

STRUCTURE-RESONANCE THEORY FOR HOMOAROMATIC BRIDGED ANNULENES

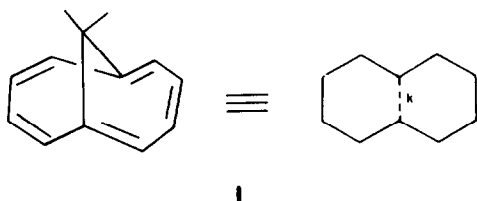
WILLIAM C. HERNDON* and CYRIL PÁRKÁNYI

Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968, U.S.A.

(Received in U.S.A. 9 December 1981)

Abstract—The π systems of bridged annulenes can be represented by π molecular graphs with homoconjugative interactions at the bridge positions. Nonbonding MO's of odd molecular graphs derived from the parent bridged annulene graphs can be used to carry out structure-resonance theory calculations. A general outline of possible applications is given. Specific comparisons are made between calculated bond orders and bond lengths, and between calculated and experimental ionization potentials. The concept of neutral homoaromaticity is supported by good agreement between calculated and experimental properties.

Bridged annulenes¹ can be represented as delocalized species in which the bridged portions of the annulene system are presumed to be linked by "through space" homoconjugative interactions.²⁻¹³ In π molecular orbital approximations the value of the transannular resonance integral is estimated to be about 40% of that between neighboring $2p_z$ orbitals in benzene.¹³ The π system of 1,6-methano[10]annulene can therefore be modeled as the perturbed naphthalene π molecular graph shown in 1.



This naive first-order approximation has been shown to be useful in interpretations of electronic spectra^{2,3,13} and photoelectron spectra,⁴⁻⁶ and in calculations of delocalization energies.^{7,9-12} The PMO theory of homoaromatic ions has also been extensively discussed^{7,8} using the perturbed annulene model.

The purposes of this paper are to demonstrate that this simplified model for bridged annulenes has a valence bond structural interpretation, and to propose that the model can therefore be used to carry out valence bond structure-resonance theory calculations,¹⁴ the results of which are related to chemical and physical properties. To do this, it will be shown that odd alternant fragments of conjugated bridged π molecular systems possess a non-binding molecular orbital (NBMO), and that the unnormalized coefficients of the NBMO can be related to numbers of Kekulé structures (structure count, SC) for reactive intermediates and for the parent even molecular systems.¹⁵⁻¹⁸ This approach will allow the definition of a new concept, the fractional non-integral Kekulé structure count for a bridged annulene molecule. Then, the newly defined SC's and other derived quantities will be compared with relevant experimental properties.

Calculations of resonance energies,¹⁹⁻²¹ Pauling bond orders,²² and correlations of the calculations with ionization potentials (IP's)²³ and bond lengths²⁴⁻²⁶ will be demonstrated. Each one of these applications is analogous to already published investigations in normal unsaturated conjugated hydrocarbons. Examples of each type of calculation for bridged annulenes will be given,

hopefully sufficient to demonstrate a potential usefulness of the theory. The justifications for the procedures to be developed are primarily based on the good agreement of experimental values with calculations in the previous work, so a brief summary of the prior results will be given where appropriate.

THEORY

NBMO's for Bridged Annulene Fragments. The deletion of one vertex from the π molecular graph of a bridged annulene gives an odd alternant graph that formally has an NBMO. The unnormalized coefficients of the NBMO can be written by inspection using the following two rules.

(1) The coefficients obey the zero sum rule, eq. 1, derivable from the secular equations.¹⁵

$$\sum_i a_i \beta_{ij} = 0 \quad (i \text{ adj. to } j) \quad (1)$$

(2) The absolute value of any coefficient corresponds to the actual number of Kekulé structures that can be written with charge or odd electron located at the self-same position.^{15,16}

As an example let us consider the fragment obtained by deletion of the α vertex from the graph of 1,6-methano[10]annulene. The coefficients at the unstarred positions are zero from rule 1. The coefficient at the indicated position (2nd graph in 2) is unity from rule 2, and the remaining coefficients follow using rule 1. Coefficients for odd fragments derived from the molecular π graphs of dibridged [14]annulenes are given as further examples in 3 and 4. The position of the deleted vertex is shown by an open circle and transannular bonds are indicated by dashed lines.

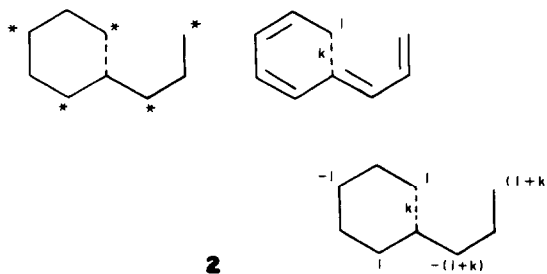


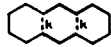
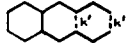
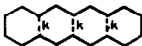

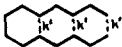

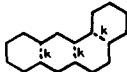
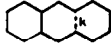
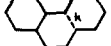
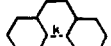


Table 1. SC's and resonance energies for bridged annulenes

Bridged Annulene π -system	SC	SC $k = 0,4$ $k' = 0,16$	RE(eV) = $1.191n(\text{SC})$	%RE ^a	Topological ^b RE(β)
	$1+k'$	1.16	0.18	21	0.180 ^c
	$2+k$	2.4	1.04	80	0.290 ^c
	$2+2k$	2.8	1.23	74	0.319 ^c
	$2+2k'$	2.32	0.84	61	
	$2+3k$	3.2	1.38	72	0.351 ^c
	$1+2k'$	1.32	0.33	25	0.248 ^c
	$1+3k'$	1.48	0.47	28	
	$2+2k+k^2$	2.96	1.29	67	0.336 ^c
	$2+3k+2k^2$	3.52	1.50	65	
	$3+k$	3.4	1.46	88	
	$3+2k$	3.8	1.59	83	
	$4+2k$	4.8	1.87	88	

^a Compared to the isostructural benzenoid hydrocarbon. ^b Graph-theoretical definition of resonance energy, ref. 9,28,29. ^c Ref. 12, 30.

According to these calculations, the bridged annulenes are substantially resonance stabilized. If one compares their resonance energies with the calculated resonance energies of the analogous benzenoids, the % resonance energies range from 21% (bridged benzene) to 88% (bridged pyrene and bridged benzo[b]naphthalene). There are no experimental thermochemical determinations of resonance energies for these systems. However, graph theoretical topological resonance energies^{9,28,29} (TRE) have been calculated for a few bridged annulenes,^{12,30} and are also listed in Table 1. The correlation coefficient of the TRE with the SC resonance energies is 0.961.

The results given in Table 1 are listed primarily to indicate the potential scope of this theoretical approach. The experimental resonance energy of any particular bridged annulene will depend upon details of ring conformation that are not included in this naive theory. However, $4n+2$ bridged annulene systems with noticeably bent aromatic rings have been demonstrated to have physical properties that are indicative of aromaticity, even with torsional angles for the bonds of the order of 30 to 50°.^{1,31-33} Consequently, for the majority of bridged

annulenes, the SC or the calculated RE should give a good qualitative ordering of stabilization due to cyclic delocalization. Of course, both SC and calculated RE depend upon the chosen value of k . One advantage of this approach is that the effects of variations in k are simply deduced from the general expressions for SC as given in Table 1.

Bond orders and bond lengths. Structure-resonance theory bond orders are compared with bond lengths for cycloheptatriene³⁴ and five recently determined bridged annulene crystal structures³⁵⁻³⁹ in Table 2. The general formulas in terms of k for the bond orders are determined as explained earlier. The predicted bond lengths are calculated from a linear bond length-bond order equation obtained by fitting Pauling bond orders to accurately known bond lengths in standard substances^{25,26} (ethylene, butadiene, benzene, graphite, ave. dev., expt. - calc., ± 0.002 Å), eqn (4). This equation correlates

$$d = 1.463 - 0.124 p(\text{Pauling}) \quad (4)$$

bond length data for alternant unsaturated and benzenoid

Table 2. Bond orders and bond lengths

# Compound	Molecular Graph and SC ($k=0.40, k'=0.16$)	Bond	Bond Order	Bond Length (Calc.)	Bond Length (Expt.)
5		a (1.0) b (k') c (1.0)	.862 .138 .862	1.356 1.446 1.356	1.356 ^a 1.446 1.356
1		a (1.0) b (1+k) c (1.0)	.417 .583 .417	1.411 1.391 1.411	1.418 ^b 1.377 1.405
3		a (1.0) b (1+2k) c (1.0) d (1+k)	.357 .643 .357 .500	1.419 1.383 1.419 1.401	1.403 ^c 1.370 1.413 1.393
7		a (1.0) b (2k) c (1.0) d (k') e (1+k')	.761 .238 .761 .119 .881	1.369 1.433 1.369 1.448 1.354	1.361 ^d 1.429 1.364 1.444 1.352
8		a (1.0) b (2k) c (1.0) d (k) e (1+k) f (0.0) g (1+2k) h (0.0)	.556 .444 .556 .222 .778 0.0 1.0 0.0	1.394 1.408 1.394 1.435 1.367 1.463 1.339 1.463	1.381 ^e 1.401 1.386 1.430 1.367 1.441 1.341 1.475
9		a (2+k) b (k') c (2.0) d (2k) e (1.0) f (1.0) g (1+2k) h (1.0)	.931 .069 .862 .138 .431 .431 .569 .431	1.348 1.454 1.356 1.446 1.410 1.410 1.392 1.410	1.326 ^f 1.434 1.335 1.451 1.433 1.408 1.358 1.391

^aRef. 34. ^bRef. 38. ^cRef. 36. ^dRef. 37. ^eRef. 35. ^fRef. 39.

hydrocarbons with an average deviation of $\pm 0.009 \text{ \AA}$, slightly better than Coulson bond orders or bond orders from LCAO-MO-SCF calculations.²⁶

The qualitative short-long characters of the predicted bond lengths are in reasonably good agreement with experimental results if $k=0.4$ is used for all of the compounds in Table 2. However, the average deviations of predicted and experimental bond lengths in the diformyl compound 7, $\pm 0.022 \text{ \AA}$, cycloheptatriene, $\pm 0.018 \text{ \AA}$, and benzoellassovalene 9, $\pm 0.023 \text{ \AA}$, are much larger than the average deviations in 1,6-methano[10]annulene, *syn*-1,6:8, 13-bis-methano-[14]annulene, and the tropone derivative 8, ± 0.007 , 0.011 , and 0.009 \AA respectively. The fact that cycloheptatriene 7, and 9 are open bridged annulenes with open bridging distances *ca.* 0.3 \AA longer than transannular distances in the other "closed" compounds infers an apt explanation in terms of a reduced value of k for the open compounds. One finds that $k'=0.16$ gives exact agreement between calculated (eqn 4) and experimental bond lengths for cycloheptatriene, and it is suggested that this lower value be used for other open bridged annulenes represented by graphs listed in Tables 1

and 2. With this approximation the resonance energy of cycloheptatriene (homobenzene) would be only 21% of the resonance energy of benzene, rather than a calculated 49% if $k=0.4$.

More crystal structures will be available in the future, and it is likely that large deviations of predicted bond lengths from experimental values will not all be as easily rationalized. Since this present paper constitutes only a general outline of possible applications of structure-resonance theory to bridged annulenes, additional comparison and discussion will therefore be left to a later date. However, one additional aspect of the bond order results is worth describing, and this is in regard to questions of bond length alternation and measures of aromaticity.⁴⁰⁻⁴³ Combining the results of Tables 1 and 2, one finds for 1,6-methano[10]annulene that as k increases, resonance energy and bond order alternation on the periphery of the molecule *both* increase. Conversely in 7 (Table 2) bond alternation will *decrease* as k and resonance energy both increase. From these results, one can see that only a regular alternation of bond lengths around the entire perimeter of an annulene is valid evidence of nonaromaticity. Complete delocalization

(high aromaticity) requires partial but substantial alterations in bond lengths, as is found, e.g. in naphthalene and anthracene.²⁴

Ionization Potentials. The lowest adiabatic IP for a particular compound is the difference in energy between neutral molecule and radical cation produced upon ionization. Assuming no major changes in underlying structures upon ionization, the IP should be a linear function of the difference in π resonance energies of neutral and ionized compound. Accordingly the first IP's of twenty-nine compounds were used to establish the linear relationship given in eqn 5.²³ The correlated compounds include cata- and peri-condensed

$$\text{IP(eV)} = 11.277 + 1.185 \ln[\text{SC(R)}] - 1.044 \ln[\text{SC(R}^{+\cdot})] \quad (5)$$

benzenoids, nonbenzenoids and nonalternant π hydrocarbons, and open chain and cyclic olefins. The average deviation between calculated and experimental IP's is ± 0.16 eV (correlation coefficient 0.996). Equation (5) shows that the lowest IP of a π molecular hydrocarbon can be interpreted as the energy to remove an electron from an isolated sp^2 hybridized carbon atom augmented

by the resonance energy of the neutral compound ($1.185 \ln[\text{SC(R)}]$) and diminished by the resonance energy of the resulting radical cation ($1.044 \ln[\text{SC(R}^{+\cdot})]$).

Calculated and experimental IP's^{5,6,44-46} for five bridged annulenes are given in Table 3. The remaining molecular graphs in the table correspond to known molecules,¹ and the range of predicted IP's is reasonably large. Therefore the calculated IP's could serve as tests of the theoretical approach when experimental results become available.

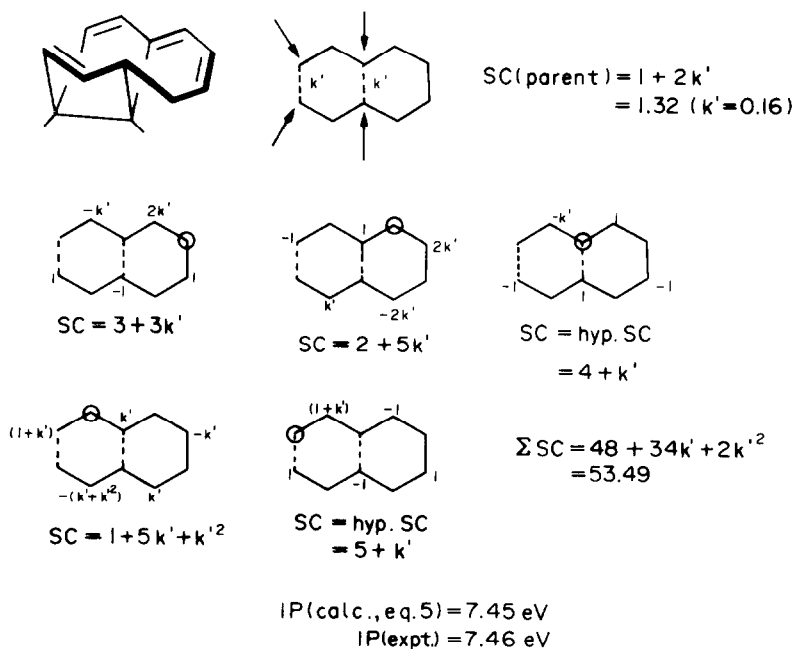
The results in Table 3 are obtained using the same k values (0.40 and 0.16) as used in the bond order calculations. The SC's for the ionized radical cations are calculated by localizing a cationic charge at each independent site in the π graph and summing the SC for the odd electron resonance structures. The cation structures are also assumed to be hyperconjugatively stabilized if the charge is located at the site of an alkyl group or methylene substituent. In line with recent results in correlating gas phase proton affinities of π hydrocarbons,⁴⁷ the hyperconjugation structures are taken to have the same weight as the other covalent structures. The SC summation is illustrated in **10** for ellassovalene⁴⁶ where the alkyl group stabilized sites are denoted by arrows.

Table 3. Ionization potentials from structure-resonance theory

Compound	Molecular Graph ^a	SC(R)	SC(R ⁺)	I.P. calc.	I.P. expt.
		$1+k'$	$18+6k'$	8.38	8.50 ^b 8.57 ^c
		$1+k'$	$24+6k'$	8.09	8.11 ^d
		$2+k$	$60+12k$	7.96	7.90 ^e
		$2+2k$	$126+56k+2k^2$	7.27	7.33 ^f
		$1+2k'$	$48+34k'+2k'^2$	7.45	7.46 ^d
		$2+3k$	$216+152k+12k^2$	6.78	-
		$3+k$	$120+28k$	7.63	-
		$3+2k$	$138+37k$	7.61	-

^aThe positions of alkyl substituents are denoted by arrows. $k=0.40$ $k'=0.16$.

^bRef. 45. ^cRef. 44. ^dRef. 46. ^eRef. 5. ^fRef. 6.



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CONCLUDING REMARKS

It is noteworthy that the same values of k and k' for the transannular interactions can be used to correlate both bond lengths and ionization potentials. This parallels earlier structure-resonance theory results where it has been shown that parameters of the theory are generally transferable in discussions of different kinds of properties.¹⁴ The calculations could be elaborated using, for example, values of overlap integrals at the transannular points³⁹ to establish the k parameters. However, the simplest possible model is preferred at present, and the good agreement between experiments and calculations may constitute support for the choices of k . The interpretation of the results seems to require that neutral homoaromaticity be an observable phenomenon, reflected in ground state and excited state properties. IP's and bond lengths are correlated correctly by the theory only if homoconjugative interactions are included, and the very small number of necessary parameters leaves little leeway for adjusting results to fit experimental data.

The calculated resonance energies (Table 1) are quite substantial, which is in disagreement with some recent opinions^{48,49} regarding the existence of neutral homoaromaticity. This question could be further considered using the procedures that have been outlined. For example, it is readily apparent that either IP's or bond lengths could be used to calculate a separate optimum value of k for each compound. This k could then be used to calculate a resonance energy the value of which could be compared with other physical and chemical criteria for aromaticity. Whether or not such procedures will yield useful information regarding homoaromaticity is under investigation.

The advantages of using the structure-resonance theory presented here are the extreme simplicity of the algorithms for the calculations and the agreement of theory with relevant experimental data. No other theoretical approach gives so many detailed "predicted"

experimental values in a wide variety of applications with so little labor. These are, of course, limitations to the structure-resonance theory approach. For example, Hückel MO calculations will give a predicted value for the first IP of a π hydrocarbon, and also values for the remaining π levels. Only the first IP is calculated by structure-resonance theory as presented in this paper. It is also appropriate to mention that Haddon's PMO approach^{7,8} can be used to obtain extremely good correlations of bond lengths in addition to estimates of resonance energies in bridged annulenes.

Structure-resonance theory can also be used to correlate the rates of cycloaddition reactions,^{50,51} and electrophilic,^{52,53} nucleophilic,³² and free radical reactions^{21,54} of benzenoid hydrocarbons. The calculations require no more than counting structures for reaction intermediates or postulated transition states to yield quantitative results. The formalism has also recently been extended to predictions of the relative stabilities of tricarbonyl(η^4 -diene)iron complexes⁵⁵ and other metal complexes. The application of these extensions to bridged annulene systems will hopefully be of interest.

Acknowledgement—The financial support of the Robert A. Welch Foundation of Houston, Texas is gratefully acknowledged.

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