Conformational Analysis of Trigonal and Planar Rotors attached to Δ^4-Azoline-2-thiones. The Effect of Ring Geometry

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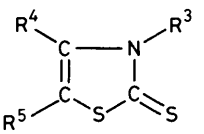
The barriers to rotation of isopropyl and aryl groups (unsubstituted in the *ortho* positions) in position 3 in 4,5-dimethyl-oxazoline-2-thiones, -imidazoline-2-thiones, and -thiazoline-2-thiones have been studied by temperature-dependent ^{1}H n.m.r. spectra. The barriers are 44.2, 50.4, and 59.0 kJ mol^{-1} for the Pr^i groups, and 38.9, 51.5, and 74.0 kJ mol^{-1} for the Ar groups. The barriers are analysed in terms of the apparent overlap of van der Waals radii in idealized transition states, and the barrier differences are shown to depend on the effects of the ring elements in position 1 on the geometry of the ring.

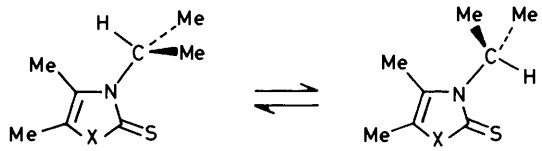
We have previously found that the thiazoline-2-thione moiety (**1**) is a suitable framework for studying the interactions of attached groups,[1-4] among other things because of the strong anisotropy of shielding of this system, which facilitates the identification of the various rotamers. Earlier studies have been concerned with the effect of the sizes of substituents R^4 and R^5 on the orientations and barriers to rotation of a variety of primary and secondary alkyl groups and analogues in position 3. In the work presented here, we have used the rotation of a 3-isopropyl and a 3-aryl group in a series of azoline-2-thiones (**2**) and (**3**) to study the effect of the ring element X on the steric environment of the 3-substituent. This ring element affects all bond lengths and angles within the ring and thereby modifies the distances between the 3-substituent and the flanking thiocarbonyl and methyl groups. It may also affect the barriers through the electron distribution. The Pr^i group was chosen as a 'rotor' in position 3 because it has been widely used as a probe for steric effects in other studies by n.m.r.[1,5,6] When attached to a planar framework, this group has been shown by ^{1}H n.m.r. shifts and solvent effects,[1] by force-field calculations,[1,5] and by analysis of coupling constants[7] to be orientated with the C–H bond in or nearly in the plane of the frame and with the methyl groups on either side of the plane. Therefore, two conformations (*syn* and *anti*) are available with an unsymmetrical framework, the one with the isopropyl methyl groups turned towards the smaller of the flanking groups being energetically favoured.

The 3,4-dimethyl-5-isopropylphenyl group was chosen as a planar rotor, in which the 5-isopropyl group serves as a ^{1}H n.m.r. probe to study the rotation of the aryl group, the isopropyl methyl groups being diastereotopic on slow rotation.

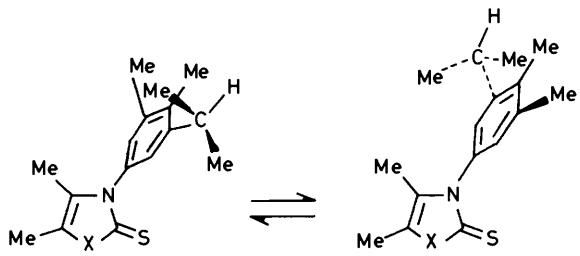


(**1**)

a; R^3 = R^4 = Pr^i, R^5 = H
b; R^3 = R^4 = Pr^i, R^5 = Me



syn (**2**) *anti*



(**3**)

a; X = O
b; X = NMe
c; X = S

Results and Discussion

The rotational barriers in each of series (**2**) and (**3**) show an important and regular increase when the ring element X changes in the series O, NMe, S (Table 1). In the 3-isopropyl derivatives (**2**), the *anti*-rotamer is favoured in all cases, and in particular when X = NMe.

The ring element X can influence the barrier to rotation of the rotor in position 3 in compounds (**2**) and (**3**), and the rotamer equilibrium in compounds (**2**) by its effect on the geometry of the molecule and on its electron distribution. To begin with the latter factor, increasing donor capacity of X increases the electron density of the thiocarbonyl sulphur atom and thereby its steric requirements. However, the donor capacity, as measured by the nucleophilic reactivity of the sulphur atom, increases in the series X = O, S, NMe, whereas the barriers increase in the order O, NMe, S indicating that this aspect of the electronic effect cannot explain the order of the rotational barriers.

Another possibility for an electronic effect is *via* an influence on the length of the C(4)–C(5) bond. However, as follows from the discussion of the geometries, this effect must be small. The differences between δ(H-5) and δ(H-4) ($\Delta\delta_{5-4}$ in Table 3) follow the order O, S, NMe, indicating that the order of effects

Table 1. Experimental and calculated free energy barriers for (**2a**—**c**) and (**3a**—**c**), and fractional populations for (**2a**—**c**)

Compound	Solvent	T/K	$\Delta G^{\ddagger}_{syn\rightarrow anti}$/kJ mol^{-1} (exp)	ΔG/kJ mol^{-1} (calc)[a] (Σr^{*})	p_{syn}
(**2a**)	$(CD_3)_2CO$ + 3% $CDCl_3$	202—223	44.3	45.2 (1.558)	0.26
	$(CD_3)_2CO$	189	*b*		
(**2b**)	$(CD_3)_2CO$[c]	248; 256	50.4	46.5 (1.607)	0.15
	$(CD_3)_2CO$ + 10% $CDCl_3$	212.5			0.05
	$CDCl_3$	203			<0.05
(**2c**)	$(CD_3)_2CO$	298	59.0	55.2 (1.941)	0.30
(**3a**)	CS_2	182	38.9	57.3 (2.025)	
(**3b**)	C_7D_8	230	51.5	59.1 (2.091)	
(**3c**)	C_7D_8	318	74.1	76.4 (2.760)	

[a] Calculated by equation (2). [b] Too low concentration for bandshape analysis. [c] At 60 MHz in Fourier transform mode (JEOL FX-60).

Table 2. Chemical shifts (δ_H) and coupling constants (Hz, in parentheses) for compounds (**2a**—**c**) in [$^2H_6$]acetone

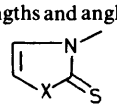
	3-Pr^i							
	CH_3		CH		4-CH_3		5-CH_3	N-CH_3
Compound	*syn*	*anti*	*syn*	*anti*	*syn*	*anti*	*syn* and *anti*	*syn* and *anti*
(**2a**)	1.65 (6.8)	1.42 (7.2)	4.34	5.18	2.15	2.29	2.16	
(**2b**)	1.74 (6.9)	1.41 (7.2)	*a*	5.63	2.14	2.29	2.14	3.47
(**2c**)	1.79 (7.2)	1.47 (7.7)	4.68	5.95	2.25	2.42	2.16	

[a] Not observable due to low population.

Table 3. Chemical shifts (δ_H) at ambient temperature for (**3a**—**c**) in $CDCl_3$

Compound	4-CH_3	5-CH_3	$\Delta\delta_{5-4}$	N-CH_3	4′-CH_3	5′-CH_3	3′-CH(CH_3)$_2$	3′-C*H*(CH_3)$_2$	CH (aromatic)
(**3a**)	1.81	2.21	0.40		2.32	2.26	1.21	3.23	6.95, 7.01
(**3b**)	1.87	2.14	0.27	3.61	2.31	2.25	1.21	3.22	6.95 (br)
(**3c**)	1.83	2.17	0.34		2.31	2.26	1.185, 1.232	3.23	6.85, 6.91

Table 4. Bond lengths (Å), bond angles at ring element X (θ_x^0), and interaction distances AB and BC (Å). Estimated bond lengths and angles in bold type

Ring system									
X	O	NR	S	O	NR	S	O	NR	S
Bond									
1—2	1.362	1.370	1.718	1.358	1.364	1.724	**1.360**	1.349	1.727
2—3	1.354	1.371	1.370	1.292	1.321	1.304	**1.320**	1.349	1.360
3—4	1.440	1.429	1.423	1.394	1.373	1.372	**1.410**	1.392	1.390[a]
4—5	1.354	1.371	1.370	1.353	1.364	1.367	**1.320**	1.325	1.350
C(2)=S							**1.670**	1.696	1.683
θ	106.6	109.8	92.1	103.9	107.4	89.3	**106**	109.2	92.1
R(A—B)							3.178	3.123	3.038
R(B—C)							3.147	3.210	3.117
Reference	14	15	16	17	18	19		11	13

[a] Corrected for effect of repulsion between 3-Pr^i and 4-Pr^i.

on the electron distribution in this part of the molecule does not follow the order of barriers.

In compounds (**3**), the aromatic ring and the azoline-2-thione ring must be nearly perpendicular in the ground state but more or less coplanar in the transition state to rotation. Therefore, the ring element X may influence the order of barriers in these compounds by different effects on the transition state energy. The transition state will be stabilized by electron donation, mainly from the highest occupied π orbital of the azolinethione to the lowest free π orbital of the benzene ring. The energy of this interaction, ΔE, will increase with diminishing splitting, $\Delta\varepsilon_{ij}$, between the two energy levels, according to conventional PMO reasoning [equation (1)].[9] In this expression, ΔH_{ij}, the matrix element between the orbitals

$$\Delta E = -2\,\Delta H_{ij}^2/\Delta\varepsilon_{ij} \qquad (1)$$

involved, can be assumed to be constant in the series. Photoelectron spectra have been recorded for 3,4,5-trimethyloxazoline-2-thione, 1,3-dimethylimidazoline-2-thione, and 3,4,5-trimethylthiazoline-2-thione, and the IPs ascribed to the highest occupied π orbitals are 7.45, 7.26, and 7.45 eV, respectively.[10] The value for 1,3,4,5-tetramethylimidazoline-2-thione is not available, but it is certainly lower than 7.26 eV. Thus, the transition state stabilization should follow the sequence (**3a**) ≈ (**3c**) < (**3b**). Evidently, this effect cannot by itself explain the order of barriers, but it may well have an observable effect on their absolute values.

Turning now to the geometric effect, the barriers may as a

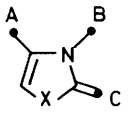


Figure.

first approximation be interpreted in terms of the distances AB and BC (Figure), where A and B are the positions of the carbon atoms in the 4-methyl and 3-isopropyl groups respectively, and C is the thiocarbonyl sulphur atom. Geometries for suitable imidazoline-2-thiones[11,12] and thiazoline-2-thiones[13] are known from *X*-ray crystallographic studies, but unfortunately no similar studies of oxazoline-2-thiones have been reported. However, using the geometries of furan,[14] pyrrole,[15] and thiophene,[16] and of oxazole,[17] imidazole,[17,18] and thiazole,[19] it is possible to make a reasonable extrapolation to a structure for an oxazoline-2-thione.

It is found that the 2–3 and 4–5 bonds are consistently longer and the 3–4 bonds shorter in the S- and N-heterocycles than in the O-analogues. The differences generally fall in the range of 0.01—0.03 Å, and they reflect the well known order of π electron delocalization ('aromaticity') increasing in the series furan, thiophene, pyrrole.

In constructing model geometries (Figure), we have assumed that the exocyclic bonds to positions 2, 3, and 4 bisect the outer ring angles. The N(3)–C_{exo} and C(4)–C_{exo} bonds are given the lengths 1.45 and 1.52 Å, respectively, in all structures. The bond lengths in the ring are chosen or estimated to apply to compounds unsubstituted except possibly in position 3, since most data are available for this group. Therefore, the 3–4 bond, which is 1.40—1.42 Å in the 3,4-di-isopropylthiazoline-2-thiones described in ref. 13, has been shortened to 1.39 Å in the model with X = S, and the angles at C(2) and C(5) have been adjusted to account for this. The only other constraint in the construction of the oxazoline-2-thione ring has been to keep these angles equal, which is in fact quite natural with the bond lengths chosen. Geometric data for the reference compounds and estimated values for the model oxazoline-2-thione are shown in Table 4.

The shortest AB and BC distances are found for the thiazoline-2-thione, whereas the values for the N and O analogues, and in particular their sums, are more equal (Table 4). However, the long BC distance when X = NMe is due to the long C=S bond, which in turn is a consequence of the strong electron donation by two nitrogen atoms. This simple model does not take the van der Waals radii of the interacting atoms into account, and in order to obtain a better appreciation of the interactions, we have employed the method of 'apparent overlap' introduced by Sternhell and co-workers.[20] as a measure of steric interaction. These authors constructed a variable, Σr^*, as a measure of apparent overlap between two interacting parts of a molecule in an idealized transition state, typically the benzene rings in a sustituted biphenyl. Each term r^* is the sum of the van der Waals radii of a pair of interacting groups after subtraction of the estimated distance between the centre of the groups in the transition state. Σr^* is the sum over all interactions, and the authors found a linear relation (2) between Σr^* and $\Delta G^{\ddagger}$ for the internal rotation.

$$\Delta G^{\ddagger} = 26\,\Sigma r^* + 4.7\ \text{kJ mol}^{-1} \qquad (2)$$

The transition state of (**2c**) and analogues have been found by molecular mechanics calculations[21] to have the isopropyl group perpendicular to the thiazoline ring, *i.e.* the C(4)-N(3)-C_α-H dihedral angle is 90°, where C_α-H is the Pr^i methine group. With this transition state for compounds (**2**) and a planar transition state for compounds (**3**) we have used equation (2) to calculate the $\Delta G_{calc.}^{\ddagger}$ values found in Table 1. The calculated barriers are with one exception reasonably close to the experimental ones, and they fall in the right order. The exception is (**3a**), and the deviation (nearly 50%) far exceeds any found in the large material of compounds studied by Sternhell and co-workers.[20] In order to reproduce the experimental barrier, Σr^* should be diminished from 2.025 to 1.315 Å, *i.e.* the sum of the distances between the interacting groups should be increased by 0.71 Å. It is difficult to envisage that the extrapolated geometric model should be so much in error, considering the good agreement between calculated and experimental barrier for (**2a**). We have at present no explanation for the observed aberration.

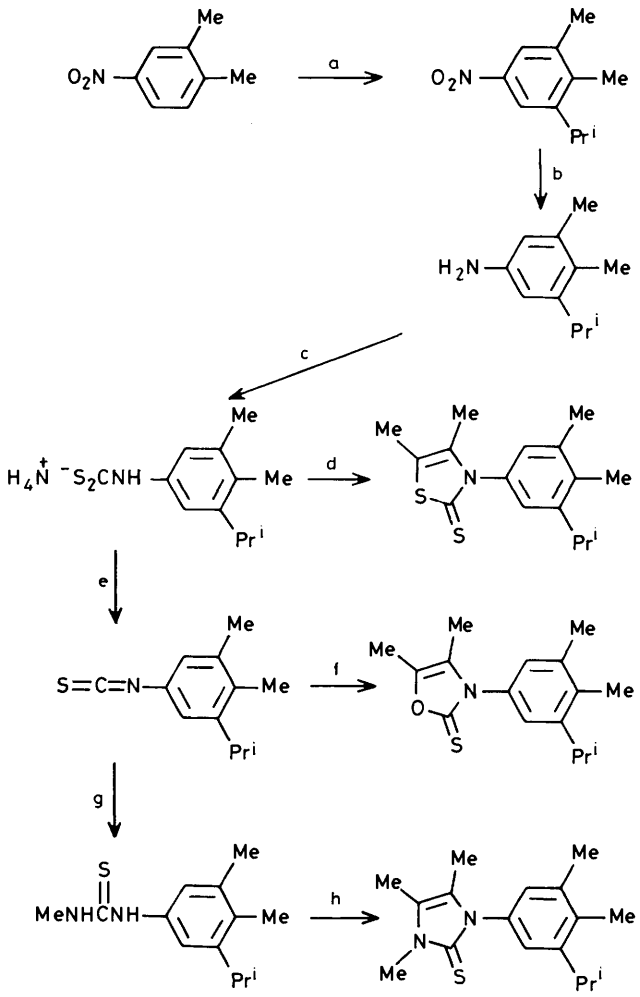
Apart from this, the geometric factor seems to account in a satisfactory way for the variation of the rotational barriers with the ring element X. Secondary effects, such as an expected stronger transition state stabilization due to conjugation in (**3b**) may well play a role, but the uncertainties in the geometries and the deviation for (**3a**) make speculations over such finer details seem futile. The effect of the ring element X seems to be similar in other planar systems. Thus Içli and co-workers.[22] report $\Delta G^{\ddagger}$ 101.2 kJ mol^{-1} for the rotation of the *o*-tolyl group in 4-oxo-3-*o*-tolyloxazolidine-2-thione, whereas the barrier in the thiazolidine analogue was estimated to be > 105 kJ mol^{-1}.

We next turn to the *syn*:*anti* ratio in compounds (**2**) (Table 1). The *anti* form is generally favoured, in particular so in (**2b**). The very high *anti* preponderance in $CDCl_3$ solution reflects the tendency of this solvent, like CH_2Cl_2, $CHCl_2F$, and $CHClF_2$, to increase the apparent steric bulk of the thiocarbonyl sulphur atom by specific solvation, possibly mediated by hydrogen bonding.[1,23]

The high proportion of *anti* form in (**2b**) in [$^2H_6$]acetone may also be a consequence of the particularly high electron density around the thiocarbonyl sulphur atom. This should increase its effective van der Waals radius and thereby disfavour the *syn* form, but it may also affect the relation between the isopropyl methine proton and the C=S group in the *anti* form. Taylor and Kennard[24] have studied a large number of crystal structures determined by neutron diffraction, and they have found that protons bound to carbon often display distances shorter than the sums of the van der Waals radii to oxygen, nitrogen, and chlorine atoms, indicating an attractive interaction resembling a hydrogen bond. A few cases involving (C–)H···S interactions are also recorded with H-S distances in the range 2.5—2.9 Å, all shorter than the sum of the van der Waals radii (3.0 Å). However, the authors hesitate to describe the interactions as attractive, since repulsive effects in other parts of the molecules could be responsible for the observed conformations.

The 3,4-di-isopropylthiazoline-2-thiones (**1a** and **b**) studied by Pèpe and Pierrot[13] provide examples where an attractive effect seems to be firmly established. In both compounds the 3-Pr^i group has the *anti* conformation in the crystal, and the distance between the 3-methine proton and the thiocarbonyl sulphur atom is 2.51 and 2.37 Å, respectively. Although the 3-Pr^i group is rotated *ca.* 5° out of the ring plane, the methine remains in the plane, which clearly indicates an attractive interaction. The same effect may contribute to the preponderance of the *anti* form in all compounds (**2a**—**c**), but it should be largest in (**2b**).

Summing up, the analysis of the interactions based on the geometries of the rings, the one for the oxazoline-2-thione extrapolated, permits the conclusion that the ring element X (O, NCH_3, S) affects the rotational barriers of the 3-substituents mainly by its influence on the geometry of the ring and thereby on the distances between the flanking groups (4-Me and 2-S) and the 3-substituent in the transition state to rotation.



Scheme. *Reagents:* a, Pr^iOH–H_2SO_4; b, NH_2NH_2–Raney Ni; c, CS_2, NH_4OH; d, 3-bromobutan-2-one; e, $Pb(NO_3)_2$; f, acetoin; g, $MeNH_2$ 41%, in water; h, acetoin

Experimental

Materials.—3-Isopropyl-4,5-dimethyl-Δ^4-oxazoline-3-thione (**2a**) was obtained by refluxing equimolecular quantities of acetoin and isopropyl isothiocyanate[25] in pyridine for 6 h, evaporating, and refluxing the residue in ethanolic hydrochloric acid for 2 h. After evaporation, the solid residue was purified by chromatography on silica (Merck Kieselgel 60, 0.063—0.2 mm) with benzene to give an oil (10%), δ_H (100 MHz; $CDCl_3$) 1.50 (6 H, d), 2.19 (6 H,br), and 5.1 (1 H, sept); *m/e* (70 eV) 171 (76%), 129 (100), 128 (15), 100 (14), 86 (24), 43 (49), 41 (29), and 39 (17).

3-Isopropyl-1,4,5-trimethyl-Δ^4-imidazoline-2-thione (**2b**) was obtained by refluxing equimolecular quantities of acetoin and *N*-methyl-*N'*-isopropylthiourea[26] in pentan-1-ol for 20 h under continuous water separation conditions. Most of the solvent was removed by distillation under reduced pressure, and the residue was purified by recrystallization from ethanol to give a 70% yield of prisms, m.p. 166—168 °C; δ_H (100 MHz; CCl_4) 1.33 (6 H, d), 1.95 (3 H,br), 2.06 (3 H, br), 3.33 (3 H, s), and 5.35 (1 H, sept); *m/e* (70 eV) 184 (64%), 142 (100), 141 (28), 127 (10), 109 (17), 56 (32), 42 (25), and 41 (19).

3-Isopropyl-4,5-dimethyl-Δ^4-thiazoline-2-thione (**2c**) has been described previously.[27]

The 3-(3,4-dimethyl-5-isopropylphenyl)-4,5-dimethyl-Δ^4-azoline-2-thiones (**3a—c**) were prepared according to the reaction sequence given in the Scheme. Isopropylation by Pr^iOH–H_2SO_4[28] of commercial 3,4-dimethylnitrobenzene afforded 3-isopropyl-4,5-dimethylnitrobenzene (17%), b.p. 125 °C at 1.6 kPa; δ_H (100 MHz; $CDCl_3$) 1.23 (6 H, d), 2.27 (3 H, s), 2.33 (3 H, s), 3.25 (1 H, sept), 7.76 (1 H, s), and 7.86 (1 H, s); *m/e* (70 eV) 193 (40%), 178 (100), 132 (21), 117 (17), and 115 (18). Reduction by hydrazine and Raney Ni[29] afforded 3-isopropyl-4,5-dimethylaniline (35%), b.p. 130 °C at 1.3 kPa; δ_H (100 MHz; $CDCl_3$) 1.15 (6 H, d), 2.06 (3 H, s), 2.15 (3 H, s), 3.06 (1 H, sept), 3.33 (2 H, s), 6.23 (1 H, s), and 6.31 (1 H, s); *m/e* (70 eV) 163 (90%), 148 (100), 133 (15), and 120 (20).

This aniline was transformed into the corresponding ammonium dithiocarbamate.[30] Without further purification this was treated with 3-bromobutan-2-one as in the preparation of (**2c**)[27] and gave in a smooth reaction 3-(3,4-dimethyl-5-isopropylphenyl)-4,5-dimethyl-Δ^4-thiazoline-2-thione (**3c**) as an oil (42%) after column chromatography (Merck Kieselgel 60, 0.063—0.2 mm, eluant benzene), *m/e* (70 eV) 291 (74%), 276 (28), 119 (52), 114 (52), 91 (68), 85 (83), 77 (62), 71 (85), 59 (95), 53 (100), and 45 (70). The ^1H n.m.r. spectra of (**3a—c**) with assignments are found in Table 3.

The ammonium dithiocarbamate was transformed[30] without isolation into 3-isopropyl-4,5-dimethylphenyl isothiocyanate in 23% yield after purification by steam distillation, δ_H (100 MHz; $CDCl_3$) 1.13 (6 H, d), 2.13 (3 H, s), 2.20 (3 H, s), 3.10 (1 H, sept), 6.70 (1 H, s), and 6.73 (1 H, s). The isothiocyanate reacted with acetoin to give 3-(3,4-dimethyl-5-isopropylphenyl)-4,5-dimethyl-Δ^4-oxazoline-2-thione (**3a**) in 8% yield after two recrystallizations from ethanol, m.p. 111 °C; *m/e* (70 eV) 275 (63%), 260 (20), 191 (61), 128 (28), 119 (63), 105 (35), 91 (53), 77 (40), 59 (100), and 53 (40).

The isothiocyanate reacted with methylamine (40% aqueous solution) under cooling (0 °C) to give *N*-methyl-*N'*-(3,4-dimethyl-5-isopropylphenyl)thiourea in 35% yield after purification by chromatography on silica as above (eluant benzene), δ_H (100 MHz; $CDCl_3$) 1.15 (6 H, d), 2.20 (3 H, s), 2.28 (3 H, s), 3.06 (3 H, s), 3.60 (1 H, sept), 6.78 (1 H, s), 6.83 (1 H, s), and 8.05 (2 H); *m/e* (70 eV) 236 (100%), 203 (47), 193 (25), 180 (42), 103 (72), 148 (68), 91 (51), 77 (42), and 74 (68).

The thiourea was treated with acetoin as in the preparation of (**2b**) to give 3-(3,4-dimethyl-5-isopropylphenyl)-4,5-dimethyl-Δ^4-imidazoline-2-thione (**3b**) as an oil in 17% yield after three purifications by column chromatography as above [ethyl acetate–benzene (20:80) as eluant], *m/e* (70 eV) 288 (40%), 273 (18), 161 (12), 141 (22), 119 (30), 105 (18), 91 (20), 77 (15), and 56 (100).

^1H N.m.r. spectra, with the exception mentioned in Table 1, were recorded on a JEOL model JNM-MH-100 n.m.r. spectrometer equipped with a standard variable-temperature attachment (VT 3-C). The spectra of (**2a—c**) were recorded with samples *ca.* 0.2M in [$^2H_6$]acetone. For solubility reasons, it was necessary to add 3% of $CDCl_3$ to the sample of (**2a**) in order to obtain a continuous wave spectrum, but this had no influence on the rotamer population. The spectra of (**3b** and **c**) were recorded in [$^2H_8$]toluene, but in this solvent no splitting of the diastereotopic Pr^i methyls in (**3a**) was observed. Instead, CS_2 gave the desired non-equivalence.

The rate constants to rotation of the 3-substituents, *k*, were evaluated by visual fitting of the experimental spectra to theoretical spectra calculated by the McConnell equation.[31] The measurements of temperatures and T_2 values were performed as described in ref. 23. The free energies of activation, $\Delta G^{\ddagger}$, were calculated using the Eyring equation (3).[32] A

$$\Delta G^{\ddagger} = RT \ln k_B T/kh \qquad (3)$$

complete bandshape analysis of (**2a**) over a 21° temperature interval gave $\Delta H^{\ddagger}$ 41.3 ± 0.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ −14.4 ± 2.5 J

mol^{-1} K^{-1}, with the error limits corresponding to the 95% confidence level. The rotamer populations for (**2a**—**c**) were evaluated by band fitting near the slow exchange limit. The free energy barriers and rotamer populations are found in Table 1, the chemical shifts of (**2a**—**c**) in Table 2, and those of (**3a**—**c**) in Table 3.

The calculations of Σr^* were performed according to ref. 20, *i.e.* the methyl groups were treated as 'united atoms' with a bond length of 1.9 Å and a van der Waals radius of 1.8 Å. The same value was used for the van der Waals radius of the sulphur atom.[33]

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