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Aromatic Electronic Delocalization of Benzo Derivatives of Five-membered Heterocycles

Achim Mehlhorn and Jürgen Fabian

*Sektion Chemie der Technischen Universität Dresden DDR-8027 Dresden,
Mommsenstr. 13*

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The aromaticity of some bicyclic heterocycles is discussed with the aid of the configuration analysis of the expansion coefficient matrices and the similarity analysis of the density matrices. The iso- π -electronic [9] annulenyl anion is taken as the aromatic reference compound for all the heterocyclic compounds considered. The results are compared with those previously obtained from considerations of energy. In addition the question is posed whether the sub-structures display aromatic features.

INTRODUCTION

As documented at a recent conference¹, aromaticity is a matter of continuing interest. Many attempts have been made to express aromaticity quantitatively and to use aromaticity indices for systematizing or predicting aromatic systems.

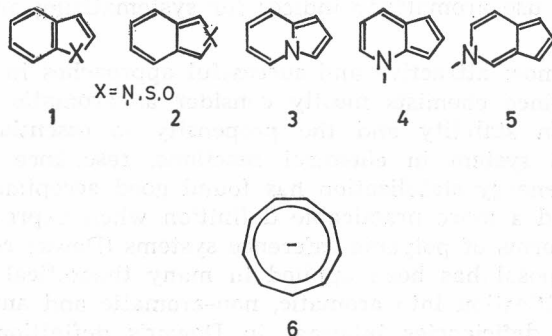
One of the most attractive and successful approaches in this field is the energetic one. Since chemists mostly consider as aromatic compounds that display a certain stability and the propensity to essentially retain their cyclic-conjugated system in chemical reactions, resonance energy (RE) as an indicator of energy stabilization has found good acceptance in chemistry. Dewar introduced a more practicable definition when expressing the energy stabilization in terms of polyenic reference systems (Dewar resonance energy, DRE)². This proposal has been applied in many theoretical papers and has resulted in classification into aromatic, non-aromatic and anti-aromatic compounds. Certain deficiencies inherent in Dewar's definition were removed more recently by Gutman, Milun and Trinajstić, who proposed a nonparametric topological resonance energy (TRE)³. Along these lines, theoretical aromaticity indices are known for a great variety of hydrocarbons and heteroconjugated systems. There is, however, a lack of experimental equivalents.

In order to gain better experimental access, alternative approaches have been advanced, linking aromaticity to the electronic structure of the molecules. Since bond lengths equalization and uniform distribution of the π -electrons are further characteristic features of aromatic parent compounds, similar properties in any other compound considered should indicate aromaticity as well. The behaviour of the compounds in the magnetic field provides a rich source of experimental information about the electronic structure. Therefore,

magnetic and magneto-optic properties⁴ are widely accepted as proper aromaticity criteria. However, this approach is not devoid of problems, either^{4,5}.

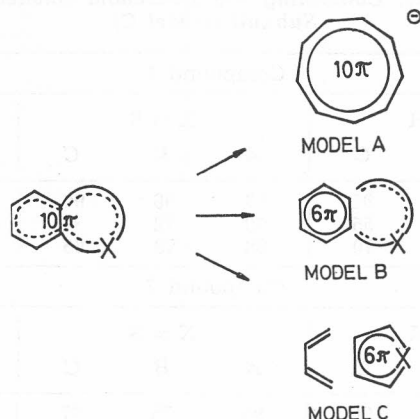
The electronic structure of a molecule is theoretically indicated by its total state wave functions and the charge-bonded order matrix derived therefrom. Consequently, a comparison of the results obtained for any cyclic conjugated system with those of the iso- π -electronic aromatic parent hydrocarbon might provide criteria of aromaticity equivalent to the energetic ones. In order to analyze both the total state wave function and the charge-bond order matrix configuration analysis⁶ and similarity analysis⁷ are appropriate techniques. In this context, the question has been recently posed whether two distinct approaches, one in terms of the energetics and the second one in terms of the electronic distribution, are compatible^{8,9}. For alternant hydrocarbons, this question got a definite answer: The energetic stability increases with the diamagnetic ring current⁸. However, experimental studies suggest that this relation no longer holds for non-alternant hydrocarbons¹⁰ and heterobenzenes¹¹.

The main aim of this paper is, therefore, to consider the compatibility of the two approaches for some heterocyclic compounds. We have chosen the compounds 1 to 5, which are iso- π -electronic to the aromatic^{3,12} [9]annuleny anion 6 (cyclononatetraenyl anion). The aromaticity of these heterocyclic compounds was extensively studied from the energy point of view and HMO^{3,13}, PPP¹⁴ and ab initio calculations¹⁵ have been carried out. These studies provided a rather concurrent picture: Replacement of the heteroatoms X in 1 and 2 on passing from nitrogen through sulphur to oxygen is accompanied by a decrease in aromatic stability. Also, compounds of the series of »benzenoid« heterocycles 1 are more stable than the isomeric »quinoid« heterocycles of the series 2.



Due to the choice of reference system 6, the degree of aromaticity calculated is not only affected by the heteroaromatic substitution and the position of the heteroatom, but also by the intra-annular bridge. If the intra-annular bridge is strong, the delocalization of π -electrons along the outer perimeter will be appreciably perturbed. In consequence, an aromatic 6π subsystem may emerge in structures of the series 1 and 2, either the aromatic benzene or the aromatic heterocycle. The second point to be considered in this paper is therefore the question whether the entire molecule's aromaticity is affected by any local aromaticity, and how far this local aromaticity is caused by one of the two sub-systems.

Thus, the structure 1 to 5 are analyzed with respect to 6 (model A) and, in addition, the structures 1 and 2 both with respect the benzene-heteroene (model B) and butadiene-heterocycle (model C) fragmented molecule.



Finally the electronic structures of excited states should be compared with that of the reference ground state. This gives information about aromatic electronic structures in excited electronic states.

At this point, the nature of the reference systems used in the distinct approaches deserves an additional comment in defining the aromatic character. Whereas the former energy analysis (DRE's) is referred to certain polyenic reference structures, the analysis of the electronic structure is referred directly to the electronic structure of an aromatic parent compound. This is, as mentioned above, the electronic structure of the [9]annulenyl anion 6 for the heteroatomic systems to be considered. Without doubt, the choice of a single reference system for the whole series of structures is a great advantage, but the examination is then restricted on the comparison between structures that are topologically and π -electronically equivalent.

THEORETICAL METHODS

Configuration analysis^{6,16} enables the wave functions of any compound to be expanded in terms of the wave functions of a topologically and π -electronically equivalent reference system; the ground state of the heterocyclic compounds is described by the ground and excited states of the reference systems. When the configuration interaction is limited to singly excited states, however, expansion is incomplete and the sum of the squared coefficients r_M is lower than unity ($r_M \leq 1$). In the expansion of the ground state wave function of the heterocycle the ground state wave function of the aromatic reference structure will dominate. The larger the squared expansion coefficients c^2 (0,0), the more closely related are the ground states of the two compared structures and consequently, the more aromatic the heterocyclic compound.

Configuration analysis provides, at the same time, a description of the excited states. The wave functions of the excited states of the heterocycle are now predominantly described by the wave functions of the excited states of the aromatic reference system. Therefore, the latter results of the analysis cannot be interpreted in terms of the ground state aromaticity of the reference systems.

Similarity analysis⁷ differs fundamentally from configuration analysis, although its principal approach is similar. Now the density matrices are compared and their similarity is determined quantitatively. The similarity index $s(I, J)$ between the

TABLE I

Appropriateness of the Ground State and Excited State Description (r_M values in%) with Respect to the Fully Delocalized [9] Annulenyli Anion (model A) or with Respect to Fragmented Molecules, Containing the Benzenoid (model B) or Heteroaromatic Subunit (model C)

Compound 1									
	X = NH			X = S			X = O		
	A	B	C	A	B	C	A	B	C
ψ_0	95	95	91	93	96	90	92	97	90
ψ_1	74	69	55	70	72	54	66	77	52
ψ_2	72	76	70	68	79	65	65	82	69
Compound 2									
	X = NH			X = S			X = O		
	A	B	C	A	B	C	A	B	C
ψ_0	95	82	96	94	75	97	92	77	97
ψ_1	77	60	79	75	54	80	71	55	81
ψ_2	73	45	69	68	42	73	65	43	73
Compounds									
	1	2	3	4	5				
ψ_0	95	95	97	97	97				
ψ_1	74	77	79	78	75				
ψ_2	72	73	76	83	82				

two electronic states I and J results from an exponential relationship of a simplified Eukclidean distance function. In contrast to the configuration analysis each state of the heterocycle can now be compared with any reference state in a separate calculation. For discussing the aromatic electronic delocalization, the comparison between the density matrices of the ground state has to be made resulting in $s(0,0)$ indices.

Another interesting comparison which cannot be undertaken by configuration analysis consists in comparing the density matrix of any excited state I with the density matrix of the ground state of the aromatic reference compound ($s(I,0)$ indices). Analysis will reveal to what extent aromatic delocalization still persists in the particular excited state. An approach like this has no equivalent in terms of energy aromaticity considerations.

Analysis of the density matrices in quantifying aromatic delocalization has some precedent: In Jug's aromaticity index¹⁷, bond orders along the perimeter are compared between the system under consideration and the aromatic reference system (benzene). Alternatively, in order to rationalize magneto-optical properties Labarre and Crasnier⁴ calculated the average difference of charge between adjacent atoms (\gg charge gradients \ll). The larger the charge gradient, the less the ring current. The similarity analysis unifies both approaches, for charge as well as bond orders are considered. In view of past experience only these two types of matrix elements are taken into account in the similarity analysis, thus neglecting all the density matrix bond orders between non-bonded atoms.

One analysis of the wavefunction shows the orthogonal transformation of delocalized orbitals into localized ones and the comparison of the degree of correspondence between the localized functions with those of the subunits. [18–20] The fact that even the highest localized molecular orbital in any cyclic conjugated system is more delocalized than the ethylene π orbital suggests a relationship between delocalization and resonance energy [18]. This approach differs, completely however, from configuration and similarity analysis.

The wave functions and density matrices subjected to analyses are obtained exclusively by π -methods, either on the PPP- or the HMO level. As to the approximation and the parameters the footnote to Table II should be consulted.

TABLE II
Results of the Configuration and Similarity Analyses with Respect to the [9] Annulenyli Anion (6)

	X	PPP-Calculations ^a			HMO-Calculations ^c		REPE ^d	TREPE ^e
		$c^2(0, 0)$	$s(0, 0)$	RE ^b	$c^2(0, 0)$	$s(0, 0)$	β	β
1	NH	65.5	42.8	23.8	63.6	38.6	0.047	0.038
	S	58.5	31.7	24.8	61.3	35.8	0.044	0.035
	O	56.0	27.8	20.3	36.1	11.0	0.0036	0.027
2	NH	66.7	46.1	11.6	71.9	52.5	0.029	0.032
	S	62.8	35.3	9.3	72.5	52.8	0.025	0.029
	O	58.1	29.5	2.4	42.0	12.8	0.002	0.011
3	—	71.9	48.4		84.4	52.8	0.027	
4	—	73.2	48.2		65.0	40.3	0.020	
5	—	72.9	43.6		73.0	43.1	0.019	

^a Variable β approximation, taking into account all singly excited states.

^b Values given in kcal/mol

^c HMO parametrization as described by Hess and Schaad¹³

^d Apart from 3 to 5 taken from Ref. 13

^e Taken from Ref. 3

RESULTS

Results of the configuration analyses are collected in Table I. The appropriateness of the ground and excited state description of the heterocyclic compounds 1 and 2 in terms of the electronic states of the aromatic reference compound 6 decreases in the sequence $\text{NH} > \text{S} > \text{O}$ in both series. This finding supports the earlier results for configuration analysis, in which the indenyl anion was taken as the reference structure²¹. The appositeness of model A in describing the different nitrogen-containing heterocycles 1—5 does not differ much, but a remarkable increase is observed on passing from 1 through 2 ($\text{X} = \text{NH}$) to 3, 4 and 5. In all cases the ground state description is considerably better than the excited state description.

The graduation between the heterocycles is rather similar when the contribution of the ground state of the aromatic reference system to the ground state of the heterocycles is considered. Therefore, the values of $c^2(0, 0)$ together with the similarity indices $s(0, 0)$ are collected in Table II. Obviously, the results of both analytical procedures are equivalent and the conclusions which can be drawn with regard to the delocalization of π electrons are consistent. According to the r_M , the $c^2(0, 0)$ and the $s(0, 0)$ values in Tables I and II, the nitrogen-containing heterocycles exhibit the closest similarity to the aromatic reference molecule 6 and can be considered the most aromatic. On the other hand, the electronic structures for oxygen-containing heterocycles differ considerably from those of the reference system and are consequently less aromatic.

Summarizing the aromaticity relations based on the electronic structure, we can conclude that among structures of type 1 and 2 aromaticity decreases in the order $\text{NH} > \text{S} > \text{O}$, and that among the different nitrogen-containing

heterocycles the aromaticity sequence $3 > 4 > 2$ ($X = \text{NH}$) $> 5 > 1$ ($X = \text{NH}$) is found. Finally, compounds of the type 2 should be more aromatic than the corresponding compounds of type 1.

Calculations on the HMO-level provided a similar picture (Table II). In order to compare the results of the analyses mentioned above with calculated stabilization energies, the Hess and Schaad's¹¹ parametrization was employed. In this parametrization, the oxygen electron pair is held more fixed than in the PPP calculations, and the oxygen heterocycles now differ more strongly from the sulphur and nitrogen heterocycles in their aromatic delocalization. However, the feature described above is essentially retained.

When we compare our results with the calculated resonance energies per electron (REPE and TREPE, respectively) some relationships are found to be in complete agreement while others are in sharp contrast. The trends are congruent when heteroatomic substitution is considered. The decrease in electronic delocalization in the sequence $\text{NH} > \text{S} > \text{O}$, for example, is associated with a decrease in aromatic stabilization energy. The higher aromatic electronic delocalization in series 2 relative to series 1, however, is in contradiction to the energy relations. Also, the extreme position of indolizine, 1-pyrindene and 2-pyrindene is incompatible with the calculated resonance energies.

These results suggest that analysis of the electronic structure obviously reveals different aspects of the property of »aromaticity« than the analysis of the energetics.

This opinion is strengthened by analysis of the excited state electronic distribution in terms of the aromatic ground state of the reference system. According to the $s(I, O)$, indices of the similarity analysis, heterocycles in the excited states may even exhibit a stronger aromatic delocalization than in the electronic ground state. This is the case, for example, in most of the second excited states of the »benzenoid« 1 and the »quinoid« 2.

The unexpectedly high degree of aromatic electronic delocalization in certain ground and excited states can be illuminated in more detail by similarity analysis, when the number of matrix elements under comparison is reduced.

This is achieved in two ways:

First, the similarities of the charges and bond orders between the molecule studied and the reference system can be considered separately. This procedure answers the question whether the aromatic electronic structure results either from an extended delocalization of the π electrons over the whole molecule or from an essential equalization of the peripheral bond orders only. The calculations show that the lower aromatic character of 1 relative to 2 in the ground state is due to the weaker donor capacity of the heteroatom in 1, whereas the equalization of the peripheral bond orders shows the opposite trend. An increasing inclination of the heteroatoms to release electrons in structure 2 appears to be due to a considerable weakening of the intra-annular bond.

Secondly, the similarity of aromatic sub-units according to models B and C can be calculated. The intra-annular bond is now an inherent part of either the local aromatic benzene sub-unit (model B) or the heterocycle aromatic sub-unit (model C).

TABLE III

Results of the Configuration and Similarity Analyses with Respect to Fragmented Molecules with Aromatic Sub-structures (model B and model C)

	X	Model B		Model C	
		c ² (0, 0)	s (0, 0)	c ² (0, 0)	s (0, 0)
1	NH	66.2	89.6	56.8	92.2
	S	74.0	94.1	53.1	90.9
	O	70.4	94.0	53.6	91.3
2	NH	41.4	69.0	69.9	95.8
	S	33.7	62.4	72.5	96.2
	O	33.5	63.0	73.1	96.7

As demonstrated in Table III, configuration and similarity analysis resulted in a consistent picture: The aromatic benzene dominates in the series of »benzenoid« heterocycles 1, while the five-membered heterocycles dominate in the series of »quinoid« heterocycles 2. The dominance of the heterocyclic delocalization in the latter case accounts for the fact that heteroatoms exert a negligible effect on the residual butadienic fragments. According to NMR-studies¹⁹, the ratio of the two coupling constants of the butadiene fragment are nearly constant, independent of the nature of the heteroatom in 2.

TABLE IV

Results of the Similarity Analysis between Different States of Heterocyclic Compounds and the Ground State of the [9] Annulenyli Anion (model A)

	X	Ground State s (0, 0)	First Excited State s (1, 0)	Second Excited State s (2, 0)
1	NH	42.8	43.4	50.3
	S	31.7	41.6	46.4
	O	27.8	27.7	26.6
2	NH	46.1	42.7	52.3
	O	35.3	33.5	46.8
	S	29.5	28.3	35.4
3	—	48.4	38.6	39.7
4	—	48.2	31.2	35.6
5	—	43.6	27.4	38.0

CONCLUSIONS

The study has revealed that the conclusions drawn from an analysis of the energetics agree only in part with those reached by an analysis of the wave functions or of the charge and bond orders. Obviously, the term »aromaticity« reflects distinct facets of a more complex behaviour pattern in cyclic-conjugated systems. In the case of heterocyclic compounds it seems impossible to characterize these features by a single index of aromaticity. The higher resonance energy stabilization of the »benzenoid« heterocycles, 1, relative to the »quinoid« heterocycles, 2 was the conclusion of former theoretical papers and quite well in agreement with the experimental experience so far. According to our study, however, electronic distribution does not necessarily exhibit the

same pattern. In contrast, the results of configuration and similarity analyses rather suggest that, in terms of electronic delocalization, compounds of series 2 should be more aromatic than compounds of series 1. This finding should be reflected both in the molecular geometry, especially the strength of the intra-annular bond, and in the magnetic properties. In order to prove this conclusion, more detailed theoretical studies on bond length characteristics and on magnetic properties, such as the diamagnetic ring current of the heterocyclic compounds and additional experimental knowledge of the molecular structure and their NMR-spectra would be highly desirable.

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SAŽETAK

Aromatička elektronska delokalizacija kod benzo derivata petočlanih heterocikla

A. Mehlhorn i J. Fabian

Studirana je aromatička stabilnost nekih cikličkih spojeva s N, S, O, kao heteroatomima u petočlanom prstenu pomoću konfiguracijske analize matrica ekspanzijskih koeficijenata i analizom sličnosti matrica gustoće. Kao aromatički referentni spoj uzet je izo- π -elektronski [9] anulenilni anion. Dobiveni rezultati su uspoređeni s ranijima iz literature temeljenima na energijskom kriteriju aromatičnosti. Također je pokušano odgovoriti na pitanje da li substrukture pokazuju aromatička svojstva.

ODJEL KEMIJE

TEHNIČKOG SVEUČILIŠTA U DRESDENU

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