meso- and (±)-Bis(phenylsulphinyl)methane. Characterization using Nuclear Magnetic Resonance Chemical Shift Reagents

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Summary *meso-* and (±) Bis(phenylsulphinyl)methane (II) have been synthesized by oxidation of bis(phenyl thio)methane (I) with hydrogen peroxide, structures are assigned to the isomers on the basis of the n m r spectrum in the presence of tris(dipivaloylmethanato)europium

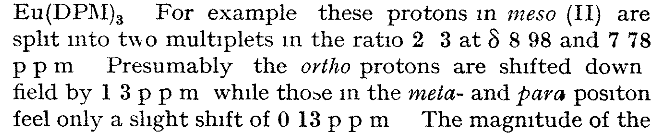
A SYNTHESIS of bis(phenylsulphinyl)methane (II) was first reported by Hinsberg [1] In this and subsequent cases[2] no mention was made of more than one diastereomer

We have synthesized the *meso* and racemic forms of (II) by the oxidation of bis(phenylthio)methane (I)[1] by hydrogen peroxide in glacial acetic acid The two diastereomers were separated by fractional crystallization from acetone m p s 118—120° and 182—183° and give identical i r spectra [ν(SO) 1045 cm^{-1}]

N m r spectroscopy should provide a means of assigning the structures of the diastereomers The racemic isomer has equivalent CH_2 protons while those in the *meso* compound should be non equivalent The spectra of each isomer in $CDCl_3$ shows a phenyl multiplet at δ 7 5—7 9 p p m and CH_2 singlets at δ 4 17 for the lower melting and 4 04 p p m for the higher melting isomer Thus, the non equivalent CH_2 protons in *meso* (II) must have the same chemical shift

Rare earth chemical shift reagents have recently been used to resolve the n m r spectra of compounds containing unshared electron pairs [3,4] and the CH_2 protons of *meso* (II) would be expected to show different chemical shifts in the presence of such a reagent The protons in the racemic compound should remain a singlet in the presence of an achiral shift reagent The spectra of the CH_2 protons of each isomer were measured in the presence of tris(dipivaloylmethanato)europium[4][$Eu(DPM)_3$] The protons of the lower melting isomer are split into an AB quartet (δ 5 90 and 6 12 p p m , $|J_{AB}| = 13$ Hz) by $Eu(DPM)_3$ and are assigned to the *meso* isomer The CH_2 protons in the higher melting isomer remain a singlet although it is shifted to 5 84 p p m In both cases $[Eu(DPM)_3]/[(II)] = 0\ 35$

We have attempted to observe separate resonances for the enantomeric protons in racemic (II) using the chiral shift reagent tris [3 (t butylhydroxymethylene)[^{1}H]camphorato]-europium developed by Whitesides and Lewis [5] However this chiral europium complex only broadens the CH_2 resonance of (±) (II) and does not split it into two peaks



(I) (II)

A striking feature of the spectra of both isomers is the nonequivalence of the aromatic protons in the presence of $Eu(DPM)_3$ For example these protons in *meso* (II) are split into two multiplets in the ratio 2 3 at δ 8 98 and 7 78 p p m Presumably the *ortho* protons are shifted down field by 1 3 p p m while those in the *meta-* and *para* positon feel only a slight shift of 0 13 p p m The magnitude of the pseudocontact shift is expected to be inversely proportional to r^3 where r is the distance of the proton from the europium atom [3] Inspection of models reveals that if co ordination takes place at the oxygen atoms the *ortho* protons are directed down and towards the europium while the *meta* and *para* protons are directed up and away from the metal We feel that it is this effect that accounts for the greater deshielding of the *ortho*-protons

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[5] G M Whitesides and D W Lewis *J Amer Chem Soc* 1970 **92** 6979