Conformational Analysis. Part 9.[1] A Lanthanide-induced Shift (LIS) Nuclear Magnetic Resonance Investigation of Conformational Isomerism and Structure in 1- and 2-Naphthaldehyde, 9-Acetylanthracene, and 9-Anthraldehyde.

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A lanthanide-induced shift n.m.r. investigation of conformational isomerism in the title molecules has been carried out, based upon the pseudo-contact shifts of all the proton and carbon nuclei in these molecules. The ^{13}C diamagnetic shifts were removed by use of La(fod)$_3$, and the pseudo-contact shifts analysed to obtain the conformational preferences of the formyl and acetyl groups. The results obtained for 9-anthraldehyde were very dependent on the concentration of the substrate. Only the pseudo-contact shifts obtained from dilute (0.2M) solutions gave good agreement between the observed and calculated shifts, with *ca.* 30° for the torsion angle between the formyl group and the aromatic rings. As starting geometries in the LIS analyses both a crystal structure of 9-anthraldehyde and fully optimized MNDO geometries for each value of the torsional angle have been used. The precise results were dependent on the starting geometry used. The results obtained for 9-acetylanthracene showed a much less marked dependence on the substrate concentration. Two different starting geometries gave the same good solution ($R_{cryst.}$ 0.07) for a torsional angle of *ca.* 70° of the acetyl group with respect to the anthracene rings. The analysis of 1-naphthaldehyde was again critically dependent on the geometrical model used. The standard geometry gave a solution ($R_{cryst.}$ 0.018) at 28% *E*-conformation but only when H-8 was removed. This proton has a large LIS and the calculated value is critically dependent on the geometry of the aldehyde at H-8. Analysis of the data using as input a fully optimized geometry for both the *E*- and *Z*-conformers from MNDO calculations gives the best solution ($R_{cryst.}$ 0.021) for 5% *E*-conformation, which now includes all the nuclei. On using the pseudo-contact shifts measured for more dilute solutions the minimum shifts to 15% *E*-conformation, without any appreciable change in the agreement factor. The use of a standard geometry as input for the LIS analysis of 2-naphthaldehyde gave a good solution ($R_{cryst.}$ 0.011) at *ca.* 80% *E*-conformation. No significant effect of the concentration of the substrate was detectable.

In previous parts of this series[1-3] and elsewhere,[4-6] it has been shown that the LIS technique, when suitable precautions are taken to remove the diamagnetic shifts, obtain over-determined data sets, and analyse the results with a chemically reasonable model, can be quantitatively applied to the determination of conformer isomerism and structure in aromatic aldehydes and ketones.

In a number of substituted benzaldehydes[1,2] the conformational preference of the aldehyde group was determined in this manner, the percentage of the *O-trans* conformer varying from 32% in *m*-methoxybenzaldehyde to 100% in *o*-chlorobenzaldehyde. In sterically hindered aldehydes and ketones, such as mesitaldehyde and 2,4,6-trimethylacetophenone, the LIS technique provides structural information on the single conformer present.[7] In mesitaldehyde the aldehyde group is coplanar with the benzene ring, but the C–C–C angles of the neighbouring 2- and 6-methyl groups relax to 126° to relieve the steric strain. In contrast in 2,4,6-trimethylacetophenone the acetyl group is almost orthogonal to the benzene ring with the methyl C–C–C angles unaffected.

In order to further investigate the complex pattern of substituent and steric effects in these molecules, we report here the LIS analyses of 1- and 2-naphthaldehyde (**1**) and (**2**), 9-acetylanthracene (**3**), and 9-anthraldehyde (**4**). These molecules have been the subject of a number of previous investigations.

The interpretation of the substituent chemical shifts of the aldehyde group in naphthaldehydes has been of some interest,[8,9] in that the orientation of the 1-aldehyde group has a profound effect on the chemical shift of the 8-H. This varies from δ 8.33 in 2-hydroxy-1-naphthaldehyde (**5**), in which the aldehyde group is in the *E*-conformation, to δ 9.51 in the tetrahydrophenanthrene derivative (**6**),[4] in which the carbonyl is in the *Z*-orientation. The ^{13}C spectra of a number of substituted naphthalenes have been assigned, using selectively deuteriated derivatives and the C–H couplings to complete the assignments.[10] Again, the ^{13}C substituent chemical shifts are very dependent on the orientation of the aldehyde group. These authors also investigated the conformational equilibria in these molecules by low-temperature ^{13}C n.m.r. spectroscopy.[11] They were able to observe the separate conformers of (**2**) at 165 K to give 80% *E*-type, but in (**1**) only a broadening of the C-2 signal at low temperatures could be seen. They estimated 90% *Z*-conformer from these results.

Salman[12] has used the long-range couplings between the aldehyde proton and the ring protons to deduce the conformational preferences of the aldehyde group. He obtained 12% *E*-type for (**1**) and 75% *E*-type for (**2**), based on model compounds of fixed conformation. This approach has been extended to the hydroxy[13] and acetyl[14] derivatives of naphthalene.

In 1- and 9-substituted anthracenes, the effect of the *peri* interaction between the substituent and the neighbouring protons on the chemical shifts of these protons has been investigated.[15] Also, Schuster[16] has given the complete assignment of the ^{13}C spectra of a number of substituted anthracenes. The conformations of some 9-substituted anthracenes were deduced from dipole moment and Kerr constant data by Le Fevre *et al.*[17] They found an essentially orthogonal

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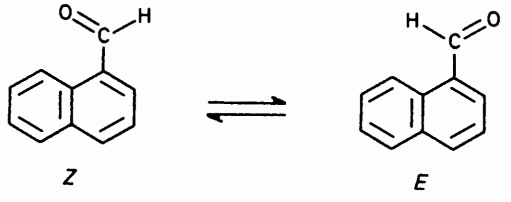

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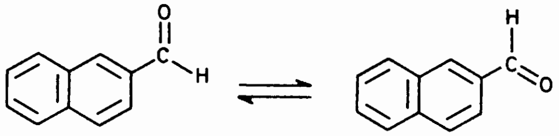

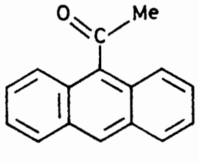

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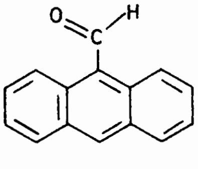

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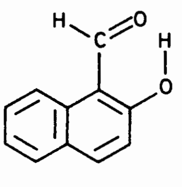

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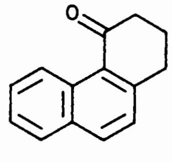

(6)

conformation of (**3**) but could not be certain about that of (**4**). Their results were consistent with the conformation found in the crystal, in which the formyl group and the ring make a dihedral angle of 27°.[18]

In a major series of investigations, Taddei and co-workers have used the LIS technique as well as theoretical calculations to study the conformer equilibrium in acetyl and formyl derivatives of condensed aromatic hydrocarbons[4] and, later, of benzofuran[5] and benzothiophene.[6] They noted that the orientation of the carbonyl group in these systems was mainly governed by the mesomeric interaction between the C=O and the adjacent C=C bond having the higher double-bond character, though earlier semi-empirical SCF-MO calculations gave contrasting results.[19]

Their LIS analyses of (**1**) and (**2**) gave conformer preferences of 23 and 86% *E*-form respectively.[4] In 9-anthraldehyde (**4**) they were not able to distinguish between two rapidly interconverting (identical) planar conformers and one orthogonal conformation; however, comparison of the H-1 chemical shift in (**4**) with those of model compounds favoured the planar model. The chemical shift of the corresponding proton in 9-acetylanthracene is more consistent with a non-planar conformation.

These investigations used Eu(fod)$_3$ as the shift reagent, and in consequence were limited to analysis of the proton LIS only, the ^{13}C shifts containing considerable contact contributions with this reagent. The system is, therefore, not very well determined (six ring proton LISs with five unknowns) which necessitates certain assumptions in the model used.

In our investigations the use of Yb(fod)$_3$ enables all the ^{1}H proton and ^{13}C LISs to be included, and it was felt that this would provide an additional and more definitive investigation of the conformer energies and molecular geometries in these molecules.

Table 1. LISs (ΔM) and diamagnetic shifts (ΔD) (p.p.m.) at various concentrations[a] of 9-anthraldehyde

	Conc.	C-F	C-10	C-9a	C-10a	C-4, -5	C-2, -7	C-3, -6	C-9	C-1, -8
ΔM	0.8398	166.67	26.02	43.35	23.28	16.17	18.15	13.45	59.73	34.51
ΔM	0.4781	163.97	23.46	40.39	20.85	13.93	16.38	11.77	56.25	32.00
ΔM	0.2029	163.99	21.93	38.67	19.08	12.57	14.70	10.14	54.90	30.77
ΔD	0.8336	9.35	6.84	3.69	0.09	0.54	2.52	0.72	−3.87	0.45
ΔD	0.4760	8.28	5.78	3.22	−0.07	0.53	1.89	0.73	−3.68	0.33
ΔD	0.1891	9.07	6.66	3.62	−0.73	0.35	2.05	0.50	−4.86	−0.09

	Conc.	H-F	H-1, -8	H-10	H-4, -5	H-2, -7	H-3, -6
ΔM	0.8398	91.56	47.42	14.69	11.41	8.32	7.70
ΔM	0.4781	90.11	44.78	12.77	9.93	7.39	6.77
ΔM	0.2029	92.00	43.59	11.41	8.85	6.70	6.00

[a] Each of the ΔM and ΔD values was obtained from two additions of Yb(fod)$_3$ or La(fod)$_3$ respectively.

Table 2. Unperturbed (ρ = 0.0) chemical shifts of 9-anthraldehyde at various concentrations

Conc.	C-F	C-10	C-9a	C-10a	C-4, -5	C-2, -7	C-3, -6	C-9	C-1, -8
0.8398	192.63	134.89	131.81	130.72	129.06	128.84	125.42	124.29	123.29
0.4781	192.75	135.01	131.95	130.89	129.17	128.96	125.54	124.52	123.41
0.2029	192.90	135.12	132.10	131.09	129.27	129.06	125.66	124.76	123.56
0.0000	192.97	135.20	132.18	131.19	129.33	129.13	125.73	124.89	123.63
Slope	−0.42	−0.40	−0.45	−0.58	−0.33	−0.34	−0.37	−0.73	−0.42
Corr. coeff.	0.9899	1.0000	0.9951	0.9922	0.9987	0.9997	0.9969	0.9959	0.9899

Conc.	H-F	H-1, -8	H-10	H-4, -5	H-2, -7	H-3, -6
0.8398	11.24	8.75	8.30	7.78	7.51	7.33
0.4781	11.35	8.84	8.45	7.89	7.58	7.40
0.2029	11.46	8.93	8.60	8.00	7.65	7.49
0.0000	11.52	8.98	8.69	8.06	7.69	7.53
Slope	−0.34	−0.28	−0.47	−0.34	−0.22	−0.25
Corr. coeff.	0.9969	0.9969	0.9969	0.9969	0.9969	0.9887

Table 3. LIS (ΔM) and diamagnetic shifts (ΔD) (p.p.m.) for 9-acetylanthracene at the concentration shown

ΔM

Conc.	CO	C-9	C-4a	C-4	C-10	C-2	C-8a	C-3	C-1
0.5929	157.22	60.04	19.91	11.71	17.69	12.86	38.01	9.67	30.26

ΔM

Conc.	C-Me	H-10	H-4, -5	H-1, -8	H-2, -7	H-3, -6	H-Me
0.5929	63.53	11.21	8.61	40.51	5.41	5.41	38.38

ΔD

Conc.	CO	C-9	C-10	C-4a	C-4	C-2	C-8a	C-3	C-1	C-Me
0.6071	13.14	−2.79	1.41	0.00	0.00	0.45	0.45	0.29	0.00	0.29

Table 4. LIS (ΔM) and diamagnetic shifts (ΔD) (p.p.m.) for 1-naphthaldehyde at the substrate concentration shown

ΔM

Conc.	CO	C-2	C-4	C-4a	C-1	C-8a	C-7	C-6	C-5	C-8
0.9905	192.80	42.43	23.38	25.22	66.59	48.60	21.70	16.67	15.61	46.66

Conc.	C-3	H-F	H-8	H-4	H-2	H-5	H-6	H-3	H-7
0.9905	21.43	100.62	71.18	13.23	32.91	10.59	9.17	13.79	12.80

ΔD

Conc.	CO	C-2	C-4	C-4a	C-1	C-8a	C-7
1.0141	12.48	5.92	4.77	0.49	−1.74	0.98	1.48

Conc.	C-6	C-5	C-8	C-3
1.0141	0.73	1.20	0.47	0.47
0.5762	0.00	0.68	0.48	0.48

Table 5. LIS (ΔM) and diamagnetic shifts (ΔD) (p.p.m.) for 2-naphthaldehyde at the substrate concentration shown

ΔM

Conc.	CO	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a
0.9895	173.66	38.44	61.05	44.52	23.83	10.61	9.57	8.61	12.52	18.35

Conc.	C-8a	H-F	H-1	H-3	H-4	H-5	H-6	H-7	H-8
0.9895	19.57	92.70	31.91	49.13	15.22	9.31	6.09	6.09	9.31

ΔD

Conc.	CO	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
0.9967	9.99	4.32	−2.19	0.94	1.69	0.26	1.95	0.68	0.51	1.19	0.09

Results

All the compounds studied give accurately linear plots of their chemical shifts *vs.* the shift reagent/substrate molar ratio. As in some cases (*vide infra*) the collection of data at different substrate concentration proved necessary, in Tables 1—5 we report for the various compounds the unperturbed chemical shifts (δ), the LISs (ΔMs) with $Yb(fod)_3$ and the diamagnetic complexation shifts (ΔDs) with $La(fod)_3$ obtained at various concentrations of the substrate.

The pseudo-contact contributions ($\Delta M - \Delta D$) were analysed with the program LIRAS-3 (described previously[3]) to obtain the required conformational information. As we have stressed repeatedly, in these studies a major problem is the provision of an over-determined set of equations. The general model derived previously is of four-site lanthanide ion complexation in which the lanthanide position is reflected in the *xy* and *xz* planes (this being equivalent, of course, to the two-site model for a planar substrate) and in which the percentage population of the lanthanide ion *exo* and *endo* to the carbonyl is allowed to vary. However, as all our previous studies with aromatic aldehydes have yielded 100% *exo*-populations, there is little point in varying this parameter, unless the aldehyde group becomes non-planar with respect to the aromatic ring. Thus, four parameters are required to fix the lanthanide complexation (one normalization factor and three lanthanide ion co-ordinates). The additional information required is the conformer population plus any geometrical distortion in these molecules. It is convenient to consider the 9-anthraldehyde first.

9-Anthraldehyde.—This molecule presented considerable difficulties in the analysis of the LIS data. Initially the *X*-ray geometry of Trotter[18] [Figure 1(a)] was used to simulate the ΔM values (obtained from 0.8M 9-anthraldehyde solutions, see Table 1), and the program searched for the best solution as a function of the dihedral angle between the formyl and the anthryl moieties. (Note that for all dihedral angles, except 90°, rapid flipping of the formyl group about two equivalent conformations is assumed, *i.e.*, H-1 and H-8 are averaged in the calculations.) However, no acceptable solution could be found for any dihedral angle [Figure 2(a)] as the agreement factor was always larger than 0.035.

Using the fully optimized MNDO geometry for each dihedral angle as input [the MNDO geometry for a 30° dihedral angle is reported in Figure 1(b)], the agreement is generally better for all dihedral angles, but the convergence to the minimum value of the agreement factor of 0.026 at ω = 50—60° is not properly defined [Figure 2(b)].

As Stothers and co-workers[20] reported n.m.r. evidence of self-association of 9-anthraldehyde molecules in chloroform solutions we decided to check if these interactions can affect the LIS analysis. In Tables 1 and 2 are reported the unperturbed chemical shifts (in absence of lanthanide) and the ΔM and ΔD values obtained at various concentrations of 9-anthraldehyde. Table 2 reveals that the chemical shifts of all the nuclei move to high field with increasing concentration, in agreement with the suggested model of a layer-like complex,[20] in which the aryl skeleton of one molecule tends to shield the nuclei of another one. Table 1 reveals that both the ΔM and ΔD values are significantly affected by the concentration of the substrate. It is

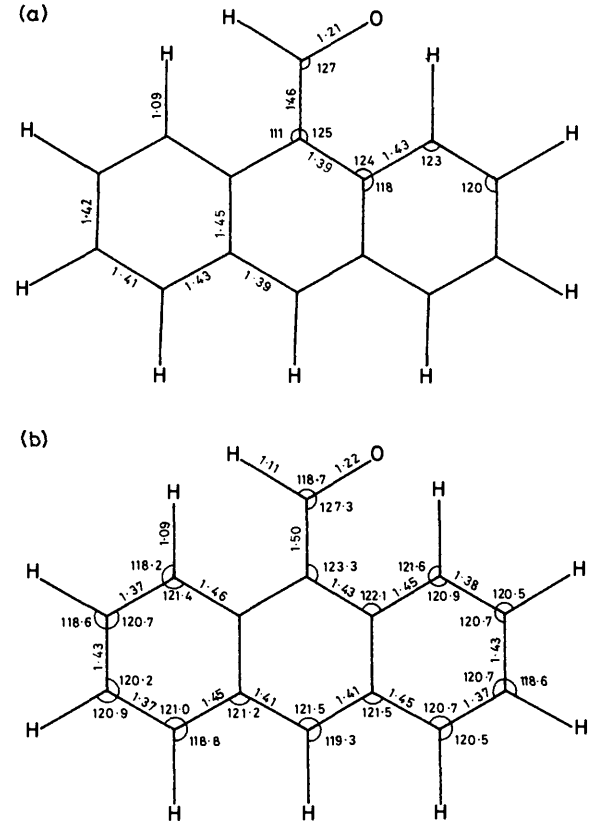

Figure 1. (a) *X*-Ray geometry[18] and (b) MNDO geometry (ω = 30°) of 9-anthraldehyde

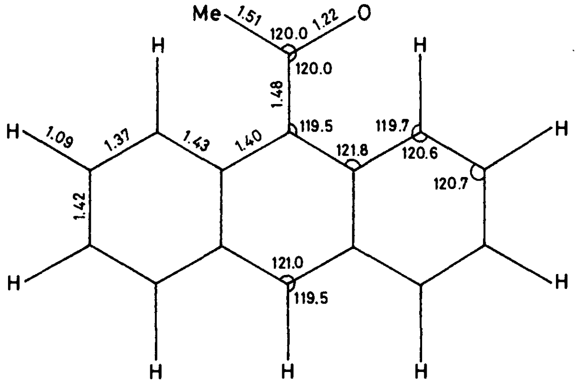

Figure 3. Geometry used for 9-acetylanthracene

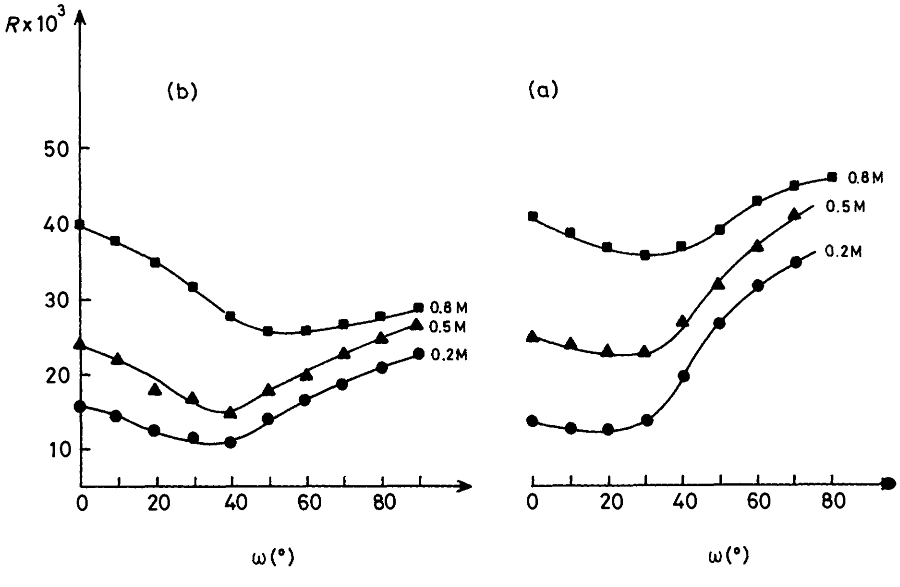

Figure 2. Plot of $R_{\text{cryst.}}$ *vs.* the torsional angle (°) of the aldehyde group in 9-anthraldehyde from results at different substrate concentrations (a) using *X*-ray geometry and (b) using MNDO geometry

important to stress that the ratios between the ΔMs and between the ΔDs vary [note that the ΔM value of the formyl proton (H-F) is practically unaffected by concentration, while all the other ones are affected], because it is on the ratios that the result of the LIS analysis depends.

Figure 2 shows that as the concentration of the substrate is lowered the simulation of the ($\Delta M - \Delta D$) values yields a

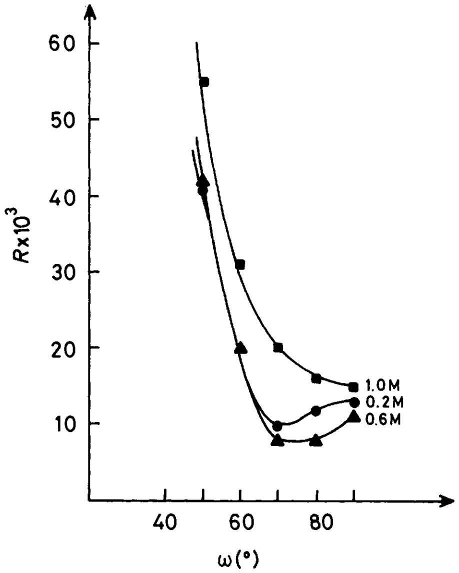

Figure 4. Plot of $R_{\text{cryst.}}$ *vs.* the torsional angle (°) of the acetyl group in 9-acetylanthracene, from results at different substrate concentrations

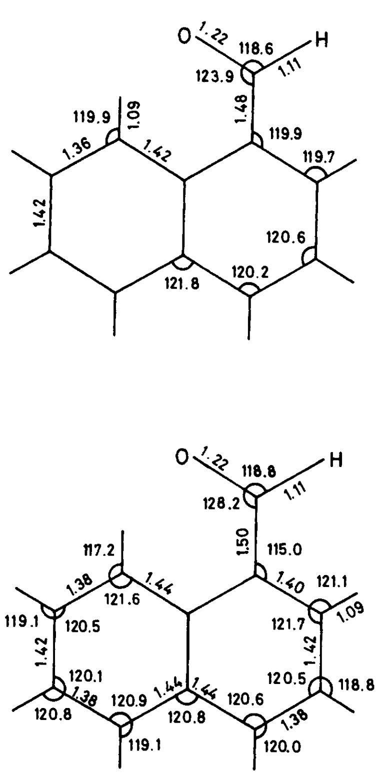

Figure 5. Standard (above) and MNDO (below) geometries for the *Z*-conformer of 1-naphthaldehyde

Table 6. Results of the analyses of the LIS

9-Anthraldehyde

Conc.	ω (°)	$R_{\text{cryst.}}$	Sum-diff. (p.p.m.)	R (Å)	φ (°)	ψ (°)	Pop. %	$K^a \times 10^3$
0.8398	50—60	0.026	1.40	2.70—2.75	85—90	140—145	100	4.5
0.4781	40	0.015	0.82	2.60	90	135	100	3.9
0.2029	20—30	0.012	0.63	2.65—2.70	70—75	130	100	4.0

9-Acetylanthracene

Conc.	ω (°)	$R_{\text{cryst.}}$	Sum-diff. (p.p.m.)	R (Å)	φ (°)	ψ (°)	Pop. %	$K \times 10^3$
1.0356	90	0.015	0.76	2.70	75	145	100	4.2
0.5929	70—80	0.008	0.38	2.70	70	145	100	4.0
0.2076	70	0.010	0.40	2.75	65	140	100	3.6

1-Naphthaldehyde

(a) Standard geometry

Conc.	*E*-conformer (%)	$R_{\text{cryst.}}$	Sum-diff. (p.p.m.)	R (Å)	φ (°)	ψ (°)	Pop. %	$K \times 10^3$
0.9905	32	0.027	1.56	2.60	85—90	120	100	4.1
0.5565	35	0.029	1.63	2.65	85—90	120	100	4.1
0.2015	34—35	0.025	1.34	2.70	80—90	115	100	3.9

(b) MNDO geometry

Conc.	*E*-conformer (%)	$R_{\text{cryst.}}$	Sum-diff. (p.p.m.)	R (Å)	φ (°)	ψ (°)	Pop. %	$K \times 10^3$
0.9905	5	0.022	1.26	2.50—2.55	80—90	135—140	100	4.4
0.5565	10	0.020	1.12	2.60	80—85	135	100	4.3
0.2015	15	0.020	1.08	2.75	60	135	100	4.5

[a] K is the proportionality constant in the McConnell–Robertson pseudo-contact shift equation.

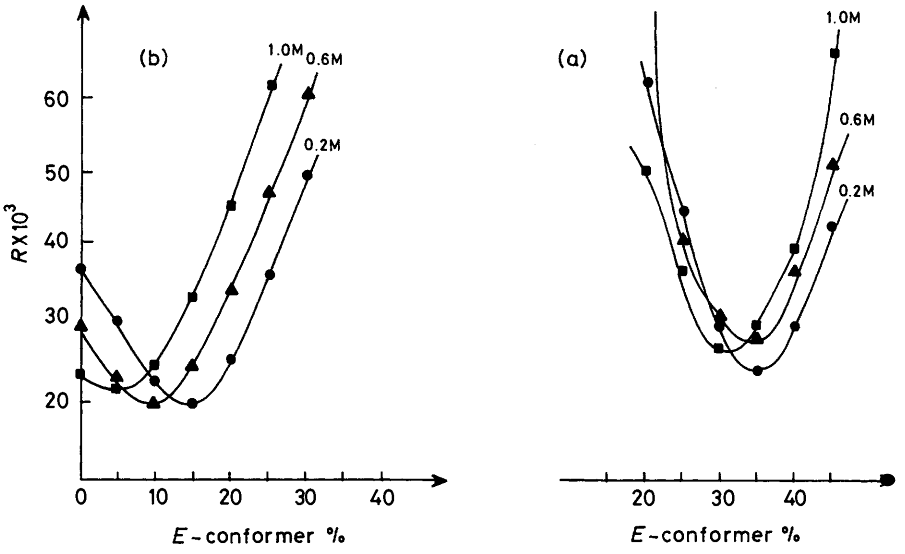

Figure 6. Plot of $R_{\text{cryst.}}$ *vs.* the percentage *E*-population of 1-naphthaldehyde, (a) using standard geometry and (b) using MNDO geometry

progressively better fit. On using the 0.2M values an agreement well inside the experimental error is obtained for low values of the torsional angle. The definition of the minimum is still not excellent, and it is somewhat dependent on the geometry used. As regards the lanthanide position, with respect to the co-ordinating atom, the 0.2M data gives a solution quite similar to the previous ones, but with the lanthanide atom out of the carbonyl plane. Table 6 gives the results using the MNDO geometry; those using the *X*-ray geometry are not significantly different.

In conclusion, the analysis of 9-anthraldehyde proved to be critically dependent on the concentration of the substrate. The use of low concentration data allows a reasonable solution to be obtained for a torsional angle less than 40°. It is difficult at the moment to say if the observed dependence of the torsional angle and of the lanthanide position on the concentration is a real effect or not.

9-*Acetylanthracene*.—We used a geometry obtained by combining the *X*-ray geometry of anthracene[21] with standard parameters for the acetyl group (Figure 3). The keto group does not affect the ring geometry significantly, as the crystal geometry of 9-anthryl styryl ketone shows no change in the geometry of the anthracene ring.[22] The analyses proceeded by varying the dihedral angle (ω) between the acetyl group and the anthracene rings.

The results are summarized in Figure 4. The simulation of the ($\Delta M - \Delta D$) values obtained from 1.0M solutions of substrate gave a minimum at values of 90°, corresponding to a good $R_{\text{cryst.}}$ value of 0.015. The use of the ($\Delta M - \Delta D$) values obtained from 0.6M solutions gave a better defined minimum at ω equal 75° with an $R_{\text{cryst.}}$ value of 0.007 (r.m.s. 0.3). Here the agreement is well inside the experimental error, and there is no reason to use more dilute solutions; thus it appears that in this case the LIS analyses is much less affected by the substrate concentration than for 9-anthraldehyde.

Once again the lanthanide co-ordinates corresponding to the best solution (Table 6) indicate that the lanthanide is not in the plane of the carbonyl group. Its position compares with that found for acetophenone[23] and particularly 2,4,6-trimethylacetophenone[7] (R 2.6 Å, φ 70°, ψ 147°, pop. 100%). As in the latter there is 100% *exo*-population of the lanthanide, *i.e.*, towards the acetyl methyl group, as is to be expected when the possible steric interactions between the bulky lanthanide in the *endo*-position and the 9-anthryl group are considered. Interestingly, there is no need to invoke any distortion of the anthryl geometry, particularly of the H-1, -8–C–C–H angles, and again this is exactly comparable to the situation in 2,4,6-trimethylacetophenone,[7] and for the same reasons.

1-*Naphthaldehyde*.—In this molecule 19 pseudo-contact shifts have been measured for the aromatic and aldehyde carbons and protons (Table 4), thus the system is considerably over-determined. In the first stage we used a standard geometry for the aldehyde group[24] added to the naphthalene geometry of reference 21 (Figure 5). The program searched for the best solution over a range of conformer populations. The data obtained from 1.0M solutions of 1-naphthaldehydes gave the curve shown in Figure 6, with a minimum at 32% *E*-conformation, corresponding to a somewhat poor (0.027) $R_{\text{cryst.}}$ value, and to a lanthanide position in the plane of the carbonyl (see Table 6). The data obtained from more dilute solutions do not cause any significant variations either in the position of the minimum or in the agreement factor; only the lanthanide position changed slightly.

The reason for the somewhat poor agreement factor is very likely related to the inadequacy of the standard geometrical parameters, particularly for bond angles around the sterically crowded area of the formyl group and H-8. Inspection of the individual solutions revealed poor agreement for H-8 in spite of the fact that this nucleus, with a large (*ca.* 70 p.p.m.) psuedo-contact shift, is of major importance in determining the solution. Thus it is possible that an incorrect geometrical relationship between H-8 and the formyl group is the cause of the unsatisfactory agreement factor.

An obvious approach was to use a more refined geometry, in which steric interactions around the aldehyde group were explicitly considered. In the absence of a crystal geometry, a fully optimized MNDO[25] geometry was obtained for the *E*, *Z*, and orthogonal conformations, *i.e.*, the dihedral angle between the aldehyde group and the rings was set at 0, 90, and 180° and not varied. It is important to note here that this type of calculation does not give the fully minimized energy, as it seriously underestimates the conjugation energy between the C=O and the aromatic ring.[26] Indeed, in these calculations the orthogonal conformation has the minimum energy. The

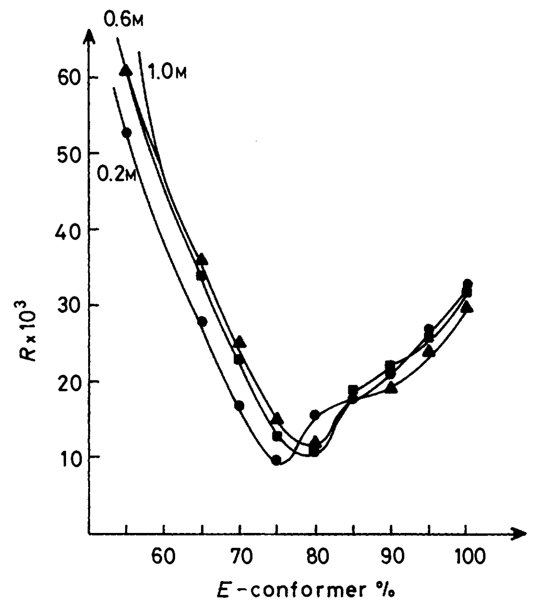

Figure 7. Plot of $R_{\text{cryst.}}$ *vs.* the percentage *E*-population of 2-naphthaldehyde

MNDO geometry of the *Z*-conformer is compared with the standard geometry used in Figure 5. It can be seen that considerable distortion of the aldehyde and of the H-8–C–C angle has occurred. Similar, but less marked, distortions are seen for the *E*-conformer whilst in the orthogonal form the aldehyde geometry is essentially identical to the standard model shown.

The use of these geometries to analyse the data obtained from 1.0M solutions of 1-naphthaldehyde gave a curve [Figure 6(b)] with a minimum at *ca.* 5% *E*-conformation, with a somewhat better $R_{\text{cryst.}}$ value (0.021) and a lanthanide position essentially in the carbonyl plane. On using the data obtained from more dilute solutions, the agreement factor only changes slightly, until 15% *E*-conformation (see Figure 6) and the corresponding lanthanide position is now out of the carbonyl plane (see Table 6).

Inspection of Figure 6 shows very clearly how sensitive the LIS analysis is to the precise geometry around the carbonyl carbon. The reason for this is that the difference in the pseudo-contact shifts on the two sides of the aldehyde group is caused mainly by the different conformer populations, but also a different bending of the formyl group in the plane of the ring in the two conformations can affect the solution. Thus, if the latter factor is not precisely known we cannot isolate the contribution of the first one, and compensations occur.

Moreover, the agreement factor is such that its value is determined mainly by the largest pseudo-contact shifts, which are observed for nuclei near to the complexing site. An incorrect location of these nuclei would lead to an incorrect solution.

2-*Naphthaldehyde*.—The 19 pseudo-contact shifts measured for all the protons and carbons of this molecule (Table 5) were simulated by the program using a standard geometry analogous to that described for 1-naphthaldehyde. In the case of the 2-isomer, there is no steric congestion which could affect the geometrical parameters. The program searched for the best agreement with the observed shifts over a range of conformer populations. Using the 1.0M data a good minimum ($R_{\text{cryst.}}$ 0.011) was obtained at 80% *E*-conformation (Figure 7), corresponding to a lanthanide position (R = 2.6 Å, φ = 75—90°, ψ = 130°, pop. = 100%). No significant variation either of the position of the minimum, or of the agreement factor, was observed on using the data obtained from more dilute solutions.

Conclusions

The present analyses of 1- and 2-napthaldehyde, 9-anthraldehyde, and 9-acetylanthracene gave results in substantial agreement with most previous studies. This demonstrates that the LIS technique, using the standard four-site model, can give reliable conformer populations in these systems. There is, however, the important caveat that when accurate geometrical parameters around the aldehyde group cannot be used, the solution is less definite.

The present study reveals for the first time a strong dependence of the LIS result on the concentration of the substrate. However, it appears that this effect is confined to 9-anthraldehyde and possibly to some other carbonyl compounds with three or more aromatic rings.

Experimental

The ^{1}H and ^{13}C spectra for the LIS analyses were recorded on a Varian FT-80 spectrometer on the same samples at probe temperatures of *ca.* 30 °C. All spectra were measured on solutions in $CDCl_3$ which had been stored over molecular sieves and passed through a dried Al_2O_3 column immediately before use. Commercial lanthanide shift reagents were dried *in vacuo* over P_4O_{10} for 24 h. Commercial substrates were distilled *in vacuo* the day before their use.

The results of the LIS experiments with Yb(fod)$_3$ (incremental weighing method) are given in Tables 1 and 3—5. The carbon assignments follow from references 10 and 16, and the proton assignments from known substituent effects, signal multiplicities, and consideration of the expected LIS. The experimental points were all obtained with a molar ratio ρ = [L]/[S] (L = shift reagent, S = substrate), in the range between 0.00—0.12. Both the correlation coefficients (>0.998) and the intercepts (which are identical to the unshifted spectra) demonstrate the accurate linearity of these plots.

The LIS data were obtained at varying concentrations of substrate for all the compounds examined. However, in those cases where varying the concentration did not lead to any significant change in the interpretation, only one concentration run has been recorded (Tables 3—5), but the analysis of the various concentration runs is given in Figures 4, 6, and 7.

La(fod)$_3$-induced shifts on carbon signals are reported in Tables 1 and 3—5 (protons did not display any meaningful shifts). Agreement factors are good only when variations in chemical shifts are not too small. However, even in such cases, the intercepts are identical to the unshifted spectra, thus demonstrating the linearity of these plots.

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