INTERPROTON ALLYLIC SPIN-SPIN DECOUPLING : FURTHER ASPECTS OF
STERIC DEPENDENCE

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We have recently demonstrated[1] that the relative magnitudes of
cisoid and transoid allylic coupling constants are a function of the dihedral
angle ϕ (see Fig. 1 for definitions), in qualitative agreement with Barfield's
calculations[2] based on the INDO approximation of molecular orbital theory but
in conflict with the earlier VB calculations[3]. The INDO and VB calculations
predict radically different values for ${}^4J_{cisoid}$ and ${}^4J_{transoid}$ when $\phi = 90°$,
viz:

	VB	INDO
${}^4J_{cisoid}$	+ 0.43 Hz	− 1.15 Hz
${}^4J_{transoid}$	+ 0.80 Hz	− 0.54 Jz

As noted before[4,5], there is a paucity of experimental data for
molecules of appropriate geometry and containing a terminal methylene group – an
essential prerequisite[1,4] for reliable comparison of relative values of cisoid
and transoid coupling constants. In fact, the only accurate data for an un-
strained system (1) were reported by Bothner-By, Naar-Colin and Günther[6] but we
have been informed by Professor Bothner-By that the signs of allylic coupling
constants could not be considered significant as they were based on the analysis
of a lightly coupled spin system only. We have prepared (1) and re-analysed its
100 MHz spectrum with the aid of the iterative computer program LAOCN3[7] and spin-
tickling experiments[8]. It can be seen that the sign of ${}^4J_{cisoid}$ reported by
Bothner-By and his collaborators[6] is correct. The transoid allylic coupling
constant in (1) is too small for reliable determination of sign by spin tickling,
but also appears to be negative from the analysis. Clearly, the INDO calculations[2]
lead to qualitatively acceptable results, while the VB calculations[3] predict
wrong signs and wrong relative magnitudes of ${}^4J_{cisoid}$ and ${}^4J_{transoid}$.

To confirm the above conclusion, we have synthesised the systems (2)[9]
and (3)[10], which are even less conformationally ambiguous than (1). The
determinations of the signs of allylic coupling constants in these systems by
double resonance proved difficult, but it can be seen that the absolute values
are in good agreement with those in (1).
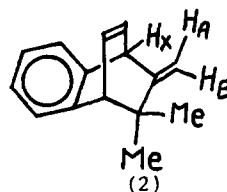
Fig. 1 : Definition of allylic coupling
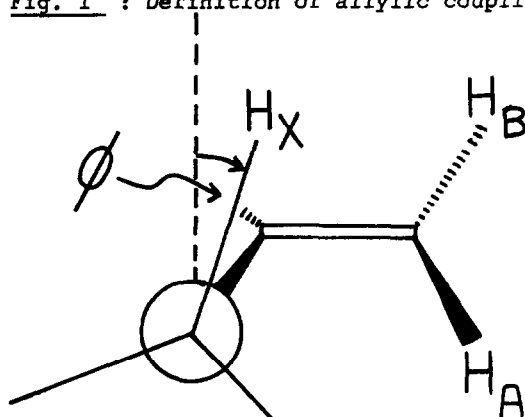
$J_{AX} = J_{allylic\ \underline{cisoid}} = {}^4J_{\underline{cisoid}}$

$J_{BX} = J_{allylic\ \underline{transoid}} = {}^4J_{\underline{transoid}}$

(1)
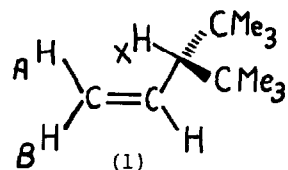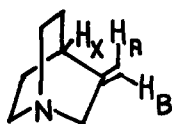
$J_{AX} = -0.66\ (-0.63)^6$

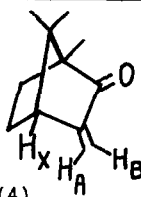$J_{BX} = -0.04\ (-0.10)^6$

(2)
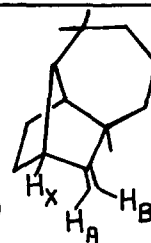
$|J_{AX}| = 0.7 \pm 0.1$

$|J_{BX}| < 0.3$

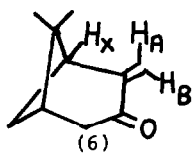(3)

$|J_{AX}| = 0.53$

$|J_{BX}| \leq 0.15$

(4)
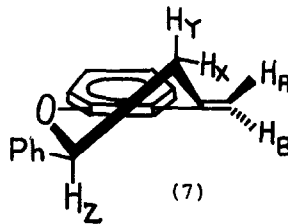
$|J_{AX}| \leq 0.4$

$|J_{BX}| = 0.8 \pm 0.1$

(5)

$|J_{AX}| = 0.55 \pm 0.1$
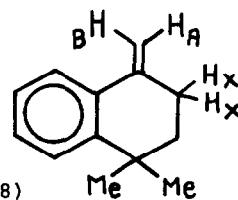
$|J_{BX}| \leq 0.10$

(6)

$|J_{AX}| \leq 0.45$

$|J_{BX}| \leq 0.1$

(7)

$J_{AX} = -0.85 \quad J_{BY} = -2.17$

$J_{BX} = -0.48 \quad J_{XZ} = 2.57$

$J_{AY} = -2.19 \quad J_{YZ} = 11.48$

(8)

$J_{AX} = (-)\ 1.48$

$J_{BX} = (-)\ 1.01$

In a number of methylene and alkylidene derivatives of bicyclo [2,2,1]heptane[11], where $\phi \sim 80°$, the relationship is "abnormal", i.e., $|{}^4J_{\text{transoid}}| > |{}^4J_{\text{cisoid}}|$. This is almost certainly <u>not</u> due to conformational non-equivalence of the E and Z isomers, because our data for methylene camphor (4) are typical for the series, while the two coupling constants in camphene[12] are of identical magnitude. Interestingly, our re-examination of the NMR spectrum of longifolene[13] (5) [gift from Dr. Sukh Dev] and of pinocarvone[14] (6) shows the "normal" relationship. We are forced to conclude that secondary effects (e.g., ring strain) present in bicyclic systems affect the magnitudes of allylic coupling constants. On the other hand, the apparently "abnormal" set of data for the isomeric ethylidene analogues of (3)[15] are probably a case of conformational non-equivalence of the E - Z isomers.

From the structural point of view, the above exceptions are not very important: both <u>cisoid</u> and <u>transoid</u> allylic coupling constants take on small values (≤ 0.8 Hz) as ϕ approaches 90°.

The relationship between <u>cisoid</u> and <u>transoid</u> allylic coupling constants demonstrated here for the region $\phi = 90°$ and previously[1] for the region corresponding to ϕ approaching 180° (or 0°) requires not only a cross-over point (which we have demonstrated)[1] but also a region where both <u>cisoid</u> and <u>transoid</u> coupling constants have significant negative values with $|{}^4J_{\text{cisoid}}|$ larger. Such relationship had been considered commonplace, in fact typical[1,5] but the examination of data shows that they all refer to flexible molecules, i.e., to averaged allylic coupling constants. In fact, we were unable to find a single example of this type involving a terminal methylene group in a molecule of defined stereochemistry.

We have prepared[9] the chroman derivative (7) whose approximate conformation follows from the magnitudes of the vicinal coupling constants, and fully analysed its NMR spectrum which yielded unique values for all signs of coupling constants except J_{AB}. It can be seen that the system exhibits just the expected relative magnitudes and signs for all allylic coupling constants, including an example of the crossover of values[1]. Furthermore, assuming the conformation of (7) to be similar to that of the two interconverting forms of (8)[1], the average coupling constants in the latter system are reasonably reproduced from the former.

In summary, it now appears that Barfield's INDO calculations[1,2] predict qualitatively the absolute and relative values of <u>cisoid</u> and <u>transoid</u> coupling constants over the range of ϕ which is accessible to direct confirmation by use of suitable unstrained but conformationally defined model substances with terminal methylene groups.

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