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ON TOPOLOGICAL CHARGE STABILIZATION IN HETEROCYCLIC COMPOUNDS*

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According to Gimarc's principle of topological charge stabilization, heteroatomic molecules are topologically stabilized when more electronegative atoms are placed in those positions where atom–atom connectivity and the electron-filling level provide the highest electron charge in the reference hydrocarbon frame. Recently, we showed that the relative atomic moments of energy (the frequencies of atomic self-returning walks) in such uniform molecular skeletons are equal to the respective squared principal eigenvector coefficients. We show here that for conjugated heterocyclic molecules these partial atomic charges follow closely the patterns mirrored by topological charge stabilization and, by producing a nonuniform charge distribution in alternant molecules, enable the broader application of this principle to such molecules.

INTRODUCTION

The last 25 years have witnessed the fast development of a new branch of theoretical chemistry called mathematical chemistry [1-8]. It includes applications of topology, graph theory, algebra and other nontraditional methods [9-15], as well as their computer-assisted applications to the solving of various structural problems in chemistry [16-19], coding and classification of chemical compounds [20-25], enumeration of isomers [26], classification and enumeration of chemical reactions [27-32], syntheses planning and elucidation of the logical structure of chemistry [33-49].

Much attention was attracted by the possibilities for topological control of molecular structure via the moments of energy method which relates molecular graphs to quantum mechanics [50-57]. The method makes use of important graph-invariants: the count of atomic and molecular self-returning walks, SRW_i^k and SRW^k, respectively. The SRW_i^k are walks of length k that start from, and end at, the same atom i without any restrictions as to how many times a certain bond or atom could be traversed. The molecular self-returning walk count is the sum of all atomic ones. Some well-known topological indices like the Wiener number [58-60] and the Zagreb group index [60, 61] were shown to be related to SRWs and via the method of moments their quantum chemical background was elucidated [62, 63].

Recently, we have found empirically [64] and then proved [65] that the limiting distribution set f_1 of the relative atomic SRWs (with the exception of the odd SRWs in bipartite graphs which are zeros) is equal to the set of squared principal eigenvector coefficients c_{1i}^2:

$$f_i = \lim_{k=\infty} (SRW_i^k / SRW^k) = c_{1i}^2 \tag{1}$$

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[*] Dedicated to N. S. Zefirov for his important contributions to mathematical chemistry, as well as for his friendly help to those who need it.

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Since SRW_i^k and SRW^k are related to the atomic and molecular moments μ_i^k and μ^k, via resonance integral β:

$$\mu_i^k = SRW_i^k \beta^k; \ \mu^k = SRW^k \beta^k \tag{2}$$

then, within the tight-binding approximation, the atomic SRW frequencies f_i are also *relative atomic moments of energy* (RAMs):

$$f_i = \lim_{k=\infty} \mu_i^k / \mu^k = c1_i^2$$

These results were used to explain some patterns in chemical architecture (molecular branching) [63] and in chemical reactivity [66, 67].

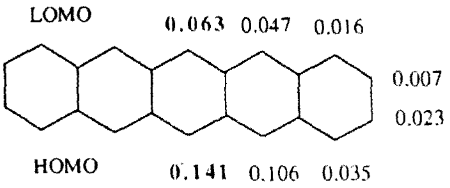
Starting in 1983, Gimarc developed in a series of papers [68-71] an earlier idea of Longuet–Higgins, Rector, and Platt [72] that atoms of greater electronegativity confer higher stability when placed in those positions where molecular topology tends to accumulate electronic charge. This important electron density trend, which stabilizes the heteroatomic molecules, is called the *principle of topological charge stabilization*. Topology plays a dominant role in this principle because uniform reference molecular frames are used in which the only factor discriminating atomic electron densities is the atom–atom connectedness. Carbon frames are thus used for organic compounds, however, in general the frames could be of any other chemical elements. The topological charge stabilization of principle has found application as a guide to synthetic efforts and as a fast method for assessing the relative stabilities of positional isomers. The pattern of charge densities makes possible the prediction of the stabilizing or destabilizing effect of various substitutions. This approach is limited to systems with nonuniform charge distribution (nonalternant systems as well as alternant systems whose number of electrons is not equal to the number of atomic orbitals), whereas for planar conjugated alternant hydrocarbons having uniform π-electron densities no predictions concerning heterocyclic substitutions can be made.

In continuing our efforts to show the potential of the relative atomic SRWs as indices of chemical reactivity [66, 67] in this paper we examine the extent to which these quantities can be used instead of the total π-electronic charge to predict topological charge stabilization. If successful, such an approach would have the advantage of no limitations in dealing with alternant systems.

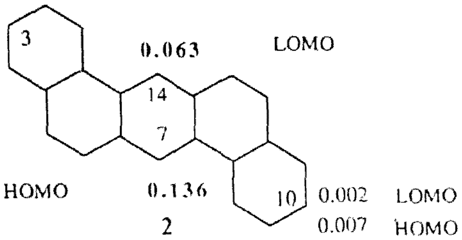
WHY RELATIVE ATOMIC SRWS?

Albeit we have shown that relative atomic SRWs (or relative atomic, moments RAMs) are one-electron charge distributions, the idea of using these quantities as chemical reactivity indices still needs some justification. This is due to the fact that for conjugated molecules these fractional charges correspond to the charges derived from the Hückel lowest occupied molecular orbital (LOMO) and LOMO electrons are generally regarded as chemically inert. Frontier orbital charges, such as those in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LOMO), are those which generally match the trends in atomic reactivity. However, for uniform (carbon) frames it is molecular topology that determines the atomic charges on all orbitals, and this impact of topology is best expressed in the lowest-energy MO. Hence, one may expect that LOMO controls in some way the other orbitals or, at least, that certain correspondence might exist between LOMO and frontier orbitals. While not transparent, this anticipated relationship may be illustrated by the comparison of the one-electron LOMO and HOMO charges of structures **1** and **2** below.

In the case of pentacene **1**, both types of charges obey the same atomic ordering (the maximum values are given in boldface). For dibenz[*a*, h]anthracene **2**, positions 3, 10 of the minimum LOMO and HOMO charges, and positions 7, 14 of the maximum charges coincide but the intermediate atom orderings differ. It should also be mentioned that generally such comparisons are instructive when made for atoms corresponding to molecular graph vertices of the same degree (in **1** and **2** only vertices of degree 2 are compared). This agrees with the common chemical sense that atoms with a lower connectivity are more reactive.



1



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The above mentioned correspondence between the extreme values of LOMO and HOMO charges of some cyclic molecules does not necessarily exist as a general trend. However, additional arguments can be offered in favor of the use of the SRWs as criteria for the topological charge stabilization. Applying SRWs (but not their limit distribution) to chemical reactivity, Jiang and Zhang [73] introduced the so-called "site energies" and advocated the idea that in alternant π-electronic compounds electrons in sites with the same total charge would be more reactive if they had more energy.

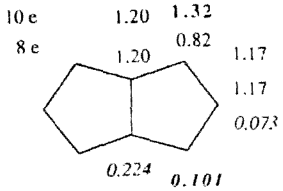
On the other hand, being an important feature of molecular topology, self-returning walks find quantum mechanical interpretations beyond molecular orbital theory; SRWs can be explained in terms of valence bond theory as well. Moreover, a reasonable interpretation of Eq. (1) is that each self-returning walk SRW_i^k in molecular graph is associated with an electron motion near the nucleus i and the relative SRWs are in fact the relative frequences of these electron motions. Thus, each SRW are in a molecular graph appears as a representation of a Feynman electron trajectory [74], a conclusion that we drew after comparing the explicit formulas for SRWs with those for Feynman's electron path counts reported recently for some simple molecules [75].

Summarizing the discussion, another useful interpretation may be introduced. Owing to the fact that the accumulation of electronic charge on different sites in the molecule is entirely topologically determined, the f_is may be regarded as *topological electronegativities*, i.e., as electronegativity that results from atom–atom connectedness but not from the different nature of atoms. Thus, the topological charge stabilization principle may be reinterpreted in a natural way by stating that more electronegative atoms are preferentially placed in sites with the highest topological electronegativity.

EXAMPLES. NONALTERNANT SYSTEMS

Proceeding from the above-mentioned ideas we re-examined most of the cases given in the basic paper of Gimarc [68] and added some more examples of alternant systems which cannot be directly treated by his approach. As advocated above, we classified separately the atoms corresponding to graph vertices of degree 2 and 3 in molecular graphs devoid of hydrogens.

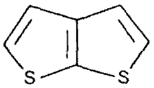
The pentalene frame **3** is a parent structure for various heterosubstituted compounds. Its total atomic charges corresponding to a radical (8-electron system) and dianion (10-electron system) are shown below along with our topological electronegativities f_i which here and thereafter are given in italics.



3

As seen, the highest f_i for a divalent atom coincides with the maximum atomic charge in the 10-electron frame. Therefore, this is in agreement with the relative stabilities of the four isomeric and isoelectronic thienothiophenes **4-7** which is evaluated, for example, by the calculated resonance energies RE in β units [76]:

$$RE(4) = RE(5) = 0{,}031 > RE(6) = 0{,}026 > RE(7) = 0{,}004$$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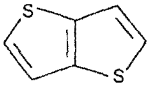
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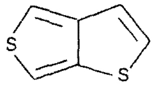
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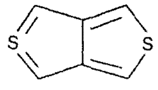
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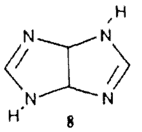
Other pentalenic heterocyclic compounds (**8-9**) that obey the topological stabilizing effect upon substitution of electronegative atoms in position 1 rather than in position 2 have been synthesized [77-79].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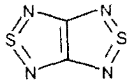
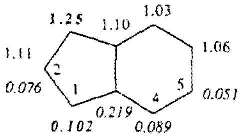
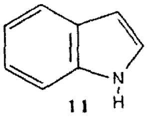

9

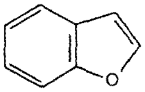
Another basic nonalternant cyclic frame, analyzed by Gimarc [68], is that of the indenyl anion **10** with nine MOs and 10 π-electrons.



10

Our f_i-indices predict correctly position 1 of the five-membered ring as a preferred position for substituting by an electronegative atom. This is illustrated by the pairs of isomers indole–isoindole (**11**, **12**), benzofuran–isobenzofuran (**13**, **14**), and benzo[b]thiophene–benzo[c]thiophene (**15**, **16**). As seen from the data for resonance energies in β units (the first row of data are taken from [80, 81], whereas the second row data are those from [75]), the substitution in position 2 is less favorable which explains (along with the *ortho*-quinonoid character) the high reactivity of these three isomers and their rather late synthesis.


11
indole
0.047
0.038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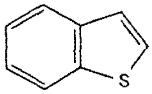
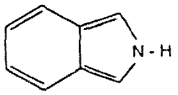
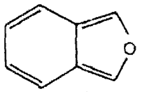
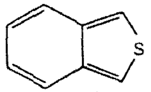
benzofuran
0.036
0.027

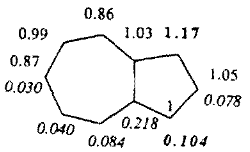

15
benzo[*b*]thiophene
0.044
0.035


12
isoindole
0.029
0.032

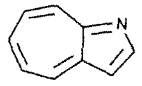

14
isobenzofuran
0.002
0.011


16
benzo[c]thiophene
0.025
0.029

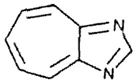
Azulene **17** is a well-known stable aromatic compound. Again, both the total π-electronic charge used by Gimarc, and our f_i-electronegativities predict correctly position 1 in the five-membered ring as the best position for topological stabilization upon the substitution of atoms more electronegative than carbon. As is well known, both 1-azaazulene **18** and 1,3-diazzaazulene **19** have been synthesized.



17

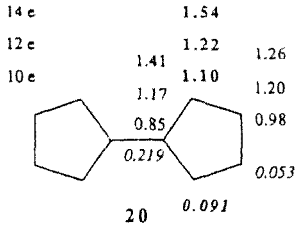


18



19

Position 1 in the five-membered ring was again shown by Gimarc [68] to be the one with the highest π-electronic charge for 10-, 12-, and 14-electron fulvalene systems **20**. We found the same position to have the highest relative atomic moment f_i. Thus, both approaches agree with the existing compounds having sulfur **21** or selenium **22** in this position.



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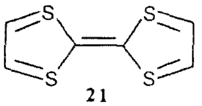

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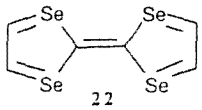
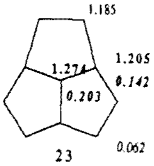
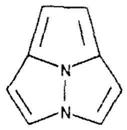


22

A similar agreement was found between our approach and that of Gimarc [68] for the reference system **23** with three *peri*-fused five-membered rings and 12 electrons. Both trivalent sites were found to have the highest charge densities, which explains the known compound **24** with two nitrogens.

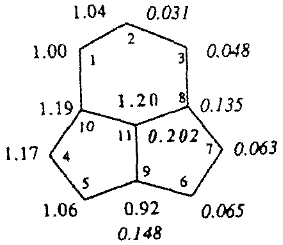


23



24

When one six-membered ring is *peri*-fused to two five-membered rings (reference structure **25**, taken by Gimarc [68] as dianion) both approaches specify the central position 11 as the most favorable and, indeed, the cyclo[3.2.2]azine **26** is known.



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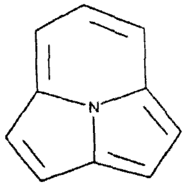
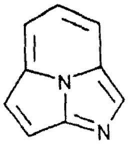


26

Both versions of the topological charge stabilization principle then specify positions 8 and 10 as the next favorable for nitrogen substitution. However, this does not happen because the nitrogen in this case would contribute two π-electrons instead of one. The next favorable positions for nitrogen substitution were found by our f_i-indices to be either 5, 6 or 4, 7 (Δf_i = 0.002). This correlates well with the existence of both **27** and **28** where the substitution takes place in 5 or 6 and in 4 or 7, respectively. The total π-electronic charge used by Gimarc favors significantly positions 4 and 7 but not 5 and 6 (q_4 = 1.17, q_5 = 1.06).



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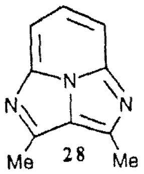
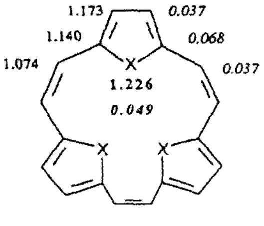


28

The macrocycles **29** and **30** contain either furan or thiophene rings linked together by ethylene bridges. Their reference frame charges were calculated by Gimarc for 24 and 32 electron systems, respectively. Both approaches predict oxygen or sulfur substitution to occur at the inner five-membered ring position (X = O or S) which has the highest charge among the divalent sites.



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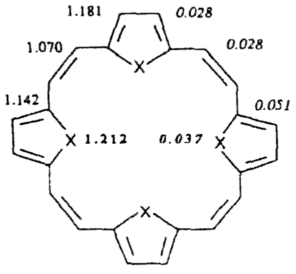
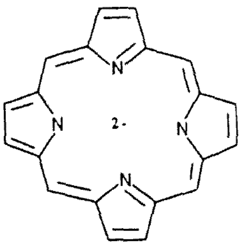


30

The porphin dianion **31** is described by the reference frame **32** with **26** electrons. The four nitrogens are located again at the inner positions of the five-membered rings, as predicted by the highest electron density in this position (q_i = 1.22) in 1950 by Longuet–Higgins, Rector, and Platt [72]. The f_i-indices reproduced this result, however, the highest value of 0.040 is degenerate, and it is also ascribed to the bridging position between the parts of rings.



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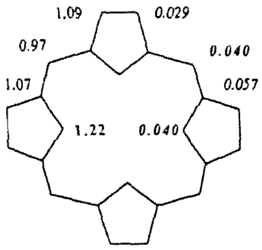
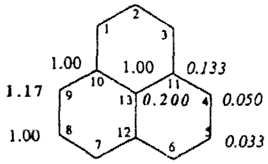


32

EXAMPLES. ALTERNANT SYSTEMS

Some of the systems analyzed by Gimarc [68] are examined first. To avoid the limitations of the uniform electron density distribution Gimarc used reference frames with number of electrons exceeding the number of orbitals. Our one-electron approach is free of these limitations.

The phenalenide anion **33** offers a variety of substitution sites. The total π-electron density predicts nitrogen substitution at the equivalent 1, 3, 4, 6, 7, and 9 positions. Topological electronegativity ranks the central position 13 first. As is well known [82] this is the position occupied not only in the monosubstituted cyclo[3.3.3]azine **34** but also in the polysubstituted compounds **35-37** having 2 to 7 nitrogens, respectively. In turn, our f_i-indices cannot correctly predict the positions of these additional nitrogens and rank second the three trivalent sites 10-12. We presume that this failure of predicting the second, third, etc. substitution position simply means that it is the electron density of the monosubstituted compound (but not that of the uniform frame) that determines the position of the second substitution, then it is the electron density of the disubstituted compound which controls the third substitution, etc. Supposedly, it is for the same reason that the topological stabilization principle cannot predict the stabilization in borazole molecule when proceeding from the uniform benzene reference frame. Work is in progress to verify these ideas by different means, including a more general treatment of the self-returning walks in molecules [83].



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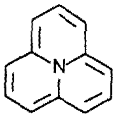

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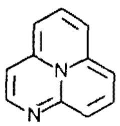

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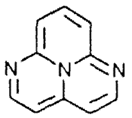

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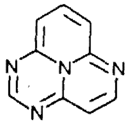

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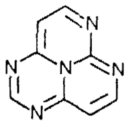

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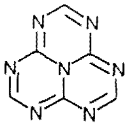
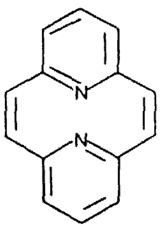


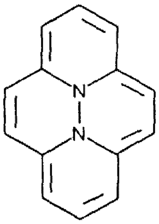
39

The present formulation of the topological charge stabilization principle faces difficulties in explaining the substitution of two nitrogens at the central positions of the valence isomers **40** and **41**. The corresponding reference frames **42** and **43** have 16 and 18 π-electrons. The uniform electron densities in **42** make impossible any prediction of the substitution positions whereas in **43** the highest charges are at external locations. The highest topological electronegativity in **38** is at the two central positions and in **42** these positions are with the highest f_is among the divalent sites.

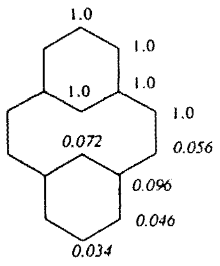
The triangulene molecule **44** with 22 electrons, if it existed, would be a highly unstable diradical. Gimarc [68] used



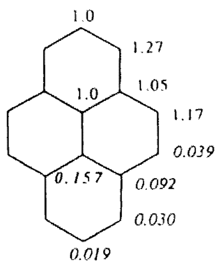
40



41

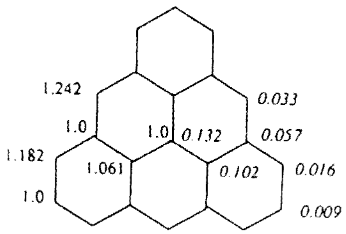


42

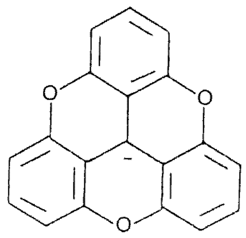


43

the triangulene dianion with 24 electrons as a reference frame and predicted correctly the oxygen substitution in the known heteroatomic anion **45**. The same positions are those with the highest topological electronegativities among the divalent sites.



44



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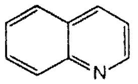
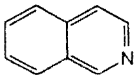
Some new examples of conjugated alternant cyclic compounds follow. Only the topological electronegativity values are given because the total π-electronic charge is evenly distributed on the atoms.

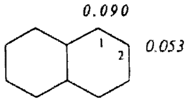
Quinoline **46** with nitrogen substitution in position 1 is known to be more stable than isoquinoline **47** in which the nitrogen is placed at position 2. This is in agreement with the resonance energy estimates of Hess and Shaad [81] (0.052 vs. 0.051) and those of Gutman et al. [76] (0.036 vs. 0.031) given in β-units. Indeed, the more central position 1 is topologically preferred among the two divalent sites by our f_1-charges as shown in the naphthalene reference frame **48**.



46

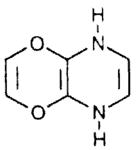


47

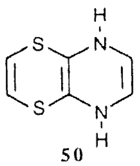


48

All four central divalent sites in **48** are also easily occupied, compounds **49** and **50** being a convenient illustration [82].

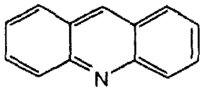


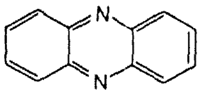
49

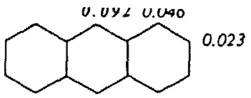


50

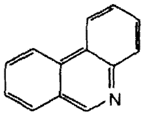
Similarly, acridine **51** and phenazine **52** with nitrogen substitution at the topologically preferred central divalent sites derived from anthracene **53** are the most stable among the monosubstituted and disubstituted anthracenes. The same arguments explain the preferential formation of phenanthridine **54** with a mononitrogen substitution at positions **5** or **6** in the reference phenanthrene frame **55**.

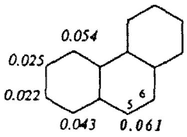

51


52



53


54



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CONCLUDING REMARKS

This work shows the potential of topological electronegativities (relative atomic moments of energy or relative atomic self-returning walks) as a criterion for the topological charge stabilization principle of Gimarc [68]. The initial results are encouraging and, after some additional studies, it would be possible to recommend the usage of this criterion in parallel with the total π-electronic energy for more reliable predictions. Our approach promises to extend the area of applicability of the topological charge stabilization to alternant systems with uniform charge densities. On the other hand, our analysis casts some doubt whether the principle in its present formulation can correctly predict the preferential orientation of more than one heteroatom, due to the neglected influence of the first substituent's electron density. These and other problems, related to the more general formulation of our approach, are to be discussed in a future publication [83].

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