

## Lanthanum-induced $^{13}\text{C}$ -N.M.R. Shifts: a Novel Probe of $\pi$ -Electron Delocalisation

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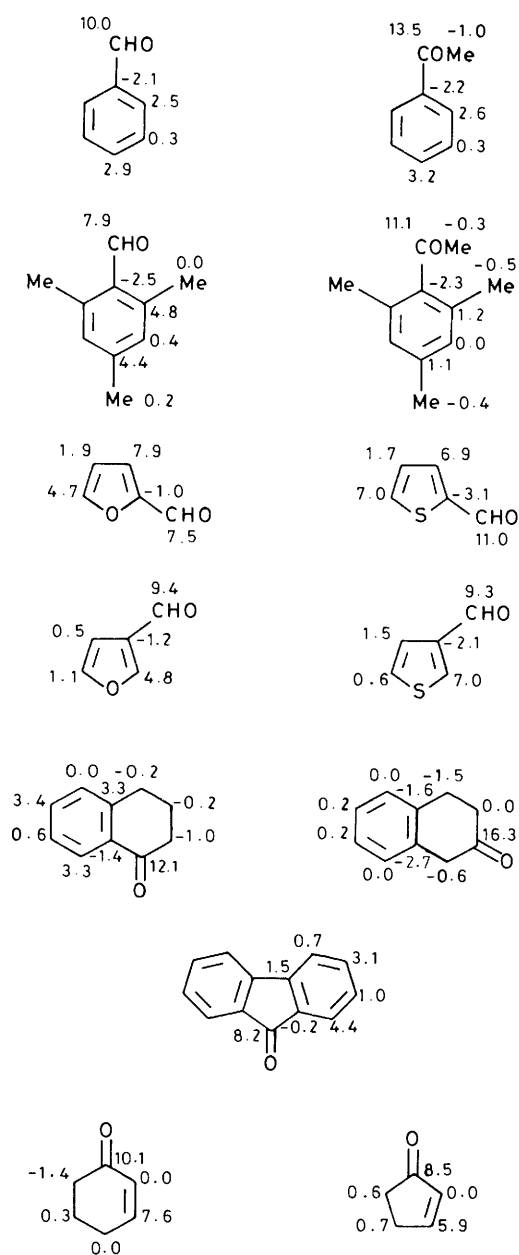
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$\text{La}(\text{fod})_3$  (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato) diamagnetic complexation shifts can be used as a sensitive probe of the extent and pattern of  $\pi$ -electron delocalisation in aromatic and olefinic aldehydes and ketones and hence as a tool for the assignment of  $^{13}\text{C}$ -n.m.r. signals in complex, unsaturated molecules.

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The use of lanthanide-induced n.m.r. shifts is commonplace in structural organic chemistry. In addition to the qualitative application of shift reagents for increased spectrum dispersion, their quantitative use in the refinement of molecular geometry is now well established.<sup>1-3</sup> It is generally recognised that the

observed shifts induced by paramagnetic lanthanide ions are a composite of three terms: the pseudo-contact shift (a through-space magnetic field effect following the McConnell-Robertson equation), the contact shift (a complex quantity arising from delocalisation of unpaired spin density from the



**Figure 1.**  $\Delta D$  values (p.p.m.) of  $\text{La}(\text{fod})_3$ -induced shifts for aldehydes and ketones in  $\text{CDCl}_3$ . The values are defined as the slopes of the plots of the  $^{13}\text{C}$  chemical shifts vs. the mole ratios of  $\text{La}(\text{fod})_3$  to substrate (generally  $<0.25$ ). Positive  $\Delta D$  values imply high frequency shifts.  $|\Delta D|$  values  $<0.5$  are within the experimental error of the measurements.

lanthanide ion into both  $\sigma$  and  $\pi$  frameworks of the substrate molecule)<sup>4,5</sup> and the complexation shift (arising from the redistribution of electron density within the substrate as it acts as a Lewis base in complex formation). This last effect is usually small and the extent to which it contributes to the observed shifts may be estimated from the shifts induced by the diamagnetic lanthanide complex  $\text{La}(\text{fod})_3$  ( $\text{fod} = 6,6,7,7,8,8,8\text{-heptafluoro-2,2-dimethyloctane-3,5-dionato}$ ).<sup>4,6,7</sup>

We now report that the diamagnetic complexation shifts induced by  $\text{La}(\text{fod})_3$  are themselves valuable n.m.r. observables furnishing an extraordinarily selective and sensitive probe of  $\pi$ -transmitted interactions. We further show that they can be used in the detection of competing  $\pi$ -transmission

mechanisms and, because of their selectivity, in the assignment of  $^{13}\text{C}$ -n.m.r. signals in complex unsaturated systems.

In Figure 1 is given a selection of complexation  $^{13}\text{C}$ -n.m.r. shifts ( $\Delta D$  values) obtained by the addition of  $\text{La}(\text{fod})_3$  to  $\text{CDCl}_3$  solutions of a range of unsaturated substrates. The pattern of the induced shifts is clearly identifiable as reflecting predominantly  $\pi$ -electron density transmission. No appreciable shifts at the saturated carbon centres in 4-phenylcyclohexanone (not shown in Figure 1) are observed (the shift at the carbonyl carbon is 14.5 p.p.m.) confirming the absence of significant  $\sigma$ -transmission. In benzaldehyde and acetophenone there are the expected large effects at the carbonyl carbon atoms and apart from the characteristic (small) negative shift at carbon-1 only the carbons *ortho* and *para* to the substituent show additional significant shifts. Insertion of ring substituents that do not complex appreciably with lanthanide ions (*e.g.*  $\text{NO}_2$ , halogen,  $\text{CH}_3$ ) does not affect this pattern substantially. Entirely comparable effects are observed in the furan and thiophen aldehydes. In the 2-substituted derivatives, simple resonance considerations predict large shifts at carbons-3 and -5 and a smaller shift at carbon-4, as is observed. The 3-substituted analogues are of particular interest since the  $\Delta D$  values provide clear evidence for differences in bond orders between furan and thiophen-3-aldehydes. Whereas in the furan case significant high frequency shifts are found only for carbons-2 and -5, in the thiophen case the largest high frequency shifts are at carbons-2 and -4 which is in agreement with the known increase in partial double bond character of the C(3)-C(4) bond in thiophen compared with furan.

Perhaps the clearest examples of the alternating  $\pi$ -mechanism for delocalisation are to be found in the polycyclic and olefinic compounds. The results for fluorenone and  $\alpha$ -tetralone beautifully illustrate the alternation, indeed in the latter compound the effect is so clear as to allow unambiguous assignment of the signals due to carbons-3 and -4 ( $\delta$ -values 126.46 and 127.00, respectively, from  $\text{Me}_4\text{Si}$ ) which would otherwise have been extremely difficult. The absence of any direct conjugative pathway connecting the carbonyl group and the benzene ring in  $\beta$ -tetralone results in either small or negligible high frequency shifts at carbons other than the carbonyl carbon and small negative shifts at the ring junction and adjacent, saturated carbon centres. The  $\alpha,\beta$ -unsaturated ketones follow the now familiar pattern in which carbons-1 and -3 display large high frequency shifts, carbon-2 a negligible shift, and the remaining carbon atoms only small shifts.

Finally (and importantly), revealing comparisons may be made between the shifts found in benzaldehyde and acetophenone, and the corresponding mesityl (2,4,6-trimethyl) derivatives. In the former pair, the ring carbon shifts are very close in magnitude and pattern: a negative shift is observed at the carbon to which the carbonyl group is attached, a small positive shift is found at the *meta* carbon, and large positive shifts at the *ortho* and *para* carbons. In stark contrast, although this pattern is preserved in the methylated analogues, the magnitudes differ considerably between aldehyde and ketone, the latter displaying much reduced shifts for the *ortho*, *meta*, and *para* ring carbons compared with the former. We regard this as evidence for deconjugation of the ketonic carbonyl and ring  $\pi$ -systems consequent on increased steric hindrance in the ketone compared with the aldehyde. It is also fascinating to compare the effects of ring methylation on the shifts of *ortho*, *meta*, and *para* carbons in the aldehydes and ketones since they are quite different. Whereas methylation of acetophenone leads to substantially decreased shifts (presumably as a result of steric destabilisation of the coplanar conformation as proposed above), methylation of the aldehyde has the reverse effect. It is tempting, in this connection, to

propose a synergic effect in the aldehyde in which the electron withdrawal on complex formation is facilitated by the electron-donating methyl groups, and it may be significant that in the trimethyl ketone the shifts on the ring methyl carbons are negative whereas they are zero or positive in the aldehyde.

In conclusion, diamagnetic lanthanum-induced shifts, which are easily and accurately measurable, provide a ready means of studying the extent of  $\pi$ -type interactions both between the carbonyl and ring  $\pi$ -systems and within the ring systems. The shifts correlate only moderately with  $^{13}\text{C}$ -n.m.r. chemical shifts (which is not surprising in view of the composite nature of the latter) and differ completely from pseudo-contact and contact shifts (the latter tending to alternate in sign rather than in size<sup>4</sup>). Recent literature data (on aromatic amines) encourage us in the view that this technique will have general applicability.<sup>5</sup>

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