

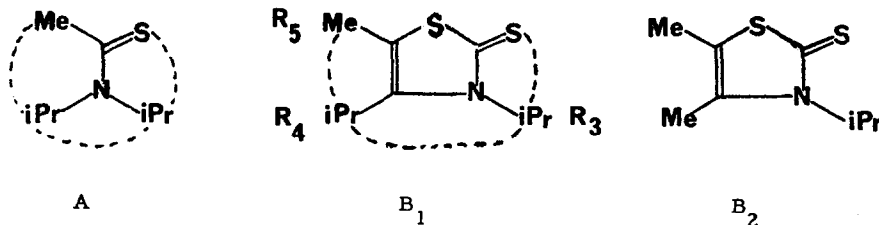
THE GEAR EFFECT, II: THE CONFORMATION OF THE N-ALKYL GROUPS
IN N,N'-DIISOPROPYL THIOACETAMIDE

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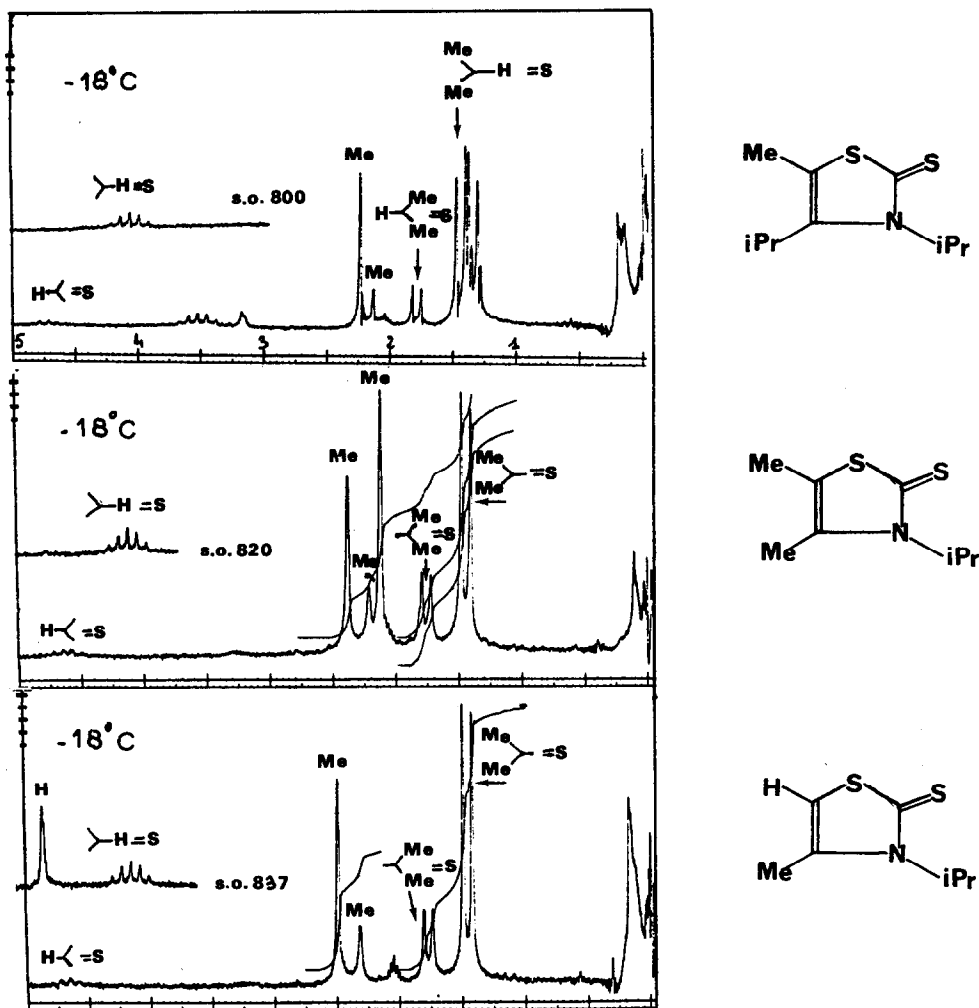
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It is well established that two types of rotational process are present in a thioamide such as is represented by (A): a) around the S=C-N bond ($\sigma + \pi$ type); b) around the N-alkyl bond (pure σ type). The first rotation is forbidden in (B) by its cyclic structure. The striking similarities of structures and of low temperature spectra for (A) and (B₁) led us to reconsider the conformations suggested by Siddall and Stewart (2) and Ramey et al. (3) for the less energetic process. The conclusions of these authors and ours are summarized in Table I. We have represented only one of each d,l pair found in (3)



and (2). The structures (A) and (B) are seen along the dashed line in a Newman-type representation. The values $C_i T_j$ in Table I correspond to the definition given by Siddall and Stewart (2).

The spectra of (B) shown below and results previously reported by us (1) show that



1) The difference in shifts between the two methyl groups of R_3 is quite independent of the nature of R_4 .

R_4	Me	Et	iPr	iBu
$\Delta\nu$ p.p.m.	0.32	0.33	0.34	0.32

The conformation of Ramey et al. which implies that the difference in shifts for R_3 depends only on the conformational state of R_4 is inconsistent with our results.

TYPE	MAJOR COMPONENT	MINOR COMPONENT	REF.
A	<p>2.73, 1.18, 1.47, 6.19, 4.12</p> <p>C_1T_4</p>	<p>1.30, 4.0, 1.70, 2.65, 4.53</p> <p>C_4T_1</p>	Siddall and Stewart (2)
A	<p>2.73</p> <p>C_1T_4</p>	<p>2.65</p> <p>C_1T_6</p>	Ramey et al. (3)
A	<p>1.18, 1.47, 2.73, 4.12, 6.19</p> <p>C_1T_4</p>	<p>1.30, 1.70, 2.65, 4.0, 4.53</p> <p>C_4T_1</p>	*Our conclusion
B ₁	<p>1.37, 1.48, 2.29, 3.59, 6.10</p>	<p>1.35, 1.82, 2.18, 3.32, 4.77</p>	*This work
B ₂	<p>1.47, 2.16, 2.42, 5.95</p>	<p>1.79, 2.16, 2.25, 4.68</p>	*This work

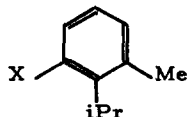
TABLE I. All shifts are given in P.P.M. (solvent C_3D_6O)

* Footnote: Further studies at much lower temperatures should show whether the proposed conformation results from the out-of-plane libration of the methine proton or from the presence of a real d, l pair, having a very low barrier of rotation.

2) The conformational effect of an isopropyl group on the shift of a neighbouring methyl group is :



These assignments are made for the B_1 and B_2 structures and in C (4).



C

This shielding effect is more or less strong depending on the geometry and no crossing has ever been observed. Furthermore the

conformational state of R_3 has no effect on the shift of the R_5 group. Therefore the conclusion of Siddall and Stewart is inconsistent with our results.

Our conclusion is that there is the same conformational "geared" state in the (A) and (B) structures. The use of heterocyclic models may be very useful in the study of the least energetic process in amides and thioamides. Energetic calculations and topographic representations as in (1) and (5) are consistent with our results for (A) and (B_1). A more complete discussion will be published elsewhere.

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