Table IV. Sensitized Photolysis Quantum Yields

Reactant (mg, mmol)	Light absorbed, mEinstein	Product (mg, mmol)	Φ (product)
1N (27.0, 0.168)	0.0449	**1E** (2.80, 0.018)	0.39 ± 0.02
1N (28.4, 0.180)	0.0449	**1E** (2.72, 0.017)	0.38 ± 0.02
1N (33.3, 0.208)	0.0160	**1E** (0.97, 0.00606)	0.38 ± 0.02
1N (26.7, 0.167)	0.0160	**1E** (1.01, 0.00632)	0.40 ± 0.03
1N (131.7, 0.823)	0.0773	**1E** (5.44, 0.0340)	0.44 ± 0.03
1N (135.5, 0.847)	0.0773	**1E** (5.28, 0.0330)	0.43 ± 0.03
1E (27.6, 0.172)	0.0449	**1N** (0.99, 0.0062)	0.14 ± 0.01
1E (26.6, 0.166)	0.0449	**1N** (0.94, 0.0059)	0.13 ± 0.01
1E (26.4, 0.165)	0.0160	**1N** (0.31, 0.00195)	0.12 ± 0.01
1E (25.3, 0.158)	0.0160	**1N** (0.30, 0.00187)	0.12 ± 0.01
1E (124.5, 0.778)	0.0773	**1N** (1.60, 0.0100)	0.13 ± 0.01
1E (127.9, 0.799)	0.0773	**1N** (1.63, 0.0102)	0.13 ± 0.01

by the cut and weigh method. The results are compiled in Table III.

Quantum Yields for Sensitized Photolyses of *exo*- and *endo*-1-Hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene. Pyrex vessels containing 6.5-ml portions of acetone solutions were degassed using the freeze–pump–thaw method at <1 μm pressure. The vessels were then sealed and irradiated on a merry-go-round apparatus at room temperature using the light from a Hanovia 450-W medium-pressure mercury arc. The light was passed through a potassium chromate filter solution (0.2994 g/250 ml of 5% aqueous potassium carbonate, 0.9 cm path length) to isolate the 313 nm band (305–322 nm). Benzophenone-benzhydrol actinometry was used to determine light output.[13] Product analyses were carried out as in the direct photolyses. The results are compiled in Table IV.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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The Gear Effect.[1-3] V. A Model for Conformational Transmission

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Abstract: Polyhedral substituents like alkyl groups can be involved in a "geared" [2] system when they are in close contact. In 3-isopropyl-4-alkyl-Δ^4-thiazoline-2-thiones and the 3-cyclohexyl analogues, the conformational state of the 3-isopropyl (3-cyclohexyl) group is strongly dependent on the substituents in positions 4 and 5, and when the 4 substituent is an isopropyl group, the conformational equilibria cannot be explained by the "classical" steric effect. In this "geared" system, substitution at one side of the structural block of two interacting groups affects the reactivity at the other end of the block. The barriers to rotamer interchange have been studied by dynamic ^{1}H NMR, and the rotations of the 3- and 4-isopropyl groups in the 3,4-diisopropyl-5-methyl derivative have been shown to be nonsynchronous. Rotamer conformations and routes of interchange are discussed in relation to calculated nonbonded energies.

A conformational transmission process may be evidenced in a molecular system in which the groups involved occupy a suitable spatial disposition to carry conformational information through the framework. Such suitable dispositions have previously been exemplified in the steroid field.[5] More recently it has been reported that the locking of a side chain in a conformation which is favorable for the reaction gives rise to spectacular rate enhancement.[6] The time honored "geminal dialkyl effect"[7,8] rests on a similar mechanism. In the biochemical field the allosteric mechanism[9] and the induced fit theory[10,11] are important applications of the induced conformational effects.

The purpose of the present communication is to show with a simple model that polyhedral substituents like alkyl

groups can be involved in a "gear system" which may transmit long-range conformational changes. This model demonstrates that long-range substituent effects can be used to increase or to decrease the population of an "active" conformation.

With the term "gear effect" we wish to imply a conformational transmission, which is caused by interaction between polyhedral substituents and which depends on their polyhedral shape. The result of the interaction depends not only on the interacting polyhedral groups but also on the sizes of flanking groups with spherical or cylindrical shape. The gear effect can be seen as a refinement and an amplification of the buttressing effect, which takes into account only the globular sizes of interacting groups.

Models

We have studied the effect of R_4 and R_5 alkyl groups on the conformational equilibrium of the 3-isopropyl and 3-cyclohexyl groups in the 3-isopropyl-4-alkyl-Δ^4-thiazoline-2-thiones (**1–10,** Scheme I) and the corresponding 3-cyclo-

Scheme I

$R^4 = CH_3$, C_2H_5 ; $CH_2CH(CH_3)_2$; $CH(CH_3)_2$; $C(CH_3)_3$

R^5= H	1	2	3	4	5
R^5= CH_3	6	7	8	9	10

hexyl compounds **1′, 2′, 4′, 5′, 6′, 7′,** and **9′**,[12] together with the 3,4-dicyclohexyl analogue. These compounds have been found convenient for the present study for the following reasons: (1) A wide variety of differently substituted derivatives is readily available by straightforward synthetic routes. (2) The thiocarbonyl group provides a source of a strong magnetic anisotropy, which facilitates the identification of the different rotamers. (3) The barriers to conformational changes in general fall in an energy range which is convenient for DNMR work. (4) The nucleophilic reactivity of the thiocarbonyl group can be used as a test for the effect of the "structural block" R_3–R_4–R_5.

Experimental Section

Preparative Part. All the Δ^4-thiazoline-2-thiones were prepared by standard syntheses from the appropriate dithiocarbamates and α-halocarbonyl compounds.[13] Compounds **1, 2, 4, 5,** and **6** have been described previously.[13] **Other compounds**: R_3, R_4, R_5, mp °C, % yield given: *i*-Pr, *i*-Bu, H, 55, 45; *i*-Pr, Et, Me, 47, 87; *i*-Pr, *i*-Bu, Me, 77, 53; *i*-Pr, *i*-Pr, Me, 72, 78; *i*-Pr, *t*-Bu, Me, 95, 5; *i*-Pr, Et, H, 73, 35; c-Hex, c-Hex, H, 108, 65; c-Hex, Me, H, 98, 92; c-Hex, Et, H, 114, 68; c-Hex, *i*-Pr, H, 90, 75; c-Hex, *t*-Bu, H, 184, 60; c-Hex, Me, Me, 100, 80; c-Hex, Et, Me, 125, 64; c-Hex, *i*-Pr, Me, 136, 58; *i*-Pr, Me, Et, oil, 40; *i*-Pr, Me, *i*-Pr, 90, 38. All these compounds gave satisfactory elemental microanalytical data.

^{1}H NMR spectra were normally recorded in acetone-d_6 but in some cases also in deuteriochloroform and toluene-d_8, employing Varian Model A-60 A, XL-100, and HA-100 spectrometers. All chemical shifts are given in ppm downfield from Me_4Si.

The barriers to rotamer exchange were measured by the complete line-shape technique, studying the temperature-dependent spectra of 3-isopropyl or 4- or 5-methyl groups. The theoretical spectra of the isopropyl groups were obtained by superposition of the spectra of two exchanging uncoupled two-site cases with the intensities weighted to account for the effect of coupling. The evaluation of rate constants and the measurement of temperature and T_2 were performed as previously described.[14,15]

Table I. Parameters in the Equation $E = A \exp(-cr) - Br^{-6}$

Interaction	A, kcal mol^{-1}	B, kcal mol^{-1} Å^6	C, Å^{-1}	Ref
S–CH_3[a]	442 000	283	3.96	
S–H	113 000	502	4.05	
H–H	65 000	150	4.80	21
H–CH_3	250 000	234	4.69	
C–CH_3	123 000	344	4.08	
C–H	30 000	140	4.17	21
N–H	61 500	141	4.55	
N–CH_3	232 000	214	4.41	
CH_3–CH_3[b]	908 600	363	4.59	
S–S	195 000	1676	3.43	22
N–N	58 000	134	4.27	22

[a] The parameters for the mixed interactions are obtained as geometric means of those for the homogeneous interactions. [b] These parameters are those proposed for a "hard" C–C interaction.[20]

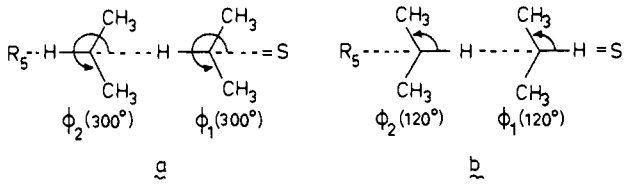
Strain energy calculations were performed in a rather simplified manner, taking only the van der Waals' interactions into account by a potential energy function of the Buckingham exp-6 type:[16]

$$E = A \exp(-cr) - Br^{-6}$$

Furthermore, the methyl groups are treated as "combined atoms".[17] The parameters used are found in Table I. We have performed the calculations with three different ring geometries (I–III). Of these, I is based on π-electron calculations by the PPP method, in which the geometry has been adapted to give the best fit between experimental and calculated ultraviolet spectra.[18] Structure II is taken from the crystal structure of 3-methylbenzothiazoline-2-thione,[19] and III is based on CNDO/S calculations.[20] Other bond lengths and angles are standard data from similar molecules.

The van der Waals' energy was calculated as a function of the angles ϕ_1 and ϕ_2, which describe the rotations of the 3 and 4 substituents (Scheme II), all other geometric parameters being held

Scheme II



fixed. These angles were varied independently in steps of 15°, which necessitates the calculation of the energy in 576 conformations. The energies are represented in maps with isoenergetic curves. The repulsive energies are vastly exaggerated by this method, but we believe that the positions of the energy minima are realistic, since they in general have very low and sometimes even negative energies. Under such circumstances, inclusion of bond bending and stretching changes the energy and geometry only slightly at the minima. The different geometries give slightly different results, but the general trends and especially the positions of the energy minima are the same. The maps presented in Figure 2 were calculated using geometry I and drawn by the computer program NIVO from CIRCE in Paris. The isoenergetic curves correspond to 0; 1, 2, 3, 5, 8, 13 kcal/mol; and $E_n = E_{n-1} + E_{n-2}$ up to a maximum of $n = 15$ (n defines the curve number).

Results

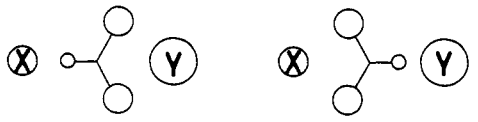
Rotamers and Assignment of NMR Signals. Several examples of hindered rotation around pure σ bonds between sp^3- and sp^2-hybridized atoms have been described.[23] It is well established in cases when two groups on the sp^3 atom are similar and considerably larger than the third one and the sp^2 atom is part of a planar system with two ortho substituents X, Y (Scheme III), that the energy minimum is obtained when the smallest substituent is in or nearly in the plane defined by X, Y, and the sp^2 atom.[24,25] This leads to a conformational equilibrium, the position of which can be

Table II. Chemical Shifts[a] and Coupling Constants[b] for the 3-*i*-Pr Protons in Compounds 1–10

	Conformer a		Conformer b		
Compd	β-Methyl	Methine	β-Methyl	Methine	% a
1	1.81 (7.2)[b]	4.70	1.49 (7.6)[b]	5.89	24
2	1.82 (7.2)	4.72	1.49 (7.6)	5.95	41
3	1.81 (7.1)	4.70	1.49 (7.6)	5.98	77
4	1.79 (7.1)	4.77	1.50 (7.7)	6.05	59
5[c]	1.83 (7.2)	4.65			100
6	1.79 (7.2)	4.68	1.47 (7.7)	5.95	25
7	1.81 (7.2)	4.65	1.47 (7.6)	6.02	61
8	1.80 (7.2)	4.64	1.46 (7.7)	6.04	90
9	1.82 (7.2)	4.77	1.48 (7.7)	6.10	20
10[c]	1.85 (7.2)	4.99			100

[a] In ppm from internal Me_4Si; solvent $(CD_3)_2CO$; temperature, −28 °C. [b] In Hz. [c] Ambient temperature; exists as a single conformer.

Scheme III



used to measure the relative sizes of different substituents Y when X is kept constant.[24,25]

The NMR spectrum of compound **1** is in agreement with this picture, featuring at ambient temperature a broadened doublet for the 3-isopropyl methyl protons, but at −20 °C two sharp doublets in the intensity ratio 28:72. The 3-isopropyl methine proton changes in this temperature region from a broad, structureless signal to two sharp septets and the 4-methyl signal from a singlet to two singlets. This indicates an exchange between two rotamers, which is slow on the NMR scale at −20 °C.

The assignment of signals (Tables II and III) to the rotamers **1a** and **1b** is based on the following observations:[26]

(1) The energy calculation for **5** predicts only one stable conformer (**5a**), and its NMR spectrum shows, independent of temperature, only one set of signals. The isopropyl methyl and methine proton chemical shifts (1.83 and 4.65 ppm) in **5a** were used to assign the low-field doublet and the high-field septet in **1** (1.81 and 4.7 ppm) to rotamer **1a**.

(2) It is well known that the thiocarbonyl group exerts a strong deshielding effect in or near the thioamide plane.[27] The low-field methine proton in **1** can therefore be assigned to rotamer **1b**. This effect is illustrated by several *N*-isopropylthioamides with conformational states analogous to those of **1a** and **1b**, e.g., **11**[28] (R = 1-naphthyl, solvent CCl_4) and **12**[29] (R = *i*-C_3H_7, solvent $(CD_3)_2CO$) (Scheme IV).

(3) Aromatic solvent molecules are known to interact with polar solute molecules in such a way that magnetic nuclei close to the negative end of the molecular dipole become less shielded than those near the positive end[30,31] (the "ASIS" effect). Calculation of the π-electron distribution in the thiazoline-2-thione nucleus[18] shows that the thiocarbonyl sulfur atom is negatively charged and that the nitrogen and ring sulfur atom bear positive charges. In agreement with this and with the previous assignment, the high-field 3-methine septet was shifted 0.8 ppm upfield, while the low-field septet was almost unaffected when toluene-d_8 was used as solvent instead of deuteriochloroform.

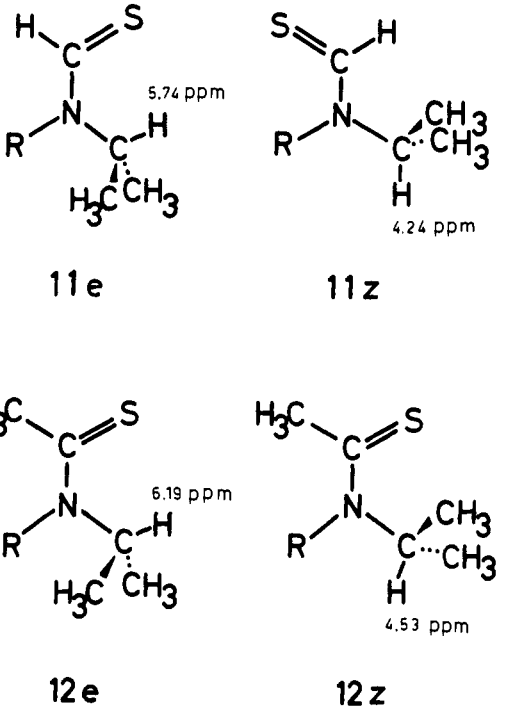
The same techniques were used to assign signals to rotamers **a** and **b** in the other compounds (**2–4, 6–9**). The mean value of the chemical shifts of the 3-isopropyl methyl protons in the rotamers given the conformation **a** is 1.81 ± 0.02 ppm and in **b** 1.48 ± 0.02 ppm (Table II). This constancy indicates that the nature of the rotamers is not drastically altered when the substituents in positions 4 and 5 are changed.

Table III. Chemical Shifts[a] of the R_4 and R_5 Groups in Compounds 1–10 and Some 3-Cyclohexyl Analogues

	Conformer a			Conformer b		
	R_4			R_4		
Compd	H–C_α	H–C_β	R_5	H–C_α	H–C_β	R_5
1	2.32		6.62	2.54		6.62
2	2.70	1.25	6.60	2.93	1.31	6.60
3	2.59	0.97[b]	6.65	2.72	1.03[b]	6.65
4	3.05	1.27	6.64	3.50	1.38	6.80
5		1.38	6.51[c]			
1'	2.37		6.62	2.56		6.62
2'	2.72	1.24	6.61	2.95	1.30	6.61
4'	n.r.[d]	1.26	6.65	n.r.	1.33	6.78
6	2.25		2.16	2.42		2.16
7	2.69	1.12	2.17	2.91	1.20	2.19
8	2.54	0.97[b]	2.17	n.r.	1.03[b]	2.20
9	3.32	1.35	2.18	3.59	1.37	2.29
10		1.51	2.28[c]			
6'	2.26		2.15	2.44		2.15
7'	2.71	1.11	2.16	2.93	1.19	2.18
9'	n.r.	1.33	2.17	n.r.	1.35	2.27

[a] In ppm from internal Me_4Si; solvent $(CD_3)_2CO$; temperature, −28 °C. [b] Methine protons are not resolved; the values given are for the γ-methyl protons. [c] Ambient temperature; exists as a single conformer. [d] Not resolved.

Scheme IV



Effect of R_4 and R_5 on Populations and Barriers to Rotation of the 3-Isopropyl Groups. The effect of substituents on the populations is shown in Figure 1. In the 5-unsubstituted compounds the population of rotamer **a** increases monotonically with the size of R_4 in the series R_4 = H, CH_3, C_2H_5, *i*-C_3H_7, *i*-C_4H_9, *t*-C_4H_9 (Figure 1). This behavior is as expected from the accepted sizes of these groups. In the series of 5-methyl analogues, the 4-methyl compound (**6**) has the same population ratio as in the 5-H series, whereas the relative population of rotamer **a** increases when R_4 = Et (**7**) and *i*-Bu (**8**). More strikingly, the 4-isopropyl compound **9** shows a strong deviation from the monotonic series, the fractional population of rotamer **9a** dropping to 0.24 (in acetone) compared with the expected ca. 0.70.

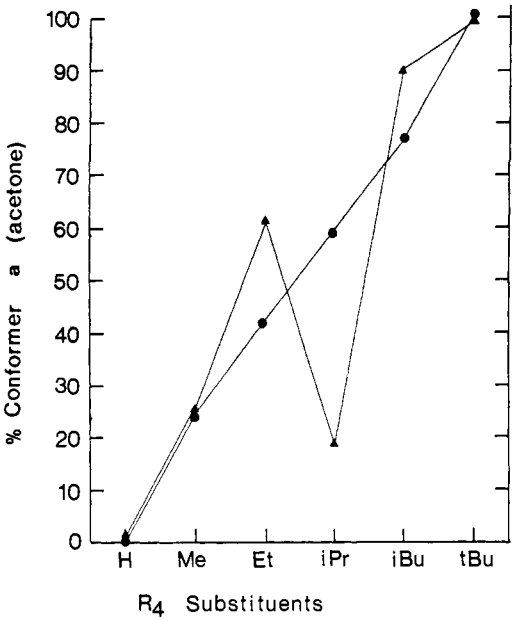


Figure 1. Fractional population of rotamer **a** as a function of R_4 in **1–5** (●) and **6–10** (▲).

Table IV. Rotamer Populations and Solvent Effects[a]

			% a		
Compd	% a[b]	Compd	C_3D_6O	$CDCl_3$	Toluene-d_8
1'	23	1	24	12	11
2'	38	2	41	30	40
4'	59	4	59	50	64
5'	100	5	100	100	100
6'	24	6	25	12	10
7'	62	7	61	45	50
9'	32	9	20	16	10

[a] At −28 °C. [b] In C_3D_6O.

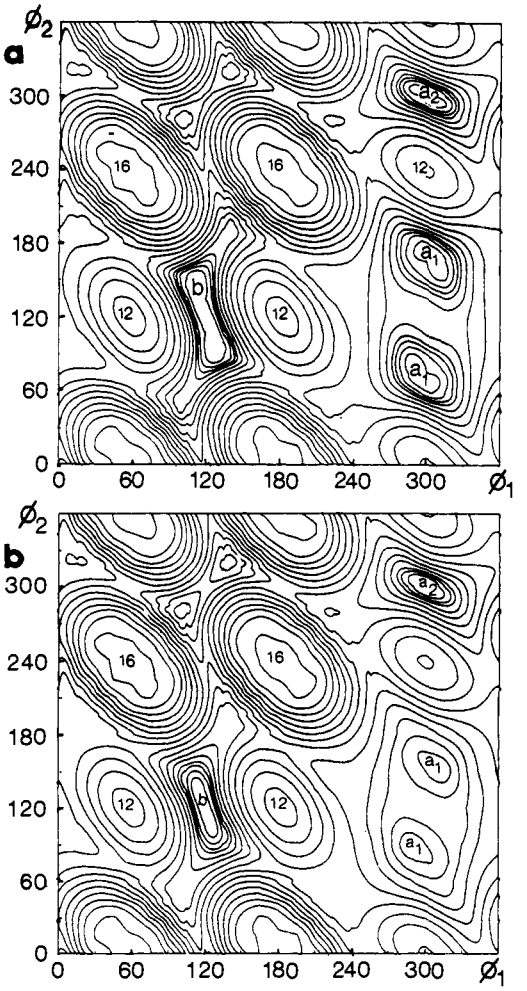


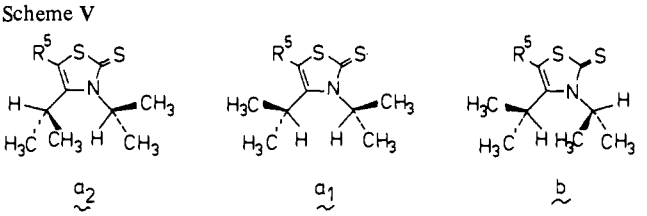
Figure 2. van der Waals' energy maps for **4** (2a) and **9** (2b).

The specific effect of the 4-isopropyl group, i.e., diminishing the relative population of rotamer **a** when R_5 is changed from H to CH_3 is also observed in the 3-cyclohexyl series (Table IV.)

The barriers to rotation of the 3-isopropyl group [$\Delta G^{\ddagger}_{298}$ for **b** → (**a**$_1$ + **a**$_2$)] listed in Table V range from 14.6 to 16.5 kcal/mol and are thus rather similar in magnitude to the corresponding barriers in the ortho,ortho'-disubstituted isopropylbenzene derivatives studied by Mannschreck and Ernst.[24] The effect of the 4 substituent is rather weak, and no significant buttressing effect of the 5-methyl group is observed except in the 4-isopropyl case.

Conformational State of the 4-Isopropyl Group. The energy maps for **4** and **9** (Figure 2) predict three energy minima, which are denoted **a**$_1$, **a**$_2$, and **b** (Scheme V), where **a**$_1$

Scheme V

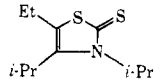
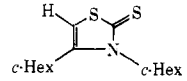


actually represents two shallow, close-lying minima. In a recent paper,[3] the observation of three rotamers, **9a**$_1$, **9a**$_2$, and **9b**, by low-temperature NMR was described. The barrier separating **9a**$_1$ from **9a**$_2$ is 11.9 kcal/mol and that separating **9b** from **9** (**a**$_1$ + **a**$_2$) is 16.5 kcal/mol. In **4** only two sets of signals were observed down to −150 °C (solvent dichlorofluoromethane), indicating either that the barrier to interconversion between **4a**$_1$ and **4a**$_2$ is very low or that one of them predominates strongly. The former explanation is quite plausible since an important obstacle to this interconversion in **9** is the 5-methyl group.

Discussion

The model presented here represents a clear-cut case where the conformational state of an isopropyl group can be varied by substitution in a neighboring position but also by substitution in the next-neighboring position. One of the most striking points is that an isopropyl group in the 4 position could have the same effect on the population and therefore, the same apparent size as a methyl group. We believe that this spectacular deviation from the expected steric effect of the 4-isopropyl group, and probably also the smaller opposite effects of the 4-Et and 4-*i*-Bu groups, are due to a specific interaction between the 4 substituent and the 5-methyl group, which gives rise to a long-range induced steric effect steering the orientation of the 3-isopropyl group. The result of exchanging H for CH_3 in position 5 is a stabilization of rotamer **b** relative to **a** by ca. 1 kcal/mol. The preferential locking of the 4-isopropyl group toward the 5-methyl group may be caused by a destabilization of **a** due to bending of the 4-isopropyl group toward the 3-isopropyl group, which in turn is bent toward the thiocarbonyl sulfur atom in such a way that the CH_3–S repulsive interaction is considerably increased. That the repulsive $C(CH_3)_2$···S interaction is more important than the CH···S interaction

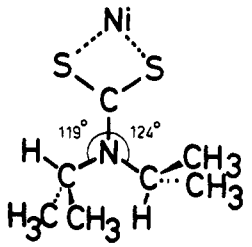
Table V. Rate Constants[a] and Activation Parameters for the Interconversion b → a

Compd	Temp, K	$\tau_{b\rightarrow a}$ (s)	$\Delta G^{\ddagger}_{T,b\rightarrow a}$, kcal/mol	$\Delta G^{\ddagger}_{298,b\rightarrow a}$,[b] kcal/mol	P_a[c]	Solvent
1	302.2	0.0137	15.1	15.1	0.15	$CDCl_3$
2	270.1	0.099	14.5	14.7	0.35	$CDCl_3$
4	300.0	0.025	15.4	15.4	0.50	$CDCl_3$
6	272.1	0.153	14.9	15.0	0.13	$CDCl_3$
6	263.1	0.168	14.4	14.6	0.30	$(CD_3)_2CO$
7	291.3	0.032	15.1	15.1	0.47	$CDCl_3$
9	299.1	0.183	16.5	16.5[d]	0.18[e]	$CHCl_2F$
	288.2	0.34	16.2	16.3	0.22	$CDCl_3$
	297.7	0.42	16.9	16.9	0.51	$CDCl_3$

[a] Obtained from fitting experimental and theoretical spectra. [b] Calculated assuming $\Delta S^{\ddagger}$ −5 cal mol^{-1} K^{-1}.[32] [c] Population of a obtained from curve fitting. [d] $\Delta G^{\ddagger}_{b\rightarrow a_1+a_2}$. [e] $a_1 + a_2$.

with equal bond angles is shown by the crystal structure of bis(*N,N*-diisopropyldithiocarbamato)nickel(II),[33] in which the (S)C-N-C angle is larger on the side where the methyl groups face the sulfur atom (Scheme VI).

Scheme VI



However, it is also possible that the 5-methyl group favors conformer **b** (and $\mathbf{a}_1$) by an attractive interaction. Models indicate that the hydrogen atoms on the respective alkyl groups may be close to 2.5 Å apart, which is the sum of their van der Waals' radii.[34]

In the present case, the balance between attractive and repulsive interactions among the 3, 4, and 5 substituents depends on the geometry of the thiazolinethione ring. It is hoped that the results of an x-ray structure investigation now under way will provide a basis for complete molecular-mechanics calculations, which may explain the observed effect.

A synchronous[35] rotation of the two isopropyl groups in **4** and **9** should have a barrier which is the sum of the barriers to rotation of each group. One isopropyl group cannot be effectively smaller than a methyl group to its neighbor, and the difference in free energy of activation between **4** and **1** (or **9** and **6**) is small and should be about the same between **4** and the 3-methyl-4-isopropyl analogue. Since the barrier to rotation of the 4-isopropyl group in **9** is 11.9 kcal/mol, the barrier to a synchronous rotation in this molecule should not be much less than 11.9 + 15.1 (14.6) = 27.0 (26.4) kcal/mol.

According to the energy maps for **4** and **9** (Figure 2), the conversion from **b** to $\mathbf{a}_2$ goes via $\mathbf{a}_1$. The interconversions $\mathbf{a}_1$–$\mathbf{a}_2$ (4-isopropyl rotation) and $\mathbf{a}_1$–**b** (3-isopropyl rotation) also involve some concerted libration of the other isopropyl group.

The same explanation (a two-step rotation) may also account for the similarity in $\Delta G^{\ddagger}$ between 3,6-dichloro-1,2-bis(dichloromethyl)benzene ($\Delta G^{\ddagger}_{356}$ = 17.7 kcal/mol)[36] and 2,4,6-trichloro(dichloromethyl)benzene ($\Delta G^{\ddagger}_{304}$ = 14.9 kcal/mol).[37] In this case the energy difference is somewhat larger, which is probably due to the closer proximity of the substituents on a benzene ring.

At this point of the discussion, it may be appropriate to outline the difference between the gear effect and the classical buttressing effect.[38] The two effects depend on different modes of minimization of the steric strain introduced by two substituents in close contact. With spherical or cylindrical substituents, the major mode of strain minimization will be bond bending (buttressing effect), as exemplified by iodine substituents in the biphenyl series.[38a] With polyhedral substituents, the major mode will be rotation of the groups (gear effect), though bond bending and other modes will also contribute. Thus the free energy of rotamer $\mathbf{9a}_2$ can be diminished by successive rotations of the 4- and 3-isopropyl groups in going via $\mathbf{9a}_1$ to **9b**, which has the lowest free energy. On the other hand, the increase in barrier to 3-isopropyl group rotation in going from **4** to **9** is probably due to a buttressing effect of the 5-methyl group in the transition state. Summing up, the buttressing effect deals with the bond-bending aspect while the gear effect deals with the conformational aspect of strain minimization.

Conformational Transmission. For geometric reasons the 3-isopropyl group cannot be in direct contact with the group in position 5. Changes in rotational barrier or conformational state for the 3-isopropyl group caused by changes in position 5 must be relayed by the 4 substituent. Thus the thiocarbonyl group is "informed" about changes in position 5 through the substituents in positions 4 and 3 acting as a gear system. Since the nucleophilic reactivity of the thiocarbonyl sulfur atom is increased by strain release,[39] it can be varied by long-range induced conformational changes of the 3-isopropyl group. The rate constants of S-alkylation by methyl iodide of some of the compounds studied here are given in Table VI.[40] It is obvious that the rate constants vary in the same sense as the populations of rotamer **a**.

In the same way, changes at the thiocarbonyl sulfur atom can result in conformational changes at the other end of the gear chain. The solvation in chloroform is different from that in acetone, the former solvent forming weak hydrogen bonds with the thiocarbonyl sulfur atom,[41,42] thus increasing its effective size. This leads to an increase in population of rotamer **b** (Table IV) which implies a change in the surroundings of R_5.

In this five-membered ring system, conformational transmission is apparently not effected by a methyl group in position 4. No change in the **a**/**b** ratio is observed in 3-isopropyl-4-methyl-Δ^4-thiazoline-2-thiones when R_5 is varied in the series H, CH_3, C_2H_5, i-C_3H_7.

Table VI. Rate Constants[a] for the Alkylation at Sulfur of Δ^4-Thiazoline-2-thiones by CH_3I

Compd	$k^b \times 10^6$	Compd	$k^b \times 10^6$
1	332	1'	380
2	368	2'	387
4	396	4'	411
5	457	5'	452
6	552	6'	603
8	648	8'	732
9	582	9'	621
10	745		

[a] Obtained by conductometry. [b] l. mol^{-1} s^{-1}, at 25 °C, precision ±1%.

Conclusions

Long-range conformational effects can be induced by substituents of the polyhedral type acting in a geared system, since the thiocarbonyl sulfur atom is informed about changes in position 5 of the ring through a geared block of polyhedral substituents occupying positions 3 and 4. The observed effects (on populations and rates of reaction) could not have been predicted using the current view of steric effects of alkyl groups. Instead, each situation involving interaction between several polyhedral groups must be analyzed separately, if possible with molecular-mechanics calculations. This is a new demonstration, if required, of the importance of the conformational aspect in discussions of the steric effect of alkyl groups.[43] The DNMR study shows that conformational transmission by the gear effect does not require synchronous rotation of the groups involved.

Our investigations of the gear effect are being continued with studies of model thiazolinethiones bearing asymmetric substituents and substituents with a functional group in position 3.

Acknowledgments. We are grateful to C.N.R.S. de France (International A.T.P. No. 9111) and to the Swedish Natural Science Research Council for financial support, and to Drs. R. E. Carter and T. Drakenberg for valuable discussions. We are also grateful to Mr. J. M. Bernasseau for his help in the use of the NIVO program.

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