

Sulfur(II)–Oxygen 1,5-Interactions of 2-Thiocyanatomethylenecycloalkanones as Studied by ^1H , ^{13}C NMR and X-Ray Crystallographic Methods

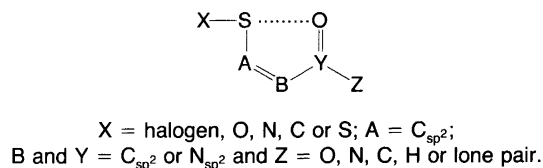
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The stereochemistry of eight thiocyanatomethylenecycloalkanones has been studied by ^1H and ^{13}C NMR spectroscopy. In addition, an LIS (lanthanide-induced-shift) study was performed for two and an X-ray diffraction study for one of the compounds. In 2-thiocyanatomethylenecycloalkanone (the only one with both *Z* and *E* isomers) the vicinal carbon–proton coupling constant of the carbonyl carbon to the side-chain proton proved to be 5 Hz larger in the *Z* isomer than in the *E* isomer. Similar, rather large, coupling constants for the other six compounds support their *Z* arrangement. In the *Z* isomer of 2-thiocyanatomethylenecycloalkanone the C=O and SCN carbons are deshielded by 5.5 ppm compared with those in the *E* isomer; this is due to the steric closeness and the 1,5-intermolecular S \cdots O interaction. In all of the compounds of *Z* stereochemistry, the SCN carbon chemical shift varied to within 1.7 ppm. LIS results for two compounds are in accordance with their assumed *Z* arrangement. 2-Thiocyanatomethylenecycloheptanone crystallizes in the triclinic space group *P*–1 (No. 2) with cell dimensions: *a* = 6.152(1), *b* = 7.855(1), *c* = 10.302(2) Å, α = 103.06(1), β = 91.58(1), γ = 104.71(1)° and *V* = 467.1(1) Å³ with *Z* = 2. Full-matrix least-squares refinement of 142 parameters gave *R* = 0.041 for 1162 reflections [*I* > 3 σ]. The S \cdots O distance is 2.537(2) Å and the angle C–S \cdots O is 172.2(1)°, indicating moderate intramolecular S \cdots O interaction in 2-thiocyanatomethylenecycloheptanone.

There is a large number of organic sulfur compounds, where the actual conformation is controlled by intramolecular sulfur–oxygen (S \cdots O) interactions.^{1,2} In these molecules the intramolecular non-bonded S \cdots O distances are significantly shorter (2.0–3.0 Å) than the corresponding sum of the van der Waals radii of S- and O-atoms (3.25 Å), but significantly longer than the range of the hypervalent S–O bond (about 1.65–1.96 Å). Compounds which have non-bonded sulfur and oxygen atoms may be classified by means of the ‘ring’ size and the sulfur valence state; in this way the non-bonded 1,3-, 1,4-, 1,5- and 1,6-S \cdots O distances can be discussed. Such 1,*n* (*n* = 3, 4, 5, 6) interactions, characterized by a planar and conjugated *n*-membered ring, are closed by the non-bonded S(II)- and O-atoms as shown (Scheme 1). The S \cdots O interaction is particularly effective if (i) the S \cdots O distance is short enough; (ii) the XSO angle is close to 180°; (iii) the ring torsional angles are close to 0° and (iv) X is an electronegative or polarizable counteratom or substituent.



Scheme 1.

In a large number of compounds of the type presented in Scheme 1, the actual conformation is often controlled by the non-bonded intramolecular S \cdots O interaction. The purpose of this study is to describe the first example of compounds, which exhibit a short 1,5-S \cdots O interaction, in which X = cyano group (–C \equiv N), Y = C_{sp²} and Z = aliphatic or aromatic carbon.

The 2-thiocyanatomethylenecycloalkanones (**1a–c**, **2c**) and benzocycloalkanones (**1d–g**) presented in Fig. 1 were prepared from the corresponding 2-chloromethylenecycloalkanones using NH₄SCN.³ Recently the thiocyanates (**1**) have been found to show remarkable fungicidal activity.^{4,5} Because most of the compounds were obtained as single

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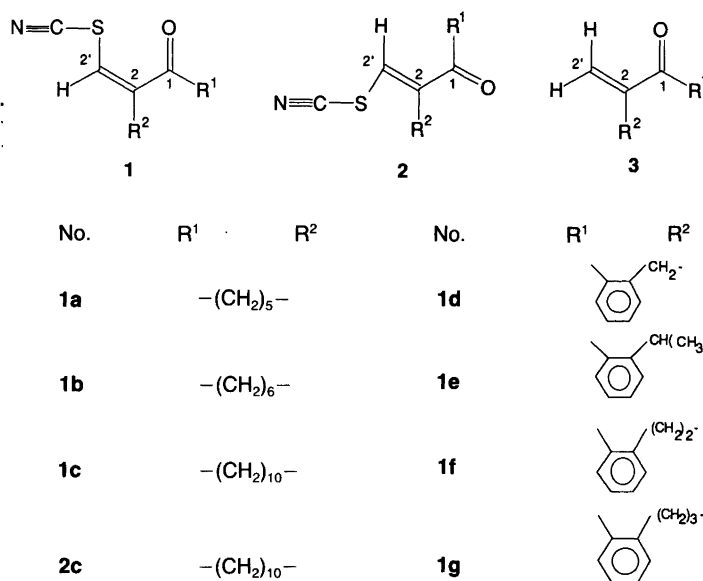


Fig. 1. The structures of (*Z*- and (*E*-thiocyanatomethylenecycloalkanones (**1** and **2**) and the corresponding methylenecycloalkanones (**3**).

isomers (compound **c** had both *E* and *Z* isomers), it was not possible to make any comparisons and the elucidation of the stereochemistry was not straightforward.

In an earlier study, based on their ¹H NMR spectra, the configurations of 2-thiocyanatomethylenecycloalkanones were found to have *E*- rather than *Z*-configurations.³ However, LIS studies of compounds **1d** and **1e**, ¹³C NMR chemical shifts and the ³J_{C=O, H2'} coupling constants now suggest that the *Z* configuration (**1**) is the more probable stereoisomer. The crystal structure study of **1a** confirms its *Z* configuration.

Experimental

NMR measurements and the preparation of compounds 1a–g. Compounds **1a–g** were synthesized in 60–90% yield as reported previously.³ The crystals were recrystallized from ethanol. The ¹³C NMR spectra were recorded on a JEOL GSX 400 MHz (in CDCl₃) spectrometer both in broadband-decoupled and fully coupled mode.⁶ The ¹H spectra were measured on JEOL GSX 400 MHz and Tesla BS 487 C CW spectrometers in CDCl₃ with tetramethylsilane (TMS) as an internal standard. In the LIS study increasing amounts of Eu(fod)₃* LIS reagent was added to the solutions of **1d** and **1e** and the ¹H spectra were recorded as before. The theoretical LIS parameter values[†] for **1d**, **2d**, **1e** and **2e** were calculated by means of the McConnell–Robertson equation for the sensible positions of the LIS reagent (the LIS reagent complexes via the C=O in prefer-

ence to the SCN group)⁷ and the fit between the experimental and the calculated LIS parameter values were estimated by means of the Hamilton agreement factor, *R* [eqns. (1) and (2)], using a computer program especially designed for this purpose.⁸

$$R = \{[\sum_i(\Delta i_{\text{exp}} - \Delta i_{\text{calc}})^2]/[\sum_i(\Delta i_{\text{exp}})^2]\}^{1/2} \quad (1)$$

$$\Delta i_{\text{calc}} = F \cdot [(3 \cos^2 \alpha - 1)/r^3] \quad (2)$$

Crystal structure analysis of 1a. The crystal data and conditions for the data collection are given in Table 1.[‡] The lattice parameters were determined by measuring 25 reflections using Mo-K_α (λ = 0.71073 Å) radiation at room temperature (296 K). Intensity data were collected on an Enraf–Nonius CAD4 diffractometer using Mo-K_α radiation and ω/2θ scan mode. The intensity data were corrected for Lorentz and polarization effects but not for extinction. 21% linear decay occurred during the data collection and was corrected by factors of 1.00–1.13 on intensity. An empirical absorption correction was done according to Walker and Stuart,⁹ the maximum and minimum correction coefficients being 1.355 and 0.718, respectively. The structure was solved by direct methods using the MULTAN 11/82 program.¹⁰ The final refinements were carried out by full matrix least-squares using the SDP-plus program package,¹¹ anisotropically for all non H-atoms. The hydrogen atoms were located from Δ*F* calculations and refined isotropically with fixed isotropic temperature factor (*B* = 5.0 Å²). The atomic scattering factors were taken

* Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)-europium(III).

† The values of experimental and calculated LIS parameters can be obtained from one of the authors (K.R.) upon request.

‡ Lists of structure factors, anisotropic temperature factors, least-squares planes and torsion angles may be obtained from one of the authors (K.R.) on request.

Table 1. Experimental crystallographic data for **1a**.

Compound	2-Thiocyanatomethylene-cycloheptanone
Formula	C ₉ H ₁₁ NOS
M _r	181.26
a/Å	6.152(1)
b/Å	7.855(1)
c/Å	10.302(2)
α°	103.06(1)
β°	91.58(1)
γ°	104.74(1)
V/Å ³	467.1(1)
Z	2
d _{calc} /Mg m ⁻³	1.289
μ/mm ⁻¹	0.28
λ/Mo-K _α	0.71073
F(000)	192
Space group	P-1 (No. 2)
T/K	296±1
Crystal size/mm	0.15×0.17×0.25
Refl. for latt. meas.	25
θ range for latt. meas./°	5–10
Scan method	ω/2θ
Scan speed/° min ⁻¹	1–17
Scan width (ω)/°	0.50+0.34 tanθ
θ range/°	2–25
h range	0→7
k range	-9→8
l range	-12→12
Variation of std. refl.	-21 % (linear)
Refl. measured	1642
Number of unique refl.	1642
Condition of obs. refl.	I > 3.0σ(I)
Refl. used in refinement	1162
Max. shift/error	<0.01
No. of param.	142
Max./min. in final Δ _o /e Å ⁻³	0.16(4)/-0.23(4)
S	0.66
R	0.041
R _w	0.040

$$w = 1/[(\sigma F_0)^2 + (aF_0)^2], a = 0.001.$$

from Ref. 12. The final coordinates are quoted in Table 2. The calculations were performed on a μ-VAX II computer at the Department of Chemistry, University of Jyväskylä. In addition to the programs quoted the PLUTO¹³ program was used.

Results

Crystal structure of 1a. A view of the compound **1a** is presented in Fig. 2 and the stereoscopic packing scheme is shown in Fig. 3. The structure of **1a** exhibits a short intramolecular N≡C–S⋯O=C 1,5-interaction. The distance between the S and O atoms is 2.537(2) Å and the C–S⋯O angle is 172.1(1)°. The S⋯O distance falls in the middle of the critical region of 2–3 Å with the X–S⋯O angle near to 180° and these are consistent with the earlier observations.^{2,14} The S⋯O interaction affects only slightly the distances to the SCN group and within it. The bond distances S–C_{sp}, S–C_{sp²} and C≡N have values of 1.697(3), 1.750(3)

and 1.144(4) Å, respectively. The first two values observed are in accordance with the values presented by Kalman and Parkanyi¹⁴ for the S⋯O 1,5-interactions. In addition all three distances do not deviate markedly from the values found in 'normal' structures containing the thiocyanate group bonded to sp²-hybridized carbon atoms.^{15,16} The C=O bond distance is more affected by the S⋯O interaction and has a value of 1.224(3) Å, again in accordance with earlier observations.¹⁴ The other bond distances and angles (Table 3) are normal. The five-membered ring (closed by the S⋯O interaction) can be regarded as planar, the maximum and minimum deviations from the calculated least-squares plane [atoms S(1), C(8), C(2), C(1) and O(1)] being -0.024(2) and 0.014(1) Å, respectively. Owing to the planarity, the important torsion angles [O(1)–C(1)–C(2)–C(8) and C(1)–C(2)–C(8)–S(1)] also have near-zero values, -4.2(4) and 0.5(3)°, respectively.

IR spectra. In the vibrational spectra of **1**, the carbonyl frequencies are dramatically shifted to lower wave numbers (1650–1655 cm⁻¹) when compared with the ν_{CO} data of unsaturated 2-methylenecycloalkanones (1690–1700 cm⁻¹).¹⁷ This weakening of the C=O bonds correlates with the shortening of the non-bonded S⋯O contact distance in the compounds studied here and is well known for other compounds with non-bonded S⋯O interactions.¹

Table 2. Fractional coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses for the compound **1a**.

Atom	x	y	z	B _{eq} /Å ² *
S(1)	0.6621(1)	0.20784(9)	0.17286(7)	4.70(2)
O(1)	0.3158(3)	0.1234(2)	0.2971(2)	5.96(5)
N(1)	1.0347(4)	0.2604(3)	0.0159(2)	6.19(7)
C(1)	0.2885(4)	-0.0398(3)	0.2830(2)	3.94(6)
C(2)	0.4570(4)	-0.1246(3)	0.2150(2)	3.56(6)
C(3)	0.4390(5)	-0.3222(3)	0.2049(3)	4.79(7)
C(4)	0.4579(5)	-0.3723(3)	0.3386(3)	5.18(8)
C(5)	0.2444(5)	-0.3935(4)	0.4107(3)	5.25(8)
C(6)	0.1636(5)	-0.2248(4)	0.4518(3)	4.66(7)
C(7)	0.0922(5)	-0.1527(4)	0.3348(3)	4.75(7)
C(8)	0.6232(4)	-0.0231(3)	0.1646(2)	3.65(6)
C(9)	0.8859(5)	0.2332(3)	0.0795(3)	4.52(7)
H(31)	0.553(5)	-0.350(4)	0.156(2)	5.0
H(32)	0.285(5)	-0.396(4)	0.149(3)	5.0
H(41)	0.585(5)	-0.279(3)	0.388(3)	5.0
H(42)	0.489(4)	-0.498(3)	0.316(2)	5.0
H(51)	0.270(5)	-0.440(3)	0.495(3)	5.0
H(52)	0.126(5)	-0.482(3)	0.351(3)	5.0
H(61)	0.285(5)	-0.125(3)	0.520(2)	5.0
H(62)	0.034(5)	-0.251(3)	0.512(2)	5.0
H(71)	0.027(5)	-0.248(4)	0.264(3)	5.0
H(72)	-0.001(5)	-0.068(4)	0.357(3)	5.0
H(8)	0.727(5)	-0.066(3)	0.121(3)	5.0

$$*B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)].$$

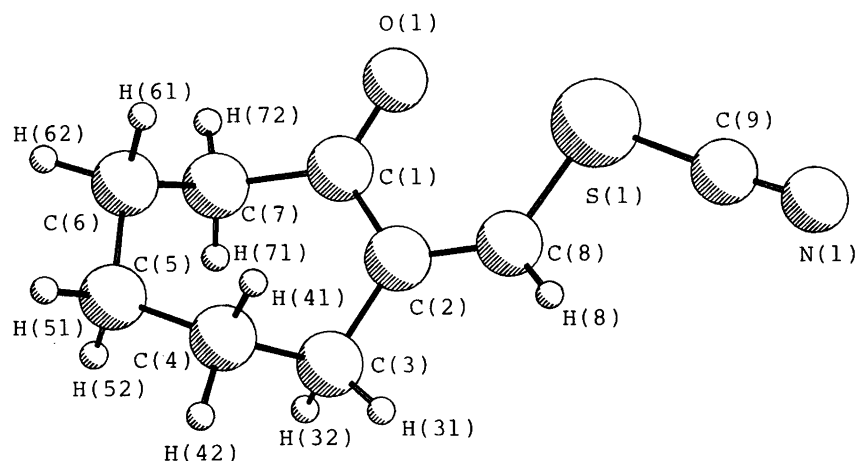


Fig. 2. PLUTO plot of the compound **1a** with the numbering scheme.

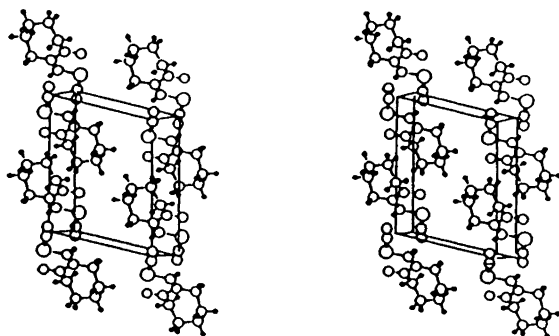


Fig. 3. Stereoscopic PLUTO plot of the compound **1a**. The *b* axis is horizontal and the *c* axis vertical.

Table 3. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses for **1a**.

S(1)–C(8)	1.750(3)	C(3)–C(4)	1.525(4)	C(5)–H(52)	0.96(2)
S(1)–C(9)	1.697(3)	C(3)–H(31)	0.92(3)	C(6)–C(7)	1.541(4)
O(1)–C(1)	1.224(3)	C(3)–H(32)	1.05(2)	C(6)–H(61)	1.04(2)
N(1)–C(9)	1.144(4)	C(4)–C(5)	1.517(4)	C(6)–H(62)	1.03(3)
C(1)–C(2)	1.479(4)	C(4)–H(41)	0.96(2)	C(7)–H(71)	0.92(2)
C(1)–C(7)	1.494(4)	C(4)–H(42)	1.03(3)	C(7)–H(72)	0.98(3)
C(2)–C(3)	1.507(4)	C(5)–C(6)	1.509(4)	C(8)–H(8)	0.88(3)
C(2)–C(8)	1.324(3)	C(5)–H(51)	1.04(3)		
C(8)–S(1)–C(9)	96.9(1)	C(3)–C(4)–H(41)	103(2)	C(7)–C(6)–H(61)	112(2)
O(1)–C(1)–C(2)	118.6(2)	C(3)–C(4)–H(42)	106(1)	C(7)–C(6)–H(62)	111(2)
O(1)–C(1)–C(7)	121.4(2)	C(5)–C(4)–H(41)	114(2)	H(61)–C(6)–H(62)	100(2)
C(2)–C(1)–C(7)	120.0(3)	C(5)–C(4)–H(42)	106(1)	C(1)–C(7)–C(6)	112.6(2)
C(1)–C(2)–C(3)	120.2(2)	H(41)–C(4)–H(42)	112(2)	C(1)–C(7)–H(71)	105(2)
C(1)–C(2)–C(8)	118.6(2)	C(4)–C(5)–C(6)	115.6(2)	C(1)–C(7)–H(72)	101(2)
C(3)–C(2)–C(8)	121.2(3)	C(4)–C(5)–H(51)	109(2)	C(6)–C(7)–H(71)	110(2)
C(2)–C(3)–C(4)	114.9(2)	C(4)–C(5)–H(52)	108(2)	C(6)–C(7)–H(72)	115(2)
C(2)–C(3)–H(31)	107(2)	C(6)–C(5)–H(51)	109(2)	H(71)–C(7)–H(72)	112(2)
C(2)–C(3)–H(32)	106(2)	C(6)–C(5)–H(52)	107(2)	S(1)–C(8)–C(2)	124.9(3)
C(4)–C(3)–H(31)	109(2)	H(51)–C(5)–H(52)	109(2)	S(1)–C(8)–H(8)	112(2)
C(4)–C(3)–H(32)	112(2)	C(5)–C(6)–C(7)	114.7(2)	C(2)–C(8)–H(8)	123(2)
H(31)–C(3)–H(32)	108(2)	C(5)–C(6)–H(61)	109(2)	S(1)–C(9)–N(1)	175.7(2)
C(3)–C(4)–C(5)	114.9(3)	C(5)–C(6)–H(62)	108(2)		

Table 4. ^{13}C NMR chemical shifts for **1a–g** and **2c** in CDCl_3 ; ppm from internal TMS.

Comp.	C1	C2	C2'	SCN	Other carbon atoms ^a				
1a	203.9	138.1	131.4	114.4	43.0	33.4	30.7	29.4	24.5
1b	205.3	137.7	131.7	114.3	38.0	31.2	30.5	28.4	25.4
1c	204.4	138.4	133.0	114.7	35.3	30.0	28.4	25.4	25.2
					24.3	23.3	22.6		
2c	198.7	145.4	127.2	109.2	38.4	28.1	26.1	26.0	24.0
					24.0	23.9	23.7	23.0	22.3
1d	193.5	137.3	135.4	113.0	149.3	135.3	128.0	126.9	126.5
					124.4	32.0			
1e	193.4	141.6	126.6	113.1	154.7	136.3	135.7	128.3	125.1
					124.2	38.1	19.8		
1f	187.5	143.3 ^b	130.2	114.2	134.6	133.7 ^b	131.9 ^b		
					128.6	127.8	127.4	30.2	28.3
1g	197.7	139.3	132.0	114.2	137.3 ^b	136.3 ^b	133.0		
					129.2	128.4	127.1	30.6	29.5
					27.1				

^aNo further assignment. ^bOr reversed.

Table 5. Stereochemically relevant C,H coupling constants for **1a–g** and **2c**, in Hz.

Comp.	$^3J_{\text{C1-H2}'}$	$^3J_{\text{C2-H4}}$	$^3J_{\text{C2'-H2}'}$	$^3J_{\text{C2'-H3}}$	$^3J_{\text{C3-H2}'}$	$^3J_{\text{SCN-H2}'}$
1a	10.1	6.0	183.1	7.2	^a	7.1
1b	9.5	6.0	182.7	7.8	^a	7.5
1c	10.9	^b	182.0	7.7	^a	7.3
2c	5.9	6.0	184.9	6.2	^a	4.7
1d	7.6	–	187.7	2.7	^a	7.5
1e	9.3	4.8 ^c	184.4	2.9	3.6	7.4
1f	^a	–	178.3	5.7	^a	7.1
1g	–	–	183.7	7.6	^a	6.8

^aNot obtained owing to too many coupling constants.

^bNot obtained. ^c $^3J_{\text{C2-CH}_3}$.

^{13}C NMR spectra. The ^{13}C chemical shifts for the thiocyanates **1a–g** and **2c** are presented in Table 4. The $^1J_{\text{C2',H2}'}$ and vicinal C,H coupling constants for the sp^2 carbons C1, C2 and C2', the ring carbon C3 (sp^3) and the thiocyanato carbon (SCN) for these compounds are presented in Table 5. The assignment of the ^{13}C chemical shifts for the various carbon atoms of the thiocyanato compounds **1a–g** is based on their proton-coupled spectra, chemical shift analogies, relative intensities of the peaks and the C,H coupling constants. The compound **c**, which has the 12-membered carbon ring skeleton, is the only compound which occurs in its two stereoisomers, *Z* and *E* (1:2); compounds **1c** and **2c**, respectively. Their vicinal C1,H2' coupling constants can be used to assign both stereoisomers unequivocally, because it is known from earlier studies that $^3J_E < ^3J_Z$ (Table 5).¹⁸ Furthermore, the ^{13}C chemical shifts of the α , β -unsaturated carbonyl carbon (C1) and the carbon of the thiocyanato group (SCN) in compound **2c** are as expected for the *E* configuration.¹⁸

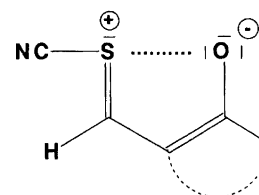


Fig. 4.

The thiocyanato carbon chemical shift has been found to be very insensitive to the adjacent carbon moiety in previously studied structures.¹⁹ The bond between C2 and C2' can be saturated or unsaturated and there can be substituents attached to C2 in *Z* or *E* to the SCN-group, and still the ^{13}C chemical shift of the thiocyanato group is between 109 and 111 ppm.^{19,20} In the thiocyanate **1c**, however, the ^{13}C chemical shifts for the C=O and SCN carbons changed dramatically owing to the steric proximity in the *Z* arrangement. The S...O 1,5-interaction deshields both of these carbons by more than 5 ppm owing to changes of the π -electron density (Fig. 4).

Within the *Z*-thiocyanato compounds **1a–g**, the carbon chemical shifts for the thiocyanato group vary very little, from 113.0 to 114.3 ppm, being almost independent of the ring size and the benzene ring. When the ^{13}C chemical shifts of the *exo*-methylene carbons (C2') are compared with compound **1a** and its non-substituted analogue **3** (Fig. 5),²¹ the following conclusions can be made. The SCN substituent, which usually has a slightly electron-withdrawing character,¹⁹ is strongly electron releasing in compound **1a**, obviously because of the intramolecular 1,5-interaction. This changes the ^{13}C chemical shifts in the SCN carbon and carbons C2 and C2' (α and β to the thiocyanato group). The chemical shifts of the C2 is moved strongly to higher field and that of C2' also strongly, but to the lower field.

LIS study. The *Z* configuration of the 2-thiocyanatomethyleneindanones (**1d** and **1e**) was confirmed by LIS (Lanthanide-Induced-Shift) studies using $\text{Eu}(\text{fod})_3$ as the reagent and CDCl_3 as the solvent. The chemical shift changes obtained for six $\text{Eu}(\text{fod})_3$ /substrate concentrations, were transformed into relative LIS parameters by linear regression for molar ratios of 0–0.7. As expected from the results of the X-ray crystallographic investigation and ^{13}C NMR spectroscopic studies, the *Z* stereoisomers display much better agreement between the theoretical and the experi-

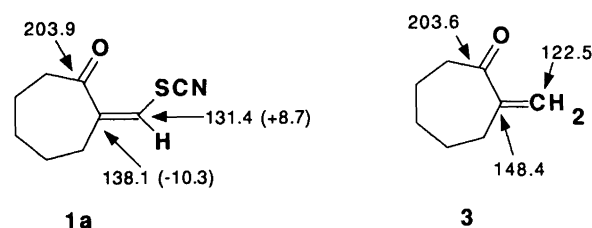


Fig. 5.

mental LIS values. Compounds **1d** and **1e**, both of *Z* configuration have agreement factors $R = 0.06$ and $R = 0.07$, respectively whereas the corresponding *E* isomers have values $R = 0.15$ (**2d**) and $R > 0.18$ (**2e**). This means that the probability of the compounds studied having a *Z* structure is over 87.5 % in the case of both **1d** and **1e**, which supports the results obtained using other techniques.

Discussion

The X-ray crystallographic and the quantitative LIS study verify the *Z* configuration for the 2-thiocyanatomethylene-cycloalkanones (**1a-g**) with a short intramolecular non-bonded S...O contact distance of 2.537(2) Å in **1a**. This 1,5-interaction has a marked influence on the ¹³C chemical shifts in these compounds which show characteristic variations for C-2, C-2' and the thiocyanato carbon situated close to the actual interaction site (S- and O-atoms).

The *Z* stereochemistry for the thiocyanates (**1**) can also be explained by the formation of these compounds via nucleophilic vinylic substitution (addition-elimination mechanism) of (*E*)-2-chloromethylenecycloalkanones^{22,23} with the ambident SCN anion. Correspondingly, (*Z*)-2-thiocyanatovinyl ketones (R¹=C₆H₅ and R²=H) are formed from the (*E*)-2-chlorovinyl compounds.²⁴ Nucleophilic substitution of (*E,Z*)-3-chloropropenals by means of the SCN anion is not stereospecific and results in (*Z,E*)-3-thiocyanatopropenals with increasing amounts of the *Z* isomers.^{25,26} Only (*Z*)-4-thiomethylene-2,2,5,5-tetraalkyltetrahydrofuran-3-one was obtained from the corresponding (*E*)-4-chloromethylene compounds.²⁷

The greater thermodynamic stability of the aliphatic thio compounds in which the carbonyl and thio groups are *cis* orientated has been described earlier.^{28,29} Investigations into the influence of non-bonded contacts between the partially negatively charged oxygen and partially positively charged sulfur on the configuration has been published for, e.g., (*Z*)-formylmethylenethiopyranones.³⁰

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