Tetrahedron Letters No. 12, pp 973 - 976, 1974. Pergamon Press. Printed in Great Britain.

ANOMALOUS SUBSTITUENT EFFECTS OBSERVED FOR LANTHANIDE-INDUCED-SHIFTS IN SUBSTITUTED PYRIDINES

G. Beech and R. J. Morgan

Department of Physical Sciences, The Polytechnic

Wolverhampton, WV1 1LY, England

(Received in UK 18 January 1974; accepted for publication 8 February 1974)

Lanthanide shift reagents have been widely applied[1] to structural studies of molecules with one or more donor atoms. In these studies it is usual to assume that a donor atom lies along a principal magnetic axis of the lanthanide complex. If this is so, the McConnell equation[2] is applicable so long as contact contributions (as opposed to pseudo contact) are negligible. In favourable cases detailed and accurate studies are possible. However, we have found that such studies may be very inaccurate when certain large steric effects are present.

We studied the interaction of tris-(1, 1, 1, 2, 2, 3, 3-heptafluoro -7,7-dimethyl -4,6-octanedione) europium (III) , $Eu(FOD)_3$, with substituted pyridines using chloroform as solvent. The deshielding gradients that we obtained are listed in Table 1.

The results for pyridine are in reasonable agreement with previously published[3] values. Also, the 6H gradients of the ligands can be arranged in a sequence:

Py > 4-CNpy > 3-CNpy > 4-Mepy > 3-Mepy > 2-Vipy > 2-Mepy > 2-Clpy > 2-CNpy > 2-Pnpy

This sequence of decreasing gradients may reflect increasing Eu-N separation; for example, the bulkier groups exert greater steric hindrance at the 2 position - increasing the bond length and decreasing the effectiveness of the shift reagent.

Anomalous results were obtained for the 2-substituted pyridines in that the 3-H deshielding gradient was always greater than that of the 5-H. By comparison, these gradients were equal for the 4-substituted pyridines. Possible ambiguities in spectrum interpretation were avoided by spin-decoupling experiments on the solutions containing $Eu(FOD)_3$ and in each case the original assignments were confirmed.

In view of the sequence of 6-H gradients, it was tempting to propose an explanation of the anomalous results based on steric arguments. In order to investigate this we calculated the relative values of the gradients by the shift-mapping method of Wing and Early.[3] However, it was not possible to obtain an adequate fit of the experimental and calculated values for any reasonable geometry of the europium-substrate complex; in fact, the angular rotation about

Table 1

Proton Deshielding Gradients of Substituted Pyridines (Vi = vinyl; Pn = 3-pentyl) using Eu $(FOD)_3$ as Shift Reagent

	6-H	5-H	4-H	3-H	2-H	CH_3
Pyridine	37.7	12.0	10.0	12.0	37.7	-
2-Mepy	13.7	4.4	6.0	7.0	-	24.3
2-CNpy	9.1	2.7	6.6	5.2	-	-
2-Clpy	12.5	4.0	5.2	7.5	-	-
2-Vipy	16.3	5.3	5.4	6.6	-	-
2-Pnpy	5.7	1.3	2.2	3.5	-	-
3-Mepy	30.8	9.1	9.6	-	29.2	6.2
4-Mepy	30.9	10.0	-	10.0	30.9	8.7
3-CNpy	33.7	12.5	10.0	-	35.7	-
4-CNpy	35.0	12.8	-	12.8	35.0	-

the N atom that would be expected on 2-substitution resulted in a calculated value of the 5-H gradient which was greater than that of the 3-H gradient. Some measure of agreement could be obtained by allowing for a simultaneous lateral shift of the substrate with respect to the Eu-N axis, but this seemed unjustified and did not give quantitative agreement. Therefore, on the basis of the above, we suggest that steric effects cannot be the major factors contributing to the observed anomalies. It seems more likely that the complex is essentially linear, the Eu-N separation being increased on 2-substitution, and that an alternative explanation should be considered.

An alternative explanation involves electronic arguments based on the π-electron distribution in the pyridine ring. So far, we have presumed that a pseudo-contact effect, governed by the McConnell equation,[2] is dominant. However, evidence is accumulating which suggests[4,5] that pure contact contributions may be important for certain combinations of shift reagent and substrate; interestingly the combination of $Eu(FOD)_3$ with strong bases can give[6] pure contact shifts which dominate the pseudo-contact contributions. Drago and Wayland[7] have measured the pure contact-shift spectra of a series of tetrahedral complexes, CoL_2X_2, in which L is a substituted pyridine. With L equal to 2-CH_3-py, it was found that although the 3-H and 5-H resonances extrapolated to a single peak in the free ligand, the contact shift of the 3-H was 560 Hz greater than that in the 5-H in the complex $Co(2\text{-}CH_3\text{-}py)_2Cl_2$. Drago and Wayland concluded that their results were best explained by a molecular orbital model in which the degree of covalency of the metal-ligand bond was altered on substitution. The difference between the 3-H and 5-H contact shifts was attributed to changes in the symmetries of the ligand wave functions compared with those of the parent compound, pyridine. In view of the similarities of our results and those of Drago and Wayland, we suggest that there may be an appreciable pure contact contribution to the resonance shifts that we have observed. We attach particular significance to the fact that the 3-H gradient is always greater than that of the 5-H with either electron-withdrawing or electron-donating 2-substituents. This is consistent with a model in which:

(i) the Eu-N bond has appreciable covalent character

(ii) pure contact contributions are present with positive spin densities at the protons, and

(iii) 2-substitution increases the spin density at the 3-, relative to the 5-proton, due to similar changes in the ring wave functions.

At this stage it is not possible to elaborate further since, from the data obtained so far, it is difficult to separate steric and electronic effects or to confirm whether the latter are σ or π in origin.

In conclusion, we suggest that our model based on pure contact contributions to the pseudocontact effects also accounts for some smaller anomalies in our results. For example, 4-substitution does not separate the 3-H and 5-H or 2-H and 6-H resonances, whereas 3-substitution causes slight separation of the 2-H and 6-H resonances; also, the 2-H and 6-H gradients are uniformly greater than their calculated values[3] and it is at these positions that pure contact effects are normally greatest.[7] Our results also indicate that it may not be possible to deduce accurate structural information from shift reagent studies if strong acceptors, such as $Eu(FOD)_3$ are used in studies of strong donors such as heterocyclic bases, with extended π-systems. The apparently simple shift mapping method may only be strictly applicable to combinations of weakly acidic shift reagents and donors which are not too basic. Shift reagents which appear to cause smaller pure contact contributions (and are, presumably, less acidic) include $Pr(FOD)_3$ and $Yb(FOD)_3$[6].

Acknowledgements

The authors thank Synthetic Chemicals Limited for a gift of 2-(3-pentyl)pyridine.

References

1. B. C. Mayo, Chem. Soc. Rev., 1, 49 (1973).
2. H. M. McConnell and R. E. Robertson, J. Chem. Phys., 29, 1361 (1958).
3. R. M. Wing and T. A. Early, Tetrahedron Lett., 4153 (1972).
4. O. A. Gansow, P. A. Loeffler, R. E. Davis, M. R. Wilcott III, R. E. Leninski, J. Amer. Chem. Soc., 95, 3389 (1973).
5. J. Briggs, F. A. Hart, G. P. Moss and E. W. Randall, Chem. Comm., 1506 (1970).
6. B. F. G. Johnson, J. Lewis, P. McArdle and J. R. Norton, Chem. Comm., 535 (1972).
7. R. S. Drago and R. B. Wayland, Inorg. Chem., 7, 628 (1968).