anisotropic effects of the two differently oriented sulfur-sulfur bonds. Although the data as presented do not unequivocally rule out such a possibility, we do not consider such a situation likely. A preliminary crystallographic investigation of I (A. Fredga, Acta Chem. Scand., **12**, 891 (1958).) indicates that I exists in the chair form (II). Although it is certainly not valid to extrapolate directly from the crystalline state to solution, it is usually the case that the conformation assumed in the crystalline state at least predominates in solution.