

EVIDENCE FOR HINDERED ROTATION OF ETHYL GROUPS AROUND sp^2-sp^3 BONDS :
N-ALKYL $\Delta 4$ -THIAZOLINE-2-THIONES.

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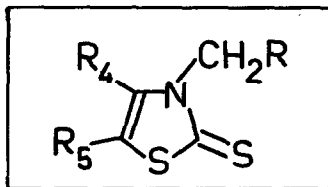
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Barriers to rotation of alkyl groups are of importance to understand both conformations and reactivities of organic molecules¹⁻³. A number of cases where hindered rotation of alkyl groups about sp^2-sp^3 bonds has been studied by D.N.M.R. are found in the literature⁴⁻⁹, but of alkyl groups of the type CH_2R only neopentyl groups have been dealt with⁷⁻⁹.

We report here the dynamic behaviour of neopentyl and ethyl groups in position 3 of the $\Delta 4$ -thiazoline-2-thione ring (I) as studied by ¹H N.M.R.



I_a, R = t.Bu, R₄ = Me, R₅ = H; Ib, R = R₅ = Me, R₄ = t.Bu;
Ic, R = Me, R₄ = t.Bu, R₅ = H; Id, R = R₄ = Me, R₅ = H.

Models as well as the known behaviour of the neopentyl group⁷⁻⁹ indicate that this group in I_a shall have a nearly perpendicular arrangement¹⁰, though in general a parallel arrangement is assumed for the benzylic groups with at least one α -proton^{10,11}. The perpendicular arrangement implies diastereotopic methylene protons, which become anisochronous on slow rotation. In agreement with this the neopentyl methylene protons give one

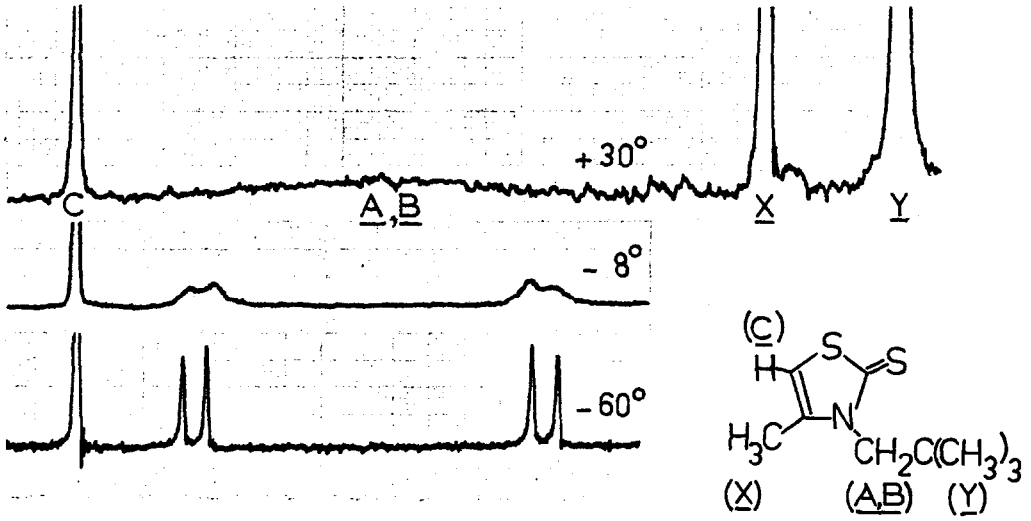


Figure 1

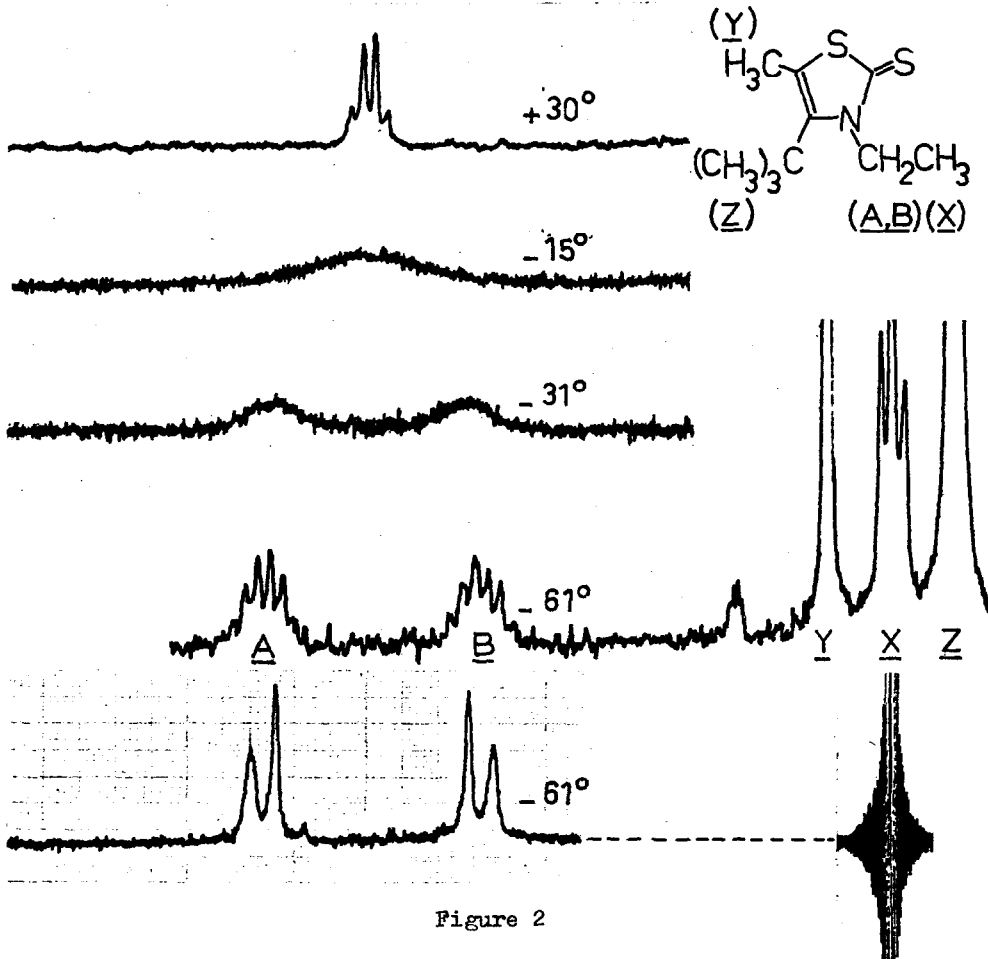
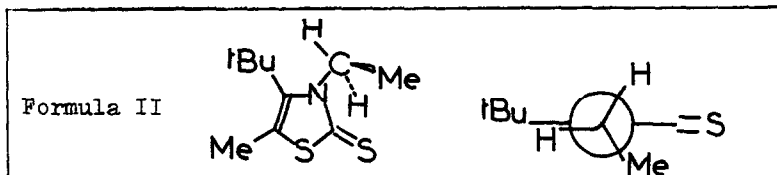


Figure 2

strongly broadened signal above + 25°C and an AB spectrum below this temperature (figure 1). The barrier ($\Delta G^\ddagger = 13.8$ kcal/mol) is mainly due to the strain created on the passage of the t-butyl group past the 4-methyl group, which is the smaller of the flanking substituents^{12, 13}. The barrier to passage of a t-butyl group past a methyl in the benzene series is 15.3 kcal/mol⁹, which reflects the angle differences in five- and six-membered rings.

The conformation of the ethyl group in Ib and Ic may be closer to the parallel arrangement (formula II), since the ethyl CH₃ will be more repelled by the 4-t.Bu than by the smaller 2-CS group. Also in this conformation the methylene protons are diastereotopic,



and the ethyl N.M.R. resonance changes from a sharp triplet and quartet at ambient temperature to an ABX₃ spectrum at lower temperatures (figure 2). Irradiation of the ethyl CH₃ resonance at - 61°C changes the methylene resonance to an AB spectrum. The coalescence temperature is the same, - 13°C, with and without decoupling, and the barrier ($\Delta G^\ddagger = 12.1$ kcal/mol) is probably mainly due to the compression caused by the passage of the ethyl past the CS group. However, some contribution probably also comes from the passage of the ethyl CH₂ past the 4-t.Bu, as evidenced by the buttressing effect of the 5-CH₃ group (Table).

TABLE

Compound	^a $\Delta\nu_{AB}$ Hz	T °C	ΔG_{Tc}^\ddagger kcal/mol
Ia	196	+25	13.8
Ib	121	-16	12.1
Ic	111	-34	11.2
Id	140 ^b	-122	6.9

^aIn toluene-d₈ at 100 MHz

^bIn toluene-d₈/freon at 100 MHz

Compounds Id shows a qualitatively similar behaviour as Ib, though at much lower temperature because of the smaller 4-substituent.

The large $\Delta\nu_{AB}$ value for Ia indicates rather different positions of the methylene protons with respect to the strongly deshielding CS group. The somewhat smaller shifts

for Ib and Ic are in agreement with the proposed conformation II, with the low-field CH_2 proton more removed from the CS group than in Ia. The large shifts values allow the rate processes to be studied over a wide range of temperatures, and complete bandshape analysis are in progress.

To our knowledge, this constitutes the first observation by D.N.M.R. of hindered rotation of ethyl groups around sp^2 - sp^3 bonds.

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13. Nitrogen inversion cannot be responsible for the observed temperature dependence, since an X-Ray crystallographic investigation shows that the ring and directly attached atoms lie in one plane (G. PEPE, to be published).