

Separation of the Energetic and Geometric Contributions to Aromaticity. 2. Analysis of the Aromatic Character of Benzene Rings in Their Various Topological Environments in the Benzenoid Hydrocarbons. Crystal and Molecular Structure of Coronene

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Statistical analysis of the aromatic character and its geometric and energetic contributions of 167 benzene rings embedded in various topological environments in 26 benzenoid hydrocarbons leads to the following conclusions: the aromatic character of benzene rings with three or fewer fused rings is due mostly to geometric contributions, whereas in other cases energetic contribution is decisive. Aromaticity indices for individual rings (local aromaticity) depend strongly on the kind of topological environment. Terminal rings always exhibit a strong aromatic character, whereas those fused to many rings are often weakly aromatic. The study is based on precisely solved X-ray or neutron crystal structure determination retrieved from Cambridge Structural Database supplemented by our own precise determination of coronene.

Aromaticity is one the most important general concepts for the understanding of organic chemistry.^{1–3} Since it is not a unique physical or chemical property, in the 1960s and 1970s it was agreed^{4–7} that the aromatic character is associated with cyclic π -electron planar systems in which delocalization of π -electrons results in a few typical, partly equivalent, physicochemical features:

- (i) an increase in stability in comparison with the olefinic analogues (resonance energy),
- (ii) averaging of the bond lengths (less bond lengths alternation than in polyenes),
- (iii) the π -electron ring current is induced when the system is exposed to the external magnetic field (typical, "aromatic" proton chemical shifts in NMR spectroscopy).

As a result, various indices of aromaticity have been defined, and many of them could be approximately related to the above three kinds of physicochemical properties. Quite recently it has been shown by use of principal component or factor analyses⁹ to matrices built up of various indices of aromatic character^{10–16} that aromaticity is a multidimensional phenomenon. Unfortunately, the structure of these factors or principal components is available only at the statistical level, i.e., for a group of systems and taking into account a set of indices of aromaticity.

The aim of this paper is to show how different topological environments of rings in benzenoid hydrocarbons are reflected in their aromatic character. Moreover, the changes in aromaticity may be divided into energetic and geometric contributions¹⁷ allowing us to get an insight into how the physicochemical properties of rings depend on the topological embedding. Additionally, we present a newly solved

structure of coronene, for which only gas electron diffraction geometry has been known so far.¹⁸

RESULTS OF X-RAY STRUCTURE DETERMINATION

Single-crystal X-ray diffraction measurement was carried out using a KUMA diffractometer with graphite monochromatic Cu K α radiation. The data were collected at room temperature using ω -2 θ scan techniques. The structure was solved in $P2_1/n$ space group (with unit cell dimensions $a = 10.122(2)$ Å, $b = 4.694(1)$ Å, $c = 15.718(3)$ Å, $\beta = 106.02(3)^\circ$ and $Z = 2$) using multiresolution direct methods (SIR92)¹⁹ and full matrix least-squares refinement (SHELX93),²⁰ to obtain the final agreement factor $R = 0.0554$ for 1483 collected reflections. Table 1 presents structural parameters for the compound whereas the numbering scheme is presented in Figure 1. Table 2 presents atomic coordinates for the compound.

SEPARATION OF THE AROMATICITY INDEX HOMA INTO ENERGETIC AND GEOMETRIC CONTRIBUTIONS¹⁷

The HOMA index (abbreviation from Harmonic Oscillator Measure of Aromaticity) was defined:^{21,22}

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum [R_{\text{opt}} - R_i]^2 \quad (1)$$

where n is the number of bonds taken into summation and α is an empirical constant fixed in the way to get $\text{HOMA} = 0$ for the Kekulé structure of the typical aromatic system, and equal to 1 for the system with all bonds equal to the optimal value R_{opt} . For CC bonds $\alpha = 257.7$ Å and $R_{\text{opt}} = 1.388$ Å. The minuend in (1) represents simply the dearomatization term since it describes a decrease in the aromatic character of the system due to the differences of bond lengths from the optimal value R_{opt} . This term however may be

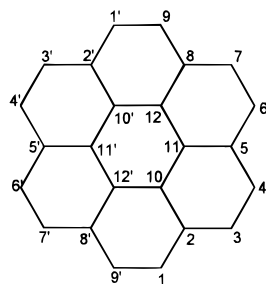
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[®] Abstract published in *Advance ACS Abstracts*, September 1, 1996.

Table 1. Bond Lengths [Å] and Angles [deg] for Coronene^a

| | | | |
|-------------------|----------|--------------------|----------|
| C(1)–C(9') | 1.355(3) | C(1)–C(2)–C(3) | 123.0(2) |
| C(1)–C(2) | 1.424(3) | C(2)–C(3)–C(4) | 121.4(2) |
| C(2)–C(3) | 1.416(3) | C(3)–C(4)–C(5) | 121.2(2) |
| C(2)–C(10) | 1.418(2) | C(4)–C(5)–C(11) | 118.7(2) |
| C(3)–C(4) | 1.367(3) | C(5)–C(11)–C(10) | 120.2(2) |
| C(1)–C(5) | 1.416(3) | C(2)–C(10)–C(11) | 119.6(2) |
| C(5)–C(6) | 1.423(3) | C(3)–C(2)–C(10) | 118.8(2) |
| C(5)–C(11) | 1.414(2) | C(4)–C(5)–C(6) | 122.8(2) |
| C(6)–C(7) | 1.350(3) | C(5)–C(6)–C(7) | 121.6(2) |
| C(7)–C(8) | 1.422(3) | C(6)–C(7)–C(8) | 121.6(2) |
| C(8)–C(9) | 1.422(3) | C(7)–C(8)–C(12) | 118.4(2) |
| C(8)–C(12) | 1.416(2) | C(8)–C(12)–C(11) | 120.1(2) |
| C(1')–C(9) | 1.355(3) | C(5)–C(11)–C(12) | 119.9(2) |
| C(10)–C(12') | 1.420(3) | C(6)–C(5)–C(11) | 118.5(2) |
| C(10)–C(11) | 1.426(2) | C(7)–C(8)–C(9) | 123.0(2) |
| C(11)–C(12) | 1.427(2) | C(1')–C(9)–C(8) | 121.3(2) |
| C(12)–C(10') | 1.420(3) | C(8)–C(12)–C(10') | 120.0(2) |
| | | C(9)–C(8)–C(12) | 118.6(2) |
| C(2)–C(1)–C(9') | 121.6(2) | C(11)–C(10)–C(12) | 120.1(2) |
| C(1)–C(2)–C(10) | 118.3(2) | C(10)–C(11)–C(12) | 119.9(2) |
| C(2)–C(10)–C(12') | 120.2(2) | C(11)–C(12)–C(10') | 120.0(2) |

^a With esd's in parentheses.**Figure 1.** The atom numbering in coronene.**Table 2.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters U_{eq} ($\text{\AA}^2 \times 10^3$)^a

| atom | x | y | z | U_{eq} |
|-------|---------|---------|----------|-----------------|
| C(1) | 7394(2) | 1575(4) | 8628(1) | 65(1) |
| C(2) | 6068(2) | 2444(4) | 8674(1) | 54(1) |
| C(3) | 5260(2) | 4477(4) | 8090(1) | 63(1) |
| C(4) | 3993(2) | 5273(4) | 8156(1) | 61(1) |
| C(5) | 3428(2) | 4065(4) | 8804(1) | 53(1) |
| C(6) | 2102(2) | 4798(4) | 8881(1) | 62(1) |
| C(7) | 1587(2) | 3615(4) | 9505(1) | 64(1) |
| C(8) | 2353(2) | 1603(4) | 10124(1) | 54(1) |
| C(9) | 1855(2) | 367(4) | 10802(1) | 65(1) |
| C(10) | 5540(2) | 1222(2) | 9337(1) | 44(1) |
| C(11) | 4212(1) | 2038(3) | 9398(1) | 43(1) |
| C(12) | 3672(2) | 803(3) | 10062(1) | 44(1) |

^a U_{eq} is defined as the one-third of the trace of the orthogonalized U_{ij} tensor.divided into two terms:¹⁷

$$\frac{\alpha}{n} \sum [R_{\text{opt}} - R_i]^2 = \alpha(R_{\text{opt}} - R_{\text{av}})^2 + \frac{\alpha}{n} \sum (R_{\text{av}} - R_i)^2 \quad (2)$$

where R_{av} is the mean bond length of all bonds taken into analysis, $i = 1, 2, \dots, n$. The first term after the equality mark depends on the mean value of bond lengths in the system under study, and hence it may be approximately related to the energetic contribution to the dearomatization term,¹⁷ hereafter abbreviated EN. The greater is this term the smaller is the resonance energy of the ring in question. The other term represents chiefly the part of dearomatization due to alternation of bond lengths, and therefore attributed to the geometric contribution to the dearomatization,¹⁷ hereafter

abbreviated GEO. Its increase means the increase of alternation of bond lengths.

It has already been shown,¹⁷ that EN terms correlated well with typical energetic indices of aromaticity, such as bond energy of the ring,^{15,23} whereas GEO terms correlated well with typical geometric indices, such as Bird's I_6 ²⁴ and BAC.^{15,25} Moreover, it was also shown that EN and GEO are not mutually correlated. In view of the above model, HOMA index should be redefined.¹⁷ In the HOMA model R_{opt} is the reference bond length for which EN = 0 and for $R_{\text{av}} > R_{\text{opt}}$ EN is by definition a positive quantity. Then for $R_{\text{av}} < R_{\text{opt}}$ the EN term must be taken with a negative sign. In this way we are able to take into consideration the rings for which the mean bond length R_{av} is lower than R_{opt} and which exhibit an energy increase. Thus in terms of energetic criteria of aromaticity, they represent a stronger aromatic character. In consequence we have to reformulate the definition of HOMA into

$$\text{HOMA} = 1 - \text{EN} - \text{GEO} \quad (3)$$

where

$$\text{GEO} = \frac{\alpha}{n} \sum (R_{\text{av}} - R_i)^2 \quad (4)$$

and

$$\text{EN} = \alpha(R_{\text{opt}} - R_{\text{av}})^2 \quad \text{for } R_{\text{av}} > R_{\text{opt}} \quad (5a)$$

$$\text{EN} = -\alpha(R_{\text{opt}} - R_{\text{av}})^2 \quad \text{for } R_{\text{av}} < R_{\text{opt}} \quad (5b)$$

The above-presented reformulation is important for this kind of rings which have the mean bond length shorter than R_{opt} . In such cases EN terms become negative and HOMA may become larger than 1.0.

RESULTS AND DISCUSSION

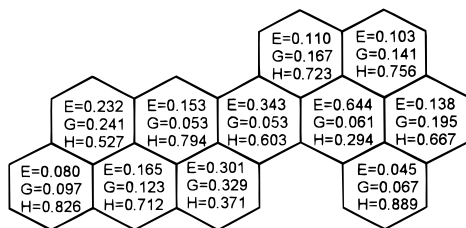
The above-presented procedure has been applied to molecular geometry of 26 benzenoid hydrocarbons, listed in Chart 1, for which the crystal structures retrieved from CSD have been solved with the highest precision, i.e., with flag AS = 1.^{26,27} The total number of benzene rings taken into analysis is 167. In many cases the formally equivalent rings have different values of aromaticity indices. This is due to the obvious fact that if the symmetric molecule does not occupy any special position in the crystal unit cell, then it need not possess any symmetry properties, since the particular "equivalent" geometrical parameters are measured with different errors. Hence we are able to estimate for this sample the mean difference between the aromaticity indices describing formally equivalent rings. They are 0.050 for HOMA, 0.048 for GEO, and 0.017 for EN. These quantities may be used further as the approximate measures of precision for estimates of HOMA, GEO, and EN terms, respectively.

Application of EN and GEO terms to benzene rings embedded in various topological environments is presented in Chart 1 which shows the values of HOMA, GEO, and EN hereafter abbreviated H, G, and E, calculated from experimental geometry.

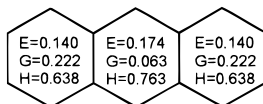
Looking at these data it is striking how strongly the aromatic character of six member rings depends on the kind of topological environment. Even in the same molecule!

Chart 1

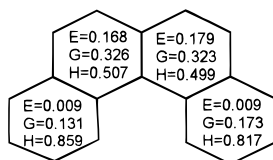
I. ANTHRABENZONAPHTHOPENTACENE



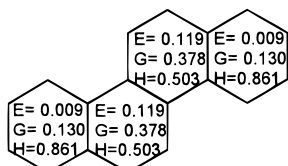
II. ANTHRACENE



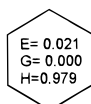
III. BENZOPHENANTHRENE



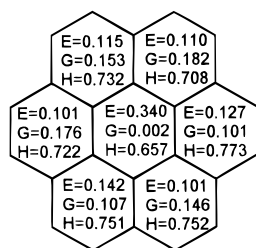
IV. CHRYSENE



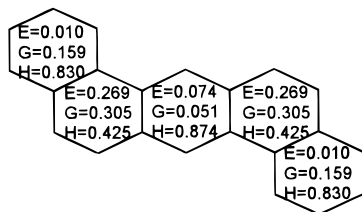
V. BENZENE



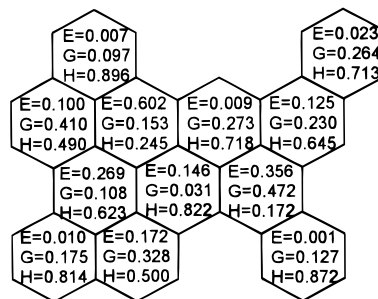
VI. CORONENE



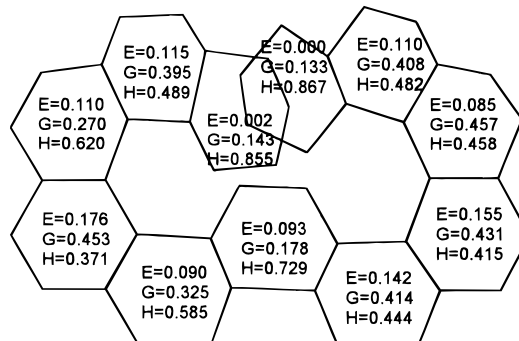
VII. DIBENZOANTHRACENE



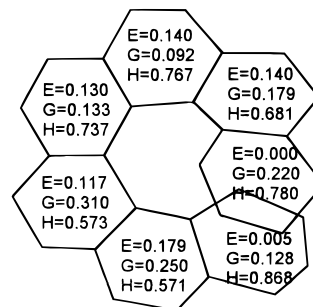
VIII. DIBENZONAPHTHOPYRANTHRENE



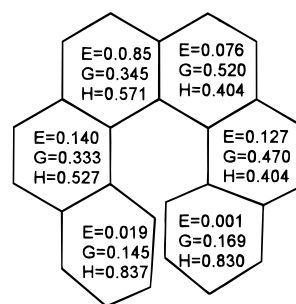
IX. DIPHENANTHROPICENE



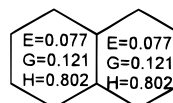
X. HEPTAHELICENE



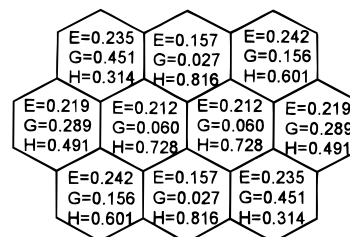
XI. HEXAHELICENE



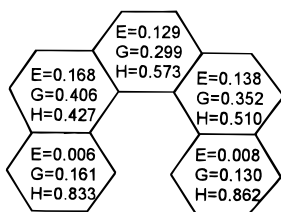
XII. NAPHTHALENE



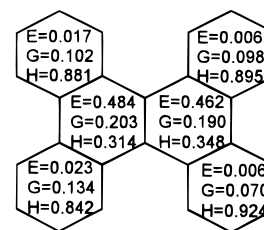
XIII. OVALENE



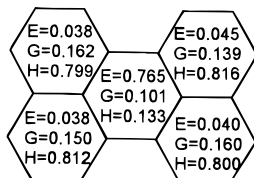
XIV. PENTAHelicene



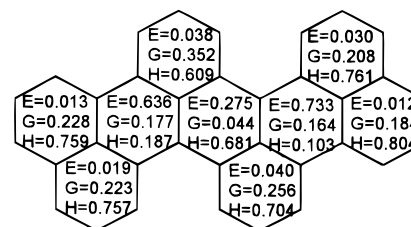
XXII. TETRABENZONAPHTHALENE



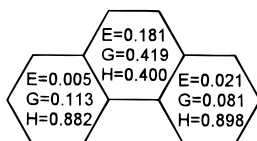
XV. PERYLENE



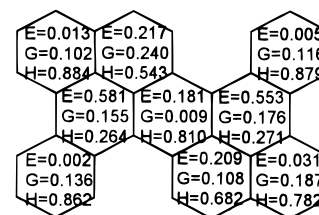
XXIII. TETRABENZOPENTACENE



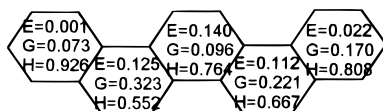
XVI. PHENANTHRENE



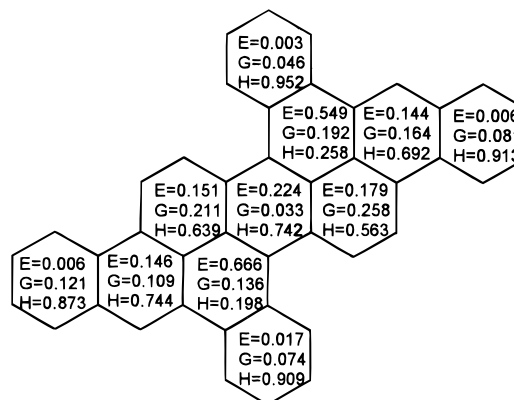
XXIV. TETRABENZOPERYLENE



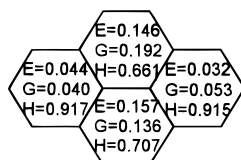
XVII. PICENE



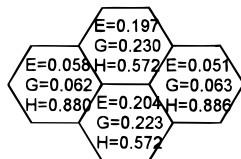
XXV. TRIBENZOPHENANTHRAPENTAPHENE



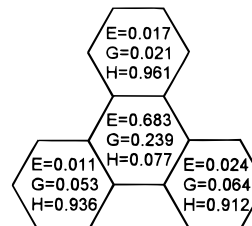
XVIII. PYRENE (neutron diffraction)



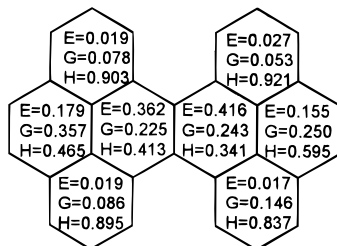
XIX. PYRENE (X-ray diffraction)



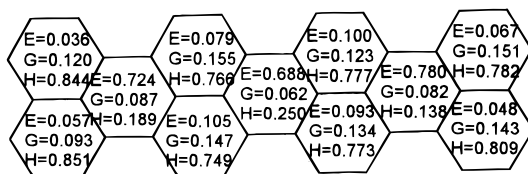
XXVI. TRIPHENYLENE



XX. PYRENOPYRENE



XXI. QUATERRYLENE



HOMA values vary from 0.077 for the central ring in triphenylene to 0.961 for its terminal rings. When we look

at the series of benzenoid hydrocarbons of Chart 1 we find that the GEO terms are also very changeable: from 0.002

Chart 2

I group



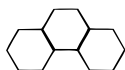
| Variable: | HOMA | H_En | H_Geo |
|---------------------|--------|---------|--------|
| Sample size | 39. | 39. | 39. |
| Average | 0.855 | 0.0213 | 0.124 |
| Median | 0.862 | 0.00928 | 0.128 |
| Lowerquartile | 0.830 | 0.00522 | 0.081 |
| Upperquartile | 0.898 | 0.0209 | 0.159 |
| Interquartile range | 0.0677 | 0.0156 | 0.0782 |

II group



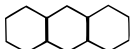
| variable: | HOMA | H_En | H_Geo |
|---------------------|--------|--------|--------|
| Sample size | 28. | 28. | 28. |
| Average | 0.827 | 0.0346 | 0.138 |
| Median | 0.821 | 0.0361 | 0.141 |
| Lowerquartile | 0.790 | 0.0190 | 0.0820 |
| Upperquartile | 0.887 | 0.0447 | 0.180 |
| Interquartile range | 0.0971 | 0.0257 | 0.0978 |

III group



| variable: | HOMA | H_En | H_Geo |
|---------------------|-------|--------|-------|
| Sample size | 32. | 32. | 32. |
| Average | 0.529 | 0.144 | 0.327 |
| Median | 0.503 | 0.134 | 0.329 |
| Lowerquartile | 0.426 | 0.114 | 0.284 |
| Upperquartile | 0.579 | 0.168 | 0.407 |
| Interquartile range | 0.153 | 0.0539 | 0.123 |

IV group



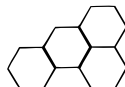
| variable: | HOMA | H_En | H_Geo |
|---------------------|-------|--------|--------|
| Sample size | 2. | 2. | 2. |
| Average | 0.818 | 0.124 | 0.0574 |
| Median | 0.818 | 0.124 | 0.0574 |
| Lowerquartile | 0.763 | 0.0745 | 0.0517 |
| Upperquartile | 0.874 | 0.174 | 0.0631 |
| Interquartile range | 0.111 | 0.0997 | 0.0113 |

V group



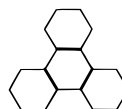
| variable: | HOMA | H_En | H_Geo |
|---------------------|-------|-------|-------|
| Sample size | 33. | 33. | 33. |
| Average | 0.617 | 0.164 | 0.219 |
| Median | 0.639 | 0.155 | 0.192 |
| Lowerquartile | 0.527 | 0.110 | 0.147 |
| Upperquartile | 0.732 | 0.217 | 0.258 |
| Interquartile range | 0.205 | 0.107 | 0.111 |

VI group



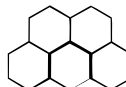
| variable: | HOMA | H_En | H_Geo |
|---------------------|-------|-------|--------|
| Sample size | 5. | 5. | 5. |
| Average | 0.490 | 0.287 | 0.222 |
| Median | 0.645 | 0.146 | 0.164 |
| Lowerquartile | 0.198 | 0.144 | 0.136 |
| Upperquartile | 0.692 | 0.356 | 0.230 |
| Interquartile range | 0.494 | 0.212 | 0.0940 |

VII group



| variable: | HOMA | H_En | H_Geo |
|---------------------|--------|-------|--------|
| Sample size | 3. | 3. | 3. |
| Average | 0.246 | 0.543 | 0.211 |
| Median | 0.314 | 0.484 | 0.202 |
| Lowerquartile | 0.0771 | 0.462 | 0.190 |
| Upperquartile | 0.348 | 0.683 | 0.239 |
| Interquartile range | 0.271 | 0.222 | 0.0490 |

VIII group



| variable: | HOMA | H_En | H_Geo |
|---------------------|--------|---------|--------|
| Sample size | 5. | 5. | 5. |
| Average | 0.771 | 0.128 | 0.101 |
| Median | 0.794 | 0.157 | 0.0531 |
| Lowerquartile | 0.718 | 0.153 | 0.0269 |
| Upperquartile | 0.816 | 0.157 | 0.123 |
| Interquartile range | 0.0986 | 0.00421 | 0.0962 |

IX group



| variable: | HOMA | H_En | H_Geo |
|---------------------|--------|-------|--------|
| Sample size | 5. | 5. | 5. |
| Average | 0.309 | 0.492 | 0.198 |
| Median | 0.271 | 0.549 | 0.192 |
| Lowerquartile | 0.264 | 0.416 | 0.176 |
| Upperquartile | 0.341 | 0.553 | 0.225 |
| Interquartile range | 0.0777 | 0.137 | 0.0485 |

X group



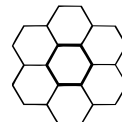
| variable: | HOMA | H_En | H_Geo |
|---------------------|-------|-------|--------|
| Sample size | 10. | 10. | 10. |
| Average | 0.384 | 0.535 | 0.0814 |
| Median | 0.219 | 0.662 | 0.0722 |
| Lowerquartile | 0.138 | 0.275 | 0.0436 |
| Upperquartile | 0.681 | 0.733 | 0.101 |
| Interquartile range | 0.543 | 0.458 | 0.0578 |

XI group



| variable: | HOMA | H_En | H_Geo |
|---------------------|-------|-------|--------|
| Sample size | 4. | 4. | 4. |
| Average | 0.496 | 0.415 | 0.0884 |
| Median | 0.459 | 0.436 | 0.0846 |
| Lowerquartile | 0.270 | 0.208 | 0.0463 |
| Upperquartile | 0.723 | 0.623 | 0.131 |
| Interquartile range | 0.453 | 0.415 | 0.0842 |

XII group



| variable: | HOMA | H_En | H_Geo |
|---------------------|--------|-------|---------|
| Sample size | 3. | 3. | 3. |
| Average | 0.705 | 0.255 | 0.0408 |
| Median | 0.728 | 0.212 | 0.0599 |
| Lowerquartile | 0.657 | 0.212 | 0.00246 |
| Upperquartile | 0.728 | 0.340 | 0.0599 |
| Interquartile range | 0.0710 | 0.128 | 0.0575 |

for internal rings in coronene-like structures to 0.419 for central rings in phenanthrene-type arrangements. The EN terms varies even more, from 0.001 for the terminal ring in

hexahelicene (XI) to 0.77 for central rings in perylene type structures. While looking at the EN and GEO terms it is apparent that the lower aromatic character, i.e., the HOMA

value of the individual ring, may have two reasons:

- (i) It may be due to the alternation of bond lengths, and then the GEO term is high. The typical cases are central rings of benzophenanthrene (III), chrysene, (IV), phenanthrene (XVI), or helicenes (X, XI).
- (ii) The other possibility is when the bond lengths in the ring are not too strongly alternated, but they are relatively long. Then the EN term becomes high and decides about lower aromaticity of the ring in question. Typical examples are central rings of coronene [VI], triphenylene (XXVI), and perylene (XV) which represent numerically the Clar concept of empty rings.²⁸

Analysis of all data presented in Chart 1 shows that aromaticity parameters, HOMA, GEO, and EN, vary considerably depending on the topological environment of the ring in question. The rings may be selected in the way to gather together those which have the same closest topological environment. In order to have a closer look at these variations we apply statistical descriptors as the mean value and the median for the central tendency of the distribution and interquartile range for the dispersion.²⁹ Chart 2 shows how these parameters depend on the kind of ring. The average or median characterizes the central tendency of the aromaticity index describing a given class of the rings in question depending on the effect of topological environment. The interquartile range shows the sensitivity of these rings of the same closest topological environment to further arrangement of rings. The following rough conclusions can be drawn:

- (i) The terminal rings (group I) are highly aromatic; dearomatization results mainly from the GEO term. The same is true of the rings of group II type.
- (ii) The angularly condensed rings (central rings in phenanthrene type, group III and pyrene type, group V) have low aromatic character, with stronger dearomatization resulting from the GEO term.
- (iii) For the rings which may be classified as belonging to the mixed group, i.e., to both the angularly condensed rings (like group III) and the linearly condensed rings (as group IV) dearomatization is due to GEO and EN at the same level (groups VI and VIII). However, this conclusion can not be treated as entirely valid, as the sample was too small.
- (iv) In the case of more than three rings condensed to the ring in question (except group VIII) dearomatization results from the energetic term and the aromatic character is usually weak.

Another important statistical descriptor of the distribution is the interquartile range, the measure of its dispersion used for distributions of unknown nature (variance may be used only for normally distributed sets of data²⁹). Only a few groups are sufficiently numerous to be analyzed. The terminal rings exhibit very low variation of all indices; nevertheless the variation of GEO is almost five times larger than that of EN. A slightly larger variation is observed for group II in which the variation of the GEO term is about four times larger than of the EN term. Much more variable are the indices for central rings of angular polyacene arrangement (group III); however, the GEO term varies twice as much as EN. In all these groups the variability of the aromatic character is mostly due to the geometric term, and

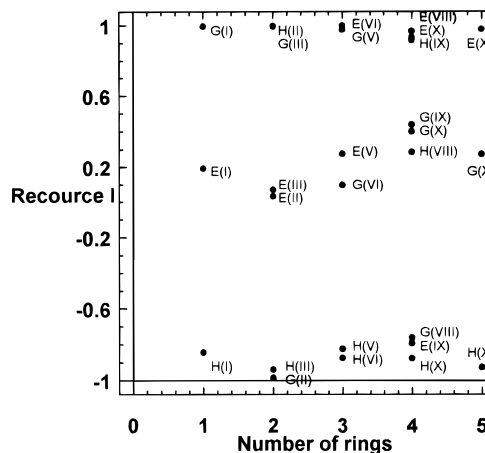


Figure 2. Plot of resources of the first factor against the number of rings fused to the ring in question. Numbers in parentheses stand for numbers of groups to which belongs to the given ring.

this term also exhibits the greatest interquartile ranges: The other groups are much less numerous, but it seems reasonable to note that if more benzene rings are fused to the ring in question, then its aromaticity decreases and energetic terms become both stronger and more varied. These conclusions are more quantitatively supported by factor analysis.⁹ If it is applied to HOMA, GEO, and EN indices for each of the groups which contain more than three rings, then due to constraints in eq 3 one obtains two independent factors. The first factor usually describes 65.7–91.9% of the total variance. Important information results from the dependence of the composition of this factor on the topological environment of the ring in question, i.e., the group in Chart 2. Figure 2 presents the graph in which the components of a given factor in H(*i*), G(*i*), and E(*i*) are plotted against the number of rings fused to the given ring (*i* stands here for the number of groups in Chart 2).

Due to the form of relations between HOMA, EN, and GEO (eq 3) at least one component has to be negative. Nevertheless the most important information is which of the two terms, GEO or EN, is a counterpart of HOMA. This counterpart is the most important contribution in determining the HOMA value. In the case where one or two rings are fused to the ring in question, independently of the way in which the fusion is realized, the HOMA and GEO terms are represented by the same factor. In the case of three fused rings the result is ambient: in group V HOMA and GEO are in the same factor, whereas in group VI EN and HOMA are represented in the first factor. In all other cases the HOMA and EN terms are mostly represented in the first factor (except group VIII, which, however, needs more data to be decisive).

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