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"GEAR EFFECT":DEFINITION AND CLEAR CUT N.M.R. EVIDENCE.

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The use of heteroaromatic substrates allows one to put into evidence in a simple manner a conformational behaviour generally present but difficult to illustrate in other structures.We propose here an ana logy between a gear system and interlocking series of alkyl groups (fig 1).This "gear effect" can be defined as being inherent to the dissymetry of alkyl groups which implies a strong conformational correlation between unbounded groups.

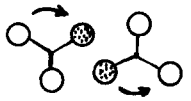
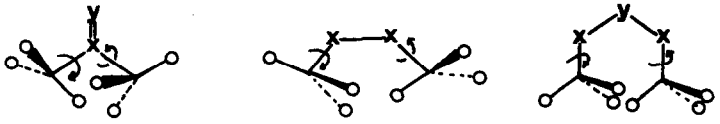


fig 1

Such a "gear effect" can be encountered in various models (fig). The 3,4-dialkyl thiazolinethiones-2 (1) which fits the type B illustrated below have been investigated[1].

fig 2



A B C

Independent 30° rotations of R_3 and R_4 give 12 x 12 = 144 possible conformational states for each molecule.The total energy (E_t) for each one of these conformational states is given by formula F1 (2) (Westheimer approach).

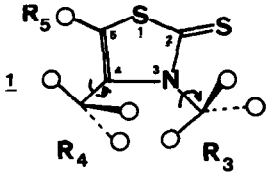
$$E_t = E_l + E_\theta + E_\phi + E_{nb} \quad (F1)$$

E_l and E_θ are Bayer's terms
E_ϕ is Pitzer's one;E_{nb} is nonbounded energy.

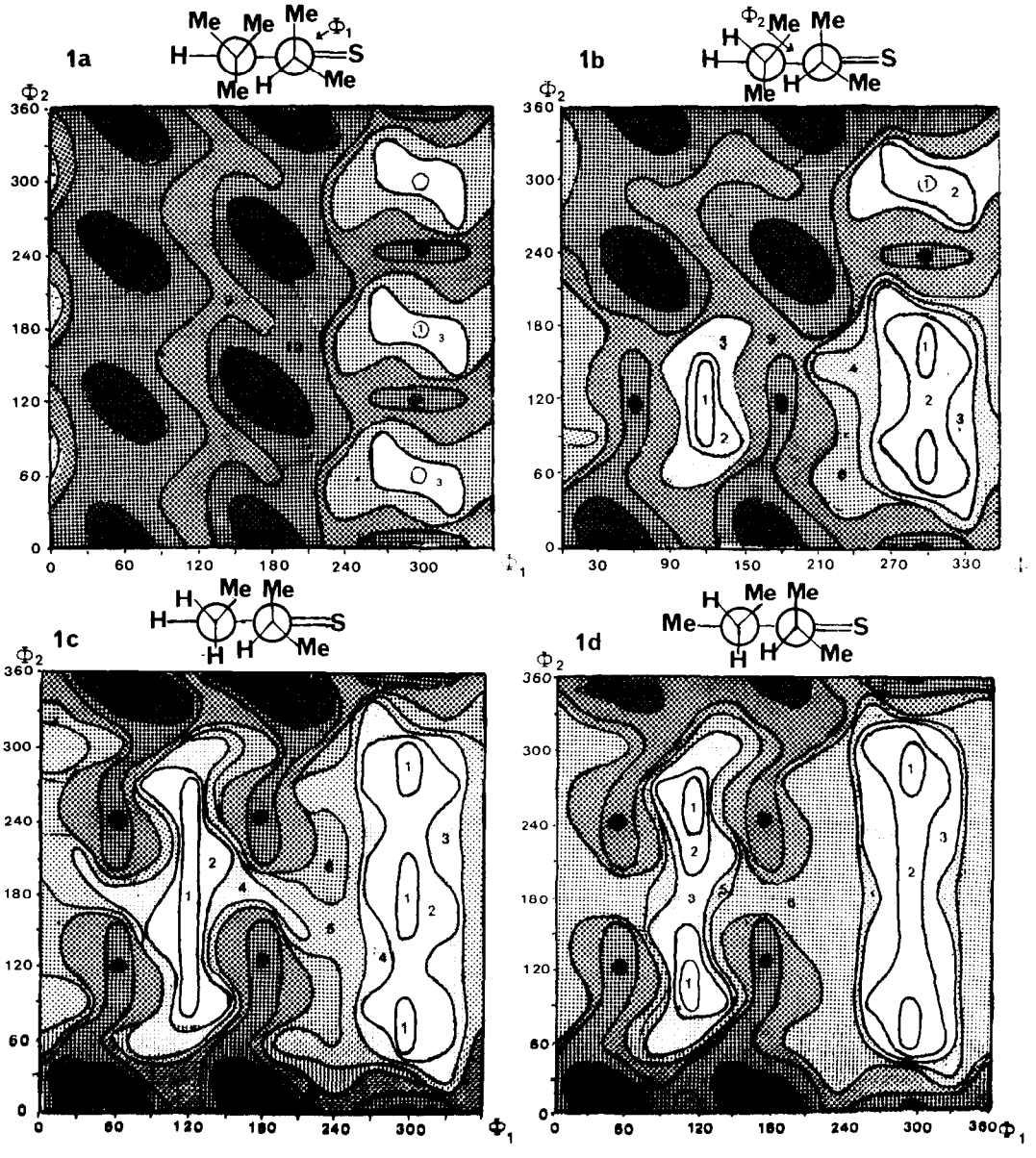
We used the Hill type approach (2) by formula F2

$$E_{nb} = A.e^{-\mu r} - B/r^6 \quad (F2)$$

The topographic representation resulting from these calculations for compounds (1) is given in fig 3



These have been confirmed independently by comparing each time the calculated conformational partition and that obtained by N.M.R..Each couple of points defines a conformational state for R_3 and R_4.The light areas are those for which the nonbounded energy is at a minimum.Isoenergetic areas are defined as: **1** = 2.5;7.5 kcal/ **2** =7.5;12.5 kcal/ **3** =12.5;17.5 kcal/ **4** =17.5;22.5 kcal/ **5**=22.5;27.5 kcal/ **6**=27.5;35 kcal./ **7**=35;45 kcal./ **9** =45;70 kcal./ **10**=70;90 kcal..Darkest areas are those for which $E_{nb} \geqslant 700$ kcal..



Discussion: As the calculations had predicted,we have observed that in each case the preferred conformations for R_3 = iPr are type I and II

I ϕ_4 = 300° H–C(Me)(Me)=S II ϕ_4 = 120° C(Me)(Me)(H)=S

These conformations I and II have a large difference in anisotropy and thus can be well differen ciated provide of course the energy barrier be high enough (3).

According to the map, (1a) must exist only in the type I state (θ_1=300°;θ_2=60°): the two methyl groups being symetrical to the plane of the ring,one could expect a good resolution of the N.M.R. signals;this is confirmed experimently : (table I).It is also predictible from the map that for (1b) the two types I and II could be observed at room temperature:the "pass" is quite high.Furthermore,at -10°c one observes a separation for R_4 group (table 1). Thus the conformation of R_3 must depend directly on the conformation of R_4 ("gear effect").

The effect on going from R_5=H to R_5=Me (1c;1d)is shown on the respective maps.This is illustrated first by a perceptible elevation of the energy pass (I/II) and second by a modication of the relative conformer population.It is in such a way that by means of a conformational transmission ,the population of R_3 is modified through R_4 (gear effect).

(1)	R_3		R_4				R_5	
1a	a Me 1.82, H 4.92, S, Me; 100%		a 1.39 S				a 6.50 S	
1b	a 1.49 1.70		a 1.28 3.10				a 6.55	
	b Me, H 4.70, S, 1.81	b Me, Me 1.47, 6.03 H, S, 40%	b 1.24 Me	3.40 CH	1.31 Me	3.00 CH	b 6.56	6.73
1c	a 1.56		a 1.22	2.72			a 6.50 T	
	b Me, H 4.60, S, 1.78	b Me, Me 1.44, 5.92 H, S, 60%	b 1.28 Me	2.64 CH_2	1.21 Me	2.87 CH_2	b 6.51 L	6.51 L
1d	b Me, H 4.56, S, 1.78	b Me, Me 1.44, 5.98 H, S, 40%	b 1.18 Me	2.63 CH_2	1.11 Me	2.86 CH_2	b 2.12	2.14

Table I : Shifts are given in δ .Spectras were recorded in D_6 aceton with T.M.S. (H.A. 100) . a) room temperature;b) -10°C.

It is indeed remarkable that the experimental and calculated datas fit so well.One reason is surely the symetry of the studied system.One must also pointed out that the use of the terms F_1,F_0,and F_0 (F1) would strongly modify the absolute values but not the general pattern of the maps (4).The topographic representation of our system puts into evidence a clear cut "gear effect".

This effect can also exist in various other systems;fom example a)in substitued toluen derivates (5),b)in amides or amines where it coexists with other phenomena (6,7,8,9),c)in cis di tBu substitued pentagonal heterocycles (10) and finally d) in some globular proteins forms as a possible mean of conformational transmission by interlocking isopropyl groups of the appropriate aminoacids.

Further quantitative studies are presently underway in our laboratory.

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