Tetrahedron Letters No. 28, pp 2619 - 2620.

0040-4039/79/0708-2619$02.00/0

DETECTION OF ENANTIOMERS IN DISSYMMETRIC BIARYLS WITH CHIRAL SHIFT REAGENTS

Basil A. Behnam, D. Muriel Hall*

Department of Chemistry, Bedford College, Regent's Park,
London NW1 4NS, England

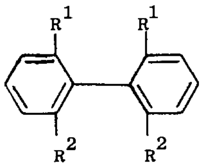
and Borzoo Modarai

Department of Chemistry, Arya-Mehr University of
Technology, Tehran, Iran

Abstract: Methoxycarbonyl groups in racemic biphenyls show separation of the methyl proton magnetic resonance signals in the presence of large amounts of chiral shift reagents.

The use of chiral shift reagents to show the presence of enantiomers in racemic mixtures is well known[1,2] but so far appears to have been limited to compounds containing an asymmetric atom and to resonances of nuclei near to the chiral centre.

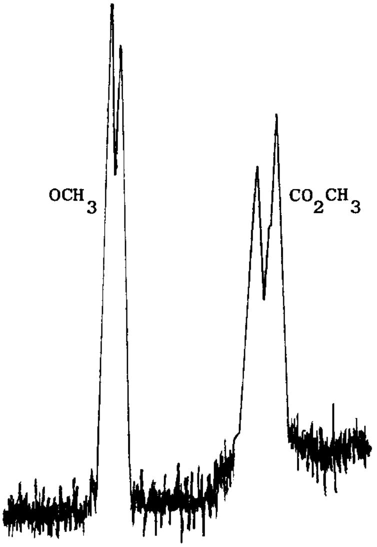
In connection with other work we wished to find conditions under which chiral shift reagents could be used to demonstrate non-equivalence of enantiomers of dissymmetric biaryls. For this purpose we used racemates of biphenyls known to have enantiomers which are optically stable at room temperature.



(1) R^1 = OMe, R^2 = CO_2Me

(2) R^1 = NO_2, R^2 = CO_2Me

(3) R^1 = OMe, R^2 = CH_2OH



The methyl proton resonances at 60 MHz of (1) (3.08 mg) in $CDCl_3$ (0.6 ml) in the presence of $Pr(tfc)_3$ (114.82 mg)

The addition of tris[3-trifluoromethylhydroxymethylene(+)-camphorato]praseodymium(III) [Pr(tfc)$_3$][2] to a solution of dimethyl 6,6'-dimethoxybiphenyl-2,2'-dicarboxylate[3] (1) in deuteriochloroform produced a separation of the signals for the ester methyl protons in the 60 MHz n.m.r. spectrum when the molar ratio was 1.68 and for the methoxyl methyl protons when the molar ratio was 7.07. At a molar ratio of 13.95 the separations were 0.05 ppm and 0.02 ppm for the ester and methoxyl protons respectively.

Ester groups coordinate to lanthanide complexes and the adjacent protons undergo moderate paramagnetic shifts[4] but aromatic ethers are poor electron donors[5]. In (1) it is clear that, as expected, the CO_2Me groups are providing the coordination site.

The methyl signals of dimethyl 6,6'-dinitrobiphenyl-2,2'-dicarboxylate[6] (2) similarly showed separation in the presence of Eu(tfc)$_3$ at a molar ratio of 3.22.

In compound (3)[7] the hydroxyl groups provide a much stronger coordination site and in this case separation of the methoxyl signals was first achieved with Eu(tfc)$_3$ at a molar ratio of 0.228. The methylene protons of CH_2OH are diastereotopic but show accidental equivalence in deuteriochloroform solution at 60 MHz. On addition of Eu(tfc)$_3$ the signal broadened, then split into two and at a molar ratio of 0.595 showed as a quartet. Owing to the broadness of the signals it was not possible to observe two quartets, corresponding to the two enantiomers.

Preliminary work with other dissymmetric compounds indicates that it is not essential for the coordination site in a biaryl to be in a sterically crowded position in order to show enantiomeric separation of signals in the presence of a chiral shift reagent. It is, however, necessary to use a large excess of the shift reagent unless the coordinating group is very strongly complexed to the lanthanide.

REFERENCES

1. G.M. Whitesides and D.W. Lewis, J. Amer. Chem. Soc., 1970, 92, 6979; 1971, 93, 5914.
   H.L. Goering, J.N. Eikenberry, G.S. Koermer and C.J. Lattimer, J. Amer. Chem. Soc., 1974, 96, 1493. R.R. Fraser, M.A. Petit and J.K. Saunders, J.C.S., Chem. Comm., 1971, 1450. M. Kainosho, K. Ajisaka, W.H. Pirkle and S.D. Beare, J. Amer. Chem. Soc., 1972, 94, 5924. K. Ajisaka and M. Kainosho, J. Amer. Chem. Soc., 1975, 97, 1761.
2. H.L. Goering, J.K. Eikenberry and G.S. Koermer, J. Amer. Chem. Soc., 1971, 93, 5913.
3. W.M. Stanley, E. McMahon and R. Adams, J. Amer. Chem. Soc., 1933, 55, 706; G. Wittig and H. Petri, Annalen, 1933, 505, 17; D.M. Hall and E.E. Turner, J. Chem. Soc., 1951, 3072; J.E. Leffler and B.M. Graybill, J. Phys. Chem., 1959, 63, 1457.
4. J.K.M. Sanders and D.H. Williams, J. Amer. Chem. Soc., 1971, 93, 641.
5. P. Joseph-Nathan and V.M. Rodriguez, Rev. Latinoamer. Quim., 1974, 5, 12.
6. A.W. Ingersoll and J.R. Little, J. Amer. Chem. Soc., 1934, 56, 2123. K. Mislow, P. Rutkin and A.K. Lazarus, J. Amer. Chem. Soc., 1957, 79, 2974.
7. D.M. Hall and J.M. Insole, J.C.S. Perkin II, 1972, 1164.

(Received in UK 9 March 1979)