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ON THE DEPENDENCE OF π-ELECTRON CHARGE DISTRIBUTION ON MOLECULAR TOPOLOGY. II

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The effect of cycles in the molecular graph on π-electron charge distribution is analysed for a number of polycyclic non-alternant conjugated systems (7 neutral hydrocarbons, 3 dications and 2 dianions). The fraction of the total π-electron charge arising from the effect of single cycles only (i.e. with the collective effects of cycles being neglected) is found to be in a rather good linear correlation with the total charge.

In the first part of this paper[1] a method has been developed for the analysis of the effect of cycles on π-electron charge distribution in conjugated hydrocarbons. This approach has been later generalized[2] to enable the study of the dependence of any π-electron property of conjugated molecules (as calculated within the framework of the Hückel molecular orbital model) on cyclic conjugation. According to refs 1 and 2, the π-electron charge q_r of the atom r can be presented as a sum of certain topological increments, viz.,

$$q_r = \sum_{a} T(a) + \sum_{a<b} T(a,b) + \sum_{a<b<c} T(a,b,c,) + \ldots, \tag{1}$$

with $T(a)$ being the effect of the cycle C_a, $T(a,b)$ being the effect of the pair of cycles C_a, C_b, $T(a,b,c)$ being the collective effect of three cycles C_a, C_b and C_c, etc. These increments are further decomposed into first order, second order etc. contributions.

The summations in eq. (1) go over all cycles, all pairs of cycles etc., contained in the molecular graph. In particular, if the molecular graph contains two cycles, say C_1 and C_2, then

$$q_r \text{ (bicyclic)} = T(1) + T(2) + T(1,2). \tag{2}$$

If the conjugated system under consideration is monocyclic, then

$$q_r \text{ (monocyclic)} = T(1). \tag{3}$$

In the following we shall use the same notation and terminology as in the first part[1] of this paper. Hence, the topological formula for $T(a)$ reads[2]

$$T(a) = 2i^{-|C_a|-1} \left\langle \frac{[G_r]\,[G-C_a]-[G]\,[G_r-C_a]}{[G]^2+4[G-C_a]^2} \right\rangle. \tag{4}$$

Note that if the size $|C_a|$ of the cycle C_a is even, then necessarily $T(a)=0$. Thus even-membered cycles (considered as being separated of all other structural details of the molecule) have no effect on the charge q_r.

The quantity $T(a)$, as given by the topological formula (4), is that fraction of the π-electron charge on the atom r, which has been induced by the cycle C_a. In the case of monocyclic molecules, eq. (4) reproduces the total π-electron charge. Therefore, in the following our consideration will be focused to polycyclic π-electron systems. In the present work we shall restrict our analysis to systems having neither empty bonding, nor occupied antibonding molecular orbital energy levels.

It can bee also shown that the first order effect of the pair of cycles C_a and C_b conforms to the relation

$$T_1(a,b) = -4i^{-|C_a|-|C_b|-1} \cdot \left\{ \left\langle \frac{[G_r][G-C_a-C_b]-[G][G_r-C_a-C_b]}{[G]^2} \right\rangle - \left\langle \frac{[G-C_a]}{[G]} \cdot \frac{[G_r][G-C_b]-[G][G_r-C_b]}{[G]^2} \right\rangle - \left\langle \frac{[G-C_b]}{[G]} \cdot \frac{[G_r][G-C_a]-[G][G_r-C_a]}{[G]^2} \right\rangle \right\} \cdot \tag{5}$$

(The above expression should bee identical with the term $T_3(a,b)$ of ref. 1. Howerer, in ref. 1 the formula given for $T_3(a,b)$ was not correct.)

From the mathematical analysis of the terms $T(a)$, $T(a,b)$ etc. a number of general topological rules about the dependence of q_r on cyclic conjugation could be deduced[1,2]. On the other hand, because of the rather complex nature of these topological formulas, a few important questions remain unsolved. The following two difficulties are especially worth mentioning.

Firstly, the central question in our considerations is whether cyclic conjugation increases or decreases the charge density on a given atom r. The answer depends, of course, on the sign and the magnitude of the increment $T(a)$. It is, however, not possible to predict the sign of $T(a)$ in the general case, using solely analytical arguments.

Secondly, by neglecting the collective effects of cycles we arrive to a simple and therefore rather attractive formula

$$q_r \approx q_r^{\star} = \sum_a T(a) \cdot \tag{6}$$

However, the legitimacy and accuracy of the approximation (6) was until now not clarified.

Another approximate topological formula for q_r would result by the inclusion of the first order collective effect of two cycles, viz.,

$$q_r \approx q_r^{\star\star} = \sum_a T(a) + \sum_{a<b} T_1(a,b) \cdot \tag{7}$$

In order to make a further step towards the understanding of the topological behavior of q_r, the quantities $T(a)$ and $T_1(a,b)$ have been computed for a series of non-alternant conjugated hydrocarbons, dications and dianions. The results obtained enable the formulation of some novel topological rules and, in particular, justify the use of the approximate formula (6). The apparently better approximation (7) is, on the other hand, shown to be less satisfactory.

RESULTS AND DISCUSSION

Calculations were performed on the conjugated systems presented in Chart 1.

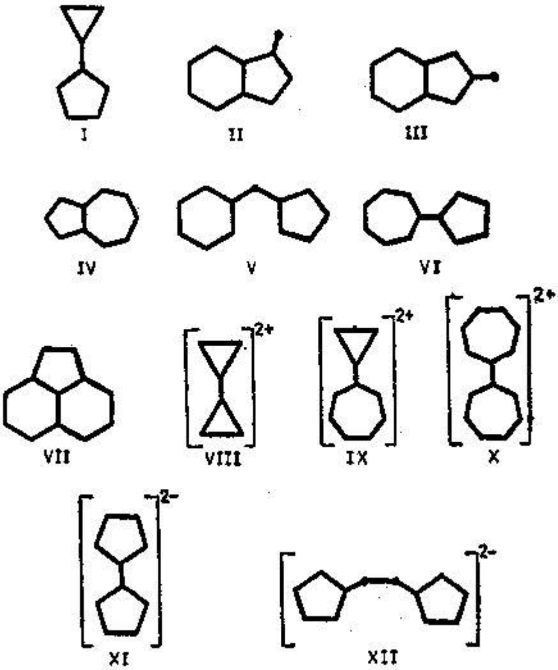
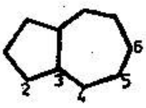


Chart 1

In Table I the computed $T(a)$, $T_1(a,b)$, q_r, $q_r{}^*$ and $q_r{}^{**}$ values for azulene are collected, whose atoms are labelled as follows.



The molecular graph of azulene possesses three cycles: a five-, a seven- and a ten-membered one. These are labelled by C_1, C_2 and C_3, respectively.

The same topological parameters have been determined for all conjugated systems given on Chart 1. A detailed tabulation is, however, omitted[9]. The case of azulene seems to reflect all the characteristic features of our analysis.

By inspection of the results given in Table I, it can be seen that the Hückel charges q_r correlate considerably better with the sum of the single ring effects, q^* (correlation coefficient $\rho=0.999$), than with the sum of the effects of single rings and pairs of rings, q^{**} ($\rho=0.928$). The same is true also for the compounds

TABLE I. The effect of cycles on the π-electron charge distribution in azulene (IV). Note that $|C_1|=5$, $|C_2|=7$, $|C_3|=10$. Since C_3 is an even-membered cycle, $T(3)=0$. Since both C_1 and C_2 are odd-membered cycles, $T_1(1,2)=0$.

r	T(1)	T(2)	$T_1(1,3)$	$T_1(2,3)$	q_r^{*}	q_r^{**}	q_r
1	−.0716	+.0186	+.0331	−.0171	−.0530	−.0369	−.0466
2	−.0927	−.1501	+.0488	+.1200	−.2428	−.0740	−.1729
3	−.0658	+.0344	+.0319	−.0197	−.0314	−.0193	−.0274
4	+.1513	+.0463	−.1432	−.0273	+.1976	+.0271	+.1451
5	−.0251	+.0375	+.0262	−.0207	+.0124	+.0180	+.0136
6	+.1362	+.0450	−.0805	−.0269	+.1812	+.0738	+.1300

II, III, V and VII. (For the other investigated systems $q^{\star}=q^{\star\star}$, because they possess no even-membered cycles and thus[1], $T_1(a,b)=0$ for all pairs of cycles C_a, C_b.) In particular, in the case of VII no correlation can be observed between $q_r^{\star\star}$ and q_r.

In the present moment we cannot offer a satisfactory explanation of this effect. It seems probable that this is a consequence of the fact that eq. (7) takes into account only the first order influence of pairs of rings. One should note that in the perturbation molecular orbital theory it occurs quite frequently that the first order approximation gives a much better description of the chemical behaviour of the molecules than higher order approximations[4].

The correlations between $q_r^{\star}$ and q_r are summarized in Table II. From the Table it can be concluded that an excellent correlation exists between the Hückel π-electron charges and the quantity $q_r^{\star}$, given by eq. (6). Moreover, q_r is found to be simply proportional to the sum of effects of single cycles. The proportionality constant (denoted by A in Table I) differs, however, from molecule to molecule. It is interesting to note that in the most examples, eq. (6) gives higher values than predicted by the HMO theory.

compound	A	B	ρ
I	0.618	$2\cdot10^{-4}$	1.000
II	0.624	$2\cdot10^{-4}$	0.995
III	0.912	$2\cdot10^{-3}$	0.998
IV	0.724	$2\cdot10^{-5}$	0.999
V	0.956	$4\cdot10^{-4}$	0.980
VI	0.620	$-1\cdot10^{-3}$	1.000
VII	0.503	$2\cdot10^{-5}$	0.991
VIII	0.560	$4\cdot10^{-5}$	1.000
IX	1.232	$1\cdot10^{-3}$	0.972
X	0.720	$-1\cdot10^{-3}$	1.000
XI	0.714	$6\cdot10^{-4}$	1.000
XII	0.857	$1\cdot10^{-3}$	1.000

TABLE II. The correlation $q_r=Aq_r^{\star}+B$ for the compounds from Chart 1. The parameters A and B are obtained by least squares fitting; the pertinent correlation coefficient is ρ. Note that in all cases studied, B is practically equal to zero

In the context of the topological theory it is of some interest to consider the effect of the size of the cycle C_a on the magnitude of $T(a)$. In Table III the ratios $T(a)/T(b)$ for several molecules are collected. Only the terms for atoms belonging to both C_a and C_b are considered.

TABLE III. Relative effects of rings of different size on the π-electron charge of an atom. Note that smaller rings have always larger effect.

compound	ring size ratio		
	five/seven	five/nine	five/eleven
II		2.62 2.20 2.36 2.22 2.31	
III		2.16 2.44 1.69	
IV	-1.91		
VII		3.23 3.33 3.14	-7.12 -7.36

The data given in Table III suggest that smaller rings have greater effects on the π-electron charge than larger rings. It is somewhat surprising that this relative effect diminishes quite slowly as the ring size increases. The data for the ratios $T(a)/T(b)$ for five- and nine-membered rings show that their value considerably depends upon the global structure of the molecule. Accordingly, there is no basis for *a priori* neglecting of the effect of large rings in the evaluation of the π-electron charge on a particular atom.

A detailed inspection of our results indicates that certain conclusions about the effect of the molecular structure on the charge on a particular atom can be drawn.

1) It is confirmed that $(4m+1)$-membered rings induce a higher electron density on the atoms which belong to these rings. The effect of $(4m-1)$-membered rings is opposite.

2) If a conjugated chain is attached to an odd-membered ring, then this ring induces charges which alternate in sign along this chain. The charge induced on the first neighbour of the ring is of opposite sign as that of the ring, the charge induced on the second neighbour is of the same sign as the charge of the ring, etc.

3) The magnitude of $T(a)$ depends on the ring size, being greater for smaller rings. Nevertheless, the $T(a)$ values of large rings are still of considerable magnitude and it is not legitimate to neglect them in eq. (6). Hence, in the analysis of the dependence of the π-electron charge distribution on molecular topology, one must consider the effect of all odd-membered rings irrespective of their size.

4) When the collective effects of cycles are taken into account (via the term $T_1(a,b)$), no improvement in the correlations could be observed. Accordingly, the use of the rather simple topological relation

$$q_r = A \sum_a T(a) \tag{8}$$

is sufficient for the prediction of charge densities, and very promising as a tool for the analysis of topological effects on the charge distribution.

ИЗВОД

О ЗАВИСНОСТИ РАСПОДЕЛЕ π-ЕЛЕКТРОНСКОГ НАБОЈА ОД МОЛЕКУЛСКЕ ТОПОЛОГИЈЕ. II

ИВАН ГУТМАН и ИВАН ЈУРАНИЋ

Природно-математички факултет у Крагујевцу и Природно-математички факултет у Београду

Анализиран је утицај прстенова у молекулском графу на расподелу π-електронског набоја за низ полицикличних неалтернантних конјугованих система (7 неутралних угљоводоника, 3 дикатјона и 2 дианјона). Нађено је да је део укупног π-електронског набоја, који настаје услед утицаја појединачних прстенова (тј. када се занемаре колективни ефекти више прстенова) у веома доброј линеарној корелацији са укупним набојем. Главни резултат рада јесте потврда ваљаности апроксимативне тополошке формуле (8).

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REFERENCES

1. I. Gutman, *Glasnik Hem. društva Beograd* **44,** 627 (1979)
2. I. Gutman, O. E. Polansky, *Theor. Chem. Acta* **60,** 203 (1981)
3. Computational details for the molecules given on Chart 1 can be obtained from the authors upon request.
4. M. J. S. Dewar, „*The Molecular Orbital Theory of Organic Chemistry*", McGraw-Hill, New York 1969, pp 191—192.