

THE USE OF A LANTHANIDE SHIFT REAGENT IN ^{19}F N.M.R. SPECTROSCOPY

THE ORIENTATION OF FLUORINE ATOMS IN A TRIFLUOROINDANOL

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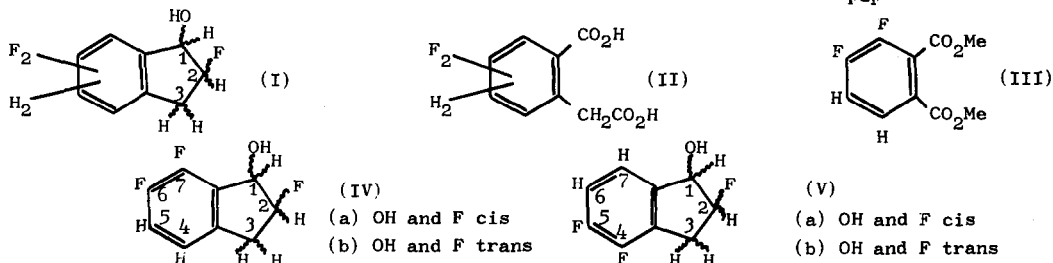
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The use of lanthanide shift reagents in ^1H n.m.r. spectroscopy for the study of stereochemical problems is well established,¹ but no application of the technique in ^{19}F n.m.r. spectroscopy has been reported.

The positions but not the stereochemical configuration of the groups bonded to the saturated carbon atoms in the trifluoroindanol (I) were readily deduced from the ^{19}F n.m.r. spectrum, which showed one fluorine atom in position 2 ($J_{\text{H-F gem}} 53 \text{ Hz}$; $J_{\text{H-F vic}} 24, 24, 12.5 \text{ Hz}$). However, an unambiguous assignment of the two fluorine atoms in the aromatic ring was not possible, because while the size of the coupling constant $J_{\text{F-F}} 21 \text{ Hz}$ excluded meta orientation of these substituents, coupling constants $J_{\text{F-F}}$ for ortho and para fluorine atoms in fused ring systems are similar in magnitude.² This problem does not arise in non-fused benzene systems.

The attempted controlled oxidation (H_2CrO_4) of the 1-keto compound derived from (I) to a homophthalic acid derivative (II) was unsuccessful;³ the further oxidised product, a difluorophthalic acid was formed which was identified as its dimethyl ester (III) ($J_{\text{F-F}} 20 \text{ Hz}$).



Compound (III) could arise from one of four precursors (IVa), (IVb), (Va) or (Vb). In order to distinguish between these alternatives, shifts in the ^{19}F n.m.r. spectrum were measured by the addition of tris(1,1,1,2,2,3,3,3-heptafluoro-7,7-dimethyloctadionato)europium [III] $[\text{Eu}(\text{fod})_3]$ to the compound in CCl_4 ; the shifts for ^1H resonance at position 2 and in the aromatic ring were measured for comparison. These results are shown in the Table together

with the relative values of the shifts $\delta\Delta$ for the possible trifluoroindanols calculated from the simplified McConnell-Robinson equation⁴ (induced shifts $\delta\Delta \propto \frac{1}{r^3}$ where r is the europium-shifted nucleus distance). For these calculations, standard bond lengths and bond angles have been used;⁵ the five-membered ring has been assumed to be coplanar with the aromatic ring; and the average position of the europium has been taken as 3\AA from and co-axial with the C-O bond; (reported iterative fittings of calculated geometries to lanthanides shift support this value¹).

Table

Atom	Position	Induced Shift (a)	Relative calculated shifts (b) $\delta\Delta$			
			IVa	IVb	Va	Vb
F	2	21.1	21.1	21.1	21.1	21.1
F	Aromatic	20.3	20.4 (7)	41.8 (7)	4.1 (4)	8.4 (4)
F	ring	6.5	6.7 (6)	13.6 (6)	3.8 (5)	7.8 (5)
H	2	9.9	11.1	41.3	11.1	41.3
H	Aromatic	4.2 (c)	4.1 (5)	8.3 (5)	19.6 (7)	40.3 (7)
H	ring	4.2 (c)	4.4 (4)	8.9 (4)	6.9 (6)	14.2 (6)

(a) Shifts are expressed in p.p.m. at extrapolated mol. ratio [mol.Eu(fod)₃ : mol.(I)] = 1; shifts were measured for a ratio of 0 to 0.7. (b) Values normalised to the shift of F-2 for comparison. The atoms to which they refer are shown in the brackets. (c) Unresolved multiplet.

It can be seen that only one specific substitution pattern for the aromatic fluorine atoms and one stereochemical configuration of the five membered ring is compatible with the magnitude of the europium-induced shifts, namely (IVa). The excellent agreement between the experimentally induced shifts and calculated values for both ¹⁹F and ¹H nuclei indicates a dominant pseudo contact mechanism for the interaction and reinforces previous observations using aniline and 2,4,6-trifluoroaniline.⁶

References

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