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AROMATIC STABILITY OF POLYCYCLIC COMPOUNDS

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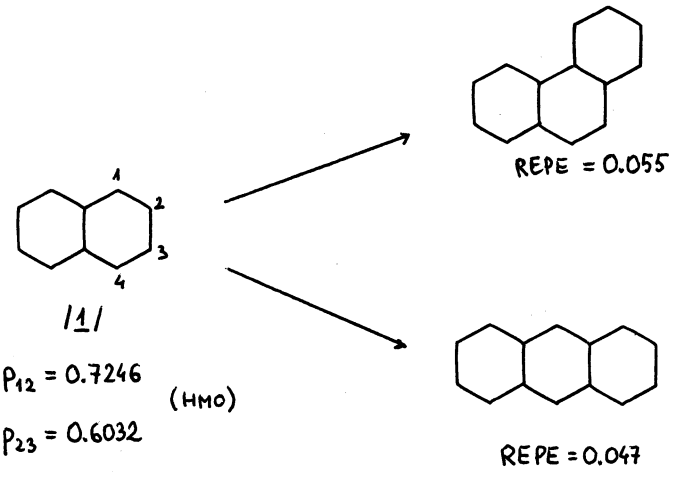
Abstract - An additional ring changes the stability of a cyclic compound. Aromatic system with condensed additional aromatic ring /e.g. benzologues/ is more stable /more aromatic/ if this ring is condensed to the bond with greater π-electron bond order, p_{rs}. If additional ring is antiaromatic the lower p_{rs} the higher stability is observed. This rule is confirmed by analysis of the REPE and HOMA indices and PPP calculations /β-Variable/. Also bond lengths in polycyclic compounds are discussed.

It is well known that the Hückel's rule works well for monocyclic systems only. Another well known rule, the Craig's one, works however only for molecular systems with some symmetrical properties, i.e. possessing C_2-axis passing across two carbon atoms of the system. Unfortunately the latter rule in some cases fails. Hence, for polycyclic systems there are known numerous attempts of estimation of the aromatic stability.

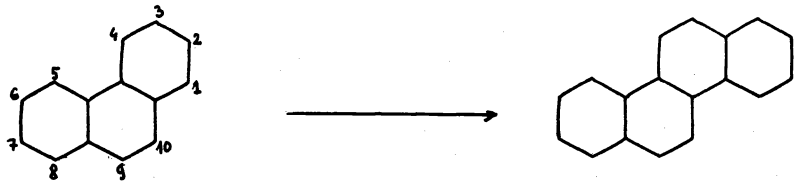
In front of good results obtained by use of the Hückel's rule for monocyclics one could be interested in the problem how the stability of the system is changed after addition of the next ring. Such introduction of an additional ring results e.g. in formation of benzologue and its stability depends upon the kind of bond to which the ring is attached. For benzologues it occurs that the greater π-electron bond order, p_{rs}, the higher stability. Let us consider as an example benzologues of naphthalene /1/ applying REPE /1/ as a stability index.



A similar relationships can be found for other benzologues of benzenoid hydrocarbons, e.g. for phenanthrene /Table 1/.

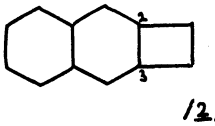
When the antiaromatic ring is attached to aromatic system, the situation observed is reverse. An addition of cyclobutadiene ring to aromatic systems results also in change of stability. The lower p_{rs} the higher stability is observed. Let us consider cyclobutanaphthalenes /2,3/ as an example.

Table 1.



REPE = REPE/chrysene/ - REPE/phenanthrene/.

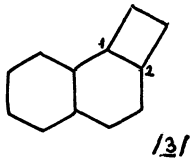
Bond order in phenanthrene /HMO/	Benzologue	
	REPE·10^3	Name
p_{12} = 0.7068	-2	Chrysene
p_{23} = 0.6228	-5	Benz/a/anthracene
p_{34} = 0.7016	-2	Tetrahelicene
$p_{9,10}$=0.7747	+1	Triphenylene



/2/

REPE = 0.007

p_{23} = 0.6032



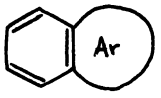
/3/

REPE = -0.012

p_{12} = 0.7246

/HMO bond orders in naphthalene/

The additional ring increases stability when added to 2-3 bond in comparison with the case when added to 1-2 bond. The additional ring influences also the mother π-electron system. If the ring is aromatic the the Kekulé's structure with the greatest contribution in the VB-method has a form as /4/ if it is antiaromatic, the structure is as /5/.



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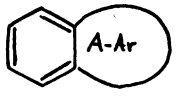
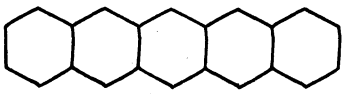
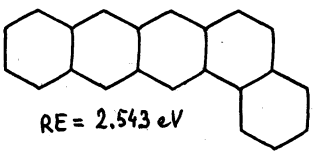


/5/

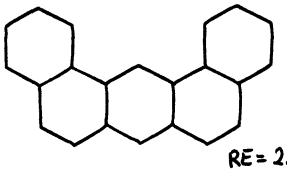
The following relationships hold for bond orders in aromatic systems: $p_{12} > p_{23}$ and $p_{34} > p_{23}$. Hence as a result the angular condensed benzenoid hydrocarbons are more stable than the linear ones. The 5-nuclear benzenoid hydrocarbons stand as good example for this rule.



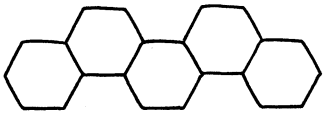
RE = 1.883 eV



RE = 2.543 eV



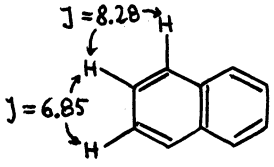
RE = 2.991 eV

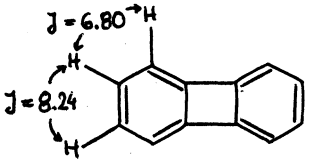


RE = 3.084 eV

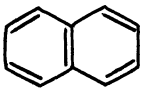
The RE are calculated here by applying Randić's conjugated circuits concept /2/.

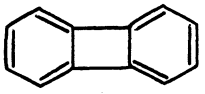
Due to the linear dependence of p_{rs} on NMR H-H coupling constants, the above mentioned conclusions can be confirmed experimentally /3/. According to Günther /3/ the ratio $Q = p_{12}/p_{23}$ can be applied as an aromaticity index, and it was shown for benzoannulenes.



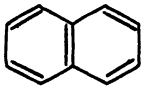


A confirmation of the above mentioned regularities is also Kekulé's index K/L/ /4/ which is a measure of the contribution of a given structure to the VB wave function. E.g. for naphthalene and biphenylene the structures with the highest contributions i.e. with the greatest values of K/L/, are as follows:

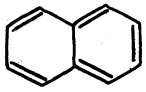




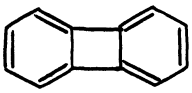
In a similar way the concept of conjugated circuits can be applied to estimate the individual contributions of the Kekulé's structures to the wave function with the same results as K/L/.



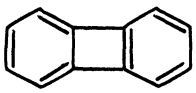
$2R_1$
1.738 eV



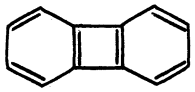
R_1+R_2
1.115 eV



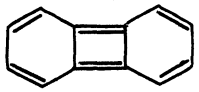
$2R_1+Q_3$
1.588 eV



$2R_1+Q_2$
1.288 eV



$2R_1+Q_1$
0.138 eV



Q_1+2Q_2
−2.500 eV

From the Kekulé's structures with the highest contributions to VB wave functions one can estimate bond lengths in real molecules. As a rule in aromatic compounds the bond lengths are averaged. Hence as an aromaticity index the quantity depending on the degree of averaging the bond lengths in the molecular systems was introduced /5,6/. For hydrocarbons one

has got /6/:

$$HOMA_d = 1 - \frac{98.89}{n} \sum_{/rs/} /1.397 - d_{rs}/^2$$

whereas for heterocompounds the formula is as below.

$$HOMA_d = 1 - \frac{98.89}{n} \left(\sum_{/rs/}^{n_{CC}} /1.397 - d_{rs}/^2 + \sum_{/rs/}^{n_{CN}} /1.338 - d_{rs}/^2 \right)$$

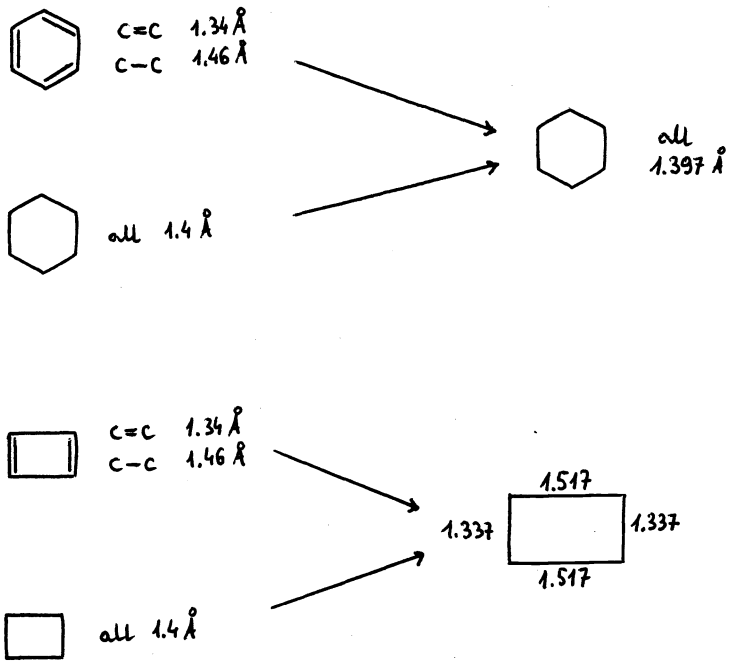
$$n = n_{CC} + n_{CN}$$

In the standard SCF PPP method the interatomic distances are taken arbitrarily and fixed. That is the reason why this method is not too convenient to study variation of bond lengths in molecules. On the other hand the application of methods AVE /e.g. CNDO/ with optimization of geometry is too time-consuming. In regard of this the version of SCF PPP mostly exploited by Nakajima /7/ with variable geometry was used in this paper. The variation of geometry after each iteration is ruled by linear relationships:

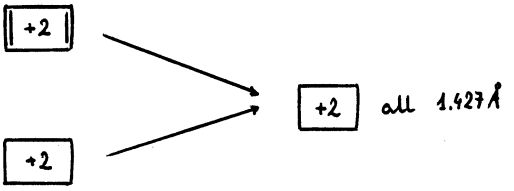
$$d_{rs} = A - B \cdot p_{rs}$$

for CC-bonds /8/: A = 1.517 Å, B = 0.180
for CN-bonds /9/: A = 1.443 Å, B = 0.167

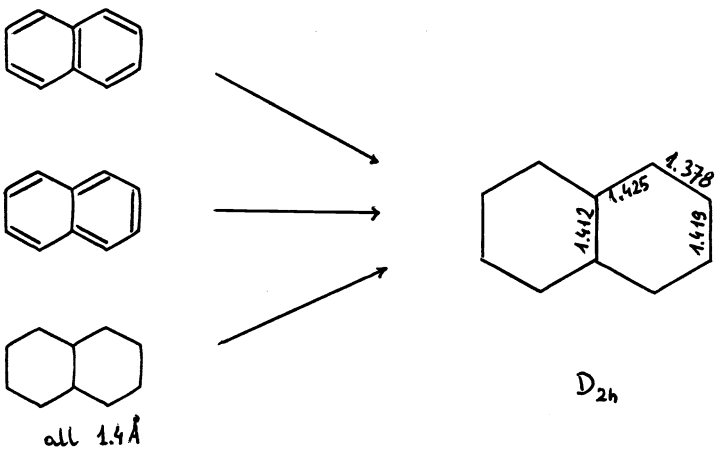
In favour of this method stand the results for benzene and cyclobutadiene. Independently of the initial geometry the final results are identical.



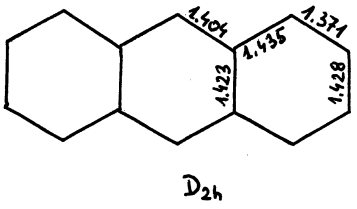
For a cyclobutadiene dication in contrast to the mother hydrocarbon the CC-bond lengths are completely equalized - but distinctly longer than in typical aromatic compound i.e. benzene.

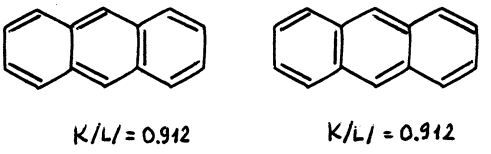


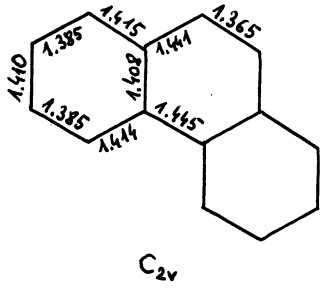
When the calculations for naphthalene are carried out starting from various geometries /the Kekulé-type ones and aromatic with CC-bond lengths 1.40 Å/ the final result is always the same.

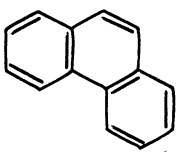


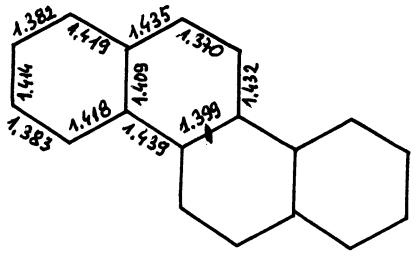
Moreover the geometry is close to that of VB-structure with the highest contribution to the wave function. The same is also observed for anthracene, phenanthrene and chrysene.



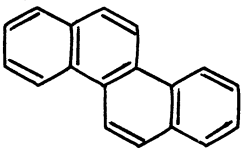




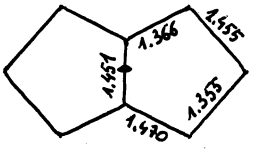




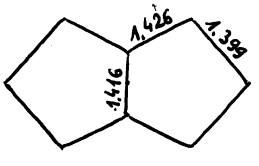
C_{2h}



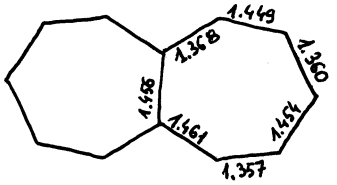
For most of the considered molecules in the final result of calculations the geometry is independent from the initial geometry except from a few cases as e.g. pentalene, heptalene and partly azulene.



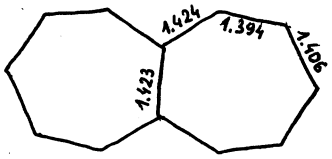
C_{2h}



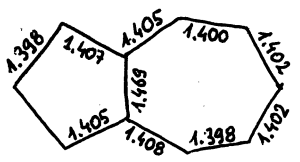
D_{2h}

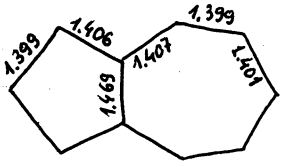


C_{2h}

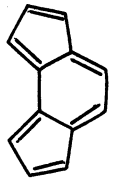


D_{2h}





A very interesting finding is for as-indacene. According to conjugated circuits concept both unexcited VB structures are equivalent. From the values of bond lengths one could conclude that structure /6/ should contribute more to the VB wave function. It seems to be possible that there works a rule that for aromatic systems /e.g. phenanthrene/ the central ring in the Kekulé's structure with the highest contribution has form as /8/ whereas for antiaromatic systems as /9/.



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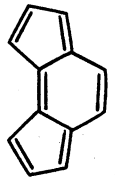

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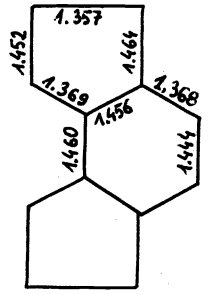

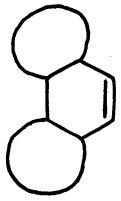

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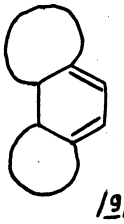
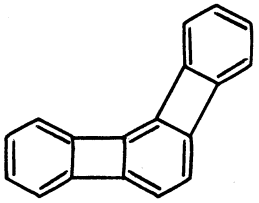
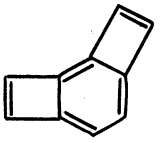


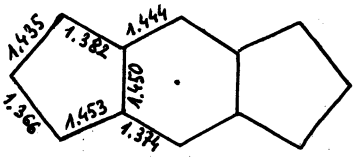
/9/

Good examples for the latter case are the following derivatives of cyclobutadiene.

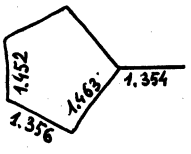


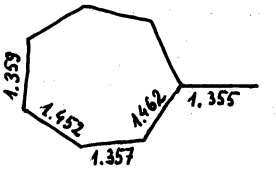


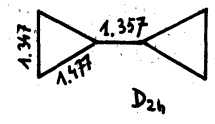
It is worth mentioning that antiaromaticity of sym-indacene is reflected in its C_{2h}-symmetry.

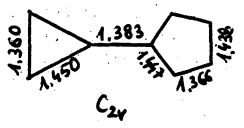


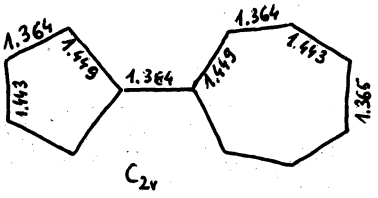
Molecules of fulvene- and fulvalene-type have got only one Kekulé's structure and their bond lengths are in good agreement with predictions, i.e. their values are close to those in polyenes. For conjugated compounds containing simultaneously rings of /4k+1/- and /4k-1/-type the bond lengths are more equalized /10/.

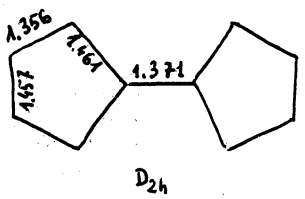


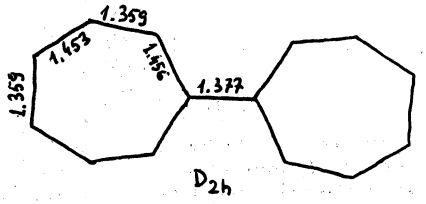




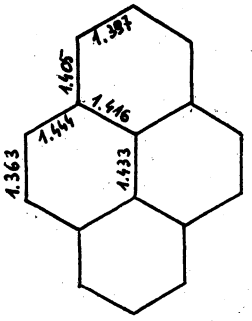


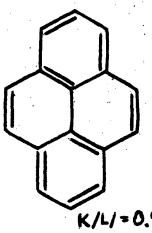




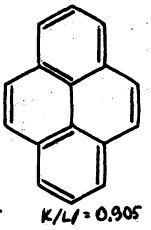


Numerous peri-condensed hydrocarbons are exemplified by considering pyrene, perylene, acenaphthylene and pleiadene.

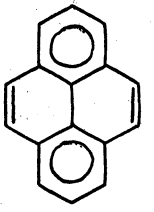


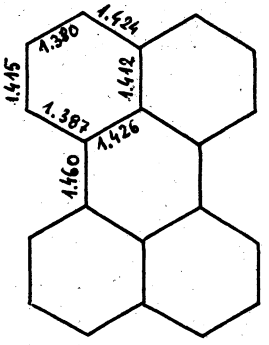


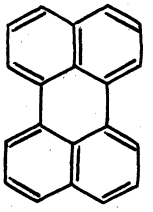
K/L/ = 0.905



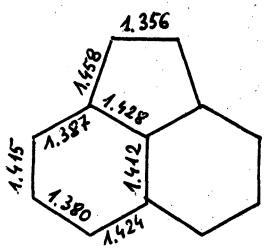
K/L/ = 0.905

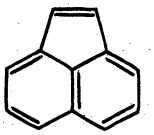


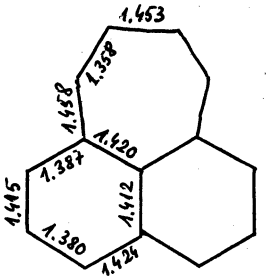


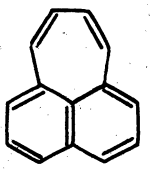


Pyrene can be considered as biphenyl with two ethylene linkages whereas perylene as two naphthalenes joined by rather long bonds. Similarly acenaphthylene can be treated as naphthalene with ethylene linkage whereas pleiadene as naphthalene with butadiene fragment. The Kekulé's structures with the greatest value of K/L/ index confirmed fully these conclusions.

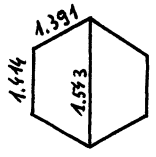




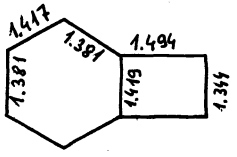


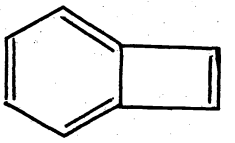


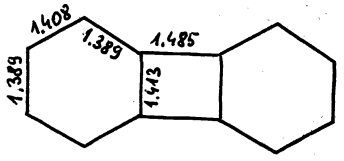
Interesting π-electron compounds are those containing 4-membered ring. For butalene /p-benzyne/ the central CC-bond is very long /the p_{rs} is negative!/. The bond lengths for molecule of this compound is given below.

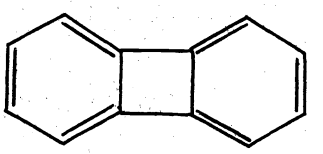


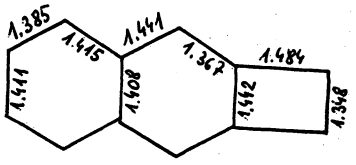
Benzocyclobutadiene, biphenylene and naphtho/b/cyclobutadiene have the bond lengths as predicted by structure with the greatest K/L/ value.

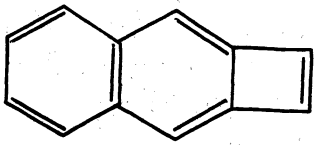




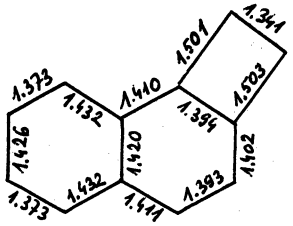


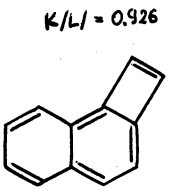


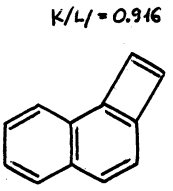




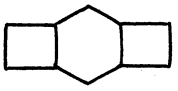
A slighty different situation is for naphtho/a/cyclobutadiene, molecular structure of which is between these predicted by two Kekulé's structures.



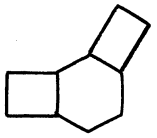




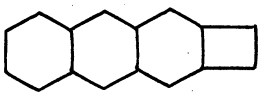
In contrast to benzenoid hydrocarbons, compounds containing cyclobutadiene ring /i.e. antiaromatic/ are more stable when they are condensed linearly. A few examples are given below. The RE-values were calculated by use of conjugated circuits concept.



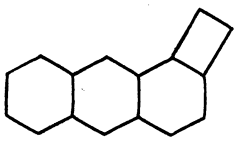
RE = -0.105 eV



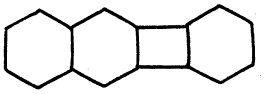
RE = -0.348 eV



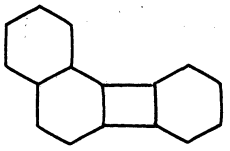
RE = 0.380 eV



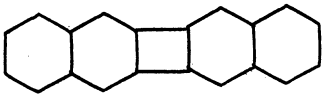
RE = -0.049 eV



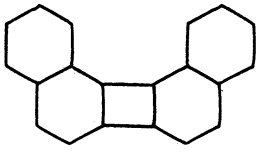
RE = 1.08 eV



RE = 0.69 eV

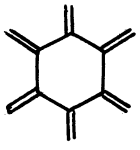


RE = 1.794 eV

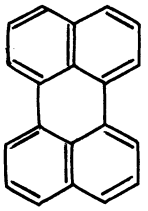
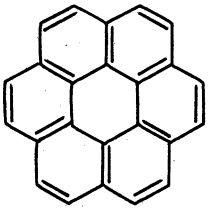
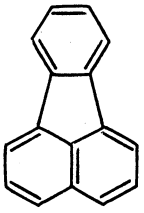
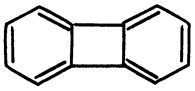
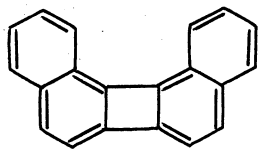


RE = 1.500 eV

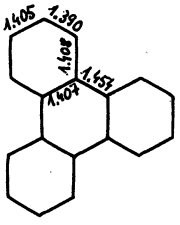
There are also known so called "empty" rings, whose presence in the molecule does not influence stability of compound. In such rings are present very long CC-bonds. Similarly long bonds are met in rings of radialenes, e.g. in radialene-/6/, where they achieve 1.466 - 1.470 Å.

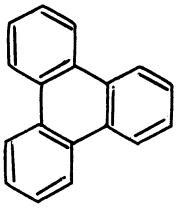


Among the structures with the greatest K/L/ values one can easily find the radialene-type fragments arround the "empty" rings.

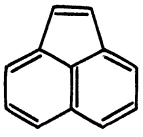
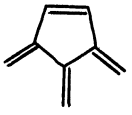
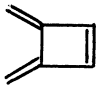






An exception to this observation is triphenylene, the bond lengths of which are in agreement with prediction for aromatic compounds and are given below.





In a similar way "partially empty" rings may be concerned as for example in acenaphthylene. The 5-membered ring looks like an ethylene linkage together with radialene fragment /10/, i.e. part of the ring is "empty". In a similar way 4-membered rings /in spite of their highly destabilizing influences/ /11/ as well as olephinic linkages in compounds /12,13,14/ can be treated.



/10/

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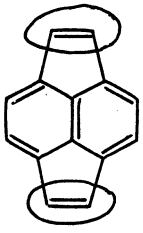
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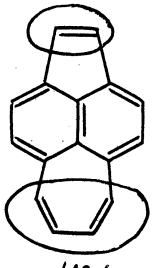
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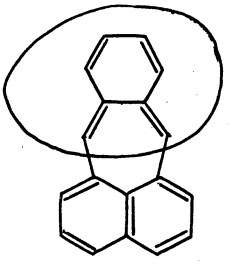
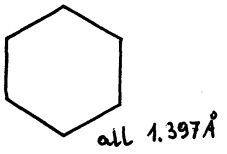
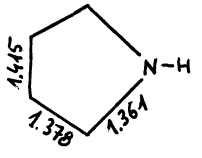
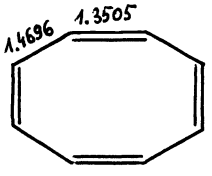

/14/

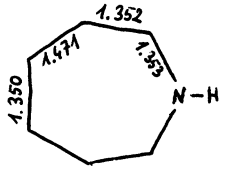
Thus one can define an olephinic fragment of polycyclic molecule which in all Kekulé's structures has got the same arrangement of single and double bonds.

Let us consider now replacing C=C bond in molecule of conjugated hydrocarbon by iso-π-electron heteroatom, say :NH /pyrrole type nitrogen/. It results in decreasing of the number of Kekulé's structure, except of the case when double bond is in the olephinic linkage, it destabilizes the molecule. As an illustration let us consider two pairs: benzene - pyrrole and cyclooctatetraene - azepine.

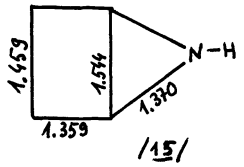




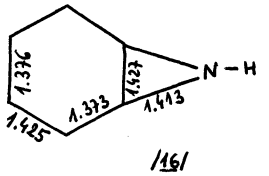




The heterocyclic analogue of butalene is cyclobutaziridine /15/. As it is clearly shown from the figures the bond lengths of both compounds are similar. The bond lengths of 6-membered ring of benzaziridine show antiaromatic property of aziridine ring /16/.

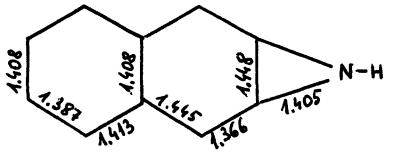


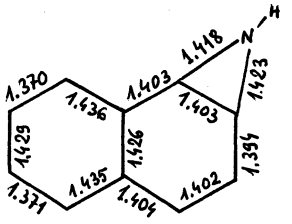
/15/



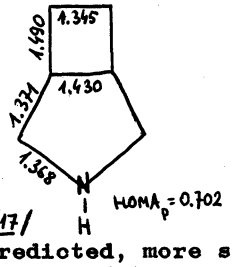
/16/

Accordingly the naphthalene condensed to aziridine recall cyclobutanaphthalenes.

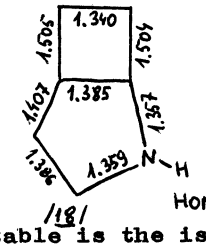




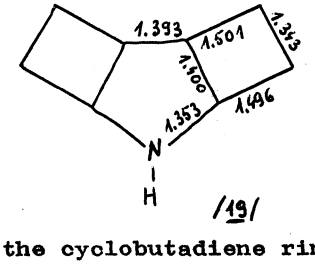
The similar regularities can be also illustrated by cyclobutapyrroles /17,18/ and cyclobutabenzene.



/17/



/18/ HOMA$_p$ = 0.659

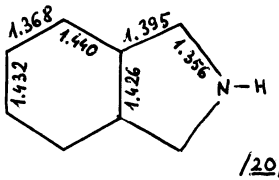


/19/

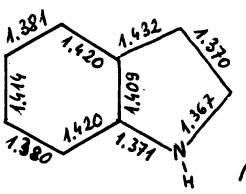
As predicted, more stable is the isomer in which the cyclobutadiene ring is condensed to more single CC-bond.

Dicyclobutapyrrole /19/ exhibit very strong equalization of bond lengths in heterocyclic ring. The HOMA-index for this ring is equal 0.9899. The 4-membered rings cause the increase of π-electron bond orders, which are in molecule of pyrrole rather single.

The bond lengths of benzopyrroles - indole and isoindole are in good agreement with prediction of VB-method.

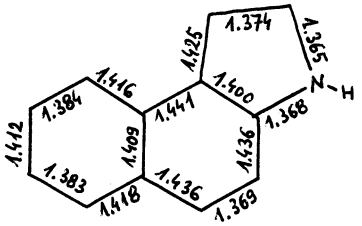


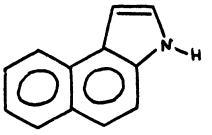
/20/

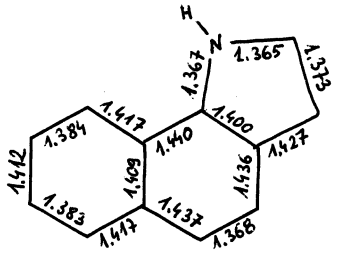


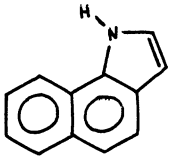
/21/

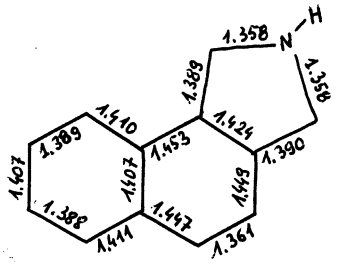
Isoindole /20/ is rather more olephinic in character whereas indole /21/ seems to be slighty aromatic. A good agreement with predictions of bond lengths is met for molecules of naphthopyrroles and carbazole /22/.

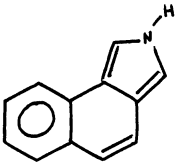


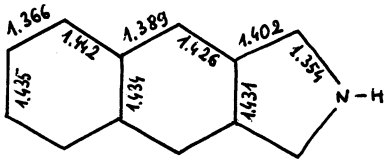


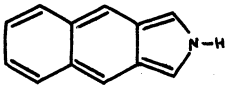


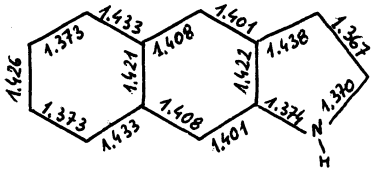


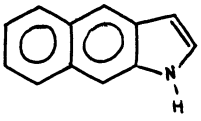


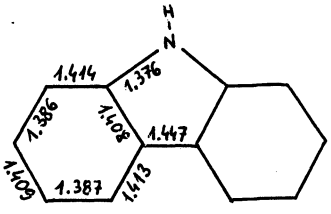


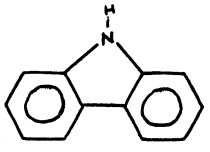




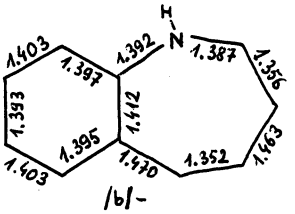




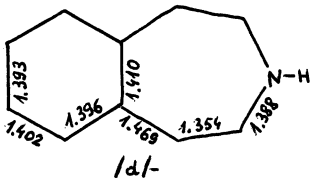




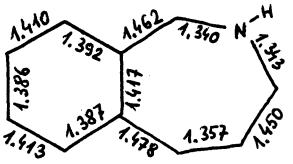
The azepine is iso-π-electronic with cyclooctatetraene. Similarly as for benzopyrroles more stable are benzologues condensed to double bond /two Kekulé's structures/ in comparison to those, with condensation to the single bond /one Kekulé's structure/. The differences between bond lengths in benzene ring for /b/- and /d/-derivatives are about 0.01 Å, whereas for /c/-isomer it is 0.025 Å.



/b/-

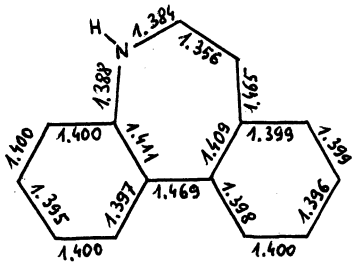


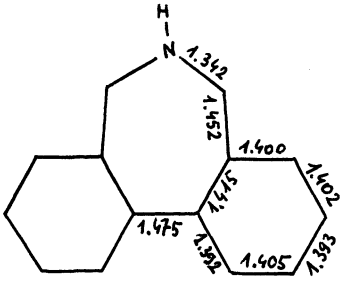
/d/-

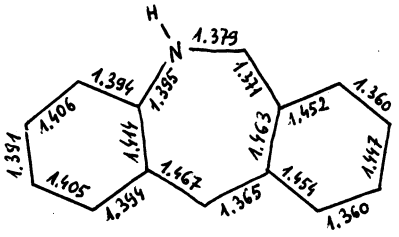


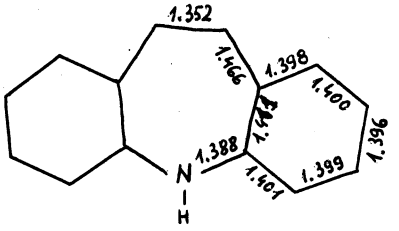
/c/-

Similar conclusions can be also drawn for dibenzazepines.

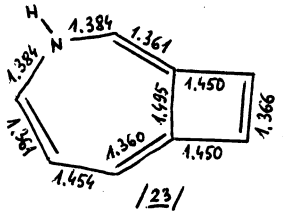








An interesting result is for molecules containing two antiaromatic rings e.g. azepine and cyclobutadiene. Cyclobuta/c/azepine /23/ has got a typical arrangement of bonds i.e. in agreement with Kekulé's structure with the highest contribution for mother hydrocarbon. For isomers /b/- and /d/-, /24/ and /25/ respectively, such situation is not possible, hence they bond lengths are as in the next /energetically privileged/ structure/.



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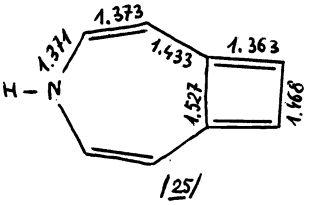

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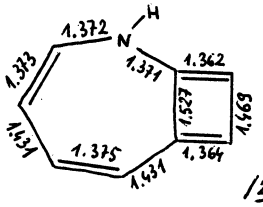

/24/

It is worth mentioning that central bond lengths /cf. butalene/ in isomers /b/ and /d/ are very long /1.527 Å/.

It may be concluded, that aromaticity of polycyclic compounds most simply can be treated with success applying conjugated circuits concept of Randić. Only in a few cases it does not differentiate in aromatic character some π-electron systems. Moreover applying this method there is no necessity of using computers. Relatively good results are also accesible by use of HMO within Hess and Schaad model of resonance energy. The PPP-method with variable geometry applied in this paper gives a good inspection into molecular structure. All valence electrons calculations applied recently very often seem to be not too convenient because of their time-consuming, in spite of their higher preciseness.

All calculations presented in this paper /11,12/ have been carried out in Computer Centre of Institute of Mathematics of University of Gdansk, for which I am highly grateful.

Finally, I would like to express my gratitude to Dr. T.M. Krygowski who discussed the material and gave valuable advices on preparation of the manuscript.

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