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Lanthanide Induced Shifts of Sterically Hindered Aromatic Carbonyl Compounds
Oxomethylene-bridged, Acetyl-, and Formyl-2,2′-Spirobiindanes*

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The lanthanide induced shift (LIS) data of 10 polysubstituted 2,2′-spirobiindanes with a carbonyl group in conjugation to an aromatic ring were simulated using the *McConnell-Robertson* equation. In the case of oxomethylene-bridged derivates (with CO incorporated in a more or less rigid ring) the classical one site or two site models gave reasonable results. For sterically hindered acetyl or formyl derivates (both *ortho* positions alkyl-substituted) a new model was developed: the carbonyl group was found to be 30° out of the aromatic plane and the possible 4 positions (± 30° and ± 150°) turned out to be populated differently depending on the *ortho* substituents. The LIS programme had to be modified to account for this situation.

(Keywords: ^{1}H-*LIS model calculation; LIS model for aromatic out of plane acetyl or formyl; Conformational analysis)*

Lanthaniden-induzierte Verschiebungen sterisch gehinderter aromatischer Carbonyl-Verbindungen. Oxomethylen-überbrückte, Acetyl- und Formyl-2,2′-Spirobiindane

Es wurden die Lanthaniden-induzierten Verschiebungen (LIS) von 10 polysubstituierten 2,2′-Spirobiindanen mit einer Carbonylgruppe in Konjugation zu einem aromatischen Ring mittels der *McConnell-Robertson*-Gleichung rechnerisch simuliert. Im Fall von Oxomethylen-überbrückten Derivaten (mit CO in einem mehr oder weniger starren Ring inkorporiert) ergaben sowohl das übliche „One Site“ — als auch das „Two Site“-Modell gute Resultate. Im Fall sterisch gehinderter Acetyl- oder Formylderivate (beide *ortho*-Positionen alkyl-substituiert) mußte ein neues Rechenmodell erstellt werden: die Carbonylgruppe erwies sich als etwa 30° aus der Benzolebene herausgedreht und die 4 möglichen Lagen (± 30° und ± 150°) zeigten dabei verschiedene Populationen. Das LIS-Programm mußte entsprechend modifiziert werden, um die Komplexierungsverhältnisse wiederzugeben.

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* Dedicated to Prof. Dr. *A. Neckel* on the occasion of his 60th birthday.

Introduction

In the course of an experimental proof for *Ruch*'s ligand parameter model [1] for the calculation of chiroptical properties a large number of poly-substituted 2,2′-spirobiindanes had been synthesised [2–4]. For sterically hindered acetyl or formyl derivates a modified set of ligand parameters had to be used to account for the out of plane conformation of the carbonyl group. By means of ^{13}C-NMR a torsional angle of ca. 30° was derived for an aromatic carbonyl function between two alkyl *ortho* substituents [5].

All these carbonyl compounds gave reliable LIS data with Eu(*fod*)$_3$. For two reasons a careful computational LIS study was of interest: (i) to support the results derived from ^{13}C-NMR concerning the conformation of the sterically hindered acetyl and formyl derivates, and (ii) to develop and test a LIS model designed to meet the requirements of sterically hindered aromatic out of plane carbonyl coordination sites. The latter task is a further example in the application of the LIS method to functional groups where the usual simple approach fails [6, 7].

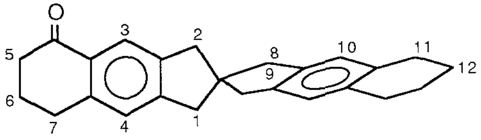
The substituted 2,2′-spirobiindanes proved to be well suited for this purpose. Since several acetyl and formyl derivates were available, the assignments of the resonances were usually straightforward, and the relatively large molecules (about 12–14 Å in length) cover enough space to give a representative set of LIS data to decide in favour or against model assumptions.

Results and Discussion

In order to gain information on the LIS behaviour of 2,2′-spirobiindanes we started to test the basic geometry of the system using sterically constrained aromatic carbonyl coordination sites (compounds **1**–**4** with cyclohexenone and cyclopentenone moieties). The studies were then extended to the conformationally free acetyl and formyl derivates **5**–**10**.

Keto Derivates **1**–**4**

Compound **1** represents a 2-cyclohexenone unit condensed to an aromatic ring of the 2,2′-spirobiindane. The two well known LIS-models [8] for ketones were applied to this compound. The geometries of the two indane moieties were assumed to be planar; for the cyclohexenone ring both possible conformations (either chair-like or boat-like) were tested. The first assumption proved to be reasonable; at least in the time average the two indane moieties are planar and orthogonal to each other. Actually a cyclopentenone ring should adopt envelope conformation; both possible conformers, however, average out on the NMR time scale since they have to be populated equally in compound **1**. The second question concerning the geometry of the cyclohexenone unit could not be answered unambiguously. The data of the cyclohexenone unit could be described fairly well for both possible conformers. Taking the *R*-values as a measure for the quality of the fit, the following results were obtained



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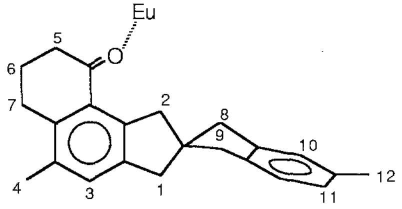

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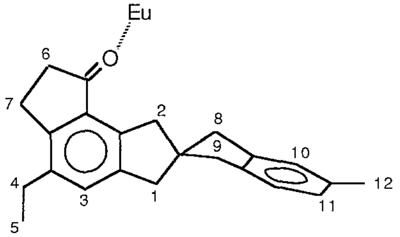

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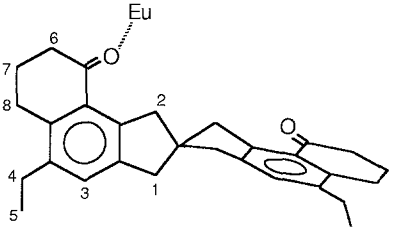

4

for the one site model: cyclohexenone chair (omitting the LIS data for the possibly contact-contaminated α-protons in the cyclohexenone ring): $R = 2.60\%$, boat (neglect of α-H): $R = 1.04\%$; chair (including α-H): $R = 2.88\%$; boat (including α-H): $R = 4.98\%$. For the two site model (constrained to sites in the $>C=O$ plane and a $C=O \ldots Eu$ angle of 35°, see Ref. [8]) the results were comparable: chair (no α-H): $R = 7.84\%$ (85% population for the site *anti* to the aromatic ring); boat (no α-H): $R = 5.32\%$ (83% *anti*). Both models are able to describe the experimental LIS; however, the calculation does not allow a clear decision between the boat-like conformation (only the β-carbon out of the aromatic plane) and the chair like conformation (α- and β-C deviating from the plane). The results are slightly in favour of a boat-like conformation with CO almost coplanar with the aromatic ring. Data for the best fit (boat-like and neglect of α-protons) are listed in Table 1.

For compound **2** the situation is somewhat different. The assumption of planar indanone moieties does not hold anymore. All fits using this assumption (independent of the adopted cyclohexene conformation or the model) yielded *R* factors > 10%. A much better fit was obtained when the cyclopentene unit of the second indanone moiety was assumed in an envelope conformation, resulting in a geometry where the second aromatic ring is bent away from the $>C=O$ group *and* the coordinating bulky reagent. The angle between the planes determined by C-1′, C-2′, and C-3′ and C-1′, 3′, 4′, 5′, 6′, 7′* turned out to be 25 ± 5°. Most indicative are the LIS values for the substituents at C-4′, 5′, 6′ and 7′ (LIS nos. 10, 12, 11, 10 in formula **2** and Table 1; LIS = −0.03, −0.10, −0.10, −0.03) which were simulated very badly by the planar structure (−0.37, −0.37, −0.41, −0.40, −0.37). To obtain less negative values a conformation with a less pronounced **U** shape of the arrangement Eu—O=C . . . H_i has to be assumed (see Ref. [9]). The best fit is tabulated (one-site model with the slightly better chair-like cyclohexenone geometry in the case of **2**). The two site model calculations gave essentially the same trends since the two site model degenerates anyhow to a one site complex with 100% population *anti* to the cyclopentenone unit (and the rest of the molecule). The complex with Eu(III) close to the spiro center is rather unreasonable which is reflected in a population of 0% in the two site model calculations.

For compound **3** with a cyclopentenone ring pointing towards the spiro center similar considerations as for compound **2** are valid. Again the cyclo-pentenone unit of the second indane moiety adopts an envelope conformation to avoid unfavourable interactions with the Eu(*fod*)$_3$ reagent. It should be emphasised that this geometry is derived for the complex only. Unfortunately no vicinal couplings are available in **2** or **3** to detect changes of conformation upon complexation. In **3** the problem of the uncertain geometry of the oxymethylene bridge is avoided, since cyclo-

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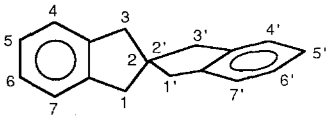
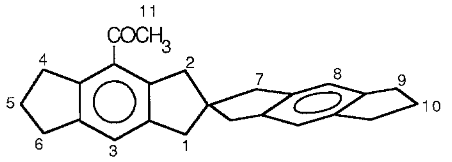
* The numbers of the carbon atoms in the text refer to the systematic ones:



The proton numbers (and corresponding LIS-values) have a separate numbering according to the formulas **1–10**.

pentenones may be assumed planar. The best fit (Table 1) is obtained for an angle of 10° between the 1′, 2′, 3′ and 1′, 3′, 4′, 5′, 6′, 7′ planes. This lower value (compared to **2**) indicates less sterical strain for the five-ring ketone. In the minimisation procedure the LIS values for the ethyl group were omitted, because of the unknown conformation. Using the known Eu(III) position, LIS-values for possible ethyl conformations may be calculated and compared with the experimental values. The best correspondence was observed for conformations *anti* to the cyclopentenone moiety [calculated LIS values for CH_2—CH_3: 0° = *syn*: 0.82 (CH_2), 0.85 (CH_3); 30°: 0.83, 0.83; 60°: 0.85, 0.77; 90°: 0.88, 0.70; 120°: 0.90, 0.66; 150°: 0.91, 0.62; 180° = *anti*: 0.91, 0.62]. The experimental values of 0.87 for CH_2 and 0.63 for CH_3 allow only to give a rather broad limit of 150 ± 30° (= *anti* with a deviation up to 60° from planarity).



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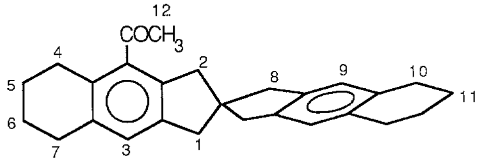

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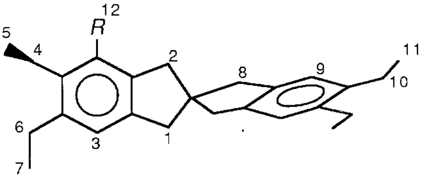
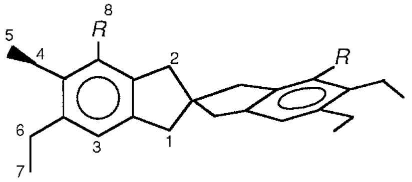


7 R = $COCH_3$

8 R = CHO



9 R = $COCH_3$

10 R = CHO

For the bifunctional derivative **4** the experience from the related

Table 1. *LIS data*[a] *for the compounds* **1–10**; *the proton numbers correlate to the numbers in the formula schemes*

LIS no.		Compound no.									
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1	exp	0.89	0.75	0.83	0.96	0.79	0.63	0.65	1.20	1.35	1.90
	calc	0.84	0.82	0.89	1.06	0.81	0.54	0.66	1.27	1.27	1.93
2		0.64	4.67	3.54	5.24	2.52	1.77	1.85	4.75	2.70	5.20
		0.67	4.67	3.57	5.13	2.50	1.82	1.87	4.76	2.63	5.00
3		7.35	0.84	1.00	0.80	0.93	0.75	0.85	1.50	0.95	1.25
		7.34	0.90	1.02	0.85	0.94	0.62	0.76	1.45	0.92	1.25
4		1.63	0.75	0.87	0.48	3.27	2.50	2.45	3.90	2.65	3.10
		1.62	0.79	0.91	0.55	3.28	2.50	2.48	3.86	2.79	3.25
5		7.14	4.41	0.63	0.20	0.63	0.32	1.25	2.45	1.45	1.85
		–	–	0.63	0.32	0.62	0.43	1.28	2.40	1.41	1.98
6		2.62	1.49	4.64	4.32	0.75	0.40	0.90	1.30	0.90	0.98
		2.65	1.41	–	–	0.78	0.49	0.76	1.42	0.85	1.11
7		2.35	1.40	1.90	1.20	0.58	0.59	0.50	0.95	0.50	0.66
		2.32	1.35	1.75	1.31	0.58	0.54	0.49	0.92	0.52	0.68
8		0.34[b]	0.33[b]	0.51	1.04	0.12	0.42	0.40	0.85	3.10	9.50
		0.30	0.24	0.55	1.21	0.07	0.38	0.46	0.93	–	–

9	0.45[b]	0.49[b]	0.55	–	0.00	0.06	−0.02	0.07	–	–
	0.44	0.53	0.60	–	−0.01	0.00	0.05	−0.03	–	–
10	0.08	−0.03	0.00	–	−0.04	−0.04	0.00	−0.15	–	–
	0.06	−0.08	−0.02	–	−0.02	−0.06	−0.01	−0.16	–	–
11	0.01	−0.10	−0.11	–	3.95	−0.06	−0.10	−0.20	–	–
	0.00	−0.13	−0.11	–	–	−0.06	−0.03	−0.15	–	–
12	0.00	−0.10	−0.10	–	–	3.21	3.40	11.50	–	–
	−0.01	−0.13	−0.10	–	–	–	–	–	–	–
R (%)	1.04	3.42	4.14	5.17	1.58	7.08	5.71[d]	3.00[e]	4.24	4.57
d (Å)	2.8	3.1	2.6	3.1	2.8	2.8	2.8	2.8	2.8	2.8
ρ (°)	30	45	42	45	27	40	50	35	50	35
φ (°)	61	45	46	45	0	20	31	−18	31	−18
% anti[c]	–	–	–	–	69	67	77	63	77	63

[a] LIS values extrapolated to the 1 : 1 complex

[b] No. 8: C 1′ and C 3′ protons *syn* to the carbonyl group (above the plane of the second indane moiety in formula **1** or **2**); no. 9: C 1′ and C 3′ protons *anti* to the carbonyl group (below the plane); due to the angle dependence in the *McConnell-Robertson* equation the LIS value for the closer protons no. 8 is smaller than for 9 (compare also the pair no. 1 and 2 of compound **1**)

[c] % Population *anti* to the spiro center and the bulk of the molecule in the case of the four positions carbonyl model (4 P-CO model)

[d] A fit omitting the ethyl groups (without LIS values no. 4, 5, 6, 7, 10, 11) gave an agreement factor of $R = 1.5\%$ at $d = 2.8$ Å, $\rho = 55°$, $\varphi = -39°$, and 78% *anti* population

[e] A fit without the ethyl groups gave $R = 2.27\%$ at $d = 2.8$ Å, $\rho = 55°$, $\varphi = -54°$, and 67% *anti* population

compounds **1–3** could be used to calculate the LIS values using known positions for Eu(III) and superposition of both independent magnetic fields of the two equally populated mono-complexes which will be the most important species in the range of low reagent concentration (cf. Ref. [10, 11] for the additivity of LIS values).

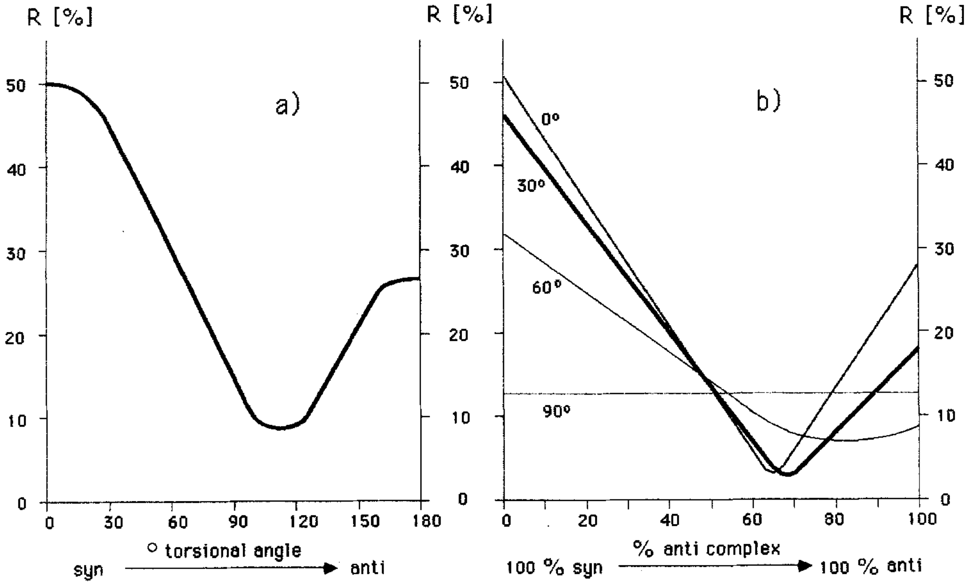


Fig. 1. *a* Dependence of the *R* factor on the torsional angle of the acetyl group of **5** according to the one site carbonyl model; *b* dependence of the *R* factor on the population ratio of the *syn* and *anti* complexes for several torsional angles of the acetyl group of **5** (0°, ± 30°, ± 60°, ± 90°) according to the four positions carbonyl LIS model for sterically hindered carbonyl compounds

Acetyl and Formyl Derivatives **5–10**

The simple use of the one site or two site carbonyl model was not successful in the case of compounds **5–10** with a conformationally mobile out of plane carbonyl coordination site. Figure 1 a depicts the dependence of the *R* factor of the torsional angle of the acetyl group of **5** relative to the aromatic plane. The minimum was found at an angle of 70° out of the benzene plane (with C=O *anti* to the spiro center and the bulk of the molecule). This torsional angle of 70 ± 20° seemed unreasonably large in the light of the ^{13}C-NMR results suggesting an angle of ca. 30°. Furthermore, the minimum *R* value of 9.5% indicated a rather poor fit.

Values below 5% are typical for good fits, up to 8% are still reasonable, but *R* factors above 10% indicate a significant deviation between the model assumption and the real geometry of the complex. This deviation may either be due to a wrong geometry of the substrate or a wrong coordination model.

The substrate geometry was proved to be essentially correct in the calculations of compounds **1**–**5** with a "rigid" carbonyl function. Therefore the one site complexation model was modified accordingly, based on reasonable considerations concerning possible conformers of the carbonyl compounds. These considerations were tested and documented most extensively for compound **5**, since this molecule may be treated approximatively as a rigid structure without any further conformational problems (the cyclopentenone rings are considered planar in the time average). However, similar comparative test calculations were done as well for **6**, **7** and **8**. In all cases the new model (see below) gave better results than a simple one or two site model.

Obviously, the assumption of only one acetyl conformer is unrealistic. In fact, due to the averaging of the LIS for the two protons at C-1 and C-3 of the indane moiety carrying the acetyl group and averaging of equivalent positions at C-1′/C-3′, C-4′/C-7′, and C-5′/C-8′ for the second indane ring two (identical) acetyl conformers are described by the usual one site model (for instance + or −30 °C gives identical results). The symmetry of the substrate molecule must be reflected in the model for the complex as well (see Ref. [12]). The reason for the bad fit is then obviously the assumption of 100% population for e.g., a torsional angle of ± 30° and neglecting the two conformers at ± 150°. In the latter conformers the deviation from the aromatic plane is again ± 30°, the relation between ± 30° and ± 150° corresponds to *syn* or *anti* conformers relative to some reference: for instance *syn* or *anti* to the spiro center (and therefore to the bulk of the spirobiindane molecule, Fig. 2 a).

The most simple way to consider these additional conformers in the LIS model is by adding corresponding symmetrical proton positions which are created by a (hypothetical) symmetry plane through the carbonyl-C and orientated orthogonal to the benzene ring (see Fig. 2 b). Similar as in previous models for 1,3-diols [6] and *o*-dimethoxybenzenes [7] the complicated relation: One set of substrate geometry parameters and several Eu(III) positions is transformed into the more convenient relation: several sets of coordinates and one Eu(III) position in the calculation. One identical LIS value is assigned to all corresponding proton positions and the geometrical factors are averaged before scaling to the experimental values. Population ratios can be considered by the use of proper weighting factors. Due to symmetry considerations (*vide supra*) the two *syn* (± 30°) and the two *anti* (± 150°) conformers must be populated equally but the population ratio *syn* : *anti* will not be 1 : 1. This means that the latter population ratio must be introduced as an additional parameter. As a consequence the weighting factors for the second (hypothetical) set of coordinates must be varied during the R factor minimisation in the course of the calculation. Figure 2 b should help to make matters clear: e.g., the protons at carbon atoms no. 7 and 7′ or 10 and 10′ must be weighted 0.345 : 0.155 for a population ratio of *anti* : *syn* = 69 : 31 (the sum of all contributions has to be 1.00 which is the weight for one measurable LIS-value).

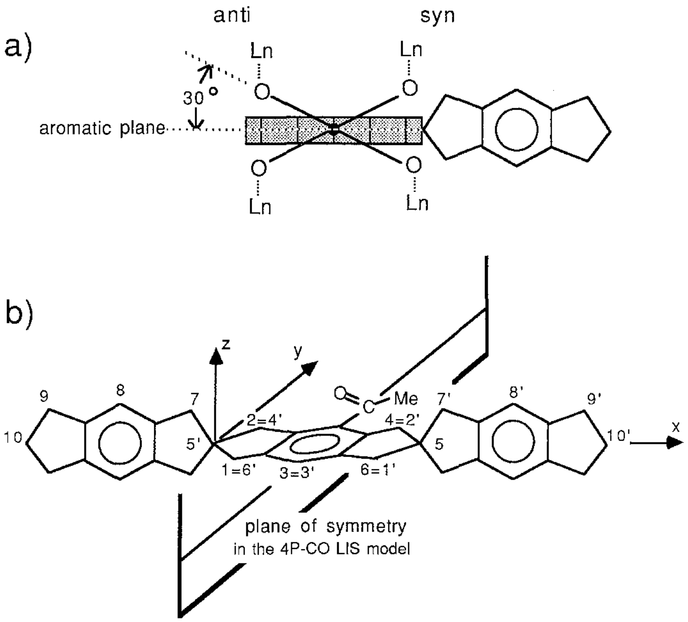


Fig. 2. Schematical presentation of the four positions carbonyl model (4 P-CO LIS model) for compound **5**: *a* *syn* and *anti* complexes for 30° torsional angle of the acetyl group; *b* illustration of the (hypothetical) plane of symmetry in the 4 P-CO LIS model, leading to a second coordinate set for all atom positions

The population ratio of 69 : 31 for ± 30° and ± 150° in favour of the *anti* configurated Eu(III) complex of **5** is the result of a study varying the torsional angle and the population ratio systematically. Fig. 1 b shows details for several torsional angles of the acetyl group of **5** over the whole population ratio range. The most striking result of this systematic study is the importance of mixing *syn* and *anti* configurated complexes in the proper ratio: very pronounced minima in the region of 60–80% *anti* conformation for a variety of torsional angles emphasize the strong dependence of the R factor on *syn-anti* mixing. The fit is less dependent on the torsional angle of the acetyl group. As a consequence, the LIS method is in this case not well suited to determine sharp torsional angles: angles of 30 ± 30° give reasonable fits (R = 1.6–4%). However, the minimum R value of 1.8% is obtained for 30° which is in perfect agreement with the ^{13}C results. Corresponding values for different acetyl torsional angles of **5** are: 0° torsion (67% *anti* complex, R = 2.8%), 15° (67% *anti*, R = 2.4%), 20° (67% *anti*, R = 2.2%), 25° (67% *anti*, R = 2.1%), 30° (69% *anti*, R = 1.6%), 35° (71% *anti*, R = 2.4%), 40° (75% *anti*, R = 3.4%), 50° (75% *anti*, R = 3.7%), 60° (75% *anti*, R = 4%).

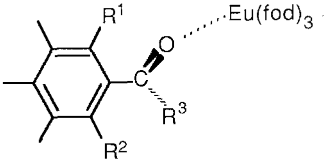
This trend, namely a strong dependence of the fit on the *syn-anti* ratio and less pronounced sensitivity towards the torsional angle, was observed for compounds **6**, **7**, and **8** as well. Despite the softness of the function towards the angle, the absolute minima for these compounds (with varied angle, population, and Eu position) were found consistent at torsional angles of ± 30°/± 150°, but at different population ratios for acetyl or formyl functions in sterically different environment.

The four-positions LIS model for compound **6** gave a minumum R-factor of 7.1% for 30° acetyl torsion and 67% population of the *anti* complex. Compared with **5** the fit is not so good due to the conformational mobility of the cyclohexenone ring (since no decision between a boat-like or chair-like conformation was possible, an average flat geometry was used in the minimisation procedure).

A similar problem is present in the tetraethyl derivatives **7** and **8**. Since the conformations of the ethyl groups are not known, the first series of test calculations was performed omitting these data. The optimal complex geometry for the acetyl derivative **7** was found at an R-factor of 1.5% for a torsional angle of 30° and 77% *anti* population, the formyl derivative **8** gave a minimum R factor of 2.3% at 30° and 63% *anti*. For this complex parameters different ethyl conformations were tested. For both compounds the best agreement between experimental and calculated LIS values was obtained for an out of plane C 5-ethyl group (90°) and in plane conformations for C 6-, C 5′-, and C 6′-ethyl groups (compare the formula scheme). The overall fits including the ethyl groups are summarised in Table 1. For the closely related bifunctional derivatives **9** and **10** identical complex geometries were assumed for the two complexation sites and the LIS data simulated by additive superposition of the corresponding geometrical factors (see Table 1).

Conclusion

The 4-positions-carbonyl model (4 P-CO LIS model) for out of plane aromatic acetyl or formyl groups gave—in accordance with ^{13}C results—in all cases torsional angles of ca. 30°. The population ratio of the *syn* : *anti* pairs (± 30° : ± 150°) is governed by the sterical requirements of the functional group, the coordinating reagent, and the *ortho* substituents. For a formyl function the $C=O$ group including the coordinating Ln(III) reagent ($>C=O\ldots Ln$) will be of most importance, in the case of acetyl the methyl group will be also important: thus the 63% *anti* complexation of the formyl derivative **8** is increased to 77% for **7** due to the interaction of acetyl methyl with the *ortho* methylene part of the *o*-ethyl group in the *syn* arrangement ($>CO$ *syn* to the five-ring of the indane moiety). In other words, in an arrangement:



the groups $-R^1$, $-R^2$, $-R^3$, and $=O\ldots Eu(III)$ must be taken into account. The residue R^3 is decisive for differences in the LIS values for different carbonyl functions like aldehydes, ketones, esters, amides, etc. The generally found torsional angle of ca. 30° for these types of sterically hindered aromatic formyl and acetyl compounds is a compromise between optimal conjugation of $C=O$ with the aromatic system and avoiding too strong non-bonded interactions of neighboring groups; larger groups R^3 may cause not only changes in the *syn* : *anti* ratio but in the carbonyl torsional angle as well.

Acknowledgements

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Experimental

Synthesis and spectral data of the compounds have been published elsewhere: **1** [4], **2–4** [3], **5** [13], **6** [4], **7–10** [3].

The LIS data were determined by stepwise addition of Eu(*fod*)$_3$ (Merck) to ca. 0.03–0.05 *M* solutions of substrate (compounds **1**, **2**, **3**, **5**, and **6**, measured on a Bruker WM-250 spectrometer), or to ca. 0.05–0.15 *M* solutions (compounds **4** and **7–10**, recorded on a Varian EM-360 spectrometer). The data for 4–5 reagent concentrations in the range of $L_0 : S_0 = 0.1$–0.6 were extrapolated to the 1 : 1 complex. Since for substrates with moderate complexing ability the extrapolated 1 : 1 values are strongly dependent on the concentration, only the relative LIS values are of interest in the computer simulation.

All computer programs were written in BASIC and run on an Apple II computer. Standard geometries for the structures were calculated using a COORD-type program. The geometrical factors [10] were calculated for all input proton positions and then weighted averaging was used to take care of the contributions of possible conformers. The populations were governed by variation of molar fractions in the program. Finally these "mixed" geometrical factors were scaled to the experimental values by means of a least-squares procedure using the crystallographic *R*-factor as a measure for the goodness of the fit. This approach afforded 5 parameters to be changed systematically: (i) the torsional angle of the carbonyl function (included in the input substrate geometry), (ii)–(iv) the three position parameters for the Eu(III) ion (the distance O . . . Eu was usually kept at 2.8 Å since this value gives in most cases good results and corresponds to experimental O . . . Eu bond length as well; in cases of less good fits the range of 2.6–3 Å was checked), and (v) the mole fraction of the *syn : anti* complex conformation pair. Weight factors of 0.0 allowed the calculation of expected LIS values for certain atom positions without using these positions in the fitting procedure (this is convenient for conformationally mobile groups attached to rigid systems, e.g. ethyl groups). The results are compiled in Table 1.

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