CONFORMATIONAL ANALYSIS BY MEANS OF LANTHANIDE INDUCED SHIFTS:
THE ARYL — METHOXY BOND

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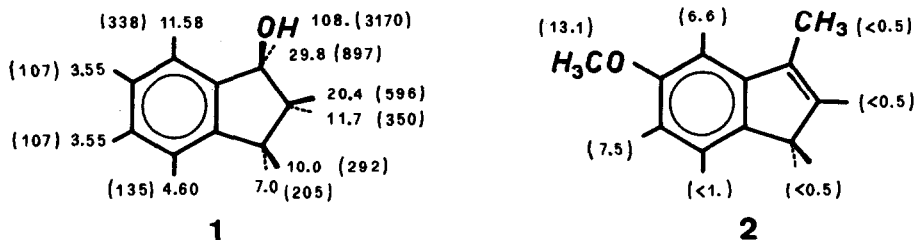
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The arrangement of C_{me}-O-C_{ar} in arylic methoxy compounds has not yet been conclusively established as far as the geometry in the dissolved state is concerned[1]. A structure where the methoxy group lies in the plane of the aromatic ring is supposed to allow for maximum overlap of the orbitals of the lone pair electrons on the oxygen and the π-orbitals of the aromatic ring. This should favor the planar conformation of the methoxy group relative to the phenyl ring. Considering steric aspects an arrangement with the methoxy group out of the plane should be favored.

Authors investigating the vibrational spectra of substituted anisoles do agree that there exists a twofold rotational barrier[2] of about 3-6 kcal/mole; whether this is due to two planar or two out of plane conformers is less clear[1,3]. Therefore it seems of interest to apply one of the most recent tools in conformational analysis to this problem - the Lanthanide Induced Shift technique (LIS)[4]. LIS calculations on methoxy xanthones did not yield unambiguous results[5]. The indanol system should provide a better framework for obtaining reliable and quantitatively interpretable LIS data:
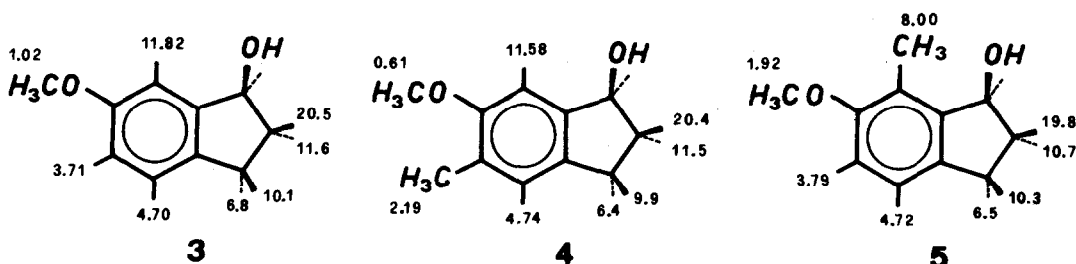
(a) Secondary alcohols coordinate strongly with tris(dipivalomethanato)-europium(III). The coordination of this reagent to the methoxy group is negligible compared to the hydroxy group. This is demonstrated by comparing the LIS values for 1-indanol (1) and 5-methoxy-3-methyl-inden (2):

(338) 11.58   *OH* 108.(3170)
(107) 3.55   29.8 (897)
                    20.4 (596)
(107) 3.55   11.7 (350)
                    10.0 (292)
(135) 4.60   7.0 (205)

1

(13.1)   (6.6)   *CH₃* (<0.5)
H₃CO   (<0.5)
(7.5)
(<1.)   (<0.5)

2

The LIS data in brackets correspond to a concentration ratio of Eu(dpm)$_3$: substrate = 0.5   (60 MHz, CDCl$_3$, values in Hz). The other data are "bound" chemical shifts[6] in ppm, determined by the method described in ref.[7] . This method allows an estimation of the equilibrium binding constant (K), assuming a 1:1 complex of reagent (L) and substrate (S): L + S $\xrightleftharpoons{K}$ LS[7a]. Even if this simple model does not account for the multitude of equilibria possible in systems of this type [4] , K should represent a good relative measure for the complexing ability of the functional groups of the compounds investigated. K for 1 is>50, K for 2 is <0.5; therefore the hydroxy group in indanols is at least 100 times stronger complexing to Eu(dpm)$_3$ than the arylic methoxy group.

(b) The lack of any symmetry planes in 1-indanol allows the calculation of a unique metal position unrestricted by any symmetry considerations [8].

(c) The molecular framework of indanol is rather rigid (motion of atoms about well defined average positions is permissible) and a sufficient number of LIS values for compounds 1 and 3-5 can be used for a reliable computational [9] analysis. The correct assignment of LIS data (especially for the C(2) and C(3) methylenic protons) was confirmed by the R-factor ratio test [10] using the computer program PDIGM [9] (confidence level better than 95%).

1.02   11.82   *OH*
H₃CO   20.5
                       11.6
3.71
4.70   6.8   10.1

3

0.61   11.58   *OH*
H₃CO   20.4
                       11.5
H₃C
2.19   4.74   6.4   9.9

4

8.00
1.92   *CH₃*   *OH*
H₃CO   19.8
                       10.7
3.79
4.72   6.5   10.3

5

The LIS data ("bound" chemical shifts, in ppm) for protons of known positions in 6-methoxy-indanol (3), 6-methoxy-5-methyl-indanol (4) and 6-methoxy--7-methyl-indanol (5) [11] can be used to calculate the proper lanthanide positions in the complexes [12]. They are virtually the same for all three compounds (distance O-Eu = 3.2 Å, angle C-O-Eu = 125° [13]; R-factors 0.03-0.06; PDIGM [9]). Knowing now the geometry of the complexes, the expected LIS for particular conformations of the methoxy group due to rotation about the C_{aryl}-O bond (angle Θ) are calculated. The results are shown in the Figure below. The shaded area allows for some uncertainties of the correct lanthanide position, the dashed lines indicate the experimental values for the methoxy LIS in 3, 4 and 5.

Inspection of the Figure shows that a conformation perpendicular to the plane of the aromatic ring should produce LIS values of about 1.1-1.3 ppm for all three compounds (the average for Θ = 90° and 270°); substitution of H by CH_3 in 5- or 7-position should not change the 6-methoxy LIS drastically.

On the other hand, the two equally populated conformers (Θ = 0° and 180°) corresponding to a planar structure of 3 (predicted LIS 1.0-1.25; obs. 1.02) should be very sensitive to substitution in 5- or 7-position. The population of the planar structures for 4 will be shifted largely towards the conformer with Θ = 180° (predicted LIS 0.55-0.75; obs. 0.61). For 5 the conformer with Θ = 0° should be the only one of importance (predicted LIS 1.5-1.85; obs. 1.92 ppm).
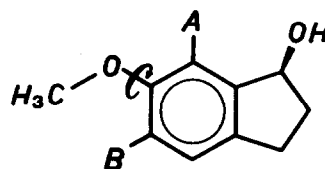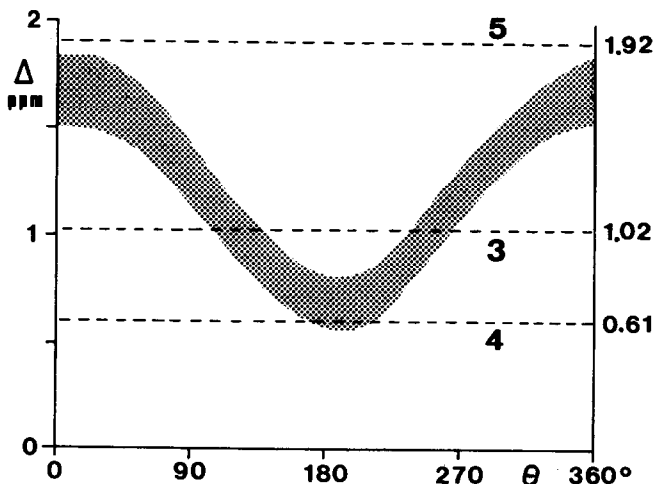
3 : A = H , B = H
4 : A = H , B = CH
5 : A = CH₃, B = H

The data reported permit the conclusion that only the assumption of essentially planar conformations of the arylic methoxy group relative to the aromatic ring accounts fully for the observed LIS values.

REFERENCES AND NOTES

1. N.L. Owen and R.E. Hester, Spectrochim. Acta, 25A, 343 (1969); and references therein.

2. Internal Rotation in Molecules, W.J. Orville-Thomas Ed., J. Wiley-Interscience, 1974; P.J.D. Park, R.A. Pethrick and B.H. Thomas, p. 94; G. Allen and S. Fewster, p. 274, 275.

3. M. Horak, E.R. Lippincott and R.K. Khanna, Spectrochim. Acta, 23A, 1111 (1967).

4. O. Hofer in "Topics in Stereochemistry", Vol. 9, N.L. Allinger and E.L. Eliel Eds., Wiley - Interscience, New York, 1975, in press.

5. M.R. Willcott III and R.E. Davis in "Nuclear Magnetic Resonance Shift Reagents", R.A. Sievers Ed., Academic Press, New York, 1973, p. 159.

6. Bound chemical shifts for $\underline{2}$ are not very reliable (too weak coordination)

7. I. Armitage, G. Dunsmore, L.D. Hall and A.G. Marshall, Can. J. Chem., 50, 2119 (1972); a) K in $1 \cdot mole^{-1}$.

8. The symmetry of the substrate has to be maintained in the calculated complex geometry (or the average of two or more complex geometries) as well which represents an additional complication [4].

9. M.R. Willcott III, R.E. Lenkinski and R.E. Davis, J. Amer. Chem. Soc., 94, 1742 (1972).

10. W.C. Hamilton, Acta Cryst., 18, 502 (1965); R.E. Davis and M.R. Willcott III, J. Amer. Chem. Soc., 94, 1744 (1972).

11. Experimental details will be presented in a later publication.

12. The C(1) proton was not used because of the unknown amount of contact shift contribution for protons close to the coordination site.

13. The dihedral angle C(2) — C(1) — O — Eu is 235° (measured clockwise, looking along C(1) → O).