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H^1 SPIN-SPIN COUPLING ACROSS ONE DOUBLE AND FOUR SINGLE BONDS

J.T. Pinhey
Department of Organic Chemistry, The University of New South Wales,
P.O. Box 1, Kensington, N.S.W.
and S. Sternhell, Division of Coal Research,
C.S.I.R.O., P.O. Box 175, Chatswood, N.S.W.

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PROTON spin-spin coupling between nuclei separated by one double and three single bonds (allylic coupling) has been investigated by a number of workers[1-12]. In most cases reported, the systems concerned permitted only a comparison between cisoid (1-4) and transoid (2-4) coupling without reference to the influence of the magnitude of the angle θ (between the plane of the double bond and the direction of the bond C_3-H_4). Recent studies of some rotamers of linear systems[6,7]

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[1] S. Alexander, J.Chem.Phys. **32**, 1700 (1960).

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[10] S.A. Barker, A.B. Foster, D.C. Lamb and L.M. Jackman, Tetrahedron **18**, 177 (1962).

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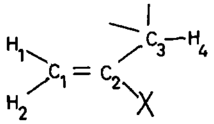

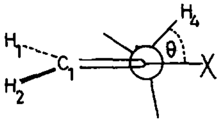

and of rigid systems[12] have shown that the occurrence of spin-spin coupling depends on the magnitude of the angle Θ.

Spin-spin coupling between protons separated by symmetrically disposed, one double and four single bonds (for which we propose the term homoallylic coupling) has also been reported[2,13,14]; but again it was possible to consider only the differences between cisoid and transoid structures (see diagram at top of this page). We wish to present evidence that homoallylic coupling, like allylic coupling[12], is influenced by the magnitude of the angle Θ. Strictly, the angle considered is a projection of a solid angle, but in the cases here investigated the departure of C_4-H_4 from vertical is small and can be neglected. Further, in the examples quoted below, the bond C_1-H_1 is a part of a methyl group, assumed to be freely rotating, and therefore the influence of the angle Θ^1 could not be determined.

We chose a number of α-santonin derivatives[15-17] (I-X) for use as model systems. In all cases the homoallylic coupling investigated is between the methyl group on C4 and H6. Table 1 shows

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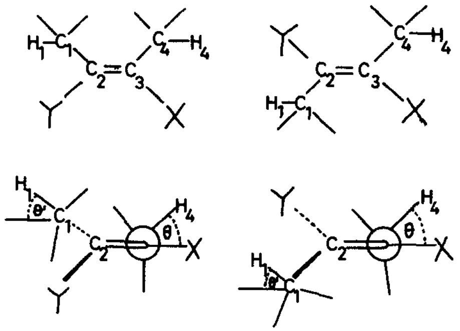
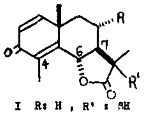


that for compounds I-V the signal assigned to the methyl group on C4 appears as a doublet while for compounds VI-VIII the signal is unsplit. In confirmation, the signal assigned to H6 in the spectra of compounds VI-VIII appears as a simple doublet (coupling to H7), while with compounds I-V the doublet assigned to H6 shows additional fine structure.

Study of Dreiding models shows that the angle θ is approximately 115° for santonin derivatives I-V with ring B in chair-like conformation and approximately 135° for the, less likely, boat-like conformation. For the 6-epi derivatives (VI-VIII) the corresponding angle with ring B in the chair-like conformation is approximately 25°.

With isophoto-α-santonic lactone IX the signal due to the methyl group on C_4 appears as a rough triplet (possibly a doublet of doublets), indicating coupling of the order of 1.5 c p s. We interpret this interaction as a spin-spin coupling of the methyl at C_4 with H_1 ($\theta = 65°$) and also with H_6. In partial confirmation, the doublet assigned to H_6 shows fine structure.

With 6-epiisophoto-α-santonic lactone X the signal assigned to the methyl at C_4 also appears as a multiplet very similar to that observed in the spectrum of IX. We interpret this as being due to coupling with H_1 ($\theta = 65°$) and also with H_6. The doublet assigned to H_6 shows fine structure. Unfortunately, the angular relationship between the methyl on C_4 and H_6 in compounds IX and X cannot be determined from the study of models, owing to flexibility of the 7-membered ring.



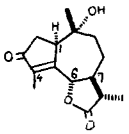
I R: H, R': βH

II R: OH, R': βH

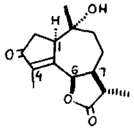
III R: OAc, R': βH

IV R: H, R': OH

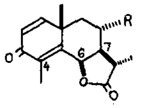
V R: H, R': OAc



IX



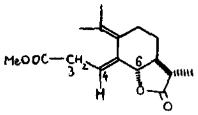
X



VI R: H

VII R: OH

VIII R: OAc



XI

The spin-spin coupling between the C_4 methyl and H_1 in IX and X is an example of homoallylic coupling in a transoid system. As with systems having undefined Θ and Θ' [2,14], homoallylic coupling appears possible for both cisoid and transoid configurations.

Both allylic (H_4-H_6) and homoallylic (methylene on C_3 - H_6) coupling have been observed[24,25] in the NMR spectrum of methyl photosantonate (XI). Here again the angle Θ is close to a right angle (115°) for the most likely conformation[24]. Surprisingly, the two

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[24] E.E. van Tamelen, S.H. Levin, G. Brenner, J. Wolinsky and P.E. Aldrich, J. Amer. Chem.Soc. **81**, 1666 (1959).

TABLE 1

NMR Data[18] on α-Santonin Derivatives[19,20]

Compound	τ C_4 CH_3 (multiplicity[21] (J) in c p s)	τ H_6 (multiplicity (J) in c p s)
I	7.88 (D, J:1.4)	5.12 (D,F,J:9)
II	7.83 (D, J:1.3)	4.85[22] (D,F[23],J:11.5)
III	7.85 (D, J:1.35)	4.99 (D,F[23],J:12)
IV	7.85 (D, J:1.3)	4.60[22] (D,F, J :9)
V	7.88 (D, J:1.4)	4.70 (D,F,J:10)
VI	7.93 (S)	4.40 (D, J:4.7)
VII	7.92 (S)	4.32 (D, J:5.5)
VIII	7.92 (S)	4.30 (D, J:5.7)
IX	8.12 (M)	5.10 (D,F, J:9)
X	8.17 (M)	4.40 (D,F, J:7.9)

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[18] Taken in dilute (less than 10%) solution in $CDCl_3$, with tetramethylsilane as internal reference, on a Varian A60 spectrometer. The τ values are believed to be accurate to within 0.03 p.p.m. and the J values to 0.2 c p s. The latter are derived from first-order considerations only. With compounds II and IV, which are sparingly soluble in $CDCl_3$, and compounds III and VIII, where the signal due to the acetate methyl obscured that due to the C_4 methyl, the J values were obtained by examination of spectra in pyridine solution.

[19] All new compounds listed gave correct analyses and spectral data.

[20] Other stereochemical implications of the NMR spectra will be discussed elsewhere.

[21] S: singlet, D: doublet, M: multiplet, F: evidence of fine structure.

[22] In pyridine.

[23] Secondary splitting (1.3 c p s) clearly visible.

vinylic methyl groups of methyl photosantonate are reported[24] to give rise to singlets.

While the bond angles discussed above cannot be determined with accuracy, and conformational changes add to uncertainty, it is clear that changes in magnitude of θ strongly influence homoallylic coupling. Further, from the limited number of examples presented here, it appears that homoallylic spin-spin coupling is strongest when θ is nearly a right angle, in line with results obtained for allylic systems[6,7,12].

Compound IV , known as α-hydroxysantonin[26], is a metabolite of I isolated from urine of dog. Chemical and spectroscopic evidence for its structure will be presented elsewhere.

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[25] J.D. Roberts, "Nuclear Magnetic Resonance", p.52. McGraw-Hill (1959).

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