CROATICA CHEMICA ACTA CCACAA **49** (3) 461—470 (1977)

YU ISSN 0011-1643
CCA-1017 547.5
Original Scientific Paper

Definition of Aromaticity on the Basis of Molecular Orbital Localizability

G. Náray-Szabó and K. Horváth*

Chinoin Pharmaceutical and Chemical Works Ltd. H-1325 Budapest, Hungary

Received June 23, 1976

A new quantitative measure is given to characterize the aromaticity of conjugated molecules. By definition the aromaticity index, A, is equal to the deviation from the unity of the average π-orbital localizability of the molecule. The localizability of molecular orbitals is defined according to Diner, Malrieu, Jordan and Claverie. Aromaticity indices were calculated for 21 homo- and heteroconjugated molecules using the CNDO/2 method. The relationship between our index and some other ones is discussed. In addition, the role of d-orbitals in aromaticity and the relation of Hückel's $4n + 2$ rule to our definition are analyzed.

INTRODUCTION

The concept of aromaticity is more than 100 years old and it has its place in modern theoretical organic chemistry, too[1]. The chemical reactivity, electronic spectra and magnetic properties of certain molecules are easily understood in terms of aromatic character. Aromaticity can be also defined theoretically, through quantum chemical models. Numerous papers deal with the quantum chemical aspects of this problem[2]. It has been found that aromaticity is related to the localizability of molecular orbitals[3,4].

Several quantitative indices have been defined to make a more precise distinction between various aromatic molecules possible. Both experimental[5] and quantum chemical[6–9] definitions are used to interpret diverse facts. For a comparative review see the paper of Kruszewski and Krygowski.[10]

However, experimental definitions possess more or less arbitrary elements. This is a consequence of the effort to choose the indices in such a way that they reflect experimental findings in the best way possible. This effort is foredoomed to failure when far lying properties, such as chemical reactivity and diamagnetic behaviour, must be interpreted uniformly. The quantum chemical indices are based preferably on resonance energy. Since the concept of resonance is rather ambigous the phenomenon of »aromaticity« becomes more difficult to understand. We feel that a thorough understanding of the problem is possible only on the basis of exact quantum chemical concepts. One of these is localization.

In this paper a suggestion is made to introduce a new aromaticity index. The definition is based on the localizability of molecular orbitals and it contains very few arbitrary elements. The index can be calculated for all

---

* Working as a guest at the Quantum Theory Group, Physical Institute, Technical University, Budapest, Hungary.

types of molecules including heteroaromatic, ionic, radical or excited ones. The numerical values for aromatic hydrocarbons were obtained by the Hückel method and for heteroaromatic molecules by the CNDO/2 method, respectively. The definition can be extended without any difficulty to molecular orbitals obtained on the basis of ab initio calculations.

The definition of the aromaticity index and the numerical values are given below. The relationship to other indices as well as some interesting individual cases are discussed.

DEFINITION

It is known that the delocalized canonical molecular orbitals, obtained on the basis of the Hartree-Fock-Roothaan equations, can be generally localized to a few atoms of the molecule[11]. Localization does not alter the physical quantities which are derived from the total wave function. Localized molecular orbitals correspond generally to the classical chemical bonds. For example, in the case of the methane molecule, localization yields four equivalent C—H bond orbitals. These have important contributions from atoms belonging to a given bond while the participation of other atoms is negligible. The molecular orbitals can therefore be localized onto two atoms. This is not the case for the π-orbitals of benzene which have non-negligible contributions from 3 or 4 centers even after localization. Therefore π-orbitals are poorly localizable.

The measure of localizability can be characterized also quantitatively. A localization index can be defined, according to Diner and coworkers[12], as follows. Let the wave function of the molecule be

$$\psi = \sum_{p}^{\text{all atoms}} \sum_{i}^{\text{on atom p}} c_{pi} \varkappa_{pi} \tag{1}$$

and let

$$c_p = \sum_{i}^{\text{on atom p}} c_{pi}^2 \tag{2}$$

Hence localizability on the p-th atom is defined as

$$l_p = c_p / \sum_{m}^{\text{all atoms}} c_m \tag{3}$$

Through summation the simultaneous localizability on atoms p, . . . , q is obtained:

$$l_{p \ldots q} = l_p + \ldots l_q \tag{4}$$

The aromaticity index, A, is defined as the measure of delocalization with respect to a given localized resonance structure of the molecule:

$$A = 100 \times (1 - L_\pi) \tag{5}$$

Here L_π is the average localizability of the π-orbitals:

$$L_\pi = \frac{1}{N_\pi} \sum_{i=1} n_i \, l_i \tag{6}$$

l_i is the localizability of the i-th π-orbital, n_i is its occupation number, N_π is the total number of π-electrons. The localized structures (see Figure 1.) contain one-center lone pair and two-center π-bond orbitals, respectively. Accordingly, l_i corresponds to one- and two-center localizability, respectively. For example, in the case of the pyrrole molecule, the localizability of the lone pair on the nitrogen is 0.792, both for the two double bonds it is 0.921, respectively. Thus L_π = 0.878 and A = 12.2% (Table I.).

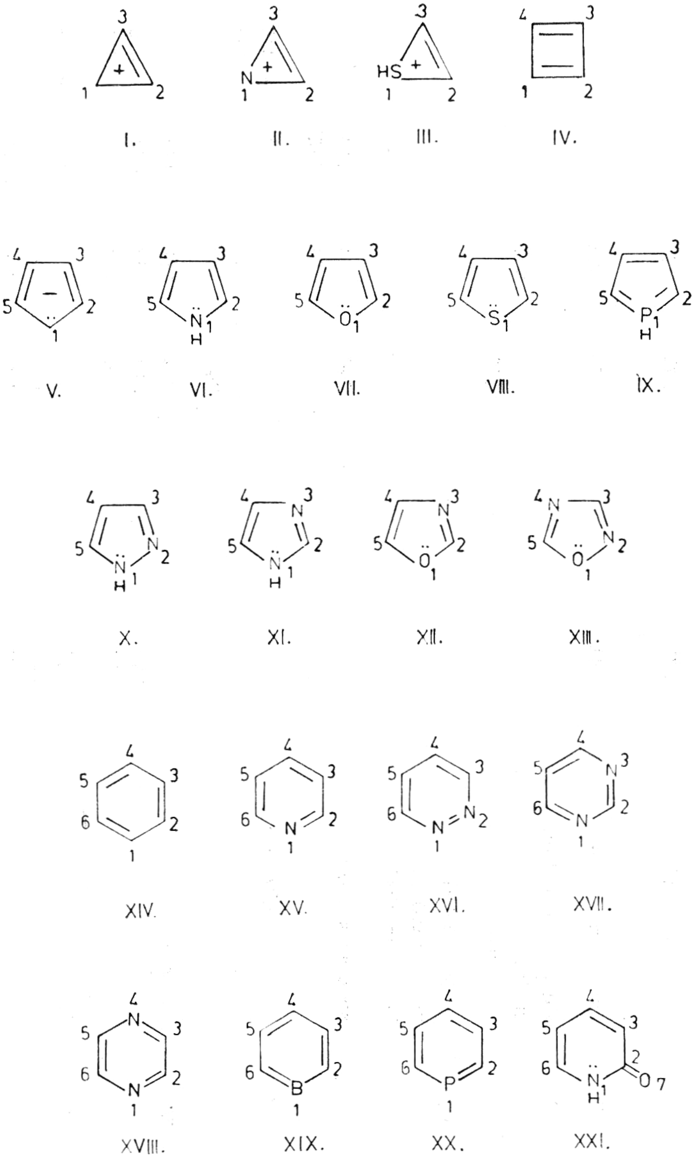

Figure 1. Localized structures of some aromatic molecules as obtained by localization of molecular orbitals calculated by the CNDO/2 method.

TABLE I

Coefficients of Atomic Orbitals in π-Type Localized Molecular Orbitals

Number	Name	AO-coefficients of π-bond orbitals/c×1000						
		1	2	3	4	5	6	7
I	cyclopropenyl cation	577	577	577				
II	azirinium cation	584	574	574				
III	thiirenium cation							
	sp-basis	0	707	707				
	spd-basis	298 0 —223	656	656				
IV	cyclobutadiene nonequivalent bond lengths[2b]	0	0	707	707			
	regular square	484	846	194	—110			
		194	—110	484	846			
V	cyclopentadienate anion	47	640	734	40	—219		
		855	—200	245	—55	408		
		—53	341	—188	776	494		
VI	pyrrole	—67	644	711	182	—206		
		890	310	—86	—86	310		
		—67	—206	182	711	644		
VII	furan	944	200	—119	200	—119		
		—7	—141	134	679	708		
		—7	679	708	—141	134		
VIII	thiophene sp-basis	952	181	—118	181	—118		
		2	—150	147	692	692		
		2	692	692	—147	150		

Table I continued

Number	Name	AO-coefficients of π-bond orbitals/c×1000								
		1			2	3	4	5	6	7
	spd-basis	—2	206	—96	675	665	172	—146		
		—2	—206	—96	—146	172	665	675		
		939	—1	—60	200	—131	—131	200		
IX	phosphole	485	—353	—138	—45	—145	214	743		
		485	353	—138	743	214	—145	—45		
		—246	0	—115	81	676	676	81		
X	pyrazole	881			163	—181	—98	394		
		79			784	571	33	—229		
		—63			—126	355	749	542		
XI	imidazole	11			—197	112	693	684		
		—46			608	752	201	—152		
		887			338	131	142	248		
XII	1,3-oxazole	—3			—143	91	703	691		
		—272			634	749	147	—118		
		940			239	—117	—113	—183		
XIII	1,2,4-oxadiazole	22			774	614	27	—148		
		—35			—115	256	754	593		
		943			123	—121	—104	264		
XIV	benzene	—235			—27	444	706	499	28	
		444			706	499	27	—235	—28	
		499			28	—235	—27	444	706	
XV	pyridine	—8			477	713	463	0	—223	
		729			455	—9	—230	—9	455	
		—8			—223	0	463	713	477	

Table I continued

Number	Name	AO-coefficients of π-bond orbitals/c × 1000								
		1			2	3	4	5	6	7
XVI	pyridazine	476			794	253	—5	—280	—5	
		—14			8	562	662	496	—7	
		491			—77	—287	6	344	743	
XVII	pyrimidine	—71			—225	69	549	707	372	
		53			541	719	370	—68	—214	
		719			378	—67	—202	73	538	
XVIII	pyrazine	—10			7	511	691	511	7	
		891			511	7	—10	7	511	
		0			—500	500	0	500	—500	
XIX	borabenzene	447			22	—230	—3	484	716	
		—203			—41	459	728	464	—36	
		442			716	489	3	—230	15	
XX	phosphabenzene	417	—125	—223	723	453	—12	—183	0	
		—255	—13	37	—5	455	736	439	—16	
		410	238	—106	—5	—169	—4	461	723	
XXI	2-pyridone	—22			—123	—109	277	737	592	45
		—5			284	734	584	76	—169	—75
		—86			479	—14	—102	40	27	866
		896			285	55	—115	—100	287	—86

The definition, given in eq (5) contains few arbitrary elements. The localization procedure and the applied quantum chemical method can be controverted, only. There exists, however no a priori prescribed, sometimes obsolete condition, such as: benzene should be the most aromatic molecule or aromaticity of certain molecules is classified on the basis of experimental findings[10].

RESULTS

In this work the results of CNDO/2 calculations[13] were used to obtain localized molecular orbitals. Localization was carried out according to Edmiston and Ruedenberg[11c] making use of the computer program of Tinland[14]. AO-coefficients of localized π-orbitals are given in Table I. When an spd-basis was used the coefficients of p_z, d_{xz} and d_{yz} (xy is the molecular plane) orbitals, respectively, were also given in the above order. Only these atomic orbitals participate in π-bond formation. MO-coefficients, corresponding to the localized structures of Figure 1., are underlined. Table II. contains aromaticity indices, as obtained from the data of Table I. Making use of the Hückel-type calculations of England and Ruedenberg[3], the aromaticity indices for several polycondensed aromatic hydrocarbons were calculated. (Table III.). It is clear that values, obtained from CNDO/2 or from the Hückel-type calculations, cannot be compared directly, however the same tendencies are expected.

TABLE II

Aromaticity Indices of Monocyclic Molecules (in per cent) as Calculated by the CNDO/2 Method

No.	*A*	PF[5b]	REPE[7] (normalized[10])	TREPE[8]
II	34.1	—	—	—
XVIII	34.1	—	0.749	0.022
I	33.4	—	—	—
XV	26.8	105	0.887	0.038
XIX	25.4	—	—	—
XX	25.4	—	—	—
XIV	25.3	222	0.994	0.046
XVI	24.0	199	—	—
XVII	19.4	198	0.749	0.032
V	15.8	147	—	—
X	14.3	121	0.841	0.047
III	13.9	—	—	—
VI	12.2	138	0.597	0.040
XXI	11.1	—	—	—
XI	11.0	126	0.642	0.033
VIII	10.8	186	0.489	0.033
IX	7.5	—	—	—
XIII	7.2	—	—	—
XII	6.1	—	0.107	0.007
VII	6.1	—	—	—
IV	0.0	—	—	—

TABLE III

Aromaticity Indices of Homoaromatic Polycyclic Molecules (in per cent) as Calculated by the Hückel-Method

Name	A	A_d[6] (normalized[10])	REPE[7] (normalized[10])
pyrene	28.3	0.216	0.769
azulene	25.2	—	0.353
anthanthrene	24.1	0.106	0.688
pentacene	23.0	— 0.200	0.582
anthracene	22.8	0.000	0.717
1,2,5,6-dibenzanthracene	22.1	0.212	0.781
1,2,7,8-dibenzanthracene	21.9	0.224	0.777
benzpyrene	20.5	0.247	0.811
naphtacene	20.5	— 0.116	0.636
benzoperylene	19.6	0.257	0.784
coronene	19.5	0.411	0.803
1,2,3,4-dibenzanthracene	19.0	0.231	0.807
triphenylene	18.8	0.691	0.865
perylene	18.5	0.257	0.739
pentaphene	18.4	0.118	0.717
benzanthracene	18.3	0.121	0.760
picene	18.2	0.284	0.801
chrysene	18.0	0.394	0.812
benzphenanthrene	17.9	—	—
phenanthrene	17.9	0.290	0.837
naphtalene	17.0	0.455	0.842

DISCUSSION

The aromaticity indices of eq (5) were compared with values obtained from other definitions. A linear regression analysis was performed with the following equation

$$A = a A_i + b \qquad (7)$$

where A_i is one of the REPE[7], TREPE[8], A_d[6] or Palmer-Findlay[5b] indices. The results are given in Table IV. The indices, obtained from the Hückel-type or from the CNDO/2 calculations were examined separately. No other significant corre-

TABLE IV

Results of Linear Regression Analysis

Pair of indices	Regression coefficients	r_e	Student-t of a	Number of points
REPE[7] — Hückel[3]	— 0.0212; 1.180	0.992	2.70	20
REPE[7] — CNDO/2*	0.0200; 0.315	0.970	2.64	9
A_d[6] — Hückel[3]	— 0.0302; 0.8345	0.799	1.90	19
Palmer-Findlay[5b] — — CNDO/2*	2.444; 115.1	0.976	1.46	11
TREPE[8] — CNDO/2*	0.00026; 0.02848	0.945	0.52	9

* This work

lations with the indices, discussed in the paper of Kruszewski and Krygowski[10], were found. It is striking that the index, calculated for polycyclic, systems varies antiparallelly with REPE and A_d respectively. We also calculated the aromaticity index of naphtalene on the basis of the CNDO/2 method. The results showed that $A = 15.8$ per cent, i. e., that it was close to the 17.0 per cent value in Table III. Thus, probably, the above antiparallelism is not a result of the differences in our computational methods of England and Ruedenberg[3]. The crucial point may be that, in the case of polycyclic molecules aromaticity is related to orbital localizability in a different way than in the case of monocyclic ones. The linear dependence between A, REPE and A_d, respectivetly, is, however, significant. Our index can be also used as a practical tool in the estimation of the aromaticity of different polycyclic hydrocarbons. In such molecules lower A values correspond to a stronger aromatic behaviour.

It is interesting to study the role of d-orbitals in the formation of the aromatic bonds in thiophene. If d-orbitals are excluded from the basis of the CNDO/2 calculations, $A = 5.9\%$. The considerable increase in aromaticity is a consequence of the delocalization of the C=C double bond orbitals to the sulphur atom. This occurs with the participation of the d-orbitals. The increase of aromaticity, relative to furan, is not due to the fact that »S is less electronegative than O and it is capable of releasing electrons into the ring«[15]. Table I proves that the lone pair is localized to almost the same extent in the two molecules ($l_O = 0.891$ in furan, $l_S = 0.885$ in thiophene). The increase in aromaticity through d-orbitals can be also observed in the case of the thiirenium cation (See Table I), $A = 0.0$ with an sp-basis while $A = 13.9\%$ is obtained with d-orbitals included.

The A aromaticity index also reflects the Hückel $4n + 2$ rule. Cyclobutadiene (4 electrons) is only slightly aromatic ($A = 5.0\%$) even if a square planar structure is assumed. In the case of furan and its aza-derivatives (VII, XII, XIII) the lone pair of the oxygen is strongly localized. The 4-electron system, obtained when excluding the O-atom, is not aromatic. The corresponding aromaticity indices are 3.7%, 2.8% and 5.3%, respectively.

A pentavalent phosphorous atom has to be assumed in phosphole if the localized orbitals of Table I are considered. This involves a localized structure, given in Figure 1. X-ray measurements contradict to these results: the experimental ring bond lengths are as follows[16]: P1C2: 1.786 Å, C2C3: 1.343 Å, C3C4: 1.438 Å. This confirms a structure similar to pyrrole: the short C2C3 bond is of double bond character, while P1C2 and C3C4 are single bonds.

Acknowledgements. The authors are indebted to Dr. I. Gutman and to Prof. N. Trinajstić (Zagreb) for fruitful discussions and for making their results available prior to publication.

REFERENCES

1. G. Binsch, *Naturwissenschaften* **69** (1974) 369; A. R. Katritzky, *Lectures in Heterocycl. Chem.* **1** (1972) S 39 (A Supplementary Issue of the *J. Heterocycl. Chem.* Vol. **9**); M. J. Cook, A. R. Katritzky, and P. Linda, *Advan. Heterocycl. Chem.* **17** (1974) 255.
2. a) A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists,* Wiley, New York—London, 1961.; b) M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry,* McGraw Hill, New York, 1969.; c) E. D. Bergman and B. Pullman (Eds.) *Aromaticity, Pseudoaromaticity, Antiaromaticity,* Proc. International Symp., Jerusalem, 1971.

3. W. England and K. Ruedenberg, *Theor. Chim. Acta* **22** (1971) 196.
4. W. England, K. Ruedenberg, *J. Amer. Chem. Soc.* **95** (1973) 8769.
5. a) A. Julg and F. François, *Theor. Chim. Acta* **7** (1967) 249. b) M. H. Palmer and R. H. Findlay, *Tetrahedron Lett.* (1974) 253.
6. W. T. Dixon, *J. Chem. Soc.* (1970) 612.
7. B. A. Hess, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.* **93** (1971) 305; B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron* **28** (1972) 3857; *ibid.* **31** (1975) 295.
8. I. Gutman, M. Milun, and N. Trinajstić, *J. Amer. Chem. Soc.* to be published.
9. J. E. Kruszewski and T. M. Krygowski, *Tetrahedron Lett.* (1970) 319.
10. J. E. Kruszewski and T. M. Krygowski, *Acta Chim.* **18** (1972) 165.
11. a) J. E. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc. London* **A 202** (1950) 166; b) S. F. Boys, *Rev. Mod. Phys.* **32** (1960) 296; c) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.* **35** (1963) 457.
12. S. Diner, J. C. Malrieu, F. Jordan, and P. Claverie, *Theor. Chim. Acta* **18** (1970) 86.
13. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *Quantum Chemistry Program Exchange* No. 142. Indiana University, Bloomington, Indiana, USA.
14. B. Tinland, *Quantum Chemistry Program Exchange* No. 191. Indiana University, Bloomington, Indiana, U.S.A.
15. K. Pihlaja, and E. Taskinen in: A. R. Katritzky (Ed.), *Physical Methods in Heterocyclic Chemistry* Vol. VI. Academic Press, New York—London, 1974, p. 244.
16. Ph. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.* **92** (1970) 5779.

SAŽETAK

Definicija aromatičnosti na temelju lokalizabilnosti molekularnih orbitala

G. Náray-Szabó i K. Horváth

Opisana je nova kvantitativna mjera za karakteriziranje aromatičnosti konjugiranih molekula. Po definiciji, indeks aromatičnosti A jednak je odstupanju prosječne lokalizabilnosti π-orbitale molekule od jedinice. Lokalizabilnost molekularnih orbitala definirana je prema Diner-u, Malrieu-u, Jordan-u i Claverie-u. Indeksi aromatičnosti izračunati su za 21 homo- i hetero-konjugiranu molekulu pomoću CNDO/2-metode. Raspravlja se o relaciji s indeksima drugih autora i tretira uloga d-orbitala u aromatičnosti i veza s Hückelovim pravilom $4n + 2$.

CHINOIN PHARMACEUTICAL AND
CHEMICAL WORKS LTD
H-1325 BUDAPEST, HUNGARY

Prispjelo 23. lipnja 1976.