

SPIN-SPIN COUPLING BETWEEN PROTONS ON
 sp^2 HYBRIDIZED BENZYLIC CARBON ATOMS AND RING PROTONS

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Protons on sp^3 hybridized benzylic carbon atoms are coupled principally to ring protons in the ortho and para positions (i.e. across four or six bonds)¹⁻⁵, while protons on sp^2 hybridized benzylic carbon atoms are coupled principally to ring protons in the meta position (i.e. across five bonds)^{6,7}. These two types of interactions are believed to involve different mechanisms of spin-spin coupling^{2,8,9}.

We now wish to present evidence, that in some molecules, protons on sp^2 hybridized benzylic carbon atoms couple principally to ring protons in the ortho position, and in other molecules, such protons couple approximately equally to ring protons in ortho and meta positions.

Deviations from symmetry in inherently symmetrical spin-spin splitting patterns (e.g. AB, A_2B_2 , AA'BB') have been advanced as evidence for long-range interactions of one of the protons (or groups of equivalent protons) with nuclei outside the apparently isolated system^{1,2,10}.

For instance, in the NMR spectrum of anisaldehyde (I), the ratio of β/α (see experimental for definition), was found to be significantly less than unity, and this was considered as confirmatory evidence for the coupling of the aldehydic protons principally to the ring protons in the meta position^{6,7} while with compounds (II) and (III), the corresponding ratios were significantly greater than unity and this was considered as

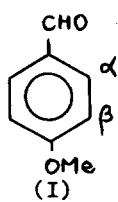
evidence for predominant coupling being across four rather than five bonds¹.

With $\beta\beta$ -dimethylstyrenes (IV) and (V), the β/a ratios indicate that, although the benzylic carbon atoms are sp^2 hybridized, the predominant coupling is across four, rather than five bonds. That this selective broadening is not primarily due to the further removed methyl groups is shown from the results with the $\alpha\beta\delta$ -trimethylstyrene (VI) and the $\alpha\alpha'$ -dimethylstilbene (VII). In the latter case, the close correspondence of the heights of the methyl and methoxyl signals affords some evidence for the absence of any significant long-range coupling, although even the methoxyl group cannot be considered as "perfectly isolated"¹². The asymmetry of the AB quartet due to the ethylenic protons in 3,4,5-trimethoxycinnamic acid (VIII) also indicates a coupling between benzylic and ortho ring protons.

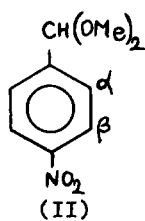
However, in the dithiolone (IX) the AA'BB' multiplet assigned to the aromatic protons is almost perfectly symmetrical; this indicates approximately equal coupling across four and five bonds but gives no information about the magnitude of the coupling constants at all.

Making the assumption that the asymmetry induced in an AA'BB' system by a long-range interaction would be essentially the same as that induced in an AB system by the same interaction (the relation between asymmetry and the absolute magnitude of the coupling constant need not be linear), allows us to obtain additional information on this point.

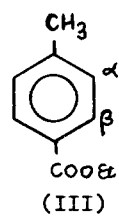
Thus while the NMR spectrum of the dithiolone (IX) gives no actual evidence for the occurrence of any long-range coupling, in the derivatives of cinnamic acid (X)-(XIII) the larger asymmetry in the AB system assigned to the olefinic protons than in the AA'BB' system assigned to the aromatic protons indicates that the benzylic protons are significantly, and approximately equally, coupled to both ortho and meta protons on the aromatic rings.



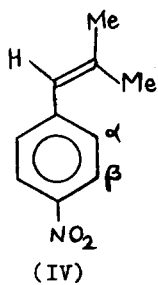
β/α : 0.87



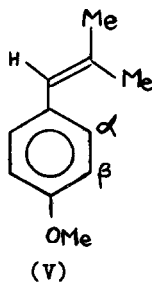
β/α : 1.23



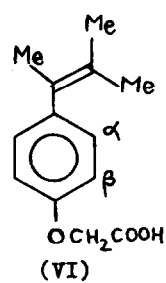
β/α : 1.32



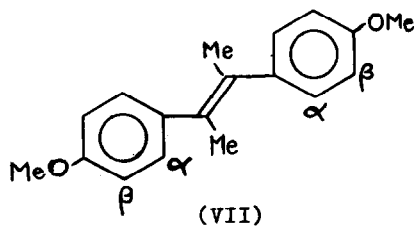
β/α : 1.24



β/α : 1.22

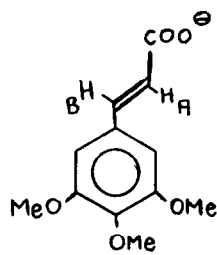


β/α : 1.03



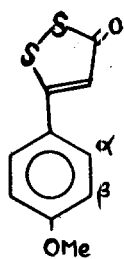
β/α : 1.03

-OMe/-Me: 1.02

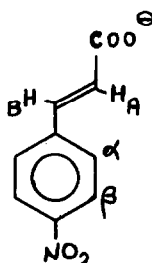


in D₂O and Et₃N

A/B: 1.12



(IX)

 β/α : 0.99

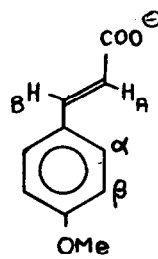
(X)

in D_2O and Et_3N

A/B: 1.25

 β/α : 1.06in D_2O and K_2CO_3

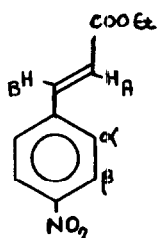
A/B: 1.34

 β/α : 1.05

(XI)

in D_2O and Et_3N

A/B: 1.19

 β/α : 1.06

(XII)

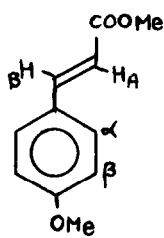
in $CDCl_3$

A/B: 1.41

 β/α : 1.02

in dioxan

A/B: 1.39

 β/α : 1.03

(XIII)

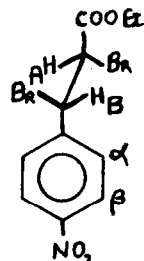
in $CDCl_3$

A/B: 1.22

 β/α : 1.08

in acetone

A/B: 1.49

 β/α : 1.06

(XIV)

A/B: 1.20

 β/α : 1.04

The same relation can be observed in a derivative with an sp^3 hybridized benzylic carbon atom (XIV), and this may be interpreted as further evidence, that while protons on sp^3 hybridized benzylic carbon atoms are coupled predominately¹⁻⁵ to the ortho and para protons, coupling to the meta protons need not be negligible.

Although the number of compounds so far examined is limited, the above results, in conjunction with other data¹⁻⁷ allow us to postulate some further, but still preliminary, hypotheses regarding the stereo-electronic requirements for effective benzyl-ring coupling:

a) Making the reasonable assumption that the cinnamic acid derivatives (X)-(XIII) are more planar than the $\beta\beta$ -dimethylstyrenes (IV and V), we suggest that coplanarity of the =C-H bond with the aromatic ring tends to suppress coupling to the ortho ring protons, for compounds with sp^2 hybridized benzylic carbon atoms, as well as with those with sp^3 hybridized carbon atoms³. This interaction across four bonds may thus involve the $\sigma-\pi$ configuration interaction mechanism^{2,5,8,13}.

Unfortunately, the properties of the AA'BB' system are such that one cannot distinguish between equal coupling to any pair of protons (ortho or meta) and selective coupling to one proton in a pair⁶.

b) It has been noted in one previous example¹ that bulky substituents on a para substituted benzyl compound with an sp^3 hybridized carbon atom (p-nitro- α -bromoethylbenzene) appeared to reduce the asymmetry in the AA'BB' system due to aromatic protons and this could be due to conformational effects. The same phenomenon is observed with compound (XIV), but additionally it may be noted that the benzylic proton is still significantly coupled to ring protons. The steric requirements for the coupling between benzylic protons on sp^3 hybridized carbon atoms with ortho ring protons thus appear to be different from the requirements for coupling with meta ring protons. In view of the reported zero coupling of benzylic and meta ring protons in acenaphthene³ but

not in 2,4,5,6-tetrachlorotoluene⁵ it is tempting to postulate that these requirements are in fact opposite.

c) The above tends to confirm that a duality^{2,8,9} of mechanisms is involved in benzyl-ring coupling. The effects of "simultaneous" coupling by two mechanisms may be expected to lead to either reinforcement or cancellation of the total effect, presumably depending on the sign of the coupling constants. Such a phenomenon has been postulated¹⁴ to explain an apparent¹⁵ discrepancy in long-range coupling in some acetylenic systems and may also be involved in the anomalous long-range coupling in strained² allylic structures and in the system H-C-CO-C-H^{2,16}. Such "simultaneous" coupling may also explain the relative magnitudes of allylic and homoallylic coupling constants^{2,11}.

Experimental: All new compounds gave correct analyses and expected spectra. The NMR spectra were obtained on an A60 spectrometer for 5-20% solutions with tetramethylsilane as internal reference. When no solvent is indicated, carbon tetrachloride or deuteriochloroform were used. The assignments of the resonances were quite unambiguous. The ratios shown with structures refer to heights of signals which should be mirror images and therefore of equal height. The measurements are averages of at least 6 (usually 8 - 12) runs, the field being swept in alternate directions, and are believed to be significant to approximately $\pm 5\%$.

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