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# Separation of the Energetic and Geometric Contributions to the Aromaticity of π-Electron carbocyclics. Part V. Analysis of the Aromatic Character of Aza-Analogues of Benzenoid Hydrocarbons.

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***Abstract.*** Analysis of the aromatic character based on the experimental geometry of 24 aza analogues of 7 benzenoid hydrocarbons led to the conclusion that presence of the nitrogen atom in the ring increases usually it's aromaticity and often increases also aromatic character of the neighbouring rings. Depending on the topological environment the increase of the aromatic character is due either to the decrease of bond length alternation or to to the increase of the mean bond length, or both. Quantitative comparison based on using of HOMA, EN and GEO[1] indices has been carried out.

## Introduction

The aromaticity of heterocyclic π-electron systems has long been a subject of intensive study. A wide collection of Bird's papers[2] mainly present the problem of various monocyclic or bicyclic heteroaromatic systems. Katritzky et al.[3] as well as Jug et al.[4] considered heteroaromatics in their fundamental papers using principal component analysis, and demonstrated the multidimensionality of the aromaticity. Schleyer also used heteroaromatic monocyles in presenting his idea of the dominant role of magnetic susceptibility as a quantitative measure of aromatic character.[5] Our own studies on the separation of aromatic character for carbocycles[1,6-7] and heterocycles[8] showed that by using the experimental bond lengths of these aromatics one can obtain information on the energetic and/or geometric descriptors of aromaticity.

In continuation of our study on the separation of the aromaticity index HOMA[9-10] into energetic and geometric contributions[1,6-7], we have undertaken analysis of similarity and dissimilarity of aza analogues of the benzenoid hydrocarbons. The aromaticity indices HOMA and its components EN and GEO for aza-analogues is compared with the respective values estimated for the geometry of benzenoid hydrocarbons.

## Results and Discussion

In the chart 1-4 are gathered indices of aromaticity HOMA, EN and GEO[1,8] estimated from experimental geometries of the most precise X-ray or neutron diffraction measurements (As=1 and 2)[11] retrieved from the CSD.[11] The indices of aromaticity are calculated by use of formulae presented in part I and IV of this series.[1,8]

Chart 1. Aromaticity indices HOMA, EN and GEO (abbreviated H, E and G) for naphthalene [ I ] and its aza-analogues [1-7]

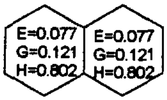
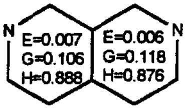
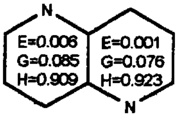
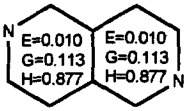
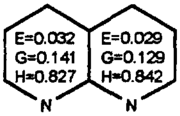
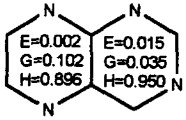
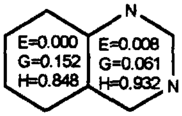
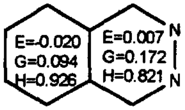
| No | Compound | No | Compound | No | Compound |
|---|---|---|---|---|---|
| I[12] |  | 1[13] |  | 2[14] |  |
| | | 3[14] |  | 4[15] |  |
| | | 5[16] |  | 6[17] |  |
| | | 7[18] |  | | |

Chart 2. Aromaticity indices HOMA, EN and GEO (abbreviated H, E and G) for three containing rings benzenoid hydrocarbons [II-III] and its aza-analogues [8-16].

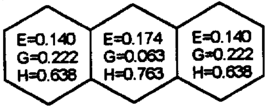
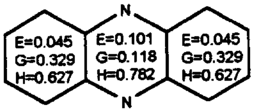
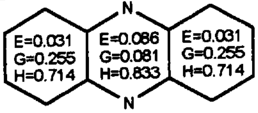
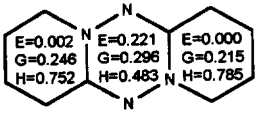
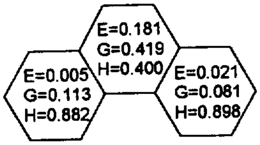
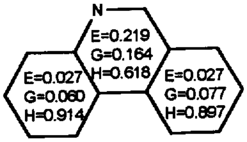
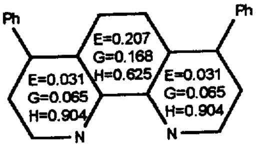
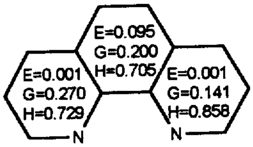
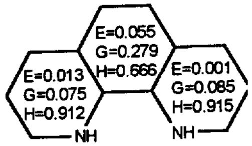
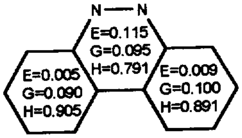
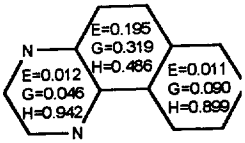
| No | Compound | No | Compound | No | Compound |
|---|---|---|---|---|---|
| II[19] |  | 8[20] |  | 9[21] |  <br>TCNQ COMPLEX |
| 7 | | 10[22] |  | | |
| III[23] |  | 11[24] |  | 12[25] |  |
| | | 13[26] |  <br>TCNQ COMPLEX | 14[27] |  <br>$ClO_4$ |
| | | 15[28] |  | 16[29] |  |

Chart 3. Aromaticity indices HOMA, EN and GEO (abbreviated H, E and G) for four and five containing rings benzenoid hydrocarbons [IV- VII]and its aza-analogues [17-20].

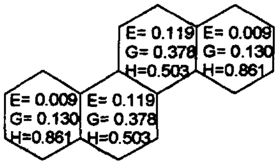
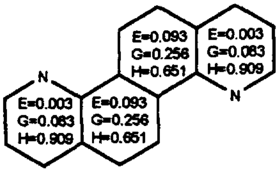
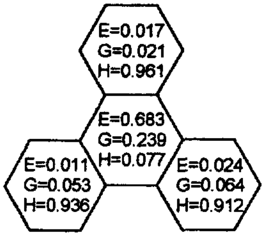
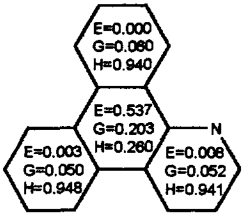
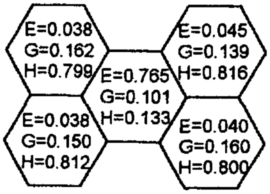
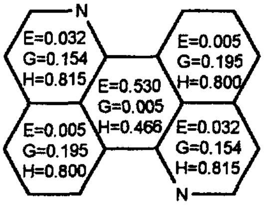
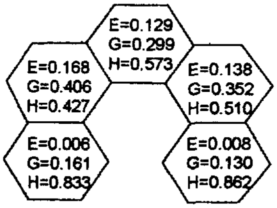
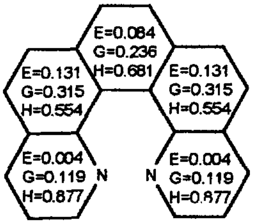
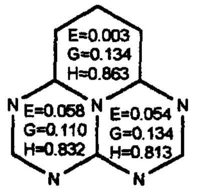
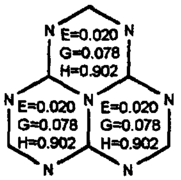
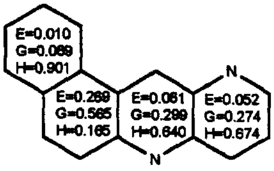
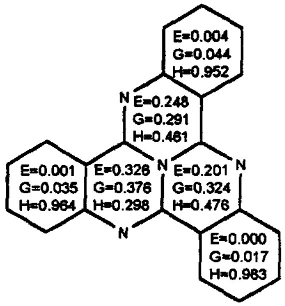
| No | Compound | No | Compound |
|---|---|---|---|
| IV[30] |  | 17[31] |  |
| V[32] |  | 18[33] |  |
| VI[30] |  | 19[34] |  |
| VII[35] |  | 20[36] |  |

Chart 4. Aromaticity indices HOMA, EN and GEO (abbreviated H, E and G) for aza-analogues of benzenoid hydrocarbons [21-24].

| No | Compound | No | Compound |
|---|---|---|---|
| 21[37] |  | 22[38] |  |
| 23[39] |  | 24[40] |  |

Even at the first glimpse it is obvious that aza-analogues of the benzenoid hydrocarbons are usually more aromatic than the parent hydrocarbons. The only exceptions are in cases where two nitrogen atoms form NN bond(s) in monocycles as presented in part IV of the series,[8] where in all cases these kinds of system are less aromatic than benzene. In the case of polycyclic systems this rule does not work so precisely. The other regularity is that an increase in aromatic character appears not only in the ring which contain(s) nitrogen atom(s) but is also often observed in the closest neighbouring rings. The nature of the latter cases depends on the kind of the topological environment of the ring. In the case of so-called "empty" rings in the Clar[41] terminology, the low values of the HOMA index are due to strong dearomatization owing to the energetic terms (elongation of bond lengths). In these cases any increase of aromaticity is due mostly to a decrease in the EN term. Aza analogues of triphenylene (1-azatriphenylene [18]) and perylene (1,7-diazaperylene [19]) are good examples.

The other class of rings are those in which considerable localisation of the π-electron structure occurs, e.g. in the central ring of phenanthrene. In these cases, HOMA has low values due mostly to the large GEO term. In these cases also an increase of aromaticity is mostly due to the decrease of bond length alternation, i.e. to the decrease of the GEO term. Good examples for these effects are aza-analogues of phenantrene (9,10-diazaphenanthrene [15], 1,4-diazaphenanthrene [16]), chrysene (quino(8,7-h)quinoline [17]) and even helicene (1,14-diaza(5)helicene [20]). In the case of phenanthridine [11] and 4,7-diphenyl-1,10-phenanthroline [12] the dearomatization is due to the GEO term as well, but the EN contribution is also very important.

A very interesting finding is observed for phenazine [8] and the phenazine-TCNQ complex [9]. Both independent rings in the heterocyclic π-electron system in the EDA complex are significantly more aromatic than in the parent phenazine. Comparison of the HOMA, EN and GEO indices for the whole moiety is even more striking: 0.719, 0.028, 0.253 for the "free molecule" vs 0.785, 0.023, 0.192 for that in EDA complex with TCNQ. The interpretation may be as follows:[1] as a result of EDA complexation phenazine loses charge of approximately q=0.1 e[42] and becomes positively charged. This partial loss of π-electrons due to intermolecular charge transfer causes an increase of aromaticity which is in line with the Hiberty and Shaik[43] idea of the decisive role of the sigma electron skeleton in determining the averaging of bond lengths in aromatic compounds. This case would be the second experimental evidence for this hypothesis, after that reported for chrysene and its complexes with TCNQ and fluoranil.[30] In both cases[1] the dominant factor in increasing the aromatic character of these π-electron systems is the decrease of the GEO term.

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