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Separation of the Energetic and Geometric Contributions to Aromaticity. Part VI. Changes of the Aromatic Character of the Rings in Naphthalene, Anthracene, Phenanthrene and Pyrene Derivatives Induced by the Charged Substituent CH_2^+

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Abstract. Ab initio 6-31G* optimised geometries of naphthalene, anthracene, phenanthrene, pyrene and all their CH_2^+ mono-substituted derivatives have been examined in respect to estimate the changes of their aromatic character due to these kinds of substitution. CH_2^+ substituent attached to aromatic hydrocarbons causes dramatic changes in their molecular geometry. This implies great changes in both local (i.e. referring to a single ring) and global aromaticity. The substituted rings always lose some part of their original aromatic character, but if the position of the substitution permits formation of the quinoidal structure *via* a short CC bond which is spread over the larger part of the molecule, the decrease of aromatic character is greater than in the other cases. Formation of quinoidal structures in a molecule leads to a long-range intramolecular charge transfer. © 1997 Elsevier Science Ltd.

Introduction

The benzylic cation and its substituted derivatives have been chosen[1] as the most effective models for determining substituent constants σ^+ describing properly the reactivity of the systems with a positively charged transition state.[2-3] They are also useful for accounting for the through resonance effect *via* the Yukawa-Tsuno equation.[4] Recently we have shown that the substituent effect in the exocyclically substituted derivatives of the benzylic cation may lead to dramatic changes of the aromatic character of the ring.[5]

Aromaticity has not been defined precisely[6] and is usually accepted as a multidimensional phenomenon.[7-11] The most practical measures of the aromatic character are based on one of the three effective criteria[7]:

i) the energetic one, by use of the resonance energy or applying a less precisely defined aromatic stability energy,[12]
ii) the geometric one by measuring the degree of bond length alternation[13-16] and
iii) the magnetic one which is either based on the NMR spectral data for proton signals[17] or on the magnetic susceptibilities.[18] Recently the theoretically calculated parameter called ***nucleus independent chemical shift*** (abbreviated NICS) has been proposed as an effective measure of the aromatic character.[19]

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Application of the geometric criterion is based upon the analysis of bond length alternation and is roughly described by a function of variance of bond lengths (or, equivalently, bond orders which replace the bond lengths in the case of heteroaromatics[15]). If the geometric criterion is used in a slightly different way, i.e. referring the bond length alternation not to the mean value but to an optimal bond length as in the definition of the HOMA index,[14,16] then it has the advantage of making it possible to examine the factors that decide about aromaticity leading to the dissection of the HOMA index into two terms, the energetic one and the purely geometric one.[20-21]

In the case of benzyl cation derivatives substituted exocyclically it was shown that for the planar systems aromaticity is decreased with an additional decrease due to the electron accepting substituents, such as CF_3. The HOMA index varied[5] from the lowest value for the o,o'-dimethyl-7-t-butylo- substituted benzylic cation, 0.605, to 0.725 for the unsubstituted benzylic cation. In opposition to that, the less co-planar is the exocyclic group (i.e. the greater is the torsion angle τ) the smaller is the loss of the aromatic character. In the case of the almost perpendicular structure of 7,7-di -t-butyl derivative, HOMA is 0.995. The aim of this paper is to show how the CH_2^+ substituent coplanar with the aromatic moiety can affect the aromatic character of the substituted benzenoid hydrocarbons and also the benzene rings embedded in various environments in the benzenoid hydrocarbons. It has already been shown that the aromaticity of benzene ring in benzenoid hydrocarbons depends markedly on its topological situation.[11,22-23] Moreover, owing to the recently invented separation of the geometric and energetic contribution to the dearomatization of the π-electron system it was possible to show which of these two factors is responsible for dearomatization.[20] The analysis was carried out for the CH_2^+ substituted derivatives of naphthalene, anthracene, phenanthrene and pyrene.

Results and discussion

Ab initio RHF/6-31G* calculations for naphthalene, anthracene, phenanthrene, pyrene and all their CH_2^+ substituted derivatives were carried out using Gaussian 94[24] program. Fig 1 presents the optimised geometry of these molecules and the values of the aromaticity index HOMA, and its contributions EN and GEO[20]:

$$\mathrm{HOMA} = 1 - \alpha\left(R_{opt} - R_{av}\right)^2 - \frac{\alpha}{N}\Sigma\left(R_{av} - R_i\right)^2 = 1 - \mathrm{EN} - \mathrm{GEO} \qquad (1)$$

The R_i stands for the bond lengths in question taken for a given molecule or its fragment, whereas R_{av} denotes the respective mean bond lengths; R_{opt} represents the optimal bond length for CC bonds.[14,16] The EN and GEO terms have the following simple interpretation: an increase of the EN term means a decrease of ring stability, i.e. a decrease of resonance energy of a given ring. An increase of the GEO term means an increase of bond length alternation in a given ring. As a rule these two terms are independent.[20-21]

Changes of aromatic character in substituted rings

While looking at the aromatic character of the substituted rings in the studied compounds it is immediately clear that it is decreased substantially as a result of substitution by CH_2^+. The HOMA, EN and GEO values for the particular rings and for the whole molecule calculated from the optimised geometry are given in Table 1. For comparison the same data are given for unsubstituted hydrocarbons at the same level of theory.

Fig. 1. 6-31G* optimised geometry (bond lengths in Å) of CH_2^+ substituted derivatives of naphthalene, anthracene, phenanthrene and pyrene and their parent hydrocarbons.

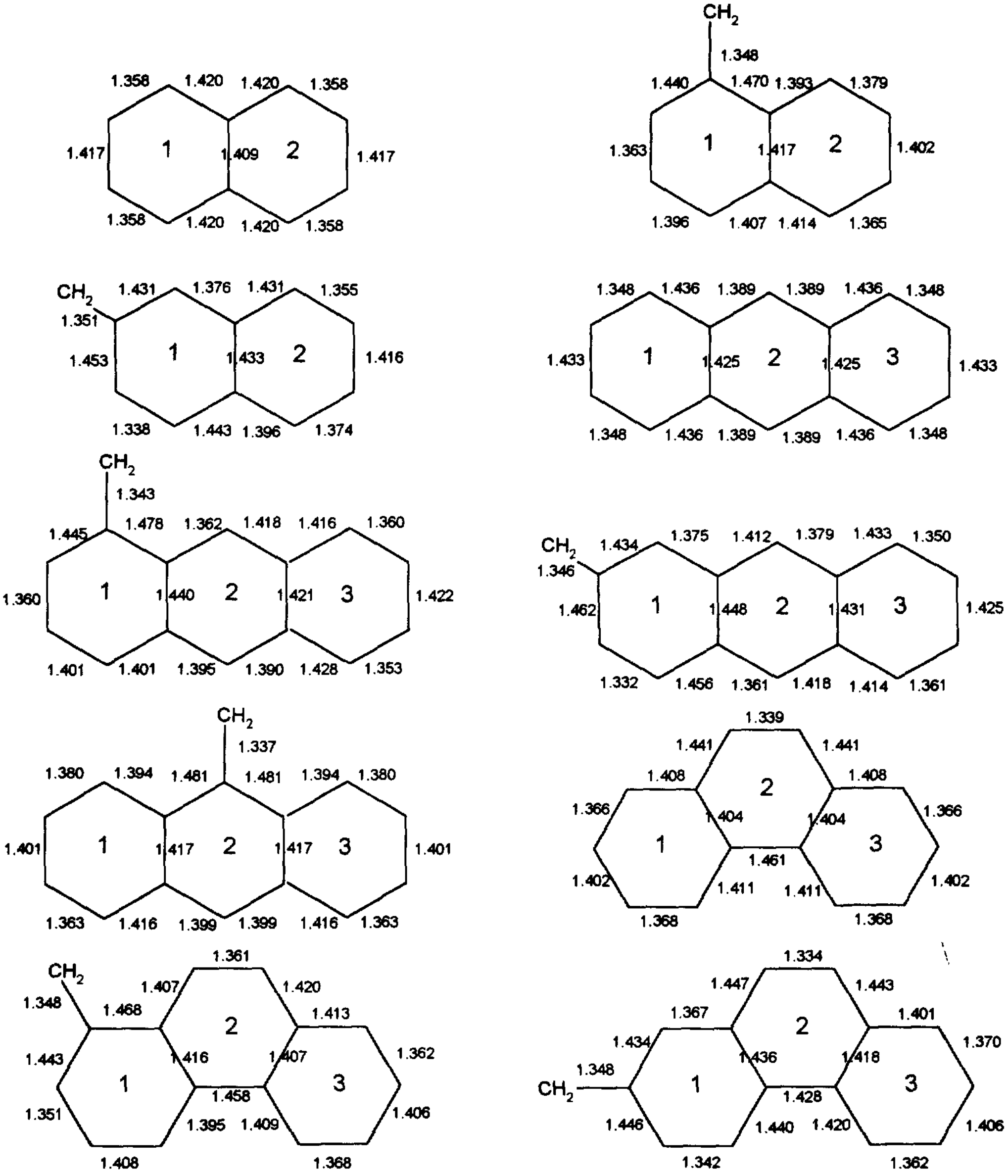


Fig. 1. Continuation.

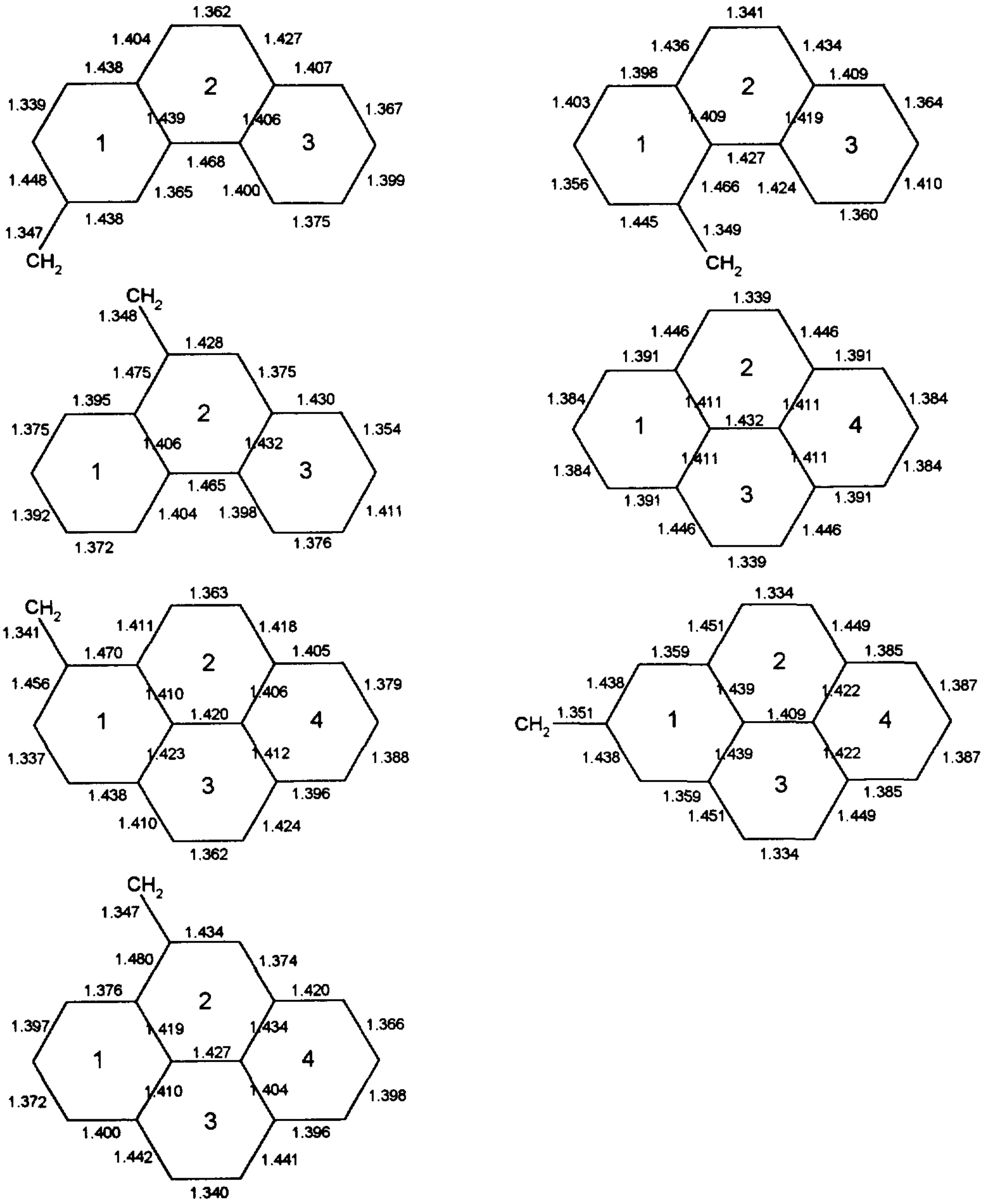


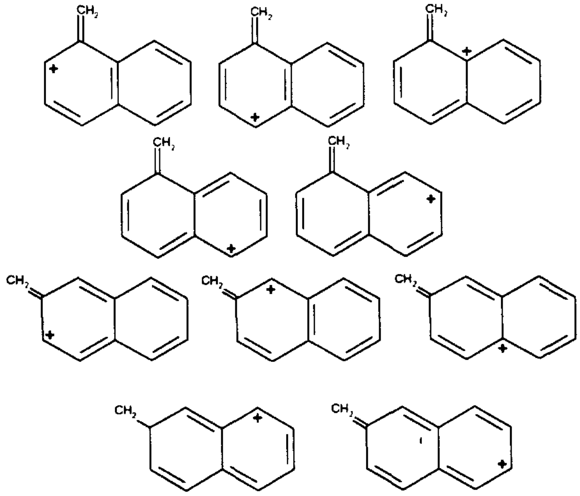
Table 1. HOMA, EN and GEO values for CH_2^+ substituted derivatives of naphthalene, anthracene, phenanthrene and pyrene and their parent hydrocarbons.

	Ring 1	Ring 2	Ring 3	Ring 4	Whole moiety
Naphthalene	HOMA=0.780	HOMA=0.780			HOMA=0.770
	EN=0.021	EN=0.021	-	-	EN=0.016
	GEO=0.199	GEO=0.199			GEO=0.214
1-Naphthalene	HOMA=0.514	HOMA=0.899			HOMA=0.699
	EN=0.195	EN=0.0126	-	-	EN=0.067
	GEO=0.291	GEO=0.0882			GEO=0.233
2-Naphthalene	HOMA=0.409	HOMA=0.742			HOMA=0.584
	EN=0.153	EN=0.042	-	-	EN=0.067
	GEO=0.439	GEO=0.216			GEO=0.348
Anthracene	HOMA=0.519	HOMA=0.882	HOMA=0.519		HOMA=0.639
	EN=0.069	EN=0.044	EN=0.069	-	EN=0.040
	GEO=0.412	GEO=0.074	GEO=0.412		GEO=0.321
1-Anthracene	HOMA=0.348	HOMA=0.767	HOMA=0.715		HOMA=0.622
	EN=0.278	EN=0.069	EN=0.037	-	EN=0.080
	GEO=0.374	GEO=0.164	GEO=0.248		GEO=0.297
2-Anthracene	HOMA=0.179	HOMA=0.668	HOMA=0.652		HOMA=0.525
	EN=0.229	EN=0.105	EN=0.053	-	EN=0.081
	GEO=0.592	GEO=0.227	GEO=0.295		GEO=0.394
9-Anthracene	HOMA=0.892	HOMA=0.174	HOMA=0.892		HOMA=0.636
	EN=0.013	EN=0.506	EN=0.013	-	EN=0.087
	GEO=0.095	GEO=0.319	GEO=0.095		GEO=0.277
Phenanthrene	HOMA=0.903	HOMA=0.405	HOMA=0.903		HOMA=0.712
	EN=0.007	EN=0.188	EN=0.007	-	EN=0.037
	GEO=0.090	GEO=0.407	GEO=0.090		GEO=0.251
1-Phenanthrene	HOMA=0.483	HOMA=0.650	HOMA=0.879		HOMA=0.648
	EN=0.168	EN=0.142	EN=0.010	-	EN=0.081
	GEO=0.349	GEO=0.208	GEO=0.112		GEO=0.271
2-Phenanthrene	HOMA=0.440	HOMA=0.389	HOMA=0.853		HOMA=0.557
	EN=0.134	EN=0.227	EN=0.017	-	EN=0.082
	GEO=0.426	GEO=0.384	GEO=0.130		GEO=0.360
3-Phenanthrene	HOMA=0.393	HOMA=0.494	HOMA=0.933		HOMA=0.605
	EN=0.138	EN=0.227	EN=0.005	-	EN=0.076
	GEO=0.469	GEO=0.279	GEO=0.062		GEO=0.320
4-Pnenanthrene	HOMA=0.522	HOMA=0.590	HOMA=0.805		HOMA=0.616
	EN=0.159	EN=0.136	EN=0.024	-	EN=0.086
	GEO=0.319	GEO=0.274	GEO=0.171		GEO=0.298
9-Phenanthrene	HOMA=0.954	HOMA=0.247	HOMA=0.758		HOMA=0.646
	EN=0.002	EN=0.458	EN=0.038	-	EN=0.079
	GEO=0.044	GEO=0.295	GEO=0.204		GEO=0.275
Pyrene	HOMA=0.952	HOMA=0.479	HOMA=0.479	HOMA=0.952	HOMA=0.696
	EN=0.013	EN=0.176	EN=0.176	EN=0.013	EN=0.051
	GEO=0.036	GEO=0.344	GEO=0.344	GEO=0.036	GEO=0.253
1-Pyrene	HOMA=0.220	HOMA=0.833	HOMA=0.773	HOMA=0.943	HOMA=0.661
	EN=0.304	EN=0.072	EN=0.108	EN=0.024	EN=0.091
	GEO=0.476	GEO=0.095	GEO=0.118	GEO=0.033	GEO=0.249
2-Pyrene	HOMA=0.490	HOMA=0.364	HOMA=0.364	HOMA=0.900	HOMA=0.513
	EN=0.148	EN=0.222	EN=0.222	EN=0.026	EN=0.095
	GEO=0.362	GEO=0.414	GEO=0.414	GEO=0.074	GEO=0.391
9-Pyrene	HOMA=0.911	HOMA=0.340	HOMA=0.558	HOMA=0.826	HOMA=0.641
	EN=0.015	EN=0.412	EN=0.132	EN=0.058	EN=0.091
	GEO=0.074	GEO=0.248	GEO=0.310	GEO=0.116	GEO=0.267

It is worth mentioning here that the decrease of the aromatic character depends strongly on the position of the substitution, and may differ in a wide range. This observation is in line with an old idea of the position dependent basicity and reactivity of benzenoid hydrocarbons[25] and the concept of the Hammett - Streitwieser position constants.[26] The effects measured as a difference between the HOMA, EN and GEO values for the substituted ring and an analogous ring in the unsubstituted hydrocarbon are considerable and amount as much as to 0.73 units of HOMA in the case of pyrene. The same trend is observed in the case of the same values estimated for the whole molecules.

The variation of HOMA, GEO and EN terms depending on the position of substitution requires deeper consideration. It is discussed in more detail in terms of the canonical structures induced by the substitution taking the substituted naphthalenes as a useful illustration (Scheme I). If the CH_2^+ substituent is in position (1) in naphthalene then the decrease of the aromatic character of the whole molecule due to the substitution is 0.07 unit of HOMA. The effect is stronger by 0.19 units of HOMA if the substitution is in position (2). In both substituted naphthalenes the EN term is the same, 0.067, and the decrease of aromaticity is due to the GEO term. While looking at the changes in the individual ring (Table 1) it is apparent that both rings in 2-substituted naphthalene lose more aromaticity than those in the 1-substituted one. The unsubstituted ring in the 1-substituted naphthalene even gains more aromatic character in comparison with the parent molecule (by 0.12 unit of HOMA). Contrary to that, both rings in 2-substituted naphthalene lose their aromatic character. This effect may be explained as follows. Transmission of the charge from CH_2^+ to the other parts of the molecule is realised *via* the quinoidal structures. The bonds which link the substituted ring with the adjacent ring are of key importance for the quinoidal structure formation. A useful measure of the intramolecular charge transfer from CH_2^+ to the terminating atom(s) of the quinoidal structure are: the total atomic charge at carbon atoms Q_C or better, the sum of the total atomic charges at the C-H group Q_{CH}. The latter is more adequate since it takes into account the possibility of the relaxation of the charge transfer from CH_2^+ group onto the H atom attached to the given carbon atom. This quantity will be used in the further analysis.

Scheme 1



A stronger dearomatization observed in the case of (2) substitution than in the case of (1) substitution is due to the more effective charge transfer from CH_2^+ group to the positions marked in Scheme 1 by (+) and accompanied with the values of the total atomic charge of the C-H moiety, Q_{CH}. Clearly the Q_{CH} values in positions C_6 and C_8 in the 2-substituted naphthalene are more positive than in positions C_5 and C_7 in the 1-substituted one: 0.14 - 0.15 vs 0.11. Note that in the case of the 2-naphthalene derivative the linking bonds are strongly alternated: 1.376, 1.433 and 1.396 Å as compared with to 1.407, 1.417 and 1.393 Å for derivative of 1-naphthalene. It seems that the bond length of the CC bond directed to the ring which is to be of quinoidal structure is of key importance. The shorter is this bond, the more localised is the quinoidal structure of the ring in question and the greater charge is transferred from CH_2^+ to the CH group terminating the quinoidal structure.

Scheme I presents clearly the above-described situations whereas Fig 2 presents the relevant data for all discussed systems. It is immediately apparent that the Q_{CH} values in the positions which may terminate quinoidal structures are much higher than the other ones, which are usually considerably smaller than 0.1, often close to 0.0. This is seen clearly for the positions C_2, C_4, C_5 and C_7 of the 1-substituted naphthalene derivative and for positions C_1, C_3, C_6 and C_8 of the 2-naphthalene derivative. In the case of the 1-naphthalene derivative the quinoidal structure is extended onto the next ring *via* the C_4C_{4a} bond in naphthalene which is relatively long (1.407 Å, Fig. 1), and in consequence the quinoidal π electron localisation of this structure is weak, and the dearomatization is also weak. Moreover, the respective carbon atoms which terminate these quinoidal structures (C_5 and C_7) in the 1-substituted derivative of naphthalene have the Q_{CH} values equal to 0.111 and 0.114, whereas for the terminating carbon atoms in the substituted ring, C_2 and C_4 these values are equal to 0.191 and 0.219, respectively. Evidently the localisation of the charge in the substituted ring is much stronger than in the other one. The situation is quite different in the case of 2-substituted naphthalene. The Q_{CH} values at carbon atoms terminating the quinoidal structure in the substituted ring, C_1 and C_3 are lower than those found in the 1-naphthalene and amount to 0.190 and 0.107, respectively. Consequently, the Q_{CH} values in the unsubstituted ring are more positive than was observed for the 1-naphthalene derivative, 0.147 and 0.141 for C_6 and C_8, respectively. In this case the extension of the quinoidal structure on the other ring is *via* a much shorter bond, C_1C_{8a} which is as short as 1.376 Å. Closer inspection of the other structural data (Fig 1) and total atomic charges (Fig. 2) and taking into account appropriate quinoid structures which may be constructed for these molecules permit us to formulate the following conclusion:

*If the CH_2^+ group is attached to the ring in the benzenoid hydrocarbon in such a way that the induction of the quinoidal structure onto the further fragments of the molecule is **via a short CC bond**, then the induced quinoidal structure has strong π bond localisation. If this is done via a long CC bond, then the localisation is much weaker. In consequence in the first case the dearomatization is greater and in the second case - weaker.*

The case of the angular molecule of phenanthrene is an even better (though more complex) illustration of the above rule. Once again the substituted species in positions (2) and (3) exhibit a lesser aromatic character of the substituted and central rings and of the whole molecule than those substituted in (1) and (4) positions. This effect is due to the fact that the quinoid structures involving the further ring(s) extended from the (2) and (3) positions are induced *via* short bonds C_1C_{10a} (1.367 Å for 2-phenanthrene derivative) and C_4C_{4a} (1.365 Å for 3-phenanthrene derivative), respectively.

Fig 2. Total atomic charges of Mulliken population analysis[27] for the CH or CH_2 groups in CH_2^+ substituted derivatives of naphthalene, anthracene, phenanthrene and pyrene and their parent hydrocarbons.

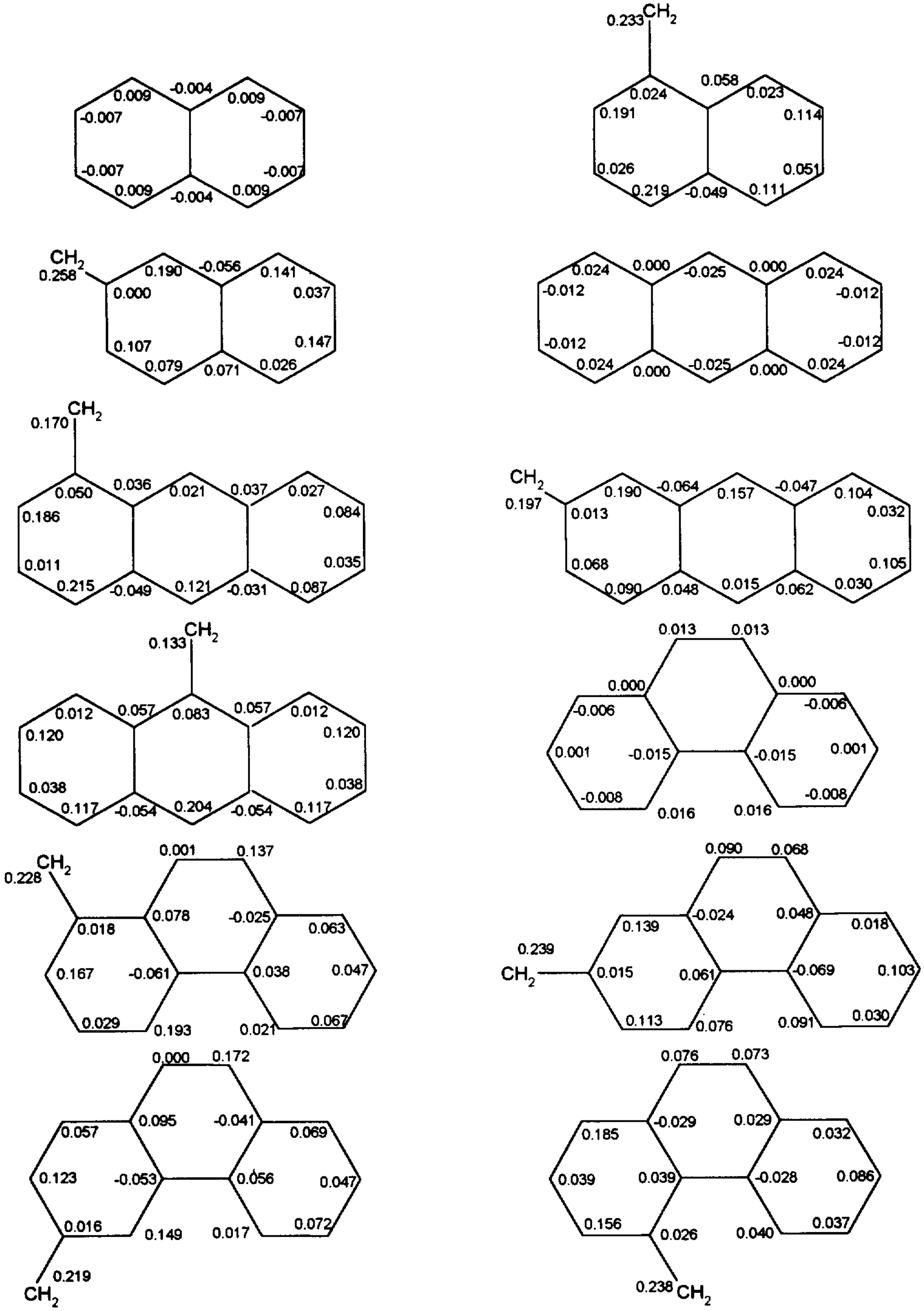
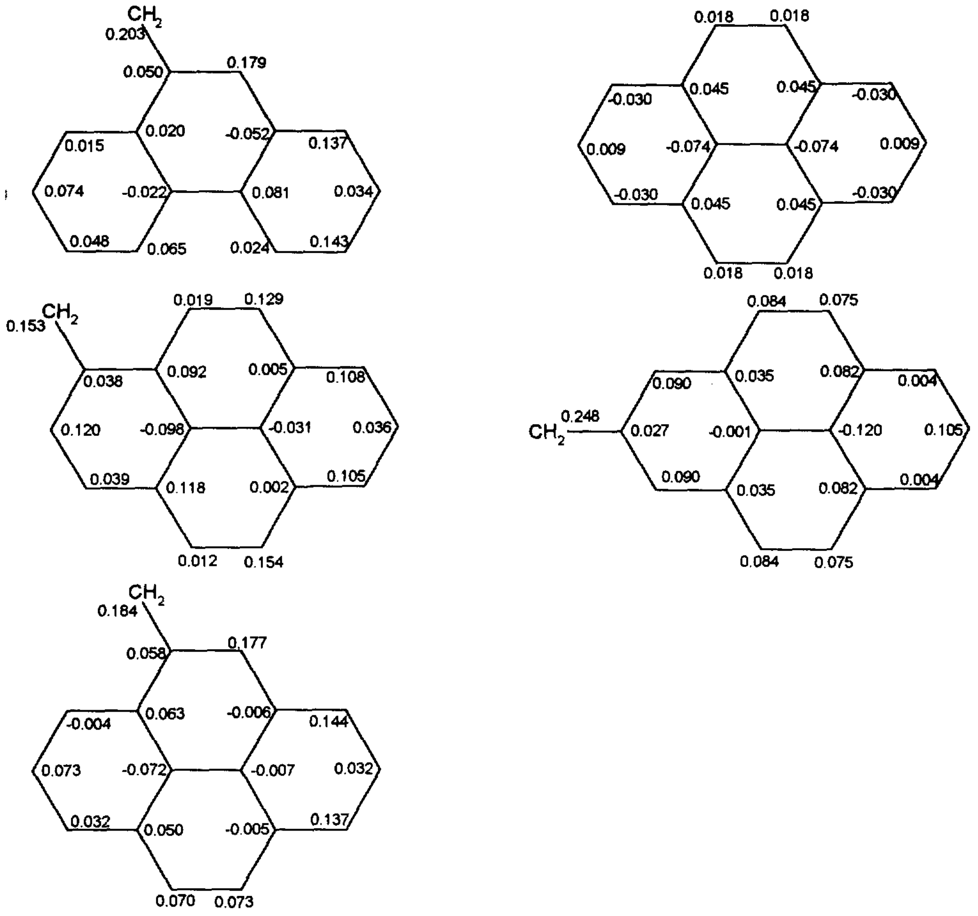


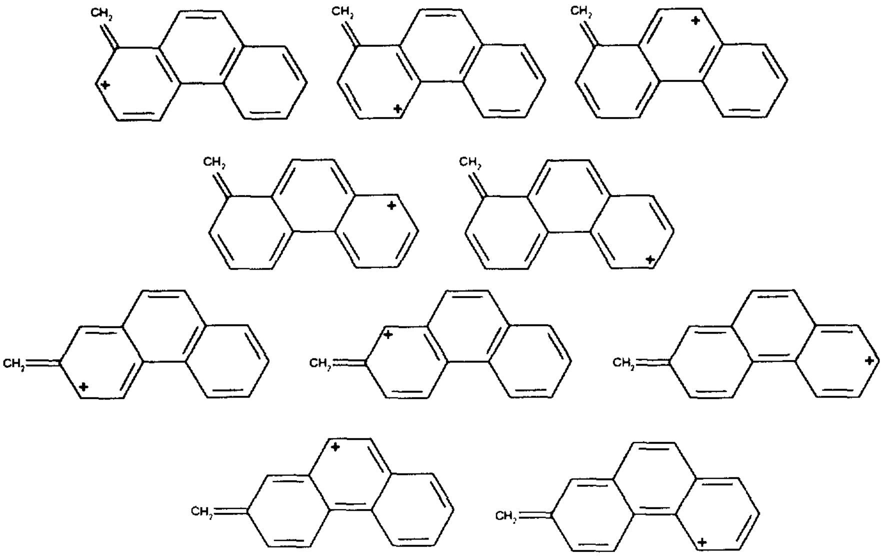
Fig 2. Continuation.



Scheme 2 shows the difference between substitution in the (1) and (2) positions, similar schemes may be done for other substituted systems discussed in this work. In the case of 1- and 4-phenanthrene derivatives the bonds inducing the quinoidal structure onto the farther fragment of the molecule are much longer: C_4C_{4a} (1.395 Å for 1-phenanthrene derivative) and C_1C_{10a} (1.398 Å for 4-phenanthrene derivative).

A very interesting effect can be observed while looking at anthracene and phenanthrene substituted in their central rings. In these cases the aromatic character of the central rings is markedly decreased, but aromaticity of the other rings in anthracene increases (from HOMA = 0.519 for the unsubstituted anthracene to 0.892 for 9-substituted one, Table 1). This finding is in line with an old observation that in linear polyacenes the central rings are inclined to become easily nonaromatic, leading to an increase in aromaticity of the other rings: typically the tautomerism of 9-hydroxyanthracene may be a good example.[28] In the case of phenanthrene the situation is more complex. If the substitution is as in Fig. 1 then the aromatic character of the left hand ring

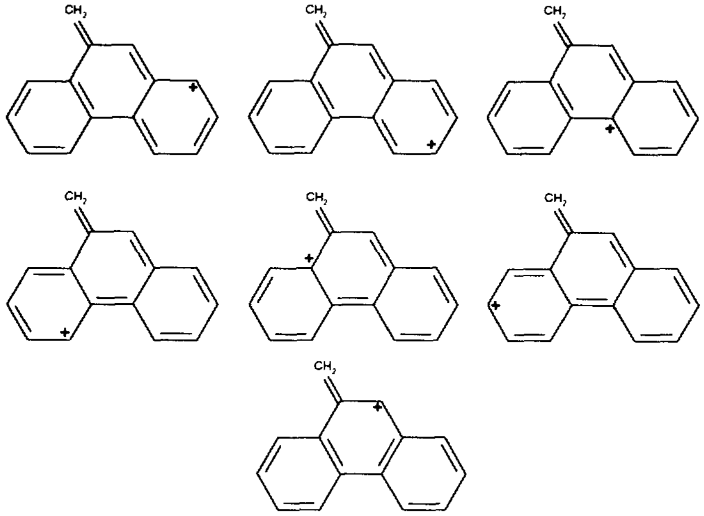
Scheme 2



(Ring 3) increases (from 0.903 for the unsubstituted species to 0.954 for 9-substituted one). But the right hand ring decreases its aromaticity to HOMA = 0.758. This effect is again due to the possibility of extension of the quinoid structure from the central ring to the other one (see Scheme 3) via a short bond $C_{10}C_{10a}$ of the length 1.375 Å. Note that in the seven canonical structures describing 9-CH_2^+ substituted phenanthrene (Scheme 3) the Q_{CH} values in positions positively charged are markedly more positive (between 0.065 and 0.137) than the other positions (less than 0.050). Again the dependence of the π electron localisation on the CC bond length of the bond inducing it in the form of a quinoidal structure is observed. The $C_{4a}C_{4b}$ bond induces two possible quinoidal structures with charge localisation in the left hand ring, but its length is 1.465 Å and it is too long to induce a strong quinoidal π electron localisation, and indeed, the Q_{CH} values at terminating positions are 0.074 and 0.065. Opposite to this is the situation in the right hand ring. The $C_{10}C_{10a}$ bond which induces the quinoidal structure in this ring is short, 1.375 Å, and induces a much stronger π electron, quinoidal localisation. The Q_{CH} values at C_3 and C_1 are 0.143 and 0.137, respectively. As a result the loss of aromatic character is greater, and it is due to the geometric factor.

Very instructive are the results for the CH_2^+ substituted derivatives of pyrene. Aromaticity of the terminal rings in the parent molecule is high (HOMA = 0.952) and drops down after substitution in this ring to 0.220 and 0.490 for the substitution in positions (1) and (2), respectively. When the central ring is substituted, the aromaticity decreases from 0.479 to 0.340. Much more interesting are, however, the consequences of these substitutions observed in further rings (see next section).

Scheme 3.



Usually the dearomatization is due to the higher GEO value, i.e. the substitution of CH_2^+ leads to a π-electron localisation. This effect remains in agreement with a general observation that doubly bonded substituents attached to the ring decrease its aromatic character due to π-electron localisation. Typically this is observed for o-[29] and p-[30] benzoquinone[31], where HOMA =-0.860 (-0.508), EN=0.469 (0.392) and GEO= 1.391 (1.116). In our case the CH_2^+ substituent is bonded with rings by a short bond of the lengths 1.34 - 1.35 Å, i.e. almost exactly double bonds (in ethene CC bond length is 1.337 Å[32]). In our case we observe that dearomatization depends on the bond length of the bond which is responsible for inducing the quinoidal structure. The EN term is always less important but still not negligible. The CH_2^+ substituent induces long CC bonds with adjacent carbon atoms, typically 1.40-1.48 Å, and therefore contributes to an increase of the mean bond lengths, and in consequence - to an increase of the EN term.

Changes in aromaticity in unsubstituted rings

The unsubstituted rings are in principle less affected by the substitution by CH_2^+ but exhibit an interesting pattern. As mentioned above, if the substituted ring may be involved in an extended system of quinoidally localised double bonds, then the fused rings which are included in this extension exhibit a stronger localisation of π electron structure and in turn are less aromatic, which is determined by an increase of the GEO term.

This rule is nicely shown by a lower aromatic character of the right hand ring (2) in the 2-substituted naphthalene than in the 1- substituted one: 0.742 vs 0.899 for the HOMA and 0.216 vs 0.088 for the GEO term, respectively. Anthracene gives an excellent example for a longer pathway of significant interactions of this type. For 1-substituted anthracene the HOMA value for the central and the right hand rings (2 and 3, Fig. 1) are 0.767 and 0.715, respectively. The GEO terms are 0.164 and 0.248, respectively. No possibility of the effective quinoidal structure exists in this case, since the C_4C_{4a} bond is relatively long, 1.401. For 2-substituted anthracene the decrease of the aromatic character is significant. The HOMA values for the central and right hand rings are

0.668 and 0.652, respectively. The GEO terms are 0.227 and 0.295. Obviously, the quinoidal structure is propagated over the whole molecule in 2-substituted anthracene and causes the decrease of the aromatic character of unsubstituted rings. This time the C_1C_{9a} bond responsible for a transmission of the quinoidal structure is short (1.375 Å) and hence the effect expected by the rule formulated in the previous section. Further transmission is realised via another short bond $C_{8a}C_9$ (1.379 Å). The above-presented effect is also shown by the HOMA and GEO values for the whole molecules. For 1-substituted naphthalene and anthracene they are 0.699 and 0.622 (HOMA) and 0.233 and 0.297 (GEO), respectively. For 2-substituted naphthalene and anthracene these data are 0.584 and 0.525 (HOMA) and 0.348 and 0.394 (GEO), respectively. The role of induction of the quinoidal structure along some lines in the molecule is well illustrated by the data from pyrene derivatives. In the case of 1-substituted derivative C_3C_{3a} and $C_{3a}C_{11}$ bonds which would be responsible for inducing the quinoidal structure in one of the central rings are rather long: 1.438 Å and 1.423 Å. In consequence, the central rings are aromatic (contrary to what was observed for the parent molecule): their HOMA values are 0.833 and 0.773. Similarly in the case of 2-substituted derivatives - the key bond, $C_{11}C_{11a}$ which is responsible for inducing the quinoidal structure in the terminal ring, is long: 1.409 Å. In consequence, the ring (4) is aromatic with HOMA = 0.900. The other key bonds C_3C_{3a} and C_1C_{10a} are very short (1.359 Å) and implicate lower aromatic character of rings (2) and (3) in comparison to the parent molecule. In the case of the 9-substituted derivative, the terminal ring to which is directed a short $C_{10}C_{10a}$ bond of the length 1.374 Å is less aromatic (HOMA = 0.826) as compared with the value for the parent molecule (HOMA=0.952). All these results illustrate well the rule which may be formulated as a conclusion of this work:

If a single substituent able to form a double bond is attached to the benzenoid hydrocarbon in a position which permits the formation of a quinoidal structure along a larger part of the π-electron moiety, then it acts as a dearomatizing factor for this fragment and in consequence for the whole system. Moreover, this effect is associated with a long-range intramolecular charge transfer from the CH_2^+ *group to the position(s) being the terminal(s) of the quinoidal structure in the molecule. This effect is also associated with an increase of the geometric term. The magnitude of the π-electron localisation via the formation of the quinoidal structures depends on the bond length of the bond which causes this induction. The shorter is this bond the greater localisation is observed.*

In view of the above it might be concluded that depending on whether or not the position of CH_2^+ substitution facilitates the formation of a long chain-quinoid structure, the charge transfer may be long range or local and hence - the global aromaticity of the molecule is not directly dependent on the charge transfer. Consequently, the local aromatic character is very informative in description of the system in question.

Correlations between the structural and electrical parameters

It is also worth mentioning that the changes in Q_{CH} on the CH_2^+ group are well correlated with the CC bond lengths linking the CH_2^+ group with the benzenoid hydrocarbon (correlation coefficient r=0.961[*]) as shown in Fig. 3. This observation is in line with a similar dependence found for the exocyclically substituted benzyl cation.[5] Another correlation (with r=-0.930) was found for the Hammett-Streitwieser position constants[25-26] and the Q_{CH2}^+ as shown in Fig. 4. It is worth mentioning that dependences on the Hammett-

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[*] In all cases data for the benzylic cation[5] was included in the correlation analysis.

Streitwieser constants were also found for changes of the CH$_2$-C bond lengths with correlation coefficient r= 0.956, and the total atomic charge at the ipso carbon atom with r= 0.794. Particularly interesting are the dependences of HOMA and EN values for the substituted rings and the position constants, r= 0.794 and 0.750, respectively, and even better, correlations between HOMA and EN with Q$_{CH}$ on CH$_2^+$ (r=0.879 and -0.810). All these correlations are significant at the significance level 0.01 or better. Interestingly, the aromatic character of the substituted rings is determined by the energetic term, since the correlation coefficient between HOMA and EN is r= -0.775 Consequently, the lack of correlation between EN and GEO (r= -0.177) is observed. Particularly interesting seems to be the good dependence of EN on the substituted ring and the sum of the total atomic charges of all carbon atoms building up the ring in question, r= 0.909. This means that an increase of this charge results in an increase of dearomatization, which is realised *via* strong quinoidal π electron localisation. The quinoidal structure is characterised by two shorter bonds and four longer ones, thus an increase of the quinoidal localisation means a longer average bond on the one hand and an increase of the total charge on the other.

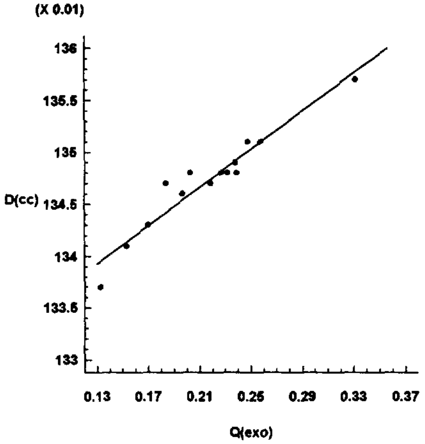

Fig. 3 Dependence of the C=CH$_2$ bond lengths on the total atomic charge at the CH$_2^+$ group.

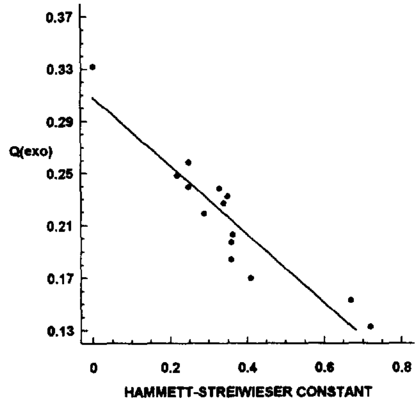

Fig. 4 Dependence of the total atomic charge at CH$_2^+$ group and the Hammett-Streitwieser position constants.

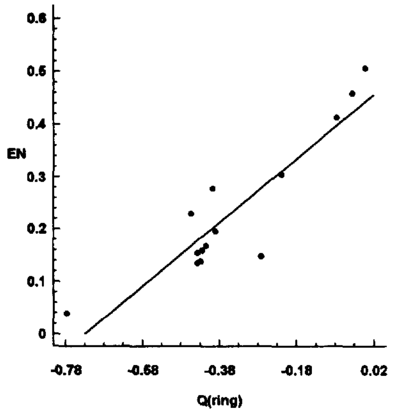

Fig. 5 Dependence of the EN term on the substituted ring and its total atomic charge calculated for all carbon atoms of the ring.

Conclusions

The aromatic character in the CH_2^+ substituted benzenoid hydrocarbons studied in this paper depends strongly on the position of the substitution. If it permits the formation of the long chained quinoidal structure, then the rings in this chain become less aromatic due to geometric term whereas the ring outside it often becomes even more aromatic than in the parent molecules. The rings in which the charge is localised in a greater degree are usually less aromatic. Variation of the aromatic character of the substituted ring depends on the Hammett-Streitwieser position constants, and *eo ipso* on the charge of CH_2^+ group and the length of the CH_2^+-C bond.

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