

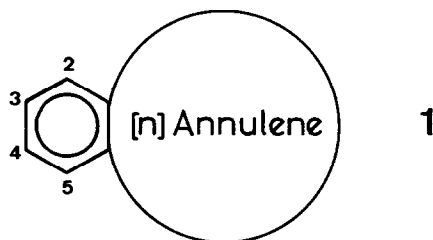
ELECTRONIC GROUND STATE PROPERTIES OF ANNULENES:
EXPERIMENTAL TEST OF THE Q-VALUE METHOD

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Recently we have shown on the basis of PPP-type SCF calculations how the ratio of the π -bond orders, $Q = P_{23}/P_{34}$, in the sixmembered ring of benzo-[n]annulenes (1) may be used to determine the electronic ground state properties of [n]annulenes¹). Delocalized $(4n+2)$ - and $4n$ - π -systems are characterized by Q-values > 1.10 and < 1.04 , respectively, whereas localized olefinic systems show Q-values of $1.04 - 1.10$.



The π -bond orders and the Q-values for a given system are obtained experimentally from the vicinal H,H coupling constants $^3J(H,H)$, measured in the 1H -NMR spectrum, via the equation

$$P_{\mu\nu}(\text{SCF}) = 0.104 \ ^3J(H,H) - 0.120 \quad (1).$$

To test the predictions summarized above, we have analyzed the 1H -NMR spectra of compounds 2 - 9²). The relevant data are collected in Table 1; further details will be given in the full paper.

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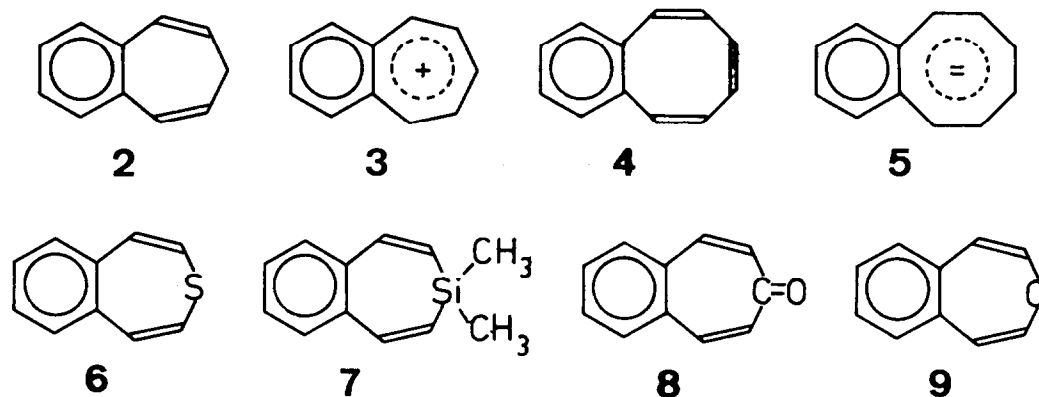


Table 1: Coupling Constants $J(i,j)$ (in Hz) of the Aromatic Protons, SCF- π -Bond Orders $P_{\mu\nu}$ from Eq. (1), and Q-Values for Compounds 2 - 9

	$J(2,3)$	$J(3,4)$	$J(2,4)$	$J(2,5)$	P_{23}	P_{34}	Q
<u>2</u>	7.83	7.36	1.36	0.49	0.694	0.645	1.076
<u>3</u>	8.37	7.05	1.28	0.52	0.750	0.613	1.223
<u>4</u>	7.73	7.29	1.39	0.54	0.684	0.638	1.072
<u>5</u>	8.51	5.80	1.55	0.47	0.765	0.483	1.584
<u>6</u>	7.87	7.44	1.33	0.67	0.698	0.653	1.069
<u>7</u>	7.89	7.34	1.42	0.30	0.701	0.643	1.090
<u>8</u>	7.86	7.34	1.26	0.56	0.697	0.643	1.084
<u>9</u>	7.54	7.58	1.32	0.47	0.664	0.668	0.994

The results obtained for 2 and 3 are in complete agreement with our predictions¹⁾. Of special importance is here the fact that a Q-value of 0.77 was recently determined for the newly prepared benzocycloheptatrienyl anion⁷⁾, the missing antiaromatic member of this series.

A Q-value of 1.072 for 4 clearly demonstrates the olefinic nature of cyclooctatetraene. This finding does not agree with the interpretation of the proton chemical shifts of 4 given by Buchanan and McCarville⁶⁾. These authors suggest that 4 displays a modest paramagnetic ring current effect.

The dramatic increase found for Q in 5 is partly due to the steric interaction expected between the peri-protons in a planar structure. It is not possible at present to correct for this effect in a quantitative way.

Extending our approach to heteroannulenes, the results for 6 and 7 classify the heterocyclic systems thiepine and silepine as olefinic. The same is true for tropone (cf. the data for 8), in accordance with conclusions reached by Bertelli et al.⁸⁾. In the case of oxepine, on the other hand, the Q -value of 0.994 obtained for 9 characterizes this compound as partly delocalized $4n-\pi$ -system. In support of this result we note that literature data for the ^1H chemical shifts of oxepines⁹⁾ indicate paratropic behaviour when compared to the resonance frequencies of the protons in the corresponding cycloheptatrienes. Other factors, as charge transfer or the diamagnetic anisotropy of the C-O-C-group may, however, cause similar shielding effects. Furthermore, cycloheptatrienes might not be suitable model compounds since they sustain a small diamagnetic ring current¹⁰⁾. Magnetic susceptibility measurements for oxepines have, therefore, been initiated.

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