

THE EFFECT OF DELOCALIZATION ON PROTON SPIN-SPIN COUPLING  
CONSTANTS IN UNSATURATED SYSTEMS

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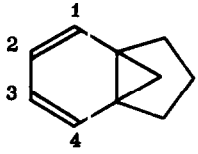
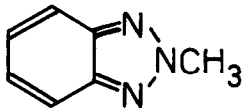
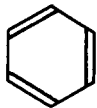
Separating  $\sigma$ -bond and  $\pi$ -bond contributions to H,H'-spin-spin coupling constants [1,2] has proven a valuable concept for the interpretation of experimental observations [3,4]. Within the limits of this model, differences in coupling constants observed for protons in unsaturated compounds with similar  $\sigma$ -bond geometry may be attributed to different  $\pi$ -electron distributions. In this sense, coupling constants have been used frequently to gain information about the electronic structure of olefinic and aromatic compounds [5a-d].

A recent paper of Smith et al. [6], which deals with the relation between vicinal coupling constants and  $\pi$ -bond order in conjugated systems, prompts us to report related observations made independently.

The consequences of different degrees of  $\pi$ -bond delocalization in cyclic polyenes on vicinal as well as on longrange H,H'-coupling constants are demonstrated by the data of table 1, that gives  $J_{H,H'}$ -values for three selected compounds obtained from the analysis of their nmr-spectra. Two reasonable assumptions concerning the structure of the six-membered ring in these systems seem justified:

- 1) The C<sub>1</sub>-C<sub>4</sub>-segment in I and II (including H-atoms) will be planar as in benzene; consequently all dihedral angles between CH-bonds are equal to zero.
- 2) All HCC-bond angles are close to 120°.

T A B L E 1

	 I	 II	 
${}^3J_C$	9.25	8.65	7.56
${}^3J_S$	5.94	6.79	7.56
${}^4J$	0.58	1.04	1.38
${}^5J$	1.31	1.03	0.68
Ref.	[7]	[8]	[9]

The trends found for the coupling constants in going from I to benzene may then be correlated with the increasing delocalization of  $\pi$ -electrons in these systems. The decrease of  ${}^3J_C$ , followed by an increase of  ${}^3J_S$  is selfexplanatory and expected on the basis of diminished bond alternation: Reduced  ${}^3J_C$ - and enhanced  ${}^3J_S$ - $\pi$ -bond contributions are accompanied by appropriate changes of  ${}^3J(\sigma)$ -terms, that are induced by the variation in bondlength [10]. The value of 7.56 cps for  $J_{ortho}$  in benzene is equal to the average of  ${}^3J_C$  and  ${}^3J_S$  in I.

The alteration observed for the longrange coupling constants  ${}^4J$  and  ${}^5J$  are best rationalized on the basis of an approximately constant (and positive)  $\sigma$ -bond and a reduced  $\pi$ -bond contribution to these interactions with increasing delocalization. Since  ${}^4J(\pi)$  in even alternant  $\pi$ -systems [11] is negative [1b],  ${}^4J$  becomes greater towards benzene. The positive sign of  ${}^5J(\pi)$  [1b] on the other side leads to the observed decrease in  ${}^5J$ . The signs of  ${}^4J(\pi)$  and  ${}^5J(\pi)$  have been confirmed experimentally by our measurements on cyclohexa-(1.3)-diene-systems of different planarity [7b].

The same mechanisms, but with varying degrees, seem therefore responsible for H,H'-spin-spin interactions in olefinic and aromatic compounds.

The dependency of  $J_{H,H'}$  on  $\pi$ -bond structure discussed above is reflected in the linear relationship existing between the  ${}^3J$ -values of table 1 and HMO-bond orders,  $p_{\mu\nu}$  [12], that extends a similar relation found earlier for benzenoid aromatic compounds [13] and is equivalent to that reported by Smith et al. [6]:

$${}^3J = 7.70 p_{\mu\nu} + 2.53 \quad [\text{cps}] \quad (1)$$

(standard deviation  $\pm 0.2$  cps) [14].

Furthermore, the ratios  $Q_1 = {}^3J_s/{}^3J_c$  and  $Q_2 = {}^4J/{}^5J$  for a given compound may serve as a qualitative measure for the degree of  $\pi$ -bond localization. For localized  $\pi$ -bonds,  $Q_1$  will be close to 0.5 and  $Q_2 < 1.0$ , whereas for delocalized systems  $Q_1$  close to 1.0 and  $Q_2 > 1.0$  will be found.

Attention must be drawn to the fact, that eq. (1) as well as the correlations between  $Q_1$  and  $Q_2$ , respectively, and  $\pi$ -bond structure are valid only, if the criteria 1) and 2), mentioned at the beginning, apply. Any change of geometry (reduced planarity, different HCC-bond angles) will have severe consequences for all  $J_{H,H'}$  values and will invalidate the quantitative aspect of the relations discussed above.

In systems with unknown molecular structure and varying ringsize no conclusions regarding the degree of  $\pi$ -electron delocalization can be reached at present on the basis of  $Q_2$ , as our results for the 1,6-bridged cyclodecapentaenes show [5j]. The alternation or non-alternation of vicinal coupling constants on neighboring HC-CH-segments, however, may be used in suitable cases to distinguish localized (olefinic) from delocalized (aromatic)  $\pi$ -systems [5j-l]. This criterium [15], i.e. the value of  $Q_1$ , will sometimes be more reliable than shift measurements [5l], but will be misleading, if non-alternating  ${}^3J$ -values are due to a fast, reversible valence tautomerism, as in the case of benzeneoxide-oxepin-systems [16].

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