THE USE OF DECEPTIVE SIMPLICITY TO DETERMINE THE SIGNS

OF COUPLING CONSTANTS IN ABX TYPE N.M.R. SPECTRA

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One of the difficulties encountered in the analysis of ABX, ABMX, and similar spin systems is to be sure of the relative signs of couplings involving the X type nuclei. It has become standard practice to use $^{13}C$ satellite spectra or sophisticated decoupling techniques to determine these signs. However, in the present study, deceptive simplicity in an ABMX system allows unequivocal assignment of signs to the X coupling constants, $J_{AX}$ and $J_{BX}$.



(I)

(II)  R $=$ C(COOH)=CH$_2$

(III)  R $=$ H
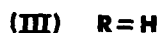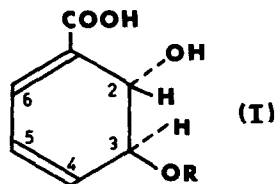
The spectra of a number of dihydrobenzoic acids of type (I) have been measured and analysed (LAOCOON III). Previous reports on compounds of this type assume that $J_{4,6}$ has a negative sign (1, 2). In spectra of these compounds, H-6 gives rise to an X type multiplet at lowest field while H-4 and H-5 form a strongly coupled AB group coupled further with H-3 which also couples with H-2. Under certain conditions the two oxygen substituents are held in the quasi-axial conformation [see (3)] and the corresponding hydrogen atoms are *trans*-quasi-equatorial. In this conformation the allylic couplings $J_{2,6}$ and $J_{3,5}$ and the vicinal coupling $J_{2,3}$ are negligible and the system reduces essentially to ABMX involving H-3, H-4, H-5, and H-6, with H-6 giving rise to a typical X type pattern. Within this pattern four lines, in pairs separated by $J_{MX}$ with centres separated by $J_{AX} + J_{BX}$, arise from

transitions between stationary state functions [see Tables and Nomograms
in (4)] and are independent of $\delta_{AB}$, the relative chemical shifts of A and B.
When $\delta_{AB}$ is reasonably large, e.g. 10 Hz or greater, the remaining four
major transitions in the X multiplet form a similar pair of doublets,
inside the lines from the stationary state transitions if the signs of $J_{AX}$
and $J_{BX}$ are the same and outside them if the signs are different.
Unfortunately, in this range of $\delta_{AB}$, mathematically valid solutions may be
computed for both sign combinations.   However, as $\delta_{AB}$ decreases, the
positions of lines from the stationary state transitions remain unaltered
while those of the other four major lines are dramatically dependent on the
size of $\delta_{AB}$.   In the deceptively simple case it is not possible to obtain a
unique analysis but the value $J_{AX} + J_{BX}$ is obtained by direct measurement,
making possible a simple and unambiguous assignment of lines in the less
strongly coupled case and eliminating one of the two solutions described above.
The characteristic variations of pattern with $\delta_{AB}$ for both sign combinations
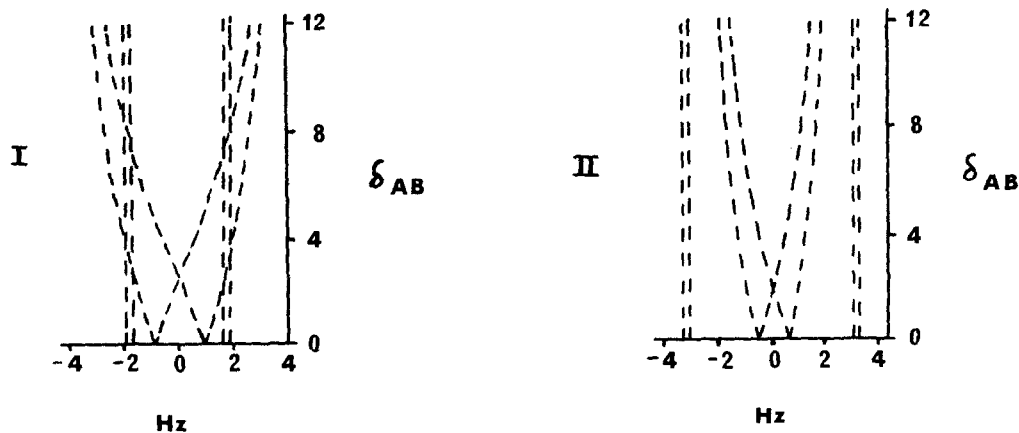are represented in Figure 1.



Figure 1. Nomograms showing variation of peak patterns with $\delta_{AB}$.

All peaks indicated are strong.

$J_{AX} + J_{BX}$ - opposite signs (I), both positive (II).

The X multiplets (H-6) from isochorismic acid (II) and 2,3-dihydro-2,3-dihydroxybenzoic acid (III) in dimethylsulphoxide $(d_6)$ at 100 MHz are shown in Figure 2.
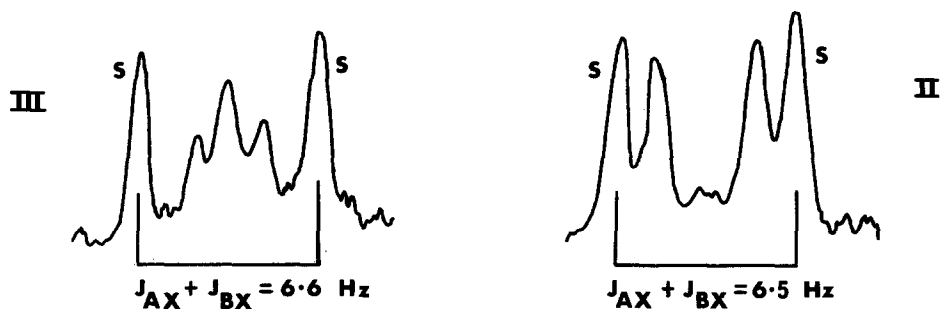


Figure 2.  X multiplets from (II) and (III). 100 MHz, DMSO$(d_6)$ solvent. S. Transitions between stationary states.

With these compounds $J_{MX}$ $(J_{3,6})$ is very small and this leads to coalescence of the pairs of lines discussed above.  $\delta_{AB}$ for isochorismic acid is 11 Hz allowing the two possible solutions listed in Table 1.  However, in the case of (III) $\delta_{AB}$ is approximately 2 Hz and the deceptively simple X multiplet gives $J_{AX} + J_{BX}$ = 6.6 Hz which when applied to the solutions in Table 1 shows unequivocally that these two couplings have the same sign, by convention positive, thus confirming the results obtained with cyclohexadiene (5).

| Table 1 Analyses of Spectra of Dihydrobenzoic Acid Derivatives Solvent - dimethylsulphoxide $(d_6)$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Chemical Shifts | | | | | Coupling Constants (Hz) | | | | |
| Compound II $J_{AX}$ and $J_{BX}$ | $\tau3$ | $\tau4$ | $\tau5$ | $\tau6$ | $\delta_{AB}$ | $J_{3,4}$ | $J_{4,5}$ | $J_{4,6}$ | $J_{5,6}$ | $J_{AX} + J_{BX}$ |
| both +ve | 5·50 | 3·74 | 3·63 | 3·04 | 11 | 4.9 | 9.5 | 1.1 | 5.4 | 6.5 |
| opposite signs | 5·50 | 3·74 | 3·63 | 3·04 | 11 | 4.9 | 9.5 | -2.3 | 6.0 | 3.7 |
| Compound III | | | | | ~2 | | | | | 6.6 |

These results lead to the conclusion that in all cyclohexa-1,3-dienes $J_{1,3}$ type couplings will be positive in sign.

This technique for determining sign is extremely simple and is applicable to systems where deceptive simplicity can be induced, as in this case, by varying substitution or, as shown in the immediately preceding communication, by changing the solvent.  Also it requires only the basic n.m.r. instrument and the decision can be made at a glance from normal proton spectra obtained from dilute solutions.

## References

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