THE PROBLEM OF A UNIQUE METAL POSITION IN LANTHANIDE SHIFT REAGENT-KETONE
COMPLEXES IN SOLUTION

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The utility of lanthanide shift reagents has been amply demonstrated[1] and rules
for their use have been established.[2] However,the basic assumption of a unique metal
ion position (which is implied by the computing methods in general use) has largely
been neglected. This assumption,which was tested for ketones using proton $Pr(dpm)_3-$
induced shifts determined for 4-t-butylcyclohexanone,is incorrect.

Two approaches to metal-ion positioning were tested,assuming the proton shifts
to be exclusively pseudo-contact in origin.[3] The molecule was set in a Cartesian
frame (diagram) and the positions of the metal ion and of the symmetry axis were
scanned over semi-spherical surfaces specified by a distance vector and four angles
at increments of .2 Å and 10°. Tolerances were set high to produce many hundreds of
solutions. Goodness of fit between observed and calculated shift ratios was estimated
by an agreement factor.[4] In the first approach (which is similar to that used
previously by the author[3]),for any ion position the shifts were calculated as averages
of two proton positions for eq.H-2 and H-6,ax.H-2 and H-6,etc.:this is equivalent to
allowing the ion to populate,equally,symmetrical positions about the X-Z plane. The
second (traditional) approach did not involve averaging,thus assuming that the ion
populates one position.

Method 1 gave two best ion positions on either side of the C=O axis (diagram)
with the symmetry axis parallel to the Pr-O vector. This agrees with an earlier
conclusion (based on a coarser ion scan) that complexation seems to occur into the
oxygen atom's lone pair orbitals[3] and not,as has been suggested,[5] along the C=O axis.
Method 2 gave one best solution with (predictably) the ion in the X-Z plane:the
symmetry axis was again parallel to the Pr-O vector. To within the same set tolerances,
method 1 produced ten times as many solutions as method 2.

Thus widely differing ion positions result from changing the computational
assumptions,and a position determined using the 'unique' assumption (which seems
unsatisfactory both intuitively and because of the above results) may have no physical
significance. That both approaches lead to similar predictions of induced shifts at
remote carbon atoms is encouraging though it may not be general. Having generated a

fictitious ion position,there seems to be no a priori reason why the predicted shifts at atoms not included in the optimisation (the carbon atoms in this case) should approximate to the values expected for the 'true' ion positions. Perhaps the only way to overcome this problem is to average the calculated shifts over all possible rotational positions of the substrate with respect to the lanthanide ion,as has recently been suggested.[6,7] Unfortunately,this introduces uncertainty concerning whether the rotation is to be assumed 'free' or weighted to particular conformations.
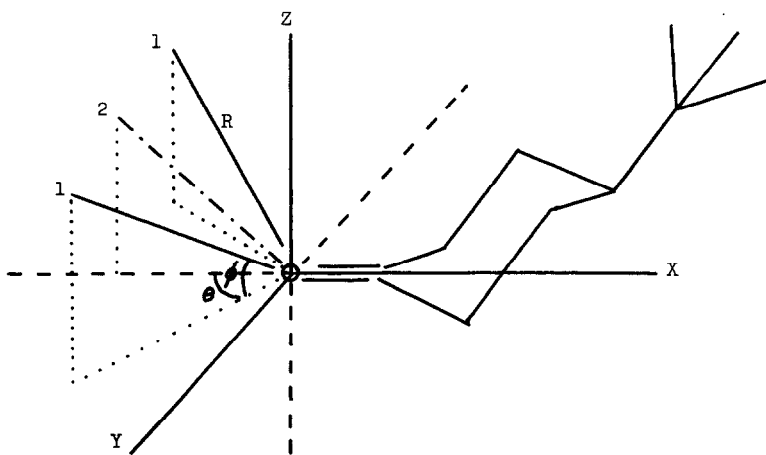
Method 1 : $R = 3\ \text{Å}$, $\theta = 50°$, $\phi = 10°$,agreement factor .247

	H-2,6eq.	H-2,6ax.	H-3,5eq.	H-3,5ax.	H-4ax.	C-1	C-2,6	C-3,5	C-4
observed	100.0	75.3	27.0	42.3	28.5				
calculated	100.0	73.9	24.9	41.6	32.7	268.8	119.8	51.6	40.0

Method 2 : $R = 2.8\ \text{Å}$, $\theta = 0°$, $\phi = 30°$,agreement factor .346

	H-2eq.	H-6eq.	H-2ax.	H-6ax.	H-3eq.	H-5eq.	H-3ax.	H-5ax.	H-4ax.
observed	100.0	100.0	75.3	75.3	27.0	27.0	42.3	42.3	28.5
calculated	100.0	100.0	74.0	74.0	30.6	30.6	38.6	38.6	34.7

	C-1	C-2	C-3	C-4	C-5	C-6
calculated	238.9	109.0	51.6	39.6	51.6	109.0

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