

An HMO »Extended« Free Valence Index and its Application

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An extended free valence index defined in the HMO framework and its modification is presented. It has been applied to several molecules containing heteroatoms and non-benzenoid systems, where the classical free valence index fails in predicting the reactivity positions. This index gives, by direct inspection, the most probable positions for electrophilic (ES) and nucleophilic (NS) substitutions.

INTRODUCTION

One of the applications of the HMO-method is the prediction of chemical reactivity in molecules with π -electrons. Several reactivity indices can be defined within the HMO framework,^{1,2,3} such as charge density, bond order, free valence, localization energy, *etc.* Among these indices, the free valence presents more difficulties in predicting chemical reactivity. Several typical examples can be found in the literature, *e.g.* azulene, fluoranthene² and most of the heterocycles to which the HMO-method can be applied.^{4,5}

In the following paragraphs it will be shown how we can re-define the free valence index in such a way that the classical definition can be considered as a particular case. This redefined free valence index will be applied to those examples where the classical index predicts incorrect behaviour.

FREE VALENCE

The free valence index is usually defined as^{6,7,8}

$$F_r = N_{\max} - \sum_s^d p_{rs} \quad (1)$$

where p_{rs} is the bond order between the r and s atoms in the π molecule, and N_{\max} is a number which can be chosen as $\sqrt{1}$, $\sqrt{2}$ and $\sqrt{3}$ and the sum runs over the d -neighbour atoms connected with the r -th atom in the mole-

cule. This index can be applied to polyenes and aromatic compounds but it fails when applied to non-benzenoid or heterocyclic molecules, where the predicted reactivity is not in agreement with the experimental facts.² Moreover, it is usual to redefine the ionic free valence indices for accounting the observed reactivity behaviour of the molecule in electrophilic and nucleophilic substitutions.⁸ Equation (1) can be deduced by reasoning as follows: The total energy of a molecule with N atoms and m occupied π -orbitals can be written as¹

$$E = \sum_s^m b_j \varepsilon_j' = \sum_r^N q_r \alpha_r + 2 \sum_r^N \sum_{s \neq r} p_{rs} \beta_{rs} = \sum_r^N \varepsilon_r \quad (2)$$

where b_j is the number of electrons at each π -molecular orbital with energy ε_j' , q_r is the charge density of the r -th atom, β_{rs} is the resonance integral between the r -th atom, ε_r is the atomic stabilization energy of the r -th atom. Within the HMO-theory $\beta_{rs} \neq 0$ only when r and s are neighbours in the molecule.

The coulomb and resonance integrals can be written as^{2,9,10}

$$\alpha_r = \alpha_0 + \delta_r^* \beta_0 \quad \text{and} \quad \beta_{rs} = k_{rs} \beta_0$$

where α_0 and β_0 are the coulomb and resonance integrals for C atoms in benzene, and δ_r^* and k_{rs} are values depending on the nature of the atoms involved in the molecule. The typical values for δ_r^* and k_{rs} can be found elsewhere (see refs. 2 and 9).

If we take $\alpha_0 = 0$, then ε_r can be written as

$$\varepsilon_r = q_r \delta_r^* \beta_0 + 2 \sum_{s \neq r}^d k_{rs} p_{rs} \beta_0 \quad (3)$$

There must exist an atom/atoms belonging to a molecule (or molecules) which is/are to be found, where this ε_r takes a minimum value. The molecule with our reference atom must fulfil some structural requirement. It can be shown that the molecule where these conditions are fulfilled are ethylene, propenylradical and 2-methylen-propenyl radical.^{2,6,7} If our reference atom is bonded to d' neighbours we can write

$$\varepsilon^0 = q^0 \delta^0 \beta_0 + 2 \sum_{s'}^{d'} k_{s'}^0 p_{s'}^0 \beta_0 \quad (3')$$

where $p_{s'}^0$ is the bond order between the reference atom and the s' atom.

Subtracting equation (3) from (3') we have

$$\varepsilon^0 - \varepsilon_r = (q^0 \delta^0 - q_r \delta_r^*) \beta_0 + 2 \beta_0 \left(\sum_{s'}^{d'} k_{s'}^0 p_{s'}^0 - \sum_s^d p_{rs} k_{rs} \right) \quad (4)$$

If for the atom in the reference molecules $\delta^0 = 0$, then

$$\varepsilon^0 - \varepsilon_r = (-q_r \delta_r^*) \beta_0 + 2 \beta_0 \left(\sum_{s'}^{d'} p_{s'}^0 k_{s'}^0 - \sum_s^d p_{rs} k_{rs} \right) \quad (4')$$

For the special case where $\delta_r^* = 0$ and $k_{rs} = 1$ it can be written thus

$$(e^0 = \varepsilon_r)/(2\beta_0) = \sum_{s'}^{d'} p_s^0 - \sum_s^d p_{rs} \quad (5)$$

If we now define the free valence index as

$$F_r = \frac{\varepsilon^0 - \varepsilon_r}{2\beta_0}$$

then

$$F_r = \sum_{s'}^{d'} p_s^0 - \sum_s^d p_{rs} \quad (6')$$

Comparing Eq. (6') with Eq. (1) we can identify

$$N_{\max} = \sum_{s'}^{d'} p_s^0 \quad (7)$$

Taking into account that (6) was obtained from (4') for a special case (that is $\delta_r^* = 0$ and $k_{rs} = 1$), then the classical free valence as given by Eq. (1) is the limiting case of a more general definition, which is that given by (6). From (4') and (6), the »free valence« index will be given as

$$F_r = N_{\max} - \frac{1}{2} q_r \delta_r^* - \sum_r^d k_{rs} p_{rs} \quad (8)$$

The problem to be considered is the value of δ_r^* and k_{rs} .

»FREE VALENCE« AND THE OMEGA METHOD

In order to calculate F_r as given by Eq. (8) we need to get a value for δ_r^* . Employing the ω -method^{2,11} this quantity is given by

$$\delta_r = (1 - q_r) \omega \quad (9)$$

For alternant hydrocarbons $q_r = 1$ and then F_r is given by Eq. (1). For non-alternant hydrocarbons and heteromolecules, where q_r is not necessarily 1, and calling $F_r(\omega)$ the »extended« free valence

$$F_r(\omega) = N_{\max} - q_r(1 - q_r)\omega/2 - \sum_s^d p_{rs} \quad (8')$$

where $k_{rs} = 1$. Without loss of generality we can put $N_{\max} = \sqrt{2}$.

FREE VALENCE AND THE ω - β -TECHNIQUE

From Eq. (8) we can derive an expression for calculating the free valence if we assume that β_{rs} is given by (12)

$$k_{rs} = \frac{\beta_{rs}}{\beta_0} = \exp. (0.55 p_{rs} - 0.3666) \quad (10)$$

Both ω and β variable techniques can be used together; then, by replacing Eq. (9) and Eq. (10) in Eq. (8) we can write

$$F_r(\omega, \beta) = N_{\max} - \frac{1}{2} q_r(1 - q_r)\omega - \sum_s^d p_{rs} \exp(0.55 p_{rs} - 0.3666) \quad (8'')$$

The values for the classical F_r can be calculated using the HMO-method, the ω -technique or the combined ω - β -method, and then we will get F_{rH} , $F_{r\omega}$ or $F_{r\omega\beta}$ respectively. As usual, for that calculation we need the corresponding bond orders. An analysis of Eq. (9) shows that the values of the extended free valence can be higher or lower than the classical F_r ; it will depend on the charge excess $(1 - q_r)$; e. g. if $q_r < 1$ then $F_r(\omega) > F_{r\omega}$. In this case we might expect an ES reaction. Otherwise, if $q_r > 1$ then $F_r(\omega) < F_{r\omega}$ and the r -th position could undergo a NS reaction.

From the exposed behaviour for $F_r(\omega)$, we should expect the highest values of this index to give the most probable position for an ES reaction and, reversely, the lowest values will correspond to the most probable position for an NS reaction.

APPLICATIONS

1. Non-benzenoid Hydrocarbons

By employing Eq. (8') and the data reported in the literature² we obtain the results shown in Table I for some non-benzoid molecules. The theoretical results can be compared with the available experimental data. As we can see, for azulene and fluoranthene the highest and the lowest values of $F_r(\omega)$ are directly connected with the most probable position for ES and NS reactions, in agreement with the known experimental results. This behaviour is not shared by the classical index.

TABLE I

A. Classical and Extended Free Valence Index in Azulene			B. Classical and Extended Free Valence Index in Fluoranthene		
position	$F_{r\omega}^a$	$F_r(\omega)^b$	position	$F_{r\omega}^a$	$F_r(\omega)^b$
1	0.3469	0.2546	1	0.09315	0.1142
2	0.1726	0.1374	2	0.07642	0.0792
4	0.0458	0.1060	3	0.12074	0.1365
5	0.0771	0.0939	7	0.10840	0.1202
6	0.0284	0.0824	8	0.09955	0.0953

experimental: ES: 1 \gg other positions
NS⁽¹³⁾: 6 $>$ 4

experimental: ES: 3 $>$ 8 $>$ 7 $>$ 1 $>$ 2

C. Classical and Extended Free Valence Index in Cyclohept-[f,g]-acenaphthylene			D. Classical and Extended Free Valence Index in Cyclohept-[d,e]-naphthylene		
position	$F_{r\omega}$	$F_r(\omega)$	position	$F_{r\omega}$	$F_r(\omega)$
1	0.1276	0.1038	1	0.1208	0.1074
2	0.1888	0.1629	2	0.1875	0.1705
3	0.1436	0.1604	3	0.1751	0.2012
4	0.1401	0.1236	4	0.0749	0.0774
5	0.1628	0.2043	5	0.1808	0.2028

^a Values taken from A. Streitwieser: *Molecular Orbital Theory for Organic Chemists*, p. 347, J. Wiley, New York, (1963) and A. Streitwieser et al., *Tetrahedron* **19** Supplement 2, (1963) 379.

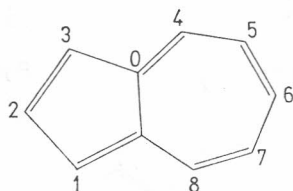
^b Calculated using Eq. (8) with $\omega = 1.4$.

Cyclohep-[f,g]-acenaphtylene and cyclohep-[c,d]-naphtylene were not so well experimentally studied as the other non-benzenoid molecules mentioned previously. The $F_r(\omega)$ predicts that the 5-th position is the most reactive for ES reactions, in agreement with other results reported in the literature.^{2,13,14} However, we have to bear in mind that these results don't take into account other factors which can affect the kinetics of ES and NS reactions.

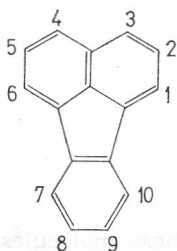
When $F_r(\omega)$ is compared with other old reactivity criteria, a close correlation with the localization energy can be found.

2. Molecules Containing Nitrogen

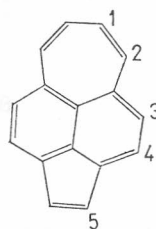
In order to analyze the predictive capability of $F_r(\omega)$ and $F_r(\omega, \beta)$ we studied some N-heterocyclic compounds where the classical F_r fails in predicting their chemical reactivity. The studied molecules are shown in Figure 2 and several obtained results with the ω - and ω - β -techniques are given in



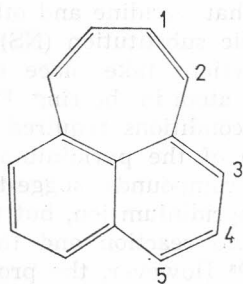
Azulene



Fluoranthene

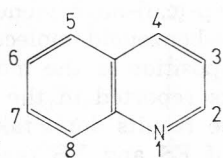


Ciclohept [f,g]-Acenaphtylene

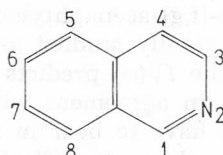


Cyclohept [d,e]-Naphthylene

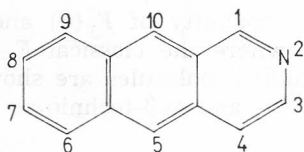
Figure 1.



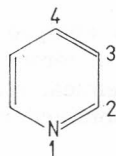
Quinoline



Isoquinoline



Benzo [g]-isoquinoline



Pyridine

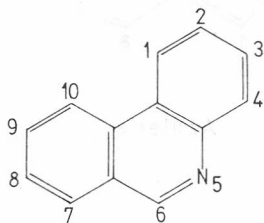
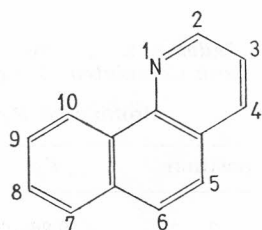
Benzo [c]-isoquinoline
(fenantridine)

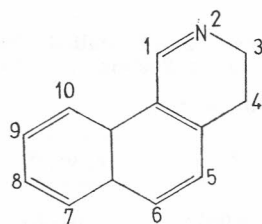
Figure 2a.

Tables II and III. The most important features of these molecules in electrophilic and nucleophilic substitution reactions are summarized in the literature (see *e. g.* ref. 15a).

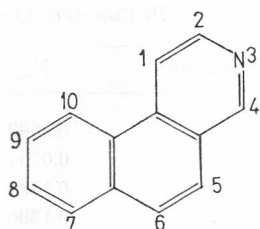
Pyridine: it is well known that pyridine and other π -defective molecules here studied undergo nucleophilic substitution (NS) rather than electrophilic reactions (ES).¹⁵ The latter reactions take place in very strong conditions because of the presence of the *N* atom in the ring. For nitration, sulphonation, halogenation, the experimental conditions required are (very high acid concentration) favour the existence of the pyridinium cation. The kinetic data for the nitration of pyridine compounds suggest that the reaction goes through direct nitration of the pyridinium ion, but the nitration of the cation is not necessarily the most rapid reaction and the direct nitration of the free base can not be excluded.^{15a} However, the process is not so simple and the direct nitration of the cation must involve two charged species. Some evidence of the complexity of these processes is known from the halogenation of pyridine. The results obtained from the application of the ω - and



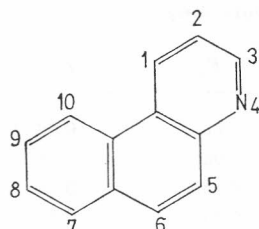
Benzo[h]-quinoline



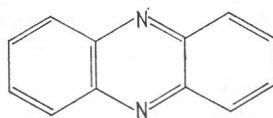
Benzo[h]-isoquinoline



Benzo[f]-isoquinoline



Benzo[f]-quinoline



Fenacine

Figure 2b.

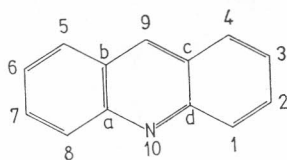


Figure 2c.

the ω - β -techniques can not be related in a direct way to the real processes which occur in the reaction, but these techniques and other more sophisticated ones can give some evidence about the electronic factors that control the reaction.

When we compare the result obtained in the free base we can see that the »extended« free valence index $F_r(\omega, \beta)$ predicts, for example, that the reactivity order is $3 > 4 > 2$, while the classical index predicts the following

TABLE II

Classical ω - and ω - β -Extended Free Valence Indexes in Several π -Defective N-Heteroatomic Systems (All the Results were Calculated Using $\omega = 1$)

Pyridine			Protonated Pyridine		
position	$F_{r\omega,\beta}$	$F_r(\omega, \beta)$	position	$F_{r\omega,\beta}$	$F_r(\omega, \beta)$
2	0.0852	0.0665	2	0.2650	0.1006
3	0.0803	0.0757	3	0.07196	0.0541
4	0.0830	0.0699	4	0.1143	0.0737

Quinoline			Protonated Quinoline		
position	$F_{r\omega}$	$F_r(\omega)$	position	$F_{r\omega}$	$F_r(\omega)$
2	0.0870	0.0659	2	0.1599	0.0829
3	0.0857	0.0825	3	0.0757	0.0633
4	0.1367	0.1108	4	0.1597	0.1029
5	0.1352	0.1325	5	0.1390	0.1283
6	0.0864	0.0849	6	0.0850	0.0797
7	0.0871	0.0831	7	0.1032	0.0790
8	0.1340	0.1348	8	0.1215	0.1236

Isoquinoline			Protonated Isoquinoline		
position	$F_{r\omega}$	$F_r(\omega)$	position	$F_{r\omega}$	$F_r(\omega)$
1	0.1139	0.0883	1	0.2027	0.0453
3	0.0768	0.0674	3	0.1477	0.1014
4	0.1314	0.1283	4	0.1273	0.1162
5	0.1330	0.1320	5	0.1925	0.1270
6	0.0830	0.0780	6	0.0934	0.0764
7	0.0844	0.0823	7	0.0868	0.0787
8	0.1315	0.1273	8	0.1429	0.1277

Fenancine				
position	$F_{r\omega}$	$F_r(\omega)$	$F_{r\omega,\beta}$	$F_r(\omega, \beta)$
1	0.1409	0.1389	0.1300	0.1278
2	0.0924	0.0903	0.0950	0.0882

TABLE II to be continued

order $2 > 4 > 3$. When we correlate the obtained results with the experimental facts, it is easy to see that the highest value for $F_r(\omega, \beta)$ corresponds to the most probable position for the ES reaction and the lowest value to the most probable position for the NS reaction. This correlation between the extreme values for $F_r(\omega)$ and $F_r(\omega, \beta)$ with ES and NS reaction was found in most cases, as shown for azulene for example, and it will be repeated later.

TABLE II continued

Benzo-[f]-quinoline

position	$F_{r\omega}$	$F_r(\omega)$	$F_{r\omega\beta}$	$F_r(\omega, \beta)$
1	0.1244	0.1095	0.1145	0.1063
2	0.0890	0.0863	0.0913	0.0878
3	0.0897	0.0633	0.0937	0.0699
5	0.1327	0.1336	0.1381	0.1384
6	0.1342	0.1289	0.1398	0.1383
7	0.1324	0.1311	0.1184	0.1232
8	0.0847	0.0839	0.0890	0.0863
9	0.0900	0.0888	0.0928	0.0913
10	0.1227	0.1219	0.1124	0.1174

experimental: ES: 7 > 10, NS: 3

Benzo-[h]-quinoline

position	$F_{r\omega}$	$F_r(\omega)$	$F_{r\omega\beta}$	$F_r(\omega, \beta)$
2	0.0948	0.0720	0.0972	0.0750
3	0.0839	0.0807	0.0878	0.0825
4	0.1339	0.1192	0.1203	0.1129
5	0.1337	0.1317	0.1394	0.1181
6	0.1335	0.1319	0.1392	0.1173
7	0.1323	0.1313	0.1183	0.1231
8	0.0848	0.0819	0.0893	0.0858
9	0.0901	0.0894	0.0926	0.0913
10	0.1230	0.1210	0.1128	0.1160

experimental: ES: 7, NS: 2

Benzo-[f]-isoquinoline

position	$F_{r\omega}$	$F_r(\omega)$	$F_{r\omega\beta}$	$F_r(\omega, \beta)$
1	0.1191	0.1192	0.1119	0.1132
2	0.7886	0.0629	0.0966	0.0821
4	0.1135	0.0900	0.1226	0.1064
5	0.1322	0.1303	0.1397	0.1177
6	0.1317	0.1297	0.1392	0.1165
7	0.1314	0.1308	0.1182	0.1230
8	0.0832	0.0816	0.0893	0.0857
9	0.0890	0.0883	0.0926	0.0912
10	0.1213	0.1196	0.1127	0.1161

Benzo-[g]-isoquinoline

position	$F_{r\omega}$	$F_r(\omega)$	$F_{r\omega\beta}$	$F_r(\omega, \beta)$
1	0.1460	0.1189	0.1160	0.0999
3	0.0952	0.0828	0.0931	0.0770
4	0.1409	0.1381	0.1178	0.1200
5	0.2018	0.2006	0.1387	0.1176
6	0.1414	0.1404	0.1398	0.1150
7	0.0911	0.0895	0.1184	0.1232
8	0.0919	0.0910	0.0891	0.0861
9	0.1416	0.1404	0.0927	0.0912
10	0.2027	0.1969	0.1123	0.1166

Benzo-[h]-isoquinoline

Nitration of benzo-[f]-quinoline gives the 7-nitro-compound. Other benzoquinolines give by nitration a mixture of isomers^{15a} although in several cases the most important is the 7-nitro derivative.

Some NS give the 2-substituted derivative (e.g. amination benzo-[h]-quinoline).¹⁷

TABLE III

*Classical and ω - β - Extended Free Valence Indexes in π -Defective Molecules
(All the Results were Calculated Using $\omega = 1$)*

Fenantridine

position	F_{rH}	$F_{r\omega\beta}$	$F_r(\omega, \beta)$
1	0.1229	0.1125	0.1165
2	0.0894	0.0926	0.0911
3	0.0852	0.0894	0.0857
4	0.1303	0.1178	0.1235
6	0.1484	0.1429	0.0943
7	0.1336	0.1194	0.1208
8	0.0846	0.0891	0.0850
9	0.0909	0.0935	0.0884
10	0.1224	0.1123	0.1188

Acridine

position	$q_r(\omega)$	$F_{r\omega}$	$F_r(\omega)$
1	1.0096	0.4396	0.4444
2	0.9555	0.4198	0.3986
3	0.9921	0.4045	0.4006
4	0.9682	0.4650	0.4497
9	0.8265	0.5392	0.4682

experimental reactivity order for ES (*e. g.* nitration, see Ref. 15)

$$3 \gg 1 > 4 > 2 \gg 9$$

Quinoline: As for pyridine an ES is harder than an NS. Many ES take place more probably in the benzene ring but there are reactions where the pyridine ring is involved. In many ES reactions the positions 5 and 8 are involved while NS reactions take place in position 2 and very rarely in position 4.

$F_r(\omega)$ was calculated for the free base and the quinolinium ion and the values are given in Table II. Our results predict that the quinolinium ion could be the species involved in the ES^{15e,16} but, like pyridine, there is no experimental evidence that this ion is more readily substituted (*e. g.* nitrated) than the free base.^{15a}

We can now compare the charge densities obtained within the ω -technique framework in both species (only relative trends are reported):

$$\text{free base} \quad (1 - q_r): 4 \approx 2 > 3 \approx 5 > 8$$

$$\text{cation} \quad (1 - q_r): 2 > 4 > 3 \approx 5 > 8$$

The charge and the $F_r(\omega)$ predict a relative order which is in good agreement with the experimental facts. Again the lowest value of the extended free valence index corresponds to the most probable position in the free base for a NS and the highest value is related to the most probable position for ES reactions.

Isoquinoline: In this molecule the ES takes place in a similar way as with quinoline. The nitration gives 5 and 8 nitroderivatives but in the ratio of 9 : 1. There is no evidence of 1, 3, 6 or 7-nitroderivatives. Other aspects of the ES reaction can be obtained from Refs. 15a and 15e. The NS reaction takes place in position 1 rather than in position 3.

By inspection of Table II it may be seen that the predicted reactivity order in our paper is better than those obtained from the classical free valence index. We should bear in mind that the method can not explain all the experimental facts, but it is able to show the most probable tendency for the reacting molecule.

Although the experimental conditions for ES reactions allow the existence of the free base, we have performed the same calculations in the protonated isoquinoline. As we can see from Table II the extended free valence method, in both cases, gives a reactivity order which is again in agreement with the experimental facts.

As it was previously done with quinoline we can compare $F_r(\omega)$ with charge density relative values. The obtained results employing $\omega = 1$ show the following tendency

$$\text{free base} \quad (1 - q_r): 1 \gg 3 > 6 > 8 > 4 > 7 > 5$$

$$\text{cation} \quad (1 - q_r): 1 \gg 3 \gg 6 \approx 8 > 4 > 7 > 5$$

Although the highest and the lowest values for $F_r(\omega)$ and $q_r(\omega)$ are in agreement, it is the latter that is in better accordance with experimental evidence.

Benzoquinolines and Benzoisoquinolines: The results reported in Table II are once again well correlated with the known experimental facts for these compounds¹⁵, the highest value of $F_r(\omega)$ predicts the most probable behaviour of the molecule in ES reactions while the lowest value corresponds to the most probable position for NS reaction. Some experimental evidence is indicated in Table II.

The charge densities which are not reported in this paper are almost independent of the employed method: for benzo-[h]-quinoline $q_2 < q_4$; for benzo-[f]-quinoline, the lowest charge densities are $q_3 < q_1$, and finally for the benzo-[f]-isoquinoline $q_4 < q_2$. Otherwise, the results on charge densities are very similar with those reported in Refs. 17 and 18.

Phenazine: The results obtained for phenazine are shown in Table II and are in agreement with other reactivity indices calculated within the framework of the HMO-method. The charge density trends predict position 1 as the most favourable for ES reaction.

Phenantridine and Acridine: For phenantridine (see Table III) the theoretical results are not so well related with the experimental facts as it was found for the benzo- and benzoisoquinolines^{15d}, that is

$$F_{rH} \quad 6 > 7 > 4 > 1 \approx 10 > 9 > 2 > 3 \approx 8$$

$$F_r(\omega, \beta) \quad 4 > 7 > 10 \approx 1 > 6 > 2 > 9 > 3 \approx 8$$

$$(1 - q_r(\omega, \beta)) \quad 6 \gg 9 \approx 7 \approx 8 \approx 3 \approx 10 \approx 1 \approx 2 \approx 4$$

However, if we take into account that for some nucleophilic substitution the reactivity order is $6 \gg 7$, we can conclude that the extended free valence index correlates this fact better than the Hückel's classical one. In some ES reactions the most reactive positions are on C_1 , C_8 and C_{10} , but this behaviour is not correlated with $F_r(\omega, \beta)$. This failure could be explained as it is done in Ref. 15d, that is the protonation of the N leads to an electrostatic repulsion for the cations which are approaching C.

Acridine is a very interesting system. The most striking result is that the different indices predict different behaviour.

The simple Hückel's calculation, like the ones performed by Zahradnik¹⁸, shows that all reactivity indices are not in any way correlated with each other. Moreover, Fukui's frontier electron density formalism¹⁹ fails in predicting the relative order of reactivity for ES.

Such miscorrelation can be found, for example, among the indices $F_r(\omega)$ and $q_r(\omega)$, as shown in Table III.

However, if we perform a CNDO/2 calculation on this system²⁰ we can see:

- a) — The acridine molecule is not strictly a planar system in agreement with X-ray diffraction studies.²¹
- b) — If we calculate the free valence employing the CNDO/2 MO-coefficients for the planar system we obtain the same behaviour as Hückel's F_r .

These failures can be possibly explained because acridine shows self-association in solution and the calculated indices are only valid for an isolated molecule.

CONCLUSIONS

In this paper we have introduced a reactivity index which resembles the classical free valence index; moreover, the classical F_r is a particular case of this new one.

Many years ago the concept of atomic stabilization energy was established as a reactivity criterion but when applied to reacting molecules it was necessary to consider some corrections so as to take into account ES and NS by introducing the well known idea of frontier electron density.²² In a similar way, the free valence index failed in predicting chemical reactivity and it was necessary to consider ionic free valence indices account for the experimental evidence. All these facts introduce as many reactivity indices as substitution reactions known, that is F_r^+ , F_r , F_r^- , ϵ_r^+ , ϵ_r , ϵ_r^- , etc.

In the literature, as far as we know, no direct definition has been reported yet of the free valence which would involve both indices as it is done here in Eq. (6). This connection enables us to extend the notion of free valence and to introduce, in an explicit way, the charge densities of the r -th atom where substitution is considered. This definition tends to unify the different indices and to introduce a more general criterion for predicting chemical reactivity which can be extended to more sophisticated methods.

This »extended free valence index« is able to predict the most probable positions for ES and NS by direct inspection of the reactivity order. The highest and lowest values for $F_r(\delta_r, k)$ can be related to the most probable

values for ES and NS because there is an explicit dependence of F_r and the charge density on the r -th atom. The electronic factors that affect the real process do not only depend on the charge density on the atom involved in the process but there must be a very important contribution of the charge between the neighbours in the early stage of the reaction. This contribution is partially contained in the bond order between atoms. Both factors are involved in only one expression in a rather simple way. This dependence of $F_r(\delta_r, k)$ on the charge density allows us to extend this index to other systems, such as heteroatomic molecular systems. When $\delta_r^* = 0$ and $k_{rs} = 1$ for every atom and pair of atoms involved in the molecule within the HMO approximation, the »extended index« is coincident with the classical one.

The behaviour shown by $F_r(\delta, k)$ prevents us from defining other indices, such as F_r^+ or F_r^- . Moreover, it must taken into consideration that such a reduction in the number of indices to be calculated should happen when a generalization of the reactivity theory can be carried out.

Although the results do not fit all the experimental facts, as one should expect, the introduced index improves the classical one as it is shown through all the examples reported in this paper. This fact can be understood if we take into account that the reactivity behaviour is not always controlled mainly by electronic factors.

The application of this index to other kinds of molecules, such as heteroatomic compounds and substituted hydrocarbons, will be reported in the near future.

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SAŽETAK

Indeks »proširene« slobodne valencije i njegove primjene

H. Villar, A. L. Capparelli i A. Spina

Prikazan je indeks »proširene« slobodne valencije. On služi za izravno predviđanje najvjerojatnijih mjesta na molekuli za ulazak elektrofilnog ili nukleofilnog supstituenta. Taj je indeks primijenjen na molekule (ne-benzenoidni ugljikovodici i heterociklički sustavi) u kojih indeks »klasične« slobodne valencije nije uspio predvidjeti najreaktivnija mjesta.