Tetrahedron Letters No. 20, pp 1685 - 1686, 1976. Pergamon Press. Printed in Great Britain.

NONANALOGOUSNESS OF 1,3,5-TRITHIANES TO OTHER CYCLIC SYSTEMS. CHEMICAL SHIFTS AND COUPLING CONSTANTS IN ^{13}C NMR SPECTRA.

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(Received in Japan 1 March 1976; received in UK for publication 29 March 1976)

While we had noticed some "anomalies" in ^{13}C NMR spectra of polymethyl-1,3,5-trithianes but had not been able to present a good rationale,1) Eliel et al recently drew attention to the similar "anomalies" in dioxane and dithiane series without furnishing the explanation 2) This publication prompts us to describe our similar findings on the chemical shifts together with a finding on an anomaly of the coupling constant in 1,3,5-trithiane derivatives in a preliminary form

^{13}C NMR spectra of polymethyl-1,3,5-trithianes (1-7) were recorded on a JEOL JNM-PFT-100 FT NMR system as 25-30% solutions in deuteriochloroform unless otherwise stated The results are given in Table 1 as chemical shifts from TMS. The coupling constants were obtained similarly except for the deuterated compounds (8-10), with which the coupling constants were obtained by deuteron decoupling on a Varian XL-100 spectrometer The results are given in Table 2.

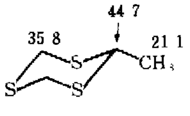
Inspecting the data in Table 1, one can immediately point out the followings 1) The γ-effect4) is present in ring carbons of the 1,3,5-trithiane series ring carbon(s) in γ-position relative to axial methyl group(s) gives a signal at a higher field than the corresponding ring carbon(s) which lacks an axial methyl carbon in γ-position. This tendency is common in the cases of cyclohexanes,5) 1,3-dioxanes,6) and 1,3-dithianes.2) 2) The signals due to axial methyl carbons are located downfield relative to those of equatorial methyls this result is contrary to the γ-effect, ordinarily observed for cyclohexanes5) and 1,3-dithianes.2) Thus the ordinary γ-effect is observed for ring carbons but not for the axial methyls in 1,3,5-trithianes

The results in Table 2 indicate that the coupling constants, $^{1}J_{CH}$, due to axial protons in trithianes are larger than the corresponding ones due to equatorial protons. This general tendency is a reversal to that in 1,3-dioxanes,6) althougn the latter tendency is common in cyclohexane series in Table 2.

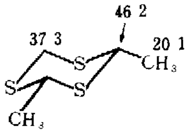
The results presented in this paper indicate that there are unknown factor in determining the chemical shifts and the coupling constants and that caution must be excercised in extending analogies to the various ring systems.

Acknowledgement We wish to express thanks to Dr. Katsumi Ajisaka of Ajinomoto Co. for the measurement of deuteron-decoupled ^{13}C NMR spectra.

Table 1. Chemical Shifts of Carbon Signals of Polymethyl-1,3,5-trithianes (δ, Estimated Error ± 0.1 ppm)



1



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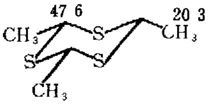

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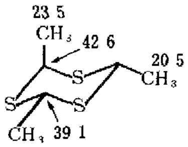

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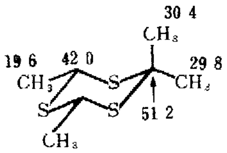
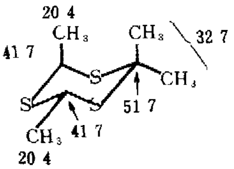
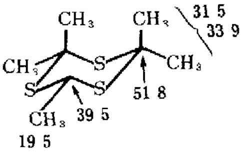


5^b



6^a



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a) This compound is known to be rapidly inverting at room temperature from ^1H NMR data.[3]

b) The two closely located signals due to methyls in position 2 were assigned by taking advantage of a fact that equatorial methyl-d_3 compound lacked the signal at the higher field due to splitting to a septet and loss of the NOE.

Table 2. Coupling Constants, $^1J_{CH}$ (Hz).

Compound	Axial Protons Assignment	J_{CH}	Equatorial Protons Assignment	J_{CH}
2	$2\text{-}H_{ax}$	158.5±0.5		
	$6\text{-}H_{ax}$	154.0±0.5	$6\text{-}H_{eq}$	148.0±0.5
3^a	$2\text{-}H_{ax}$	155.5±0.5		
4^a	$6\text{-}H_{ax}$	155.0±0.5	$2\text{-}H_{eq}$	144.0±0.5
trans-4-t-Butylcyclohexan-1-ol-2,2,6,6-d_4 (8)	$1\text{-}H_{ax}$	139.1±0.3		
cis-4-t-butylcyclohexan-1-ol-2,2,6,6-d_4 (9)			$1\text{-}H_{eq}$	143.8±0.3
Cyclohexanol-2,2,6,6-d_4 (10)		$1\text{-}H_{eq\text{-}ax}$	140.3±0.3	

a) These data were obtained with carbon tetrachloride solutions.

References

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