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ELUCIDATION OF RELATIVE CONFIGURATION OF THIADECALONES WITH Eu(dpm)$_3$; PREFERRED SITE OF COMPLEXATION

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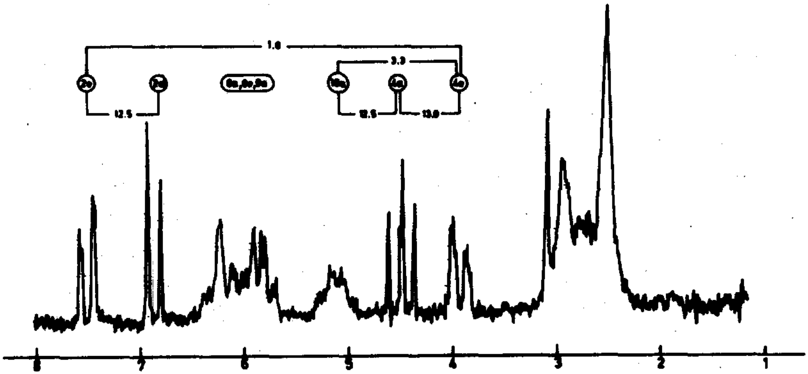
Although various thiadecalones have been described in the literature[1], no direct spectroscopical method has been used to establish their ring fusion. We wish to report direct evidence for the stereochemical structures of 3-thiadecalone (I) and 4-thiadecalone (II)[2] by means of shift reagents.

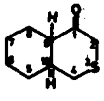
Knowledge of the co-ordination site of shift reagents in polyfunctional molecules is essential[3,4] for their effective use in structure elucidation by NMR techniques. Recent literature gives contradictory information concerning ketosulphides. Some authors[3] assume thioethers to be more effective than ketones in intra-molecular competition for Eu(dpm)$_3$, others[5] find the carbonyl group to be the site of preference.

Inspection of the 100 MHz NMR spectra of I and II gives no relevant information. Complexation with Eu(dpm)$_3$, however, allows complete analysis of the spectrum by means of multiple resonance and shows the ring fusion to be trans in both cases. Moreover, the carbonyl group turns out to be the preferred site of complexation in both I and II. The last observation is in contradiction with the literature[3], and prompted us to reinvestigate the published ΔEu[3,7] values on 4-thia-cyclohexanone (IV), which must have been based on erroneous signal interpretation.

The complexed spectra of I, II and 2,2,9-D$_3$-4-thiadecalone (III)[6] were taken in CCl_4 (100 MHz) at 31°, and are shown in fig. 1, 2 and 3, respectively. In the uncomplexed spectrum of I the signals of H2$_a$ and H2$_e$ appear at δ3.32 and 2.80 ppm as doublet (J 12.5 Hz), and double doublet (J 12.5 and 1.8 Hz), respectively.

Inspection of molecular models suggests that J 1.8 Hz could arise from long range coupling H2$_e$ / H9$_e$ in certain conformations of a cis fused molecule, or from H2$_e$ / H4$_e$ interaction in both cis and trans fused systems. The various J values, however, displayed by the H10$_a$ signal of the complexed spectrum (fig. 1) are consistent with a <u>trans</u> chair-chair ring fusion only. Consequently, the long range coupling must arise from $H2_e$ / $H4_e$ interaction. The strongly different ΔEu values of $H2_e$ and $H4_e$ prove that complexation takes place at the carbonyl group.





I

Fig. 1

100 MHz, CCl_4, 31°, $Eu(dpm)_3$/substrate = 0,48

The <u>trans</u> chair-chair structure of II clearly follows from the various signal multiplicities and J values in fig. 2. The complexation site, however, can not be derived directly, since as a consequence of molecular symmetry, the signals arising from the symmetrically equivalent position (e.g. $H2_e$, $H3_e$ or $H9_a$, $H10_a$) can not be assigned unambiguously. This ambiguity is eliminated by the introduction of deuterium at C_2 and C_9. Comparison of the spectra of II and III (fig. 3 and 4) shows that the exchangeable hydrogen atoms ($H2_{a,e}$ and $H9_a$) undergo a much stronger deshielding effect. Consequently, the remaining signals must be assigned to $H3_{a,e}$ and $H10_a$. This demonstrates the preference for complexation at the carbonyl group.

TABLE I

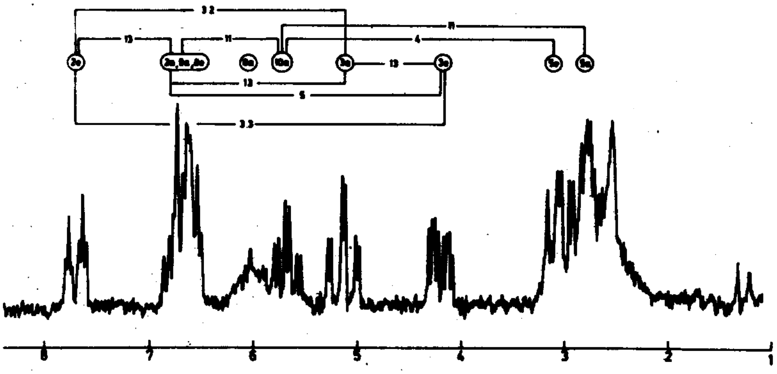
Δ Eu values[7] of I, II and IV in CCl_4 at 31°

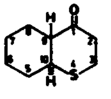
	<u>I</u>	<u>II</u>*	<u>IV</u>
$H2_e$	- 9.9	- 13.4	- 12.7 ($H2_{a,e}$)
$H2_a$	- 7.4	- 10.7	
$H3_e$		- 6.5	- 5.7 ($H3_{a,e}$)
$H3_a$		- 3.6	

*calculated from the estimated δvalues in the uncomplexed spectrum

Table I gives the ΔEu values for some signals in I, II and 4-thia-cyclohexanone (IV)[6]. The average values in II for $H2_{a,e}$ and $H3_{a,e}$ are in reasonable agreement with the corresponding values in IV[8]. This can be interpreted in terms of equal complex formation constants and complex geometry of II and IV. The ΔEu values calculated for I are markedly lower than the corresponding values in II and IV. This is possibly caused by a smaller complex formation constant for II, although trivial decomposition[9] can not be excluded.

Attempts to determine $K_{complex}$ values are in progress.

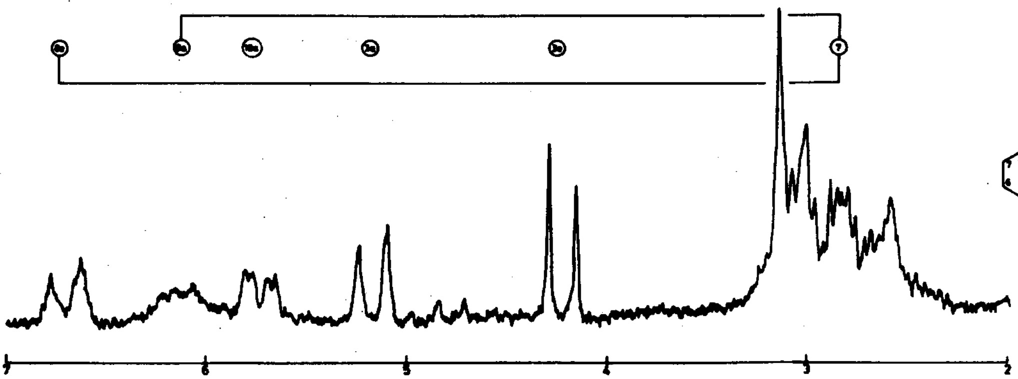


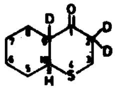


I

Fig. 2

100 MHz, CCl_4, 31°, $Eu(dpm)_3$/substrate = 0,38





II

Fig. 3

100 MHz, CCl_4, 31°, $Eu(dpm)_3$/substrate = 0,38

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6. Prepared by acid catalysed D/H exchange in D_2O/dioxane
7. As defined by P.V. Demarco, T.K. Elzey, R.B. Lewis, E. Wenkert, J.Am.Chem.Soc. 92, 5734 (1970), for equimolar amounts of substrate and $Eu(dpm)_3$
8. The line positions of the AA'XX' spectrum of IV were calculated from the corresponding 2,2,6,6-D_4 compound; see reference 6
9. The induced shifts have been noted to decrease slowly upon standing of samples. The time necessary to obtain a homogeneous complex solution of II was considerably longer than in case of I and IV.