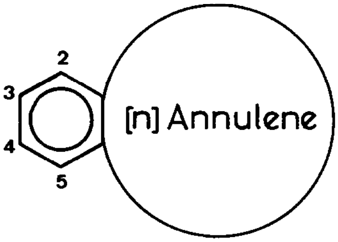
Tetrahedron Letters No. 9, pp 781 - 783, 1974. Pergamon Press. Printed in Great Britain.

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

Harald Günther, Ali Shyoukh, Dieter Cremer, and Karl Heinz Frisch (†)
Institute of Organic Chemistry, University of Cologne
Zülpicher Str. 47, 5000 Köln/Germany

(Received in UK 17 December 1973; accepted for publication 24 January 1974)

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]annulenes[1)]. 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.



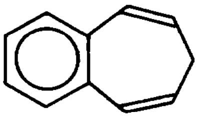
1

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 ^{1}H-NMR spectrum, via the equation

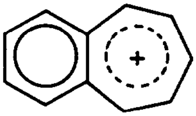
$$P_{\mu\nu}(SCF) = 0.104\ ^3J(H,H) - 0.120 \qquad (1).$$

To test the predictions summarized above, we have analyzed the ^{1}H-NMR spectra of compounds 2 - 9[2)]. The relevant data are collected in Table 1; further details will be given in the full paper.

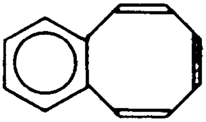
+ Deceased September 10, 1970



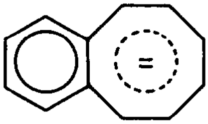
2



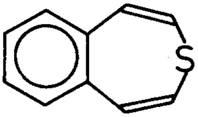
3



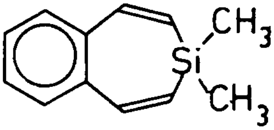
4



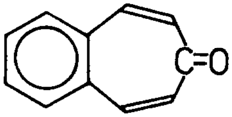
5



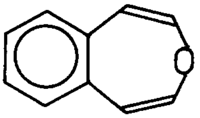
6



7



8



9

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
2	7.83	7.36	1.36	0.49	0.694	0.645	1.076
3	8.37	7.05	1.28	0.52	0.750	0.613	1.223
4	7.73	7.29	1.39	0.54	0.684	0.638	1.072
5	8.51	5.80	1.55	0.47	0.765	0.483	1.584
6	7.87	7.44	1.33	0.67	0.698	0.653	1.069
7	7.89	7.34	1.42	0.30	0.701	0.643	1.090
8	7.86	7.34	1.26	0.56	0.697	0.643	1.084
9	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 predictions[1). Of special importance is here the fact that a Q-value of 0.77 was recently determined for the newly prepared benzocycloheptatrienyl anion[7), 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 McCarville[6). 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 $4n$- π-system. In support of this result we note that literature data for the ^{1}H 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 suszeptibility measurements for oxepines have, therefore, been initiated.

We are indebted to Prof. Dr. E. Vogel and Dr. W. Büschken, Köln, and Prof. Dr. L. Birkofer and Dr. H. Haddad, Düsseldorf, for samples of 6 an 7. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

1) D. Cremer and H. Günther, Liebigs Ann. Chem. 763, 87 (1972).

2) At least ten spectra of each compound, obtained with a VARIAN HA 100 spectrometer, were averaged to yield the experimental line frequencies within 0.1 Hz. Analysis was performed by the direct method3) followed by iterative parameter improvement with the help of LAOCOON II4). Approximate data for 2, 3, and 8 have been given by Bertelli et al.5). The spectrum of 4 has recently been analyzed by Buchanan and McCarville6).

3) B. Dischler, Z. Naturforsch. 20a, 888 (1965); see als H. Günther, Angew. Chem. 84, 907 (1972); Angew. Chem. Int. Ed. Engl. 11, 861 (1972).

4) S. Castellano and A. A. Bothner-By, J. Chem. Phys. 41, 3863 (1964).

5) D. J. Bertelli and P. Crews, Tetrahedron 26, 4717 (1970).

6) G. W. Buchanan and A. R. McCarville, Can. J. Chem. 51, 177 (1973).

7) S. W. Staley and A. W. Orvedal, J. Amer. Chem. Soc. 95, 3382 (1973).

8) D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, ibid. 91, 5286 (1969).

9) H. Günther, R. Schubart, and E. Vogel, Z. Naturforsch. 22b, 25 (1967); E. Vogel and H. Günther, Angew. Chem. 79, 429 (1967).

10) a) H. Günther, Z. Naturforsch. 20b, 948 (1965); b) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, J. Amer. Chem. Soc. 91, 1991 (1969).