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Configurationally and Conformationally Homogeneous Cyclic *N*-Aryl Sulfimides. II.

^{13}C- and ^{1}H NMR Spectra

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The configuration and (in case of mobile ring systems) the preferred conformation in a series of thiane- and of *cis*- and *trans*-1-thiadecalin-1-*N*-4-chlorophenyl imides were assigned by means of ^{13}C- and ^{1}H nmr spectroscopy. ^{1}H nmr criteria known to be valid for determination of the stereochemistry of cyclic sulfoxides may be applied (with limitations) to cyclic *N*-aryl sulfimides, if both isomers (S—N bond equatorial and axial, respectively) are known. The assignments are easier, and unambiguous for single isomers, by comparison of ^{13}C nmr chemical shifts of ring carbon atoms of sulfimides and sulfides. The influence of equatorially and axially oriented sulfimide groups on the chemical shifts of neighbouring protons, and on the carbon atoms of the heterocyclic rings are discussed in detail.

Konfigurativ und konformationell einheitliche cyclische N-Aryl-sulfimide. II. ^{13}C- und ^{1}H-NMR-Spektroskopie

Die Konfiguration und (bei beweglichen Ringsystemen) die bevorzugte Konformation einer Reihe von Thian- und von *cis*- und *trans*-1-Thiadekalin-1-*N*-4-chlorophenylimiden wurde durch ^{13}C- und ^{1}H-NMR-Spektroskopie bestimmt. Bekannte ^{1}H-NMR-Kriterien zur Festlegung der Stereochemie cyclischer Sulfoxide sind (mit Einschränkungen) auch bei cyclischen *N*-Arylsulfimiden anwendbar, wenn beide Isomere (S—N-Bindung äquatorial bzw. axial) bekannt sind. Leichter, und auch bei Vorliegen von nur einem Isomeren eindeutig, gelingt die Zuordnung durch Vergleich der ^{13}C-NMR-Verschiebungen der Ringkohlenstoffatome von Sulfimiden und Sulfiden. Die Einflüsse äquatorial oder axial orientierter Sulfimidgruppen auf die chemischen Verschiebungen benachbarter Wasserstoffe und der Kohlenstoffe des Heterorings werden diskutiert.

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Introduction

In order to get information about the stereospecifity of rearrangements of *N*-aryl sulfimides (**1 d**)[1], a series of configurationally and conformationally homogeneous cyclic *N*-aryl sulfimides were prepared. Synthetic procedures and considerations about the reaction mechanism are reported in a preceding paper[2]. To assign the configurations on sulfur we examined the ^{13}C- and ^{1}H nmr spectra of these compounds.

^{1}H nmr spectroscopy has been shown to be a useful technique to define the configuration of the sulfoxide bond in cyclic sulfoxides (**2**); the observed effects of the sulfoxide group on the ^{1}H chemical shifts and coupling constants depending on the steric orientation of the S—O bond have recently been summarized[3,4]. ^{13}C nmr spectroscopy has been used in a number of investigations to determine the stereochemistry of cyclic sulfoxides[5–10]. Analogous investigations on sulfimides are few, with the exception of studies, by *Lambert et al.*[11], of the conformational behaviour of cyclic *N*-arylsulfonyl- and *N*-acylsulfimides (**1 a, 1 c**).

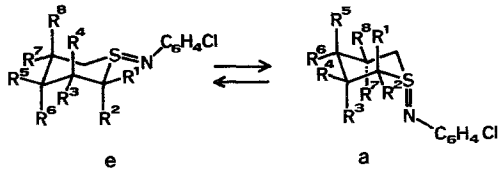
From the available data the double bond character of the S—X bond in **1 d** ($X = N$; 45-58%[12]) has to be placed between that of N-tosyl sulfimides **1 a** ($X = N$; 45%[13]) and that of dimethyl sulfoxide ($X = O$; 65.5%[12]). Hence one may conclude that the introduction of an *N*-aryl imide moiety will have effects comparable to **1 a** and **2** on the protons of a thiane ring, especially on the protons bound to carbon atoms next to sulfur (α-hydrogens), anisotropy effects of the phenyl ring in a preferentially transoid orientation hopefully being negligible.

^{13}C nmr spectra of cyclic sulfimides proved far more useful than proton spectra for identification of configurational and conformational isomers, the chemical shifts being very sensitive to steric factors, and the spectra being easier to interpret. The reasonable expectation that the shift effects caused by equatorial and axial *N*-aryl imide groups should be similar to the ones observed for other six-membered cyclic systems, especially the thiane-1-oxides, was confirmed. A communication reporting some of the results described in the sequel has been published[14].

The formulas of the compounds investigated are collected in Schemes 1 (thiane-), 2 (*trans*-1-thiadecalin-) and 3 (*cis*-1-thiadecalin-1-*N*-4-chlorophenyl-imides). Most of the compounds investigated proved to be largely or completely conformationally homogeneous, due to the presence of biasing substituents (in the thiane-1-imide series), the rigidity of the ring system (in the *trans*-1-thiadecalin-1-imides series) or severe *syn*-axial interactions in one of the conformers (in the *cis*-1-thiadecalin-1-imide series). For the rest of compounds which represent conformationally mobile systems (**3**, **4**, and **25** β) the *N*-aryl imide

function on sulfur leads to a preference of conformations **3e**, **4e**, and **25βA** with S—N equatorial[14,15] (see Schemes 1 and 3; for discussion see[2]).

Scheme 1

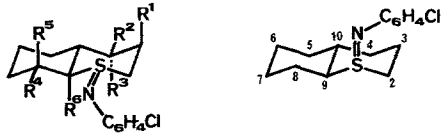


e a

All *R*'s = H, unless noted

3	all *R*'s = H	**9**	$R^3 = R^7 = CH_3$
4	$R^5 = R^6 = CH_3$	**10**	$R^4 = R^8 = CH_3$
5	$R^5 = CH_3$	**11**	$R^3 = R^8 = CH_3$
6	$R^6 = CH_3$	**12**	$R^1 = R^2 = R^5 = CH_3$
7	$R^5 = tert\text{-}C_4H_9$	**14**	$R^1 = R^5 = R^6 = CH_3$
8	$R^6 = tert\text{-}C_4H_9$	**16**	$R^3 = R^4 = R^7 = CH_3$

Scheme 2



18α – 24α **18β**

All *R*'s = H, unless noted

18α	all *R*'s = H	**19α**	$R^1 = CH_3$ (3β-CH_3)
20α	$R^2 = CH_3$ (4β-CH_3)	**21α**	$R^3 = CH_3$ (4α-CH_3)
22α	$R^4 = CH_3$ (8α-CH_3)	**23α**	$R^5 = CH_3$ (8β-CH_3)

24α $R^6 = CH_3$ (9-CH_3)

Additionally, the spectra of some cyclic *N*-acyl sulfimides of the general type **35** are included, since they were formed as by-products of the syntheses of the *N*-4-chlorophenyl sulfimides and their configuration was relevant for the elucidation of the reaction mechanism.

^{13}C NMR Spectra

Assignment of the observed signals to the carbon atoms of the compounds in Schemes 1–3 was accomplished by the following criteria: a) differences in the chemical shifts of the aromatic (> 100 ppm from

Table 1. ^{13}C *Chemical shifts*[a] *of cyclic N-p-chlorophenyl sulfimides*

Compounds	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-CH_3
a) Thiane-1-imides[b]										
3[c]	46.80	21.87	24.55	21.87	46.80	—	—	—	—	—
3e[c,d]	47.93	24.08	24.08	24.08	47.93	—	—	—	—	—
3a[c,d]	40.92	16.53	24.08	16.53	40.92	—	—	—	—	—
4[c]	42.13	33.51	29.08	33.51	42.13	—	—	—	—	27.25, 28.50
4e[c,e]	43.30	35.92	29.01	35.92	43.30	—	—	—	—	23.32 (CH_3-4a)
										31.80 (CH_3-4e)
4a[c,e]	37.34	28.34	29.01	28.34	37.34	—	—	—	—	23.03 (CH_3-4a)
										32.46 (CH_3-4e)
5	48.05	31.90	30.92	31.90	48.05	—	—	—	—	21.44
6	42.18	25.27	29.96	25.27	42.18	—	—	—	—	21.33
6[c,f]	41.22	24.57	30.91	24.57	41.22	—	—	—	—	22.83
7	48.70	25.39	46.26	25.39	48.70	—	—	—	—	27.43 [C($\mathbf{C}H_3$)$_3$]
										32.55 [$\mathbf{C}$(CH_3)$_3$]
8	42.73	17.63	46.85	17.63	42.73	—	—	—	—	27.18 [C($\mathbf{C}H_3$)$_3$]
										32.94 [$\mathbf{C}$(CH_3)$_3$]
9	54.28	30.05	41.67	30.05	54.28	—	—	—	—	21.90
10	47.49	23.00	42.14	23.00	47.49	—	—	—	—	22.01
11	55.19	25.49	38.43	28.66	53.57	—	—	—	—	18.80 (CH_3-5a)
										22.05 (CH_3-3e)
12[h]	55.70	46.50	26.56	32.50	42.33	—	—	—	—	16.14 (CH_3-2a)
										21.76 (CH_3-4e)
										28.12 (CH_3-2e)
14[i]	53.34	45.56	30.37	36.74	44.37	—	—	—	—	17.26 (CH_3-2e)
										24.17 (CH_3-4a)
										32.00 (CH_3-4e)
16	59.18	33.62	46.33	26.74	54.81	—	—	—	—	22.09 (CH_3-5e)
										25.58 (CH_3-3a)
										32.16 (CH_3-3e)

18 α	48.55	22.94	32.37	33.34	(25.54)	(25.28)	27.62	66.55	40.03	—
18 β[k]	43.67	16.49	32.66	34.07	(25.86)	(25.24)	28.11	59.46	31.75	—
19 α	54.73	28.70	38.24	33.56	(25.64)	(25.42)	27.70	67.50	34.68	18.89
20 α	47.55	31.96	36.57	30.52	25.36	25.36	27.87	66.01	45.79	18.93
21 α	42.12	(30.29)	(30.84)	(30.84)	25.58	25.58	28.42	59.25	42.96	12.47
22 α[l]	50.47	23.35	32.93	34.42	25.19	37.25	37.04	71.84	40.89	21.21
23 α[m]	48.94	22.86	(33.39)	(34.54)	19.48	(32.67)	26.35	70.28	34.66	13.59
24 α[n]	42.26	23.69	26.86	29.20	25.94	21.57	36.66	61.34	43.68	7.99
c) *cis*-1-Thiadecalin-1-imides[o, q]										
25 α	39.80	(23.36)	(23.07)	32.56	20.78	25.95	16.34	54.37	35.38	—
25 β	47.79	19.70	30.34	25.61	27.97	21.81	25.61	63.25	37.44	—
25 β[g]	48.04	19.82	30.60	(25.53)	26.97	21.16	(25.79)	63.84	38.05	—
26 α	46.34	30.14	(32.39)	(32.49)	20.70	25.98	16.13	53.15	34.57	22.15
27 β	55.45	26.29	40.06	26.53	28.16	21.28	25.53	63.21	38.36	22.06
28 β	48.88	20.01	30.89	36.11	32.88	29.90	25.79	63.63	38.45	22.45
29 β[p]	50.77	20.02	31.14	(26.50)	(27.07)	30.84	38.36	68.56	40.24	20.67
30 β	48.09	19.11	39.97	31.65	21.06	(21.06)	(21.45)	69.08	36.78	27.36

[a] In ppm from internal $(CH_3)_4Si$ in $CDCl_3$ at ambient temperature unless indicated. Parentheses indicate that assignments are not unambiguous.

[b] Aromatic ring carbons (unless indicated): C-1′ 153.91-154.17 (S—N equatorial), 154.57-155.54 (S—N axial or important contribution of the conformer with S—N axial); C-2′, 6′ 118.90-119.23; C-3′, 5′ 128.67-128.92; C-4′ 120.81-121.14 (S—N equatorial), 120.12-120.64 (S—N axial).

[c] Solvent: CH_2Cl_2 + 20% CD_3COCD_3.

[d] —90°. [e] —80°. [f] —85°. [g] —69°.

[h] C-1′ 156.07, C-2′, 6′ 119.44, C-3′, 5′ 128.52, C-4′ 120.47.

[i] C-1′ 155.42.

[j] Aromatic ring carbons (unless indicated): C-1′ 155.72-155.86, C-2′, 6′ 118.83-118.93, C-3′, 5′ 128.42-128.78, C-4′ 120.23-120.53.

[k] C-1′ 156.50, C-2′, 6′ 119.84.

[l] C-1′ 154.46, C-2′, 6′ 119.29.

[m] C-2′, 6′ 119.33.

[n] C-2′, 6′ 119.50.

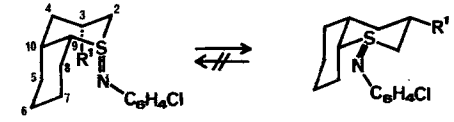
[o] Aromatic ring carbons (unless indicated): C-1′ 155.65-156.11 (**A** forms), 154.62-154.65 (**B** forms), C-2′, 6′ 118.85-118.93 (**A**), 119.01-119.03 (**B**), C-3′, 5′ 128.61-128.75, C-4′ 120.33-120.57.

[p] C-1′ 154.62, C-2′, 6′ 119.29, C-4′ 120.09.

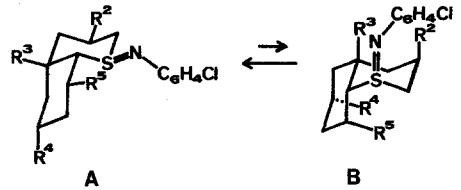
[q] "β": the substituent is on the same side of the ring as the hydrogen (or substituent) on C-10 of the 1-thiadecalin; "α": on the opposite ringside to this hydrogen (or substituent); see Schemes 2 and 3.

Me_4Si) and heterocyclic (< 100 ppm from Me_4Si) carbon atoms, b) multiplicities of signals in the off-resonance decoupled spectra, c) comparison with the spectra of the parent sulfides[16–18], d) comparison of the spectra of the thiane, *trans*-1-thiadecalin and *cis*-1-thiadecalin sulfimide series, and e) use of additive substituent effects for methyl substitution[19,20]. ^{13}C shifts determined in this way are collected in Table 1; signals occuring too close together for accurate assignment by one of the procedures listed above are parenthesized.

Scheme 3



25α, 26α

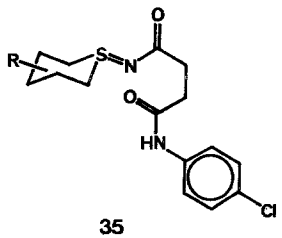


25β, 27β – 30β

All R's = H, unless noted

25 α, **25** β	all R's = H	**26** α	$R^1 = CH_3$ (3α-CH_3)
27 β	$R^2 = CH_3$ (3β-CH_3)	**28** β	$R^4 = CH_3$ (6α-CH_3)
29 β	$R^5 = CH_3$ (8α-CH_3)	**30** β	$R^3 = CH_3$ (10-CH_3)

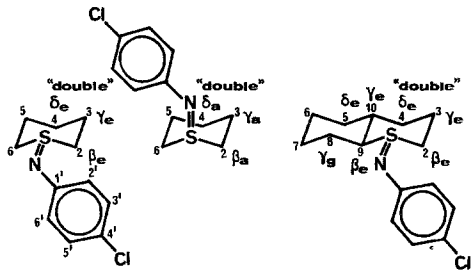
Introduction of an axial or equatorial *N*-aryl imide group on sulfur leads to sizeable changes in chemical shifts of the carbon atoms of the heterocyclic ring. The observed effects are very similar both in direction (shielding or deshielding) and in order or magnitude to the ones reported



35

for the corresponding sulfoxides[5,10]. The resulting parameters can be described as β_e, γ_e, β_a, γ_a etc. (Scheme 4), in analogy to effects observed with methylcyclohexanes; in case of 2-substituted thianes (e.g. thiadecalins), additional parameters have to be calculated to allow for the various steric effects of 1,2-disubstitution[19]. In case of the methylcyclohexanes these additional parameters still gave a manageable number of values for the estimation of the chemical shift of a certain carbon atom[19,20]; the large number of different situations for instance in thiadecalin-1-*N*-aryl imides necessitates an excessive number of additional parameters. It seems more reasonable to tabulate the observed shift differences $\delta_{sulfimide}$-$\delta_{sulfide}$ (Table 2) and to discuss the effects in a general way.

Scheme 4



Comparison between sulfimides without methyl substituents **3e, 3a, 18**α, **18**β, **25**α, and **25**β with the methyl derivatives allows the calculation of parameters for methyl substitution. The results are in close similarity to those obtained with methylcyclohexanes[19], methyldecalins[19], methyldecahydroquinolines[21] and with the parent thianes [17,18] and thiadecalins[16b]; thus a tabulation was not considered necessary.

β-*Effects*

Carbon atoms next to sulfur (α-carbons, but β to the substituent) are strongly deshielded by the *N*-aryl imide group. As in the case of the sulfoxides ($\beta_e \sim +22$ ppm, $\beta_a \sim +17$ ppm)[5,10,14] the deshielding effect of an equatorial substituent ($\beta_e \sim +19$ ppm) is larger than that of an axial one ($\beta_a \sim +12.5$ ppm). These values apply to all thiane sulfimides without substituents at C-2.

The situation is more complex in case of **12**, **14** and of all the thiadecalin sulfimides with an equatorial *N*-aryl imide group. C-2 (or C-9) now is substituted with either an equatorial (**14**, **18**α-**23**α, **25**β-**30**β) or an axial (**25**α, **26**α) methyl or methylene group, or both

Table 2. *Effects*[a] *of imide substitution*[b] *on* ^{13}C *chemical shifts in cyclic sulfides*

Compounds	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-CH_3
a) Thiane-1-imides										
3e[c]	+ 18.87	—5.89	—2.37	—5.89	+ 18.87	—	—	—	—	—
3a[c]	+ 11.86	—11.23	—2.37	—11.23	+ 11.86	—	—	—	—	—
5	+ 19.25	—4.11	—1.39	—4.11	+ 19.25	—	—	—	—	—1.57
6	+ 13.38	—10.74	—2.35	—10.74	+ 13.38	—	—	—	—	—1.68
6a[c]	+ 12.42	—11.44	—1.40	—11.44	+ 12.42	—	—	—	—	—0.18
7	+ 18.91	—3.67	—1.76	—3.67	+ 18.91	—	—	—	—	+ 0.10 (CH_3), —0,27 (q)
8	+ 12.94	—11.43	—1.17	—11.43	+ 12.94	—	—	—	—	—0.15 (CH_3), + 0.12 (q)
9	+ 19.04	—4.27	—2.33	—4.27	+ 19.04	—	—	—	—	—1.10
10	+ 12.25	—11.32	—1.86	—11.32	+ 12.25	—	—	—	—	—0.99
11[d]	+ 19.42	—1.31	—1.71	+ 0.69	+ 19.44	—	—	—	—	+ 1.58 (CH_3-5a) —1.38 (CH_3-3e)
12	+ 15.38	—3.84	—1.52	—3.08	+ 15.86	—	—	—	—	—11.18 (CH_3-2a) —3.99 (CH_3-2e) —1.46 (CH_3-4e)
14	+ 20.69	—3.92	—0.19	—2.40	+ 19.06	—	—	—	—	—4.65 (CH_3-2e) —1.46 (CH_3-4e) + 0.42 (CH_3-4a)
16	+ 18.76	+ 2.42	—2.08	—2.71	+ 19.22	—	—	—	—	—0.49 (CH_3-3e) + 1.30 (CH_3-3a) —0.98 (CH_3-5e)

b) *trans*-1-Thiadecalin-1-imides

18 α	+ 18.51	—5.29	—2.03	—1.22	—0.80	—1.48	—4.96	+ 19.54	—4.24	—
18 β	+ 13.63	—11.74	—1.74	—0.49	—1.10	—0.90	—4.47	+ 12.45	—12.52	—
19 α	+ 18.52	+ 0.60	—2.03	—1.20	—1.19	—1.03	—4.73	+ 19.85	—3.04	+ 1.52
20 α	+ 18.27	—5.42	—1.15	+ 0.31	—1.21	—1.21	—4.88	+ 19.57	—4.60	—1.17
21 α	+ 19.02	—5.01	—1.60	—1.15	—1.15	—1.15	—4.81	+ 20.75	—4.24	+ 0.15
22 α	+ 20.51	—4.75	—1.73	—0.45	—0.51	+ 1.06	—0.19	+ 17.20	—3.14	+ 0.85
23 α	+ 18.85	—5.33	—1.86	—0.62	—0.66	—1.10	—6.08	+ 18.87	—2.05	—0.22
24 α	+ 15.80	—5.16	—2.27	—1.47	—0.94	—0.58	—3.80	+ 17.38	—3.69	—10.20

c) *cis*-1-Thiadecalin-1-imides

25 α (**B**)[e]	+ 16.21	—4.92	—1.85	—1.66	+ 1.17	—2.33	—11.00	+ 13.96	—1.37	—
25 β (**A**)[e]	+ 18.12	—1.28	—1.90	+ 2.57	—0.90	+ 0.28	—6.33	+ 20.73	+ 2.04	—
26 α (**B**)	+ 15.64	—4.71	—1.89	—1.97	+ 0.77	—2.58	—11.37	+ 13.14	—3.24	—0.95
27 β (**A**)	+ 18.85	—0.19	—1.34	+ 3.02	—0.43	+ 0.45	—5.71	+ 20.54	+ 1.21	—0.79
28 β (**A**)	+ 18.81	—1.41	—1.87	+ 2.50	—0.68	+ 0.22	—6.30	+ 21.02	+ 1.92	—0.23
29 β (**A**)	+ 21.24	—2.26	—1.89	+ 2.75	—0.29	+ 1.75	+ 0.22	+ 17.81	+ 2.74	+ 0.64
30 β (**A**)[e]	+ 18.06	—4.23	—1.38	+ 3.37	—0.81	+ 0.51	—5.56	+ 22.03	+ 4.08	+ 0.04

[a] $\delta_{\text{Sulfimide}}-\delta_{\text{Sulfide}}$ in ppm; a plus sign indicates that the signal is more downfield in the sulfimide. Chemical shifts have been measured at room temperature in $CDCl_3$ unless indicated. Thiane values from[18], 1-thiadecalin values from[16b].

[b] 1-*N*-*p*-chlorophenyl.

[c] Sulfimide at low temperature (see Table 1) in CH_2Cl_2 + 20% CD_3COCD_3; sulfide at room temperature in $CDCl_3$.

[d] Sulfimide at room temperature in $CDCl_3$; sulfide at —95° in CH_2Cl_2 + 20% CD_3COCD_3.

[e] Sulfimide at room temperature in $CDCl_3$; sulfide at —68° in $CDCl_3$.

(**12**, **24** α). Equatorial substitution of C-2 (or C-9) does not lead to significant changes of the β_e-effect on either carbon atom adjacent to sulfur. Axial substitution, on the other hand, leads to a palpable reduction in deshielding, both for the substituted C-atom (C-2 or C-9) and for the second carbon atom adjacent to sulfur (C-6 or C-2), by about 3-4 ppm. This reduction finds an analogy in the $\alpha_a\beta_e$- and $\beta_e\gamma_a$-effects observed in 1,2-disubstituted methylcyclohexanes[19], and results from the steric constraint of the two *gauche* substituents. Another remarkable deviation from an "undisturbed" β_e-effect, also due to sterical strain, is observed in the cases of **22** α and **29** β. Here the *syn*-axial* interaction between the equatorial methyl group at C-8 and the equatorial sulfimide nitrogen gives rise to a deformation of the molecule which is visible in nearly all ring positions; β_e-effects are reduced to + 17.2 and + 17.8 ppm for C-9 and enlarged to + 20.5 and + 21.2 ppm for C-2.

Of the five compounds with axial S—N bond available **8** and **10** embody an "undisturbed" β_a-effect. The value derived from **3** α suffers from a temperature effect (sulfimide spectrum recorded at —90°, sulfide at + 30°), which amounts to an upfield shift of 0.6 to 0.9 ppm for lowering the probe temperature by ~ 100°. The β_a effect of + 13.4 in case of **6** indicates a sizeable contribution of conformation **6e**[15b]; the 4-methyl group is insufficient as a holding group (note also the reduced γ_a-effect of —10.7 compared to the normal ~ —11.5 ppm). Finally, in the case of **18** β, the differences of β_a for C-2 and C-9 again correspond to analogous situations in the methylcyclohexane series[19]: a downfield shifting $\beta_a\gamma_e$-effect must be included for C-2 and an upfield shifting $\alpha_e\beta_a$-effect for C-9.

γ-*Effects*

The influence of an *N*-aryl imide group on sulfur at the carbon atoms two bonds away (β-carbons, but γ to the substituent; cf. Scheme 4) depends very much on the sterical orientation. Both equatorial and axial *N*-aryl imide substituents have a shielding effect; but while the equatorial imide produces but a moderate upfield shift (γ_e ~ —4 ppm), the axial group is very strongly shielding (γ_a ~ —11.5 ppm). These differences, in complete agreement with observations made in other carbocyclic[19] and heterocyclic[5, 16, 18, 21] systems are the most important proof for the configurational and conformational situation in the compounds investigated; the correctness of the conclusions has meanwhile been confirmed by X-ray analysis of selected compounds[22].

In the thiadecalin series C-3 and C-10 are affected differently by the equatorial substituent on sulfur. C-3 of the *trans*-1-thiadecalin

* Methyl group and sulfimide nitrogen in these compounds are not really *syn*-axial, but the interaction is of comparable size and subsequently termed so.

sulfimides is shifted by ~ -5.3 ppm, C-10 by ~ -4.2 ppm; this difference is due to the causes discussed earlier. Major deviations from these values are observed for **22** α, and for **23** α and **24** α at C-10, also for reasons of strain. More interesting is **19** α: here C-3 is shifted not to higher, but to slightly lower field (+ 0.6 ppm), and the influence on C-10 is diminished (−3 ppm). A similar effect is observed for the axially methyl substituted C-5 in **11** (+ 0.69 ppm). The reason for this reversal of shielding to deshielding is uncertain; a similar change has been observed upon (equatorial) *N*-methylation of 3β-CH_3-*trans*-decahydroquinoline[21a] in contrast to other *trans*-decahydroquinolines.

cis-1-Thiadecalin sulfimides in conformation **B** (Scheme 4, **25** α, **26** α) also display shielding for C-3 (~ -4.8 ppm) and C-10 (−1.4 and −3.2 ppm). The compounds of conformation **A** are different: as in **19** α and **11** they are axially substituted at one of the β-carbons (C-10), and so the other one is only slightly shielded (C-3: between 1 and 2 ppm; an exception is the equatorially methyl substituted C-3 in **27** β), whereas C-10 is deshielded by roughly the same amount. One likely reason for this unusual behaviour is a reduction in puckering of this part (C-3, C-4, C-10) of the thiane ring compared to the parent sulfide upon introduction of the sulfimide functionality, and thus a lesser steric compression. Notable differences arise from additional steric strain as in **29** β, already discussed, and in 10-methyl-*cis*-1-thiadecalin-1β-sulfimide (**30** β). In this case the quarternary C-10 leads to an exceptional situation already in the parent sulfide; the chemical shifts of the sulfimide **30** β are not very different from the ones estimated with the aid of methyl substitution parameters[19].

Additional C-atoms (besides the ring carbon atoms 3 and 5, or 3 and 10 in the thiadecalin series) may be in a γ-position to the *N*-aryl imide group: C-8 in the thiadecalin series, and the methyl carbons at C-2 in **12** and **14**, and at C-9 in **24** α. The differences in the effects of the equatorial *N*-aryl imide groups on these carbon atoms, depending on their axial or equatorial position on the thiane ring, are as pronounced as the one between γ_a- and γ_e-effects. Equatorial carbon atoms (C-8 in **18** α–**21** α, **25** β, **27** β, **28** β, or CH_3-2_e in **12** and **14**) are shifted upfield by −6.3 ppm, at most; an axial carbon (CH_3-2 a in **14**, CH_3-9 in **24** α and C-8 in **25** α, **26** α) is shifted upfield by −10 to −11 ppm. Only part of this difference can be rationalized by a "buttressing" effect as observed in the carbocyclic series[19b]. In both cases the carbon atoms affected are oriented *gauche* to the nitrogen, but the equatorial carbons are positioned *gauche*, whereas the axial carbons are *anti-periplanar*, to the lone pair on sulfur. *Anti-periplanar* orientation of the carbon atom under consideration and the lone pair is the situation in the γ_a-effect, *gauche* orientation is the case for γ_e. Thus, although the affected C-8 in

18β is *gauche* to the upfield shifting nitrogen, a small γ-effect (—4.5 ppm) is observed: C-8 has *gauche* orientation to the lone pair. Only when the affected carbon is *gauche* both to the sulfimide nitrogen and to an α-carbon on sulfur (and *anti-periplanar* to the lone pair) is an exceptional upfield shift observed. Similar effects have been reported in the decahydroquinoline series[21a, b].

δ-*Effects*

δ-Effects in thiane- and thiadecalin-1-imides are generally upfield shifting, by about the same amount for axial and equatorial *N*-aryl imide groups. The effect is larger when transmitted two ways ("double δ"; e.g. C-4 in thiane- and thiadecalin-1-imides) than one way (e.g. C-5 in *trans*-1-thiadecalin-1-imides, CH_3 in **9**, **10**). An exception are axial substituents at C-3 (CH_3 in **16**) or C-5 (CH_3 in **11**) or at C-3, C-10 and C-8 in the thiadecalin series (CH_3 in **19**α, **22**α; C-5 and C-7 in **25**β-**30**β) which are deshielded. Recently it has been pointed out that δ-effects in methylcyclohexanes vary depending on the position of the causative and affected atom[20].

Carbon atoms more remote (> δ; e.g. C-6 in the thiadecalin series) are also significantly shifted by the *N*-aryl imide group. On the basis of the available information it is not clear if this shift reflects changes in molecular geometry, or an inductive effect of the sulfimide group, or both.

Aryl-C *Atoms*

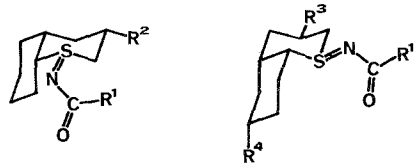
The carbon atoms of the aromatic nucleus show chemical shifts that vary in a very narrow range. The axial or equatorial substitution of the heterocycle is reflected only by the N-substituted carbon (C-1'), by shift differences of 0.86 ppm, at most. Effects are more pronounced if the thiane ring is substituted at C-2, or in the 8-CH_3 substituted thiadecalin sulfimides **22**α and **29**β; in these cases the aryl ring apparently is prevented from assuming its otherwise most preferred position.

N-Acyl Sulfimides (Succinimidyl Ring Opened Products **35**)[2]

^{13}C spectra of the ring-opened products **35** are characterized by the two signals at 183 to 184.5 ppm and 171.7 to 172.0 ppm from TMS, corresponding to the two carbonyl carbons; by a more pronounced shielding of C-1' (137.8 ppm instead of ~ 155 ppm in the *N*-aryl sulfimides); by a noticeably smaller deshielding of the α-carbons in the heteroring (i.e. smaller β_e-effect, + 10 to + 16 ppm); and by two additional signals at 32.5 to 34.8 ppm, corresponding to the two methylene carbons of the opened succinimide ring. Shift effects are

otherwise similar to those observed for the matching *N*-aryl sulfimides (Table 2). Assignment of configuration α and conformation **B** to the product obtained from *cis*-1-thiadecalin (**37** α **B**) is based on a comparison of the shift data of **37** α **B** with those of ring-opened products and of *N*-benzoyl sulfimides[23] derived from conformationally homogeneous *cis*-1-thiadecalins (e.g. 3α-CH_3-*cis*-1-thiadecalin, 3β-CH_3-*cis*-1-thiadecalin and 6α-CH_3-*cis*-1-thiadecalin; cf. Scheme 5). A comparison of the chemical shifts of the two types of *N*-acyl sulfimides is permissible, as shown by a comparison of **37** α **B** with **38** α[23]; the maximum deviation between corresponding ring carbons is 0.66 ppm. **37** α is locked in conformation **B** because of *syn*-axial interactions of the nitrogen on sulfur with C-5 and C-7 upon ring inversion (cf. corresponding conformations in Scheme 3). The ring-opened product derived from thiane (**35**, R = H), on the other hand, is conformationally mobile. The ^{13}C shifts measured at room temperature indicate a considerable proportion of the conformation with axial S—N bond, in agreement with results from experiments with other thiane-1-*N*-acyl imides[15].

Scheme 5



37α**B**, **38**α **39**β

37 α **B**:	R^1 = $(CH_2)_2$-CO-NH-C_6H_4Cl, R^2 = H
3α-CH_3-**37** α **B**:	R^1 = $(CH_2)_2$-CO-NH-C_6H_4Cl, R^2 = CH_3
38 α[23]:	R^1 = C_6H_5, R^2 = H
3β-CH_3-**39** β[23]:	R^1 = C_6H_5, R^3 = CH_3, R^4 = H
6α-CH_3-**39** β[23]:	R^1 = C_6H_5, R^3 = H, R^4 = CH_3

^1H NMR Spectra

α-*Hydrogens*

The equatorial proton at the α-carbon, H-2 e, resonates at lower field than the axial proton, H-2 a, in thiane sulfimides with an equatorial or with an axial S—N bond (Scheme 6, **e** and **a**: see Table 3). The chemical shifts of these protons, $\delta_{H\text{-}2e}$ and $\delta_{H\text{-}2a}$, are strongly dependent on the other substituents on the thiane ring and therefore provide no satisfactory criteria for the configurational and conformational properties of the compounds. The difference in chemical shifts of these protons, $\Delta\delta H\alpha = \delta_{H\text{-}2e} - \delta_{H\text{-}2a}$, on the other hand, was found to be in

Table 3. *Pertinent* ^{1}H *nmr chemical shifts of cyclic N-aryl sulfimides*[a]

Compounds	H-2e	H-6e	H-2a	H-6a	Others
a) Thiane-1-*N*-*p*-chlorophenyl-imides					
3[b]	3.07		2.67 (d, 12, of d, 13)		
4[b]	2.85		2.85		1.89 (d, 14.5, of t, 5; H-3, 5e), 1.58 (m, H-3, 5a), 1.03 (s, CH_3-4), 0.97 (s, CH_3-4)
5	3.16 (d, 12)		2.68 (dd, 12 13)		2.01 (m, H-3, 5e), 0.92 (d, 6; CH_3-4e)
6[b]	2.87		2.66		2.18 (d, 14, of t, 10.5, of d, 3; H-3, 5a), 1.68 (m, H-3, 5e), 1.02 (d, 6.5; CH_3-4)
7	3.27 (d, 12)		2.70 (dd, 12 13)		2.17 (d, ~ 14; H-3, 5e), 1.57 (dt, 11-14; H-3, 5a), 1.19 (t, 11.5; H-4a), 0.91 (s, C_4H_9)
8	2.96 (d,12)		2.61 (dd, 12 13)		2.32 (dt, 12-13; H-3, 5a), 1.76 (d, 13; H-3, 5e), 0.91 (s, C_4H_9)
9	3.12 (d, 12)		2.30 (dd, 12 13)		1.86 (m, H-3, 5a), 1.72 (d, 13.5; H-4e), 1.03 (d, 6; CH_3-3, 5e), 0.77 (m, H-4a)
10	2.70 (d, 12)		2.02 (dd, 12-13)		~ 2.65 (m, H-3, 5a), 1.74 (d, 14; H-4e), 0.95 (d, 6; CH_3-3, 5e)
11	3.10		2.74 (d, 12, of d, 3)	2.35 (dd, 12)	1.58 (d, 13; H-4e), 1.21 (d, 7; CH_3-5a), 1.05 (d, 6; CH_3-3e)
12		2.76		2.96 (dd, 13, of d, 3)	1.36 (s, CH_3-2), 1.20 (s, CH_3-2), 0.91 (d, 6; CH_3-4)
14		3.0	2.97		1.27 (d, 7; CH_3-2),

			1.15 (s, CH_3-3), 1.09 (s, CH_3-3), 1.06 (d, 6; CH_3-5)

b) *trans*-1-Thiadecalin-1-*N*-*p*-chlorophenyl-imides

18 α	3.13 (d, 12)	2.74 (dd, 12, of d. 3.5)	—
18 β	2.75	2.60	—
19 α	3.00	3.00	1.25 (d, 7; CH_3-3)
20 α	3.12 (d, 12, of dd, 3.5)	2.86 (dd, 12, of d, 3)	0.96 (d, 5; CH_3-4e)
21 α	2.95 (?)	3.1 (?)	1.03 (d, 7; CH_3-4a)
22 α	3.05	2.92 (dd, ~ 12, of d, 4)	2.45 (dd, 10; H-9), 1.05 (d, 6; CH_3-8c)
23 α	3.20 (d, 12)	?	1.03 (d, 7; CH_3-8a)
24 α	2.83 (?)	3.00 (?)	1.39 (s, CH_3-9)

c) *cis*-1-Thiadecalin-1-*N*-*p*-chlorophenyl-imides

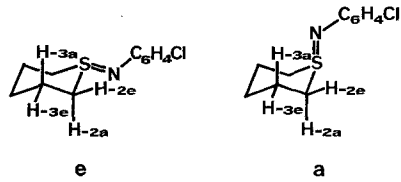
25 α	~ 2.85	~ 2.85	3.16 (d. 12: H-9)
25 β	3.16	2.67	~ 3.15 (H-9)
26 α	2.82 (d, 12, of d, 4.5)	2.71 (dd, 12)	3.17 (d, 12.5, of dd, 3.5; H-9), 1.09 (d, 6; CH_3-3)
27 β	3.10 (d, 12)	2.41 (dd, 12)	2.93 (H-9), 1.01 (d, 6; CH_3-3)
28 β	3.23 (d, 12, of dd, 3.5)	2.69	3.02 (H-9), 0.99 (d, 5; CH_3-6)
29 β	3.14	2.80	3.14 (H-9), 1.06 (d, 7; CH_3-8)
30 β	3.18 (d, 12, of dd, 3)	2.67	2.73 (H-9), 1.14 (s, CH_3-10)

[a] δ-values in ppm from $(CH_3)_4Si$ at 100 MHz, solvent $CDCl_3$. Since most signals are incompletely resolved multiplets, the reported values are centers of signals in the spectra. Only clearly recognizable coupling patterns are reported, and only apparent coupling constants (in Hz) are given; dd, 12, indicates a doublet of doublets with nearly identical coupling constants resulting in a degenerate triplet of (usually multiplet) signals. AA'BB' system of the aromatic protons for all compounds at 6.7—7.1 ppm.

[b] Averaged spectrum, owing to rapid ring inversion at ambient temperatures. All other thiane-imides are conformationally nearly or completely homogeneous due to biasing substituents at the heteroring.

accord with observations made with thiane sulfoxides[3, 4] when both equatorial and axial sulfimides could be isolated: $\Delta\delta$ Hα is larger for the "equatorial" than for the "axial" sulfimide. Thus $\Delta\delta$ Hα is 0.48, 0.57, 0.82 and 0.39 ppm for **5, 7, 9** and **18**α, respectively, but 0.21, 0.35, 0.68 and $\sim$ 0.15 ppm for **6, 8, 10** and **18**β.

Scheme 6



The low temperature ^{1}H nmr spectrum of the thiane sulfimide without additional substituent on the thiane ring, **3**, shows the α-protons of the predominant conformer[14] with equatorial S—N (Scheme 6, **e**) at 3.2 (H-2e) and 2.6 ppm (H-2a), and the α-protons of the minor conformer with axial S—N (Scheme 6, **a**) at 2.9 (H-2e) and 2.6 ppm (H-2a): as before, $\Delta\delta$ Hα**e** is noticeably larger than $\Delta\delta$ Hα**a**.

While the criterion $\Delta\delta$ Hα**e** > $\Delta\delta$ Hα**a** seems to hold for thiane sulfimides, the above data demonstrate the necessity to know the spectra of both S—N axial and S—N equatorial isomers to assign configurations, since the absolute numerical values for $\Delta\delta$ Hα are as strongly substituent dependent as the chemical shifts themselves. This is most evident in case of 2-substituted thiane sulfimides (e.g. the thiadecalin sulfimides): $\Delta\delta$ Hα in case of **20**α and **22**α, both clearly compounds with equatorial S—N, are only 0.26 and 0.11 ppm, respectively, which on the basis of the data reported above would suggest the opposite configuration.

The difference in chemical shifts of H-2e and H-2a and the resulting differences of $\Delta\delta$ Hα upon introduction of methyl substituents β to the heteroatom are largely consistent with expectations based on effects of equatorial or axial methyl groups on the proton shifts in methylcyclohexanes[24]. H-2e in **9** or **10** is slightly and H-2a very noticeably shifted upfield, compared to H-2e and H-2a in unsubstituted thiane-1-*N*-aryl imide, by the introduction of the equatorial (*gauche*) methyl groups (upfield shifting in methylcyclohexanes); $\Delta\delta$ Hα in both cases is therefore rather large. In the isomer with one axial and one equatorial methyl group, **11**, the signals of the two equatorial protons H-2e and H-6e are again hardly changed; H-2a, next to the equatorial 3-CH_3 group, is strongly overlaid but definitely shifted upfield ($\delta \simeq 2.4$ ppm), whereas H-6a, adjacent to the axial 5-CH_3, is deshielded by about 0.2 ppm.

A number of methyl-*trans*-1-thiadecalin-1α-imides displays very small geminal shift differences for the protons at C-2, for a variety of reasons. The opposing effects of the axial 3-CH_3 group in **19**α on the shifts of H-2e and H-2a lead to a reduction of $\Delta\delta$ H α to nearly zero. In **20**α H-2a is shifted downfield by the equatorial 4-methyl substituent (similar effects are seen in methylcyclohexanes[24]). Although three signals strongly overlap in the spectrum of **21**α, the most downfield one seems to be H-2a, which is deshielded by a *van der Waals* compression. In **22**α the phenyl ring is forced from its normal position, and the shifts of the α-protons are influenced by the change in anisotropy due to the aromatic ring; the same happens in **24**α, where the different pattern of the aromatic protons also reflect that change. In **23**α, finally, H-9 is shifted downfield (to coincide with H-2a) by the *anti* methyl group, and the signals are not resolved.

Both sulfimides from *cis*-1-thiadecalin (Scheme 3, **25**α**B** and **25**β**A**) are equatorially S—N substituted[14], but differ with respect to the fusion of the cyclohexane ring to the thiane ring (form **A** and **B**). H-9 in **25**α**B** appears at 3.19 ppm in the region typical for H-αe-protons; the two upfield shifting *gauche* interactions with C-5 and C-7 compensate for the fact that H-9 is on a tertiary carbon and should thus be more downfield. H-2e is shifted upfield by ~0.3 ppm, presumably as a result of displacement of the aryl ring by the axial methylene group on C-9 (see above for **24**α). H-2a is practically unchanged, and as a result the chemical shifts between these two protons are very close, and the coupling between them is degenerate. In **25**β**A**, on the other hand, H-9 is indeed downfield from the normal position of an H-αa, and both H-2e and H-2a are in the normal region. We also note the coupling of H-9, which is significant for structures **A** and **B** (and an important configurational proof in addition to the ^{13}C data): in **B** (**25**α**B**, **26**α**B**), H-9 has a large *anti* coupling with H-8a and small *gauche* couplings with H-10 and H-8e and appears as a doublet of triplets. In **A**, H-9 has only three small couplings to the protons at C-8 and C-10, and appears as a broad singlet with a half width of ~8 Hz.

Analysis of the ^1H nmr spectrum and configurational assignment on the basis of ^1H nmr data is particularly difficult in case of the only known thiadecalin-1-*N*-aryl imide with axial S—N, **18**β, because the signals of five protons (H-2e, H-2a, H-9 and presumably H-3a and H-10) are strongly overlaid.

Only limited use can be made of the geminal coupling constant between the α-protons ($^2J_2$) as a configurational and conformational criterium in the compounds investigated. Numerous additional couplings and multiple overlap with other signals as well as the fact that only in a few cases have both isomers been available cause problems in

the interpretation. In **5, 7,** and **9** (equatorial S—N) $^2J_2$ is ~ 12 Hz, close to the value reported by *Lambert*[11] for the conformers of cyclic sulfimides **1a** and **1c** with equatorial S—N. If $^2J_2$ can be read off the spectra of the other sulfimides with equatorial S—N, values between 11.5 and 12.5 Hz are found as one should expect from the S—N equatorial orientation. In **8** (axial S—N) $^2J_2$ is also ~ 12 Hz and thus very similar to the geminal coupling constant in **7.** In the spectrum of **10** a $^2J_2$ of ~ 13 Hz (compared to ~ 12 Hz in **9**) can be measured, while the signals for α-protons in the 100 MHz spectra of **6** and **18** β are too badly overlaid for measurement of $^2J_2$.

β-Hydrogens

In most instances the signals of the protons at C-3 and C-5 (see Scheme 6) were strongly overlaid; only in a few cases was an interpretation possible. In the pairs of isomers with equatorial or axial S—N bond, **5**-**6**, **7**-**8**, and **9**-**10** (the signals for H-3a,e of **18**α and **18**β are strongly overlaid), one sees that in the S—N axial isomers H-3,5a is shifted downfield by 0.7-0.8 ppm and H-3,5e is shifted upfield by 0.3-0.4 ppm. These observations agree with expectation: the axial protons suffer an additional *van der Waals* compression; effects for equatorial protons similar to those seen here have been reported for cyclohexanols by *Anteunis*[25].

N-Acyl Sulfimides (Succinimidyl Ring Opened Products **35**)

The ring-opened products are characterized by the following ^{1}H nmr data: the AA'BB' system of the *p*-substituted phenyl ring appears at lower field (by about 0.5 ppm) than in the corresponding *N*-aryl sulfimides; the signals of the α-protons of the hetero-ring also appear more downfield (between 3.0 and 3.7 ppm). Also significant is the broad NH singlet at ~ 10 ppm, and a singlet due to the four methylene protons of the opened succinimide at ~ 2.7 ppm.

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Experimental

The synthesis and the characterization of the compounds discussed has been described in detail in a preceding paper[2].

60 MHz ^{1}H nmr spectra were recorded on a Varian EM 360 spectrometer equipped with an internal lock facility. Reference substance Me_4Si provided the lock signal.

100 MHz ^{1}H- and ^{13}C nmr spectra were recorded on a Varian XL 100 pulsed *Fourier* transform nmr spectrometer. ^{1}H nmr spectra were recorded in the C.W. mode, in 5 mm o.d. tubes. The solvents reported in Table 3 and in the sequel were used, and the reference substance Me_4Si provided the lock signal. ^{13}C spectra were recorded in the pulsed mode, at 25.16 MHz. Samples were dissolved in the solvents listed in Table 1 and in the sequel, and were measured in 12 mm o.d. tubes. The solvents provided the lock signal, and 2% Me_4Si was added as an internal reference. Digital resolution was 1.25 Hz (0.05 ppm) at 4 k data points and 5,000 Hz sweep width.

The spectral data of the *N*-benzoyl sulfimides **38** α and **39** β will be reported elsewhere[23]. The ^{1}H and ^{13}C spectra of some succinimidyl ring-opened products are reported below:

Thiane-1-N-propionyl[3'-(N-4-chlorophenyl)-carboxamido]imide (**35**, R = H)

^{1}H nmr (60 MHz, $CDCl_3$, ppm): 1.5-2.5 (m, 6 H); 2.72 (s, 4 H); 2.85-3.20 (m, 4 H); 7.15-7.65 (m, 4 H); 9.98 (s, broad, 1 H).

^{13}C nmr ($CDCl_3$, ppm): 183.60, 171.77 (2 **C**O); 137.78 (C-1'); 128.68 (C-3', C-5'); 128.7 (C-4', superimposed); 120.88 (C-2', C-6'); 41.20 (C-2, C-6); 34.51, 33.01 (2 **C**H_2); 24.17 (C-4); 20.15 (C-3, C-5).

trans-1-Thiadecalin-1α-N-propionyl[3'-N-4-chlorophenyl)carboxamido]imide (ring opened product **35** from *trans*-1-thiadecalin)

^{1}H nmr (100 MHz, $CDCl_3$, ppm): 0.9-2.9 (m, 15 H); 2.71 (s, 4 H); 3.53 (d, J = 12 Hz, 1 H); 7.15-7.65 (m, 4 H); 10.06 (s, broad, 1 H).

^{13}C nmr ($CDCl_3$, ppm): 184.51, 171.77 (2 **C**O); 137.78 (C-1'); 128.62 (C-3', C-5'); 128.10 (C-4'); 120.88 (C-2', C-6'); 60.96 (C-9); 44.97 (C-2); 39.58 (C-10); 34.51, 33.28 (2 signals superimposed); 32.43 (2 **C**H_2, C-4, C-5); 27.75 (C-8); 25.35, 25.15 (C-6, C-7); 22.49 (C-3).

cis-1-Thiadecalin-1α-N-propionyl[3'-(N-4-chlorophenyl)-carboxamido]imide (**37** α **B**)

^{1}H nmr (100 MHz, $CDCl_3$, ppm): 1.1-2.2 (m, 13 H); 2.55-3.05 (m, 2 H); 2.72 (s, 4 H); 3.68 (d, J = 11 Hz, 1 H); 7.15-7.60 (m, 4 H); 9.94 (s, broad, 1 H).

^{13}C nmr ($CDCl_3$, ppm): 183.14, 171.70 (2 **C**O); 137.84 (C-1'); 128.68 (C-3', C-5'); ~ 128.5 (C-4', superimposed); 120.88 (C-2', C-6'); 51.15 (C-9); 35.61 (C-2); 34.77 (C-10); 34.57 (**C**H_2); 32.89; 32.63 (**C**H_2, C-5); 25.80 (C-7); 23.66 (C-3); 22.68 (C-4); 20.47 (C-6), 17.16 (C-8).

3α-Methyl-cis-1-thiadecalin-1α-N-propionyl[3'-(N-4-chlorophenyl)-carboxamido]imide (3α-CH_3-**37** α **B**)

^{1}H nmr (60 MHz, $CDCl_3$, ppm): 1.11 (d, J = 6 Hz, 3 H); 1.1-2.25 (m, 12 H); 2.4-3.1 (m, 2 H); 2.73 (s, 4 H); 3.71 (m, 1 H); 7.15-7.70 (m, 4 H); 9.75 (s, broad, 1 H).

^{13}C nmr ($CDCl_3$, ppm): 182.95, 171.69 (2 **C**O); 137.77 (C-1′); 128.57 (C-3′, C-5′); 127.99 (C-4′); 120.83 (C-2′, C-6′); 49.97 (C-9); 41.70 (C-2); 34.37 (C-10); 34.16 (**C**H_2); 32.71, 32.54, 32.39 (**C**H_2, C-4, C-5); 29.69 (C-3); 25.75 (C-7); 21.99 (**C**H_3); 20.25 (C-6); 16.89 (C-8).

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