Tetrahedron Vol. 38, No. 10, pp. 1485 to 1491, 1982
Printed in Great Britain.

0040-4020/82/101485-07$03.00/0
Pergamon Press Ltd.

CONFORMATIONAL ANALYSIS—III†

A LANTHANIDE INDUCED SHIFT (LIS) NMR INVESTIGATION OF BENZALDEHYDE, AND THIOPHEN- AND FURAN-2-ALDEHYDE

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(*Received in UK* 21 *September* 1981)

Abstract—A rigorous error analysis of LIS is described which avoids the use of any normalising atom. This analysis is used to investigate the LIS of benzaldehyde and thiophen- and furan-2-aldehyde. The non pseudo-contact components of the *Yb*(fod)$_3$ induced shifts are isolated and found to be appreciable at the carbonyl carbon and the ortho and para carbons. Estimation of the diamagnetic contribution to these shifts with *La*(fod)$_3$ allows a precise analysis of the ^{1}H and ^{13}C LIS of these aldehydes without the need to invoke any contact shifts. The lanthanide-complex geometry found is essentially one-site, i.e. 100% population on the unhindered exo side of the carbonyl. The lanthanide is in the molecular plane of the aldehydes with Ln–O and Ln.O.C. parameters of *ca* 2.5Å and 140°, respectively. This procedure also gives the percent population of the O-cis conformer of furfural as *ca* 70–75% in CDCl$_3$ solution.

Conformational isomerism in the carbonyl derivatives of benzene, furan and thiophen has been the subject of many investigations in the last two decades, utilising IR,[1] microwave,[2,3] electron diffraction,[4] dipole moments,[5] CNDO[6] and *ab-initio*[7,8] methods, as well as a variety of NMR techniques. In the last, the observation of the coalescence of the NMR signals at low temperatures due to restricted rotation about the Ar–CHO bond has led to the direct determination of this energy barrier and to the relative conformer energies of those molecules with sufficiently high barriers to rotation to be observed by this technique ($\geqslant$ *ca*7 kcals/mole).[9-11] Long-range couplings,[12] nematic solvents[13] and lanthanide shift reagents (LSR)[14] have also been used to investigate these molecules. In principle, LSR should be able to provide both geometric and conformational information; however, previous LSR studies have not been entirely successful.

The central problem in these studies is that the system is often not mathematically well-determined. If the lanthanide induced shift (ΔM_i) of any nucleus i is solely due to the pseudo-contact term, it can be expressed by the McConnell–Robertson eqn (1)

$$\Delta M_i = k(3\cos^2 X_i - 1)/r_i^3 \qquad (1)$$

in terms of X_i the O–Ln–M angle and r_i the Ln–M distance. To determine the lanthanide position with respect to the substrate from such measurements requires at least four values of ΔM_i as there are three co-ordinates to be obtained and the proportionality constant in eqn (1) is unknown. To investigate any substrate properties such as conformer populations, molecular geometries etc requires the measurement of an equal additional number of ΔM_i values. However, it has been shown[15,16] that the ^{13}C LIS of aromatic compounds may have a considerable percentage of contact contribution and these therefore cannot be used with eqn (1) to provide additional equations. Unfortunately, there are not enough hydrogen nuclei (for which the contact contribution may be safely ignored under certain conditions, *vide infra*) in these molecules both to solve the set of eqn (1) for the lanthanide position *and* to determine the molecular parameters. For example, furan-2-aldehyde provides four proton ΔM values, which may be used to obtain the geometry of the aldehyde–lanthanide complex *or*, assuming the geometry, to provide information on the aldehyde molecule. One cannot, however, do both.

This problem is illustrated in the series of investigations by Montaudo *et al.*[17,18] They used *Eu*(fod)$_3$ which is known to give large contact shifts for ^{13}C,[16] and consequently measured only the proton LIS. In order to obtain the relative conformer populations in furan- and thiophen-2-aldehydes they either used a one-site geometry and kept the Ln–O distance constant at 3.0Å,[17] or allowed the Ln–O distance to vary using a two-site model with CO Ln angles fixed at 120 and 240°.[18] These procedures gave agreement factors (AF) for the thiophen, which is known to be entirely in the S-*cis* form, of 0.152, 0.025 and 0.023. None of these can be considered as entirely satisfactory, though the latter are within the range of acceptability given by Hofer (0.04).[14]

Nagata *et al.*[19] used a similar procedure to determine the conformer populations in the 2-formyl and 2-acetyl derivatives of furan and thiophen. Again the Eu–O position was fixed at 3.0Å, but now an equally-populated two-site model was used with an Eu$_1$–O–Eu$_2$ angle of only 30°. They obtained very poor agreement between observed and calculated shifts.

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†For Part II see Ref. 22.

An attempt to overcome the indeterminacy problem was made by Ammon *et al.*[20] who utilised both ^1H and ^{13}C LIS in their studies of aromatic ketones. To reduce contact shifts of ^{13}C they used *Yb*(fod)$_3$, and to combine the ^1H and ^{13}C data they normalised separately the ^1H and ^{13}C data sets, i.e. the shift data was used in the form of $^1H/^1H$ and $^{13}C/^{13}C$ shift ratios. This both removes one shift value unnecessarily and also does not directly relate the ^1H and ^{13}C LIS. They overcame the problem of the normalising atom (*vide infra*) by determining all the possible ratios M_i/M_j and averaging. This approach proved qualitatively useful (e.g. in obtaining ^{13}C assignments) but little quantitative data was produced.

We have recently shown[21,22] that LSR can be used to give detailed information about conformer geometries and relative energies in cyclic ketones. Our procedure is based on: (1) the *simultaneous* measurement of the ^1H and ^{13}C LIS which avoids any separate normalisation of the ^1H and ^{13}C data sets; (2) the use of *Yb*(fod)$_3$ to minimise contact shifts, which may be neglected in saturated carbonyl compounds for all atoms except possibly the CO carbon; (3) the adoption of a chemically reasonable multisite model of Ln–O complexation. For the axially symmetric ketones studied, two and four site models have been used, in which the lanthanide co-ordinates (r, θ, ϕ) are freely varied, but in order to avoid the problems of indeterminacy the remaining sites are obtained by reflection in the xy and/or xz planes (Fig. 1). However, only the populations of the different sites about the xz plane may be varied.

It seemed of some interest to establish whether this type of procedure could be used with aromatic carbonyl compounds and in particular whether the problems detailed above, i.e. lack of data using only ^1H LIS and possible non-pseudo-contact contributions to the ^{13}C LIS, could be solved successfully. We show here that it is indeed possible to obtain precise agreement between measured and calculated ^1H and ^{13}C LIS provided that

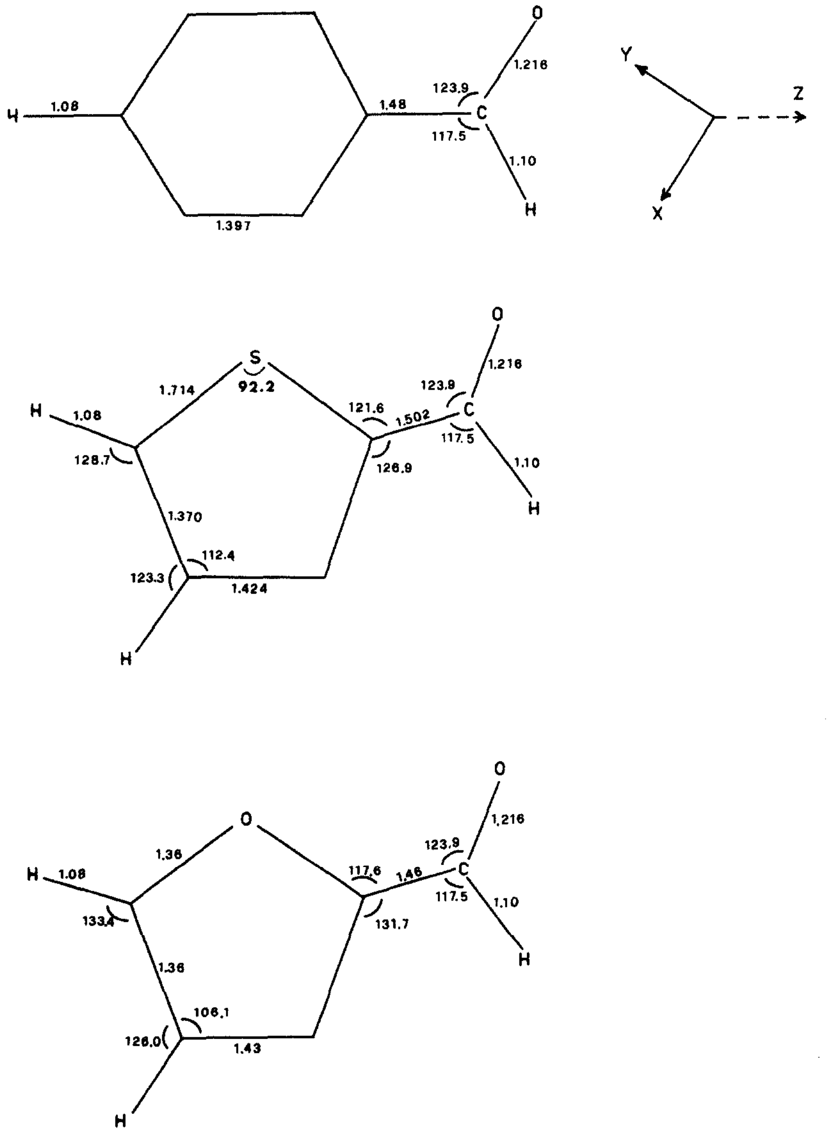

Fig. 1. Co-ordinate axes and geometries of aromatic aldehydes.

other contributions to the ^{13}C LIS can be determined. We show further that these contributions in the aromatic aldehydes are complexation shifts, not contact shifts, and as such can be easily measured using diamagnetic lanthanides, and eliminated. A preliminary account of some of these results has already appeared.[23]

Theory, the normalisation problem

The procedure now invariably used to determine the goodness of fit of the calculated vs the observed LIS is by means of the Hamilton R-value or agreement factor (AF), defined as[24]

$$R = \left\{ \sum_i (\Delta M^i_{\text{obs}} - f \cdot \Delta M^i_{\text{calc}})^2 \Big/ \sum_i (\Delta M^i_{\text{obs}})^2 \right\}^{1/2} \tag{2}$$

with $f = 1$, where the observed and calculated shifts are scaled by the use of a normalising atom i.e. the quantities in eqn (2) are all *ratios* $\Delta M^i/\Delta M^0$ of the LIS with respect to one particular atom. In this way the constant k in eqn (1) is eliminated. This implicitly assumes that the normalising atom is "reliable", i.e. error-free, without any non-pseudo-contact contribution, of well-defined geometry, etc. In the molecules we wished to investigate, some of the ^{13}C nuclei were known to experience non pseudo-contact contributions and it has been suggested that this is also true for formyl hydrogen. Thus all those nuclei with the largest LIS are necessarily excluded as the normalising atom, leaving a choice of those protons in the aromatic ring at some distance from the site of complexation with possible geometric and experimental errors.

Clearly it would be preferable to develop an approach which did not involve the subjective choice of a normalising atom. This can be done simply as follows. We need to determine that value of f, eqn (2), which for any given solution will minimise the R-value (note that we are referring now to the actual observed and calculated ΔM^i values, not their ratios). This is given by the condition

$$(\partial R/\partial f) = 0$$

from which we obtain directly

$$f = \sum_i (\Delta M^i_{\text{calc}} \cdot \Delta M^i_{\text{obs}}) \Big/ \sum_i (\Delta M^i_{\text{calc}})^2. \tag{3}$$

Thus our procedure is now to determine the goodness of fit of any solution by eqn (2) in which the normalising factor f is given by eqn (3). This procedure requires neither a normalising atom nor any implicit assumptions and we recommend its use for all future LIS studies.† Note, however, that the use of eqns (2) and (3) is still a normalising procedure involving the loss of one degree of freedom. This amendment has been incorporated into our existing computer program (LIRAS-3 is the amended version of LIRAS[25]), and could easily be inserted into any other comparable LIS program. This amended program requires slightly more cpu time than the original one, mainly due to the fact that the f values for solutions which generate ΔM^i_{calc} values outside the set tolerances on ΔM^i_{obs} have to be calculated before the solutions can be rejected. (Previously, a solution could be rejected as soon as one ΔM^i_{calc} exceeded $\Delta M^i_{\text{obs}} \pm$ tolerance). However, the time factor is not great, varying from a 10 to 30% increase.

RESULTS

The program described above can be used to investigate the extent to which the ΔM_i values contain appreciable non-pseudo-contact contributions, as now the goodness-of-fit is only determined by the set of nuclei included. It is convenient to consider each molecule in turn.

Benzaldehyde

The symmetry of the benzene ring makes this the obvious molecule to consider first. There is only one conformation, which is planar. The molecular geometry was obtained by a combination of the microwave geometries of acetaldehyde[26] and benzaldehyde[3] with the *ab-initio* calculations on aldehydes.[8] This gave the geometry of Fig. 1. Rapid rotation of the phenyl ring (on the NMR time scale) equalises the ortho and meta nuclei giving a set of nine ΔM_i values (Table 1). Initially, all these values were included except for the CO carbon, following our usual procedure.[21] This analysis has, therefore, eight equations in five unknowns (one normalising factor, three lanthanide co-ordinates and *exo*/*endo* lanthanide populations on the two-site C=O binding model) and produced an unacceptably large R-value of 0.027 (Case A, Table 4). However, the lanthanide position was as expected (ϕ90°, ψ *ca* 140°) and was essentially one site (population 95%). This is to be expected as the approach of the lanthanide to the *endo* side of the CO will be severely restricted by the phenyl group. Trial and error with LIRAS-3 eventually identified the erroneous ΔM values. Case B, Table 4 shows the results of the analysis in which C atoms $C_{2,6}$ and C_4 (as well as C=O) have been removed. In order to prevent indeterminacy in this case we restricted the search to 100% *exo* population of the lanthanide and ϕ90° to give six equations in three unknowns. The R-value (0.015) is acceptable, and a reasonable solution is obtained, but the analysis does not provide any indication of the cause of the non pseudo-contact contributions. These were then identified as diamagnetic complexation shifts by an identical LIS experiment in which the diamagnetic *La*(fod)$_3$ replaced *Yb*(fod)$_3$. The diamagnetic contribution of the *Yb*(fod)$_3$ shifts has been shown previously to be given, to a good approximation, by the *La*(fod)$_3$ shifts.[27] These diamagnetic complexation shift (ΔD) values are listed in Table 1 and can be seen to be appreciable, particularly for the C=O, $C_{2,6}$ and C_4 carbons, as indicated by the above analysis. (Intriguingly the C_1 diamagnetic shift is also appreciable and negative, but this was not indicated so clearly in the LIS analysis). However, unequivocal proof of the correctness of this interpretation is provided by the results of the analysis of the residual ($\Delta M^i - \Delta D^i$) shifts (Case C, Table 4). Under case C are given two solutions, one (C1) in which the lanthanide co-ordinates are freely variable, the other (C2) in which the lanthanide is restricted to the benzaldehyde molecular plane, i.e. $\phi = 90°$. Although case C1 is a marginally better solution, case C2 is also well within acceptable error limits. Thus the lanthanide may be considered to be essentially in the molecular plane and the lower R-value for case C1 is probably due to this, essentially four-site,

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[†] The alternative tests proposed by Richardson *et al.*[37] cannot be used here as in our problems the number of variables *differs* in the cases considered (see later).

model taking better account of the molecular motions in the complex. The *R*-values obtained are well within the acceptable margin of error and the best solution listed is again a chemically reasonable one with essentially a 100% population on the unhindered *exo* side of the CO. (In this case as there are now nine equations the percent population was included as a variable). Most important is that this solution was obtained from an analysis which utilised *all* the ΔM values (including even the CO) and shows very clearly that a complete explanation of the LIS of all the proton and carbon nuclei in benzaldehyde may be obtained *without the need to invoke contact shifts at all.* We defer further consideration of this result until the other aldehydes have been considered.

Thiophen-2-aldehyde

This molecule may be considered to exist solely in one conformation, as all previous investigations of rotational isomerism in thiophen-2-aldehyde have failed to show any population of the S-*trans* conformation.[1,2,13,17] The geometry of the predominant S-*cis* conformer was obtained by a combination of the accurate microwave geometries of the formyl group[26] and of thiophen, with *ab-initio* calculations on substituted thiophens.[8] (This reference collates also all the experimental data on thiophen geometry). The resultant geometry is shown in Fig. 1.

Using this geometry, the analysis of the thiophen LIS data proceeded in a similar manner to that of benzaldehyde. The initial analysis (Case A, Table 4) included all the C and H ΔM values (except the C=O), giving eight equations in five unknowns (the *exo*/*endo* lanthanide population was allowed to vary). Again this analysis produced very large *R*-values, well above any experimental error, but a not unrealistic lanthanide geometry with a 100% *exo* population. However, the Ln-O distance is somewhat larger than expected (3.3Å) which, in our experience, nearly always indicates errors in the analysis. Removal of the C_3 and C_5 carbons (as well as the C=O) gave Case B which has an acceptable *R*-value with now a better Ln-O distance (3.0Å). The diamagnetic contributions to the LIS were then measured (Table 2) and found to be surprisingly large, contributing over 25% to the ΔM values of C atoms 3 and 5. Clearly, any analysis of the LIS which does not explicitly take into account these contributions will be substantially in error. The analysis of the residual ($\Delta M^i - \Delta D^i$) shifts (Case C) gave a good *R*-value and an acceptable complex geometry with now a Ln-O distance of 2.55Å comparing precisely with that found in benzaldehyde, as may be expected. Again this analysis has utilised *all* the carbon and hydrogen ΔM values, including the C=O, and no constraints have been applied.

Although the microwave geometries of thiophen and of the formyl group are definitive, there remains, in the absence of an experimental study of thiophen-2-aldehyde, some doubt as to the precise geometry of this molecule, with particular reference to the attachment of the formyl group. For this reason, Kao and Radom optimised all the substituent parameters at the STO-3G level[8] and Fig. 1 incorporates their values of the C_2–CO bond length and $C_3.C_2CO$ angle. Comparison of these data with those of benzaldehyde and furan-2-aldehyde suggests that the *ab-initio* value of the C_2–CO bond length (1.50Å) is slightly too long. The other optimised parameter may also be in error. Thus it seemed of interest to explore whether the LIS procedure could be used to refine these parameters. However, over a range of bond lengths of ±0.05Å and bond angles ±5° the agreement factor was essentially unchanged. Thus at this level of approximation the procedure could not be used to optimise these parameters.

Furan-2-aldehyde

The presence of two roughly equally populated conformers of this molecule in $CDCl_3$ solution makes this a much more complex case, and this complexity is reflected in the analysis. A number of structural determinations of furan-2-aldehyde have been performed, most of them making assumptions of one sort or another.[4]

Thus, we combine the well-known structure for furan (see Ref. 7 for a comparison of experimental and *ab initio* geometries) and the known structure of the formyl group[26] with the microwave[2] and electron diffraction[4] studies of furan-2-aldehyde and the crystal structure determination of 4-bromo-furan-2-aldehyde.[28] All these are in reasonable agreement giving the averaged parameters shown in Fig. 1.

Note that these assume, following all the other investigations, the same geometry for the two conformers apart from the O.C.C.O dihedral angle (*vide infra*).

In this case it is convenient to present the results of the analysis in the form of a curve showing the best

Table 1. Observed shifts (δ_0), LIS (ΔM) and diamagnetic shifts (ΔD) (ppm) for benzaldehyde

	C=O	C_1	$C_{2\ 6}$	$C_{3\ 5}$	C_4	CHO	$H_{2\ 6}$	$H_{3\ 5}$ [c]	H_4 [c]
δ_o [a]	192.34	136.46	129.75	129.03	134.48	10.01	7.88	7.52	7.63
ΔM [b]	131.92	46.55	31.50	15.54	14.54	69.75	29.98	10.07	7.96
intercept	192.37	136.47	129.74	129.03	134.47	10.02	7.88	7.51	7.62
ΔD [d]	10.01	-2.11	2.52	0.25	2.89	-	-	-	-

a) $[S]_o$ 0.947 ml^{-1} in $CDCl_3$, b) from three additions of $Yb(fod)_3$, ρ 3.54, 6.81, 11.16 x 10^{-2} , all correlation coefficients $\geqslant$ 0.999 .

c) 120 MHz spectra, normalised by $H_{2,6}$ see text.

d) $[S]_o$ 0.442 ml^{-1}, ρ 0.197 , normalised to CO $[S]_o$ 1.017 ml^{-1}, ρ 0.109 , see text.

Table 2. Observed shifts (δ_0), LIS (ΔM) and diamagnetic shifts (ΔD) ppm for thiophen-2-aldehyde

	C=O	C_2	C_3	C_4	C_5	CHO	H_3	H_4	H_5
$\delta_0{}^a$	182.88	144.18	136.21	128.35	135.06	9.94	7.76	7.21	7.76
ΔM^b	151.18	52.77	32.93	18.46	23.13	81.52	22.57	11.52	12.63
intercept	182.98	144.20	136.23	128.36	135.06	10.00	7.78	7.21	7.76
ΔD^c	10.99	-3.10	6.92	1.69	7.01	-	-	-	-

a) $[S]_0$ 1.057 ml^{-1} in $CDCl_3$.

b) from three additions of $Yb(fod)_3$, ρ 2.18, 4.48, 7.36 x 10^{-2} ; all corr. coeff. $\overset{\sim}{>}$ 0.9995.

c) $[S]_0$ 0.656 $m\ell^{-1}$, ρ 0.190 , normalised to CO $[S]_0$ 1.21 $m\ell^{-1}$, ρ .0746 .

R-value vs the percent population of the O-*cis* conformer. In this instance, for any given population, the program obtained the best R-value by optimising all the other variables (normalisation, lanthanide coordinates and *endo*/*exo* lanthanide populations). Thus for each *cis*/*trans* population this corresponds to the solution of nine equations (for all the nuclei) in five unknowns. Following the usual procedure, i.e. using all the nuclear ΔM values of Table 3 (except the C=O) resulted always in a poor R-value (Fig. 2a). The curve does show a slight minimum at *ca* 80% *cis* population, but the differential is so small that it could not be justified as a determination of the *cis*/*trans* ratio. Furthermore, both the lanthanide-substrate co-ordinates and the *exo*/*endo* populations (Case A, Table 4) differ appreciably from the "normal" values. Note especially the large Ln–O distances 3.1–3.6Å.

The alternative procedure follows that adopted in the above analyses. Here, all the nuclear LIS were used after correction for the diamagnetic contributions (Table 3). The curve obtained (Fig. 2b) shows much better R-values at all compositions and gives an acceptable minimum at *ca* 70–75% population of the *cis* conformer with an R-value of 0.017. Furthermore, the lanthanide co-ordinates at the minimum are now much more reasonable (Case B, Table 4). The Ln–O distance is much shorter and compares well with the other substrates, the lanthanide is in the aldehyde's molecular plane ($\phi = 90°$) and is 100% in the *exo* position, as expected. The value of 70–75% (± 10) for the *cis* population also appears reasonable. Abraham and Siverns calculated $\Delta E(cis\text{-}trans) \simeq 0$ for a solvent of dielectric constant *ca* 5.[12] Chadwick,[11] from low temperature NMR measurements, suggested $\Delta E \simeq 0$ in a lower dielectric medium ($\epsilon \simeq 3$). The percentage of the *cis* form in $CDCl_3$, obtained from long range ^1H couplings by Bertran and Rodriguez,[12] is 71% in pleasing, but probably fortuitous, agreement with the value obtained here.[22]

The major uncertainties in the above analysis stem from the presence of two very different conformations rather than inadequacies in the analysis. The assumption of identical *cis* vs *trans* geometry (except for the O.C.C:O dihedral angle) does not seem a very good one. However, in the absence of any further geometrical information, there is no better assumption to be made. Also there is no good reason to suppose that the diamagnetic complexation shifts would be identical in the two isomers. This could also introduce a systematic error into the analysis. But the above analysis does show that even in this complex and not very well-determined case, the LIS procedure, when due account is taken of the diamagnetic complexation shifts, can give a quantitative measure of the molecular energies.

CONCLUSIONS

The major conclusions which emerge from these studies are the importance of the diamagnetic contribution to the C shifts and the apparently negligible contact shift

Table 3. Observed shifts (δ_0) LIS (ΔM) and diamagnetic shifts (ΔD), ppm for furan-2-aldehyde

	C=O	C_2	C_3	C_4	C_5	CHO	H_3	H_4	H_5
$\delta_0{}^a$	177.85	153.21	120.85	112.63	148.10	9.67	7.26	6.61	7.70
ΔM^b	133.93	53.07	33.94	18.28	22.73	69.39	23.41	10.63	12.85
intercept	178.00	153.26	120.90	112.64	148.12	9.75	7.28	6.62	7.71
ΔD	7.48	-1.00	7.90	1.87	4.68	-	-	-	-

a) $[S]_0$ 1.013 ml^{-1}

b) from three additions of $Yb(fod)_3$, ρ 2.61, 4.87, 8.66 x 10^{-2} , all corr. coeff. $\overset{\sim}{>}$ 0.9994.

c) $[S]_0$ 0.516 $m\ell^{-1}$, ρ 0.190 , normalised to CO $[S]_0$ 1.037 $m\ell^{-1}$, ρ .098 .

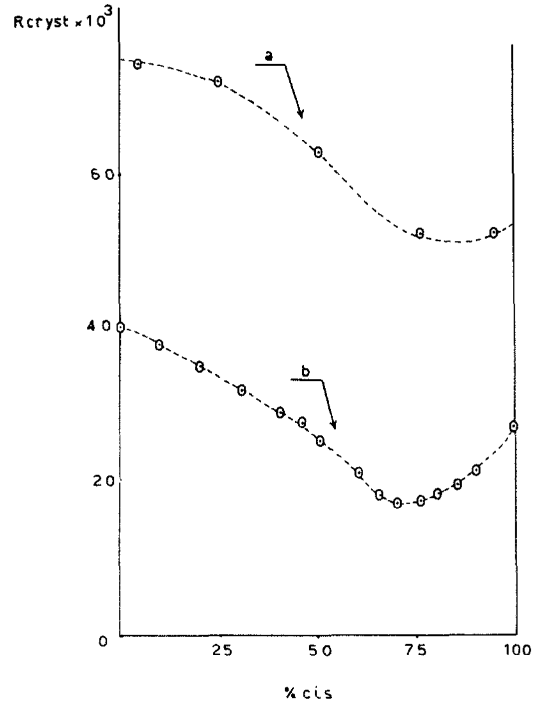

Fig. 2. The agreement factor $R(\times 10^2)$ vs the percent of *cis* conformer in furan-2-aldehyde (a) using ΔM values and (b) correcting for the diamagnetic complexation shifts ($\Delta M - \Delta D$) values.

contribution. There have been only few previous systematic studies of the diamagnetic shifts. Chadwick and Williams[27] have shown them to be small (< 1 ppm) in saturated ketones for all carbons except the CO carbon, for which ΔD values of *ca* 10 ppm were reported. (We have recently confirmed these findings for 4-phenylcyclohexanone). In a survey of saturated ketones, alcohols and amines, they observed sizeable diamagnetic contributions over more than two bonds only for amines.

Tori *et al.*[29] measured the diamagnetic shifts in pyridine, pyridine N-oxide, aniline and phenol, and obtained results in general similarity to the above, although the shifts were usually smaller, e.g. in aniline the diamagnetic shifts were −1.6, 2.8, 0.7 and 3.3 for carbons 1–4 which are almost identical to those for benzaldehyde (Table 1). Both the alternation effect and the lack of observable shifts in saturated ketones support a π-mechanism for these shifts, rather than the alternative electric field effect.[30] Indeed, the alternation effect is so regular for multi-ring aromatic ketones that it may be used as a valuable aid in the assignment of the ^{13}C spectra.[31] Although the contact shift is also mainly a π-transmitted effect (in aromatic compounds) there is a considerable difference between contact and complexation shifts in practice in that the contact shifts alternate in *sign* rather than in *size*, e.g. for aniline Tori *et al.*[29] quote the Ni(acac)$_2$ shifts, which are thought to be entirely contact, as −1.0, 0.68, −0.38, 0.53 for carbons 1–4. Similarly in pyridines the diamagnetic shifts, Ni(acac)$_2$ shifts and the contact contributions to the Eu(dmp)$_3$ shifts are for carbons 2,3,4,–0.9, 0.2, 2.2;[29] −1.00,2.81, −0.63,[29] and −22,25, −11;[32] again only for the diamagnetic shifts is C$_3$ unchanged. The alternating effect is almost exactly paralleled by the observed hyperfine coupling of the protons in the ESR spectra of quinone radical ions,[33] again confirming the π-transmission mechanism. Detailed consideration of this analogy will be deferred until further results can be considered.[31]

The apparently negligible contact shift contribution for the C shifts may not be as surprising as it at first seems. Due to the r^{-3} dependence of the pseudo-contact term, the CO carbon is in a unique position, with a much larger shift (by a factor of 2–3) than any other nucleus. Thus the fact that this C can be included in the LIS analysis does not mean that there is no contact term for it, as ±5 ppm on its ΔM value would not seriously affect the analysis. However, the analysis shows conclusively the lack of any contact shift on the other C atoms. It will be of some interest to test the generality of these findings, particularly as contact shifts have been previously implicated as the excuse for other uncertainties in the LIS analysis. Further work in this area is in progress.

Table 4. Results of analyses of LIS shifts

	Benzaldehyde.	R[a]	R.M.S.[b]	Lanthanide Co-ordinates.				
				r(Å)	ϕ°	ψ°	Pop.[c]	f
A)	All nuclei (–C=O)	.027	0.95	2.90	90	140	95%	3450
B)	–CO;C$_{2,6}$;C$_4$	.015	0.5	2.60	90[e]	130	100%[e]	2875
C1)	Corrected Shifts	.005	0.2	2.60	60	140	100%	2970
C2)		.013	0.7	2.50	90[e]	140	95%	2870
	Thiophen-2-aldehyde							
A)	All nuclei (–CO)	.051	2.0	3.3	80-90	145	100%	4870
B)	–CO, C$_3$, C$_5$	.011	0.5	3.0	90[e]	140	100%[e]	4170
C)	Corrected Shifts	.015	0.9	2.55	80- 90	140	95%	3425
	Furan-2-aldehyde[d]							
A)	All nuclei (–CO)	.052	1.9	3.1-3.6	55- 90	160-170	70-100	4640-5100
B)	Corrected Shifts	.017	0.9	2.30-2.35	80-90	150-155	100%	2770

[a] Agreement (R) factor, [b] r.m.s. error, [c] % Population of exo w.r.t. endo (see text); [d] best solution; [e] not varied in search procedure.

EXPERIMENTAL

The ^1H and ^{13}C spectra were run at 80 and 20 MHz, respectively, on the same samples with a Varian FT-80 spectrometer, with probe temp about 30°. As the H-3 and H-4 benzaldehyde absorptions, even after LIS additions, were very strongly coupled ,the proton spectra for this compound were run also with a PE R-34 (220 MHz) spectrometer, and the latter data were normalised to the former ones, using H-2 as the normalising shift.

All spectra were obtained in $CDCl_3$ which was stored over molecular sieves and passed through a dried alumina column immediately before use. Commercial lanthanide shift reagents were dried *in vacuo* over P_4O_{10} for 24 hr. Commercial samples of the aldehydes were distilled *in vacuo* the day before their use.

The results of the LIS experiments with *Yb*(fod)$_3$ (incremental weighing method) on the three aldehydes are given in Tables 1-3. The proton assignments follow from many previous studies,[34] the C-13 assignments for benzaldehyde and furan-2-aldehyde from Ref. 35, and those for thiophen-2-aldehyde from Ref. 36. The experimental points were all obtained with a molar ratio $\rho = [L]_0/[S]_0$ in the range between 0.0 and 0.1. Both the correlation coefficients (≥ 0.999) and the intercepts (which are identical to the unshifted spectra) demonstrate the accurate linearity of these plots.

As *La*(fod)$_3$ yields much smaller shifts, the latter were determined by addition of comparatively large amount of the reagent to the substrate solution to obtain a 0.2 $[L]_0/[S]_0$ molar ratio so as to minimise the importance of experimental errors. However, the ΔM's obtained from this broader concentration range are always significantly lower than those obtained from the 0.0 to 0.1 range, because of the curvature of the ΔM vs $[L]_0/[S]_0$ plots for molar ratios larger than 0.1. Therefore, it was necessary to use a value of ΔM determined from the narrow range to normalise the values of ΔM obtained from the broad one. Fortunately the ΔM value of the CO carbon was always large enough to be reliable when obtained from the narrow range. Thus we used it as the normalising shift. The results of the *La*(fod)$_3$ experiments for the three aldehydes are also given in Tables 1-3. Only carbon shifts are reported, as protons did not give any meaningful shifts.

Acknowledgements—We acknowledge a British Council Substantive Award and thank Dr. R. Podestà for considerable computing assistance in writing LIRAS-3, and Miss C. Lasagna for technical assistance.

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