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USE OF THE DISTANCE/SIMILARITY MEASURE FOR ESTIMATING LOCAL AROMATICITY IN BENZENEOID HYDROCARBONS

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Abstract—The distance/similarity[1] between an individual benzene ring in a benzeneoid hydrocarbon and benzene itself, with respect to their electronic structure, is used to define a new local aromaticity index. The electronic structure in ground and excited state is assumed to be adequately represented by the charge-bond order matrix calculated in a LCAO-MO quantum chemical approximation. The overall correctness of the index is verified for the ground state, but it should be especially useful for estimating the (S_1)-excited-state-benzene character of benzeneoid rings in excited molecules.

Local aromatic properties in benzeneoid hydrocarbons have been qualitatively and quantitatively estimated by Clar[2] ("full and empty rings"), Polansky and Derflinger[3] ("benzeneoid character"), Dewar[4], Kruszewski[5], Randic[6] ("benzene-like character"), Herndon and Ellzey[7], Fratev *et al.*[8] ("information index of ring aromaticity"). As an application of the distance/similarity approach,[1] it seems possible to define yet another local aromaticity index by calculation of the *distance/similarity between an individual benzene ring in a benzeneoid hydrocarbon and benzene itself, with respect to their electronic structure.*

METHOD

It is assumed that the electronic structure is adequately represented by the charge-bond order matrix ($p_{\mu\nu}$) obtained in routine LCAO-MO quantum-chemical calculations. In this paper PPP with standard parameters was used,[9] in tight-binding approximation (i.e. only actual chemical bonds were taken into account). The distance/similarity between a 6-membered ring r in the studied compound in electronic state I and benzene itself in electronic state J, with respect to their electronic structure, was calculated according to the Euclidean distance norm[1]:

$$d^r(I, J) = \left[\sum_{\substack{\mu \leq \nu \\ \mu,\, \nu \in r}} \left\{ p_{\mu\nu}^{\text{studied molecule}}(I) - p_{\mu\nu}^{\text{benzene}}(J) \right\}^2 \right]^{1/2}.$$

RESULTS AND DISCUSSION

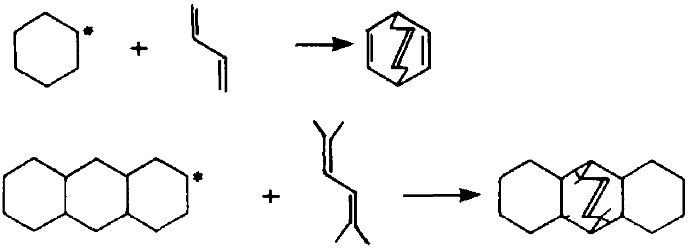
27 benzeneoid hydrocarbons and 6 related compounds were studied (Fig. 1, Table 1).

The benzeneoid rings in each compound are marked according to their topological embedding (Fig. 2).

As mentioned in the Introduction, this paper is an elaboration of the concept of partial distance/similarity introduced in a previous paper (Ref. 1, p. 251) under the heading "Comparison of a molecular subunit (fragment) M_i of M with a corresponding reference fragment L_i". Thus, the standard for aromaticity taken here is benzene itself, and benzeneoid rings are compared to it with respect to their electronic structure as represented by the PPP atomic charges and bond orders. To simplify the approach, only distance (dissimilarity) is presented, and d varies from 0 to infinity. (Of course, it is always possible to transform to complementary similarity s by an arbitrarily chosen transformation such as $S = (1/1 + d)$ or $S = e^{-1.61d^2}$, $0 \leq S \leq 1$). A unidirectional scale of aromaticity results, rings having small values of d being most similar to benzene, and thus most "aromatic" in character.

$d(S_0, S_0)$ Estimates the ground-state-benzene character of benzeneoid rings, and thus their local aromatic properties in ground state S_0. Its overall correctness was verified by correlating it with local aromaticity indices proposed by other authors for the studied compounds—the correlation coefficient R for 69 points was for Polansky and Derflinger[3] −0.919, Randic[6] −0.855, Herndon and Ellzey[7] −0.918, Fratev *et al.*[8] −0.963.

Ironically enough, good correlation means that nothing new can be expected from this local aromaticity index as compared with already existing ones. This is true, however, only for the ground state. Having tested it on a well-studied traditional set of compounds, we propose to use this index for estimating the (S_1)-excited-state-benzene character of benzeneoid rings in (S_1)-excited molecules. Thus we can expect that if a $d(S_1, S_1)$ value for a given ring r is very small, such a ring will take part in reactions characteristic for S_1-benzene itself. We note now that indeed the middle rings in anthracene **3**($d^{III}(S_1, S_1) = 0.051$), triphenylene **11**($d^{VI}(S_1, S_1) = 0.086$), perylene **13**($d^{X}(S_1, S_1) = 0.034$), 2,3,10,11-dibenzoberylene **28**($d^{X}(S_1, S_1) = 0.035$) have especially high S_1-excited-state-benzene character, and thus should, for example, partake in the photoreaction:[10, 11]



Chemical 1.

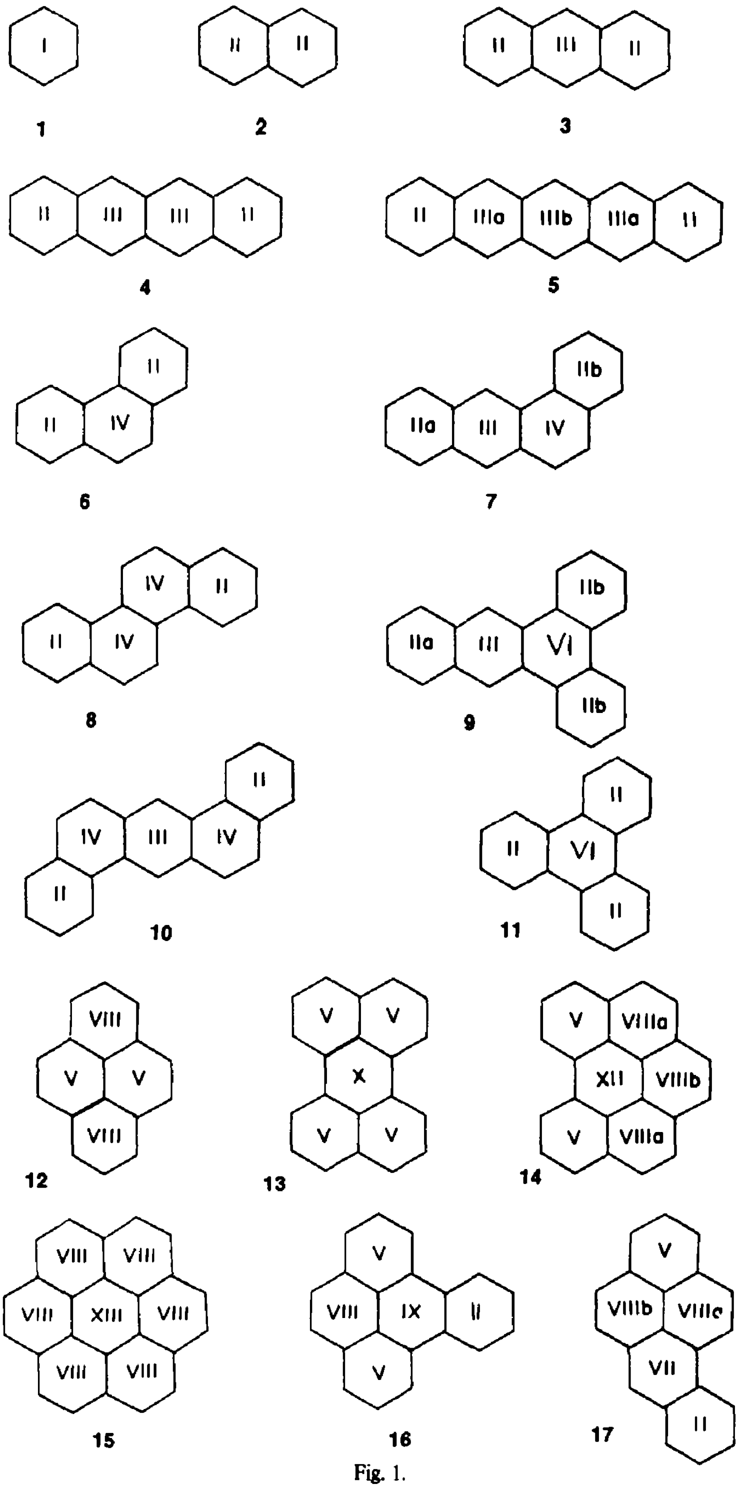
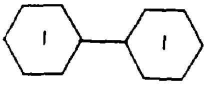


Fig. 1.



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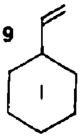

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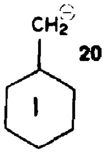

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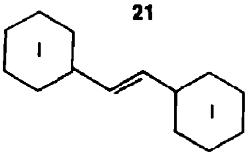

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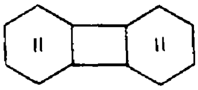

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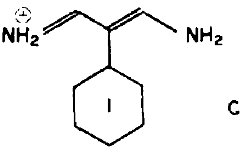

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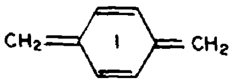

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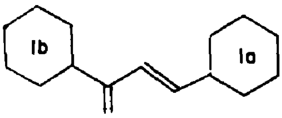

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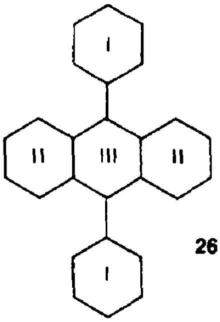

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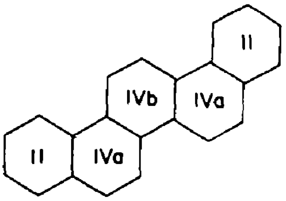

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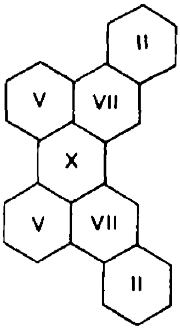

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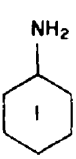

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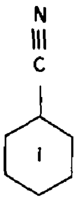

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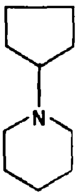

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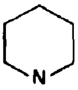

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Fig. 1. Compounds studied. Non-equivalent rings of same topological embedding are discriminated by small letters a, b, . . .

Table 1. $d(S_0, S_0)$: ground-state-benzene character of benzeneoid rings in studied compounds. $d(S_1, S_1)$: S_1-excited-state-benzene character of benzeneoid rings in S_1-excited state of studied compounds†

Compound	Ring	$d(S_0,S_0)$	$d(S_1,S_1)$
1	I	0	0
2	II	0.256	1.423
3	II	0.326	0.257
	III	0.259	0.051
4	II	0.350	0.301
	III	0.298	0.254
5	II	0.358	0.330
	IIIa	0.314	0.162
	IIIb	0.322	0.128
6	II	0.130	0.244
	IV	0.409	0.213
7	IIa	0.297	0.313
	III	0.246	0.188
	IV	0.459	0.252
	IIb	0.161	0.272
8	II	0.294	0.287
	IV	0.353	0.205
9	IIa	0.277	0.303
	III	0.251	0.124
	VI	0.530	0.139
	IIb	0.119	0.209
10	II	0.169	0.297
	IV	0.438	0.258
	III	0.208	0.172
11	II	0.129	0.259
	VI	0.497	0.086
12	V	0.202	0.195
	VIII	0.526	0.283
13	V	0.245	0.245
	X	0.470	0.034
14	V	0.198	0.240
	VIIIa	0.365	0.242
	XII	0.444	0.104
	VIIIb	0.284	0.170
15	VIII	0.315	0.220

Compound	Ring	$d(S_0,S_0)$	$d(S_1,S_1)$
	XIII	0.393	0.062
16	VIII	0.396	0.256
	IX	0.476	0.127
	II	0.123	0.295
	V	0.107	0.207
17	VIIIa	0.343	0.212
	VIIIb	0.445	0.194
	II	0.238	0.308
	V	0.209	0.245
	VII	0.325	0.136
18	I	0.054	0.383
19	I	0.062	0.420
20	I	0.307	0.101
21	I	0.055	0.343
22	II	0.095	0.383
23	I	0.115	0.340
24	I	0.048	0.383
25	Ia	0.049	0.343
	Ib	0.041	0.371
26	II	0.295	0.301
	III	0.302	0.097
	I	0.071	0.351
27	II	0.162	0.312
	IVa	0.445	0.060
	IVb	0.254	0.175
28	II	0.186	0.330
	VII	0.391	0.135
	V	0.101	0.271
	X	0.500	0.035
29	I	0.136	0.073
30	I	0.042	0.034
31	I	0.141	0.036
32		0.229	0.418
33		0.014	0.008

†Only a selection of data is presented. $d(S_1, S_0)$, $d(S_2, S_0)$, $s(S_1, S_0)$, $s(S_2, S_0)$, $s(S_1, S_1)$ etc. are available on request.

Table 2. Correlation for pairs of aromaticity indices after topological embedding breakdown (missing data due to too few points available)

	Correlation coefficient R			
Topol. embed.	$d(S_0,S_0)$/Polansky	$d(S_0,S_0)$/Randic	$d(S_0,S_0)$/Herndon	$d(S_0,S_0)$/Fratev
I	-0.923	-	-	-
II	-0.998	-0.999	-0.956	-0.999
III	-0.918	-0.890	-0.967	-0.991
IV	-0.997	-0.997	-0.826	-0.999
V	-0.868	-0.931	-0.883	-0.976
VIII	-0.930	-0.808	-0.907	-0.844

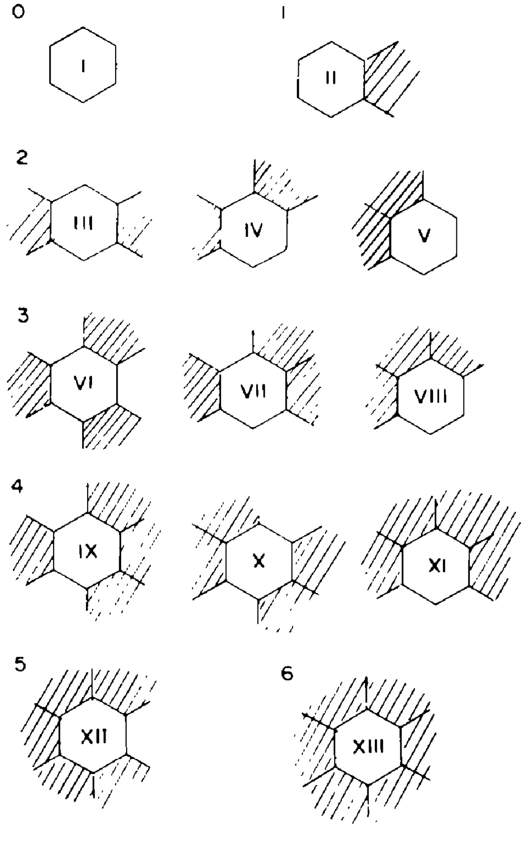

Fig. 2. Different possibilities for topological embedding of polycondensed benzene rings. Figures in upper left denote number of condensed neighbours.

We have used $d(S_1, S_1)$ successfully for interpretation of the character of excited states and photochemical behaviour of a large class of phenylbenzthiazole and phenylbenzoxazole compounds.[12]

Lastly, a topological embedding breakdown attempt according to Fig. 2 and Table 2 failed to confirm our hypothesis that for any given topological embedding (I, II, . . .) a very high correlation would be observed with respect to any given pair of local aromaticity indices. As can be seen, this is only partly true for II and IV. This should mean that a topological embedding structural factor does not predominate in any of the indices considered.

CONCLUSION

A benzene-character index has been introduced using calculated atomic charges and bond orders of benzene rings, in ground and excited state, for the purpose of estimating local aromaticity in ground and (S_1) excited state in benzene-containing compounds. This index is based on partial distance/similarity, and thus comes in-between atomic reactivity calculations (a total breakdown to atoms) and overall aromaticity estimation. The index is validated for ground state ring aromaticity, and could be especially useful for estimating excited state aromaticity (or more exactly, excited-state-benzene character). In principle, the method is applicable in any LCAO-MO scheme, no additional parameters, beside routine quantum-chemical assumptions, need be specified, any calculable excited state could be interpreted, and lastly, a generalisation to an n-atomic fragment ($n \neq 6$) could be made, thus leading, for instance, to butadiene, azulene, etc. character indices.

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