

Enumeration of Kekulé Structures in Defective Patterns of Rectangular Graphite

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Keywords The number of Kekulé structures is an indicator of the aromatic character of the underlying conjugated systems polybenzenoid. Graphite is a polybenzenoid. In this paper, a new algorithm is proposed for determining the number of Kekulé structures in rectangular graphite and its incomplete and defective variants. Defective patterns model functionalized structures. Moderate functionalization aromatic character will cause a slight increase in the aromatic properties of the underlying patterns. aromaticity

INTRODUCTION

Graphite is a polybenzenoid and is a highly aromatic system. The number of Kekulé structures of polybenzenoids, K , is closely related to the concept of the aromatic character of these structures. The greater K , the more aromatic is the underlying structure. Aromatic molecules, though unsaturated, cannot be readily saturated by using addition reactions, though they can enter substitution reactions. Substitution reactions are infeasible in graphite. No experimental method providing a quantitative measure of »aromaticity« has been devised so far, partly because of the vagueness of the concept. A review on aromaticity and ring currents was written by Gomes and Mallion.¹ The extension of the concept of aromaticity to three-dimensional polyhedral boranes and related molecules was reviewed by King.²

Enumeration of Kekulé structures^{3,4} and of conjugated circuits^{5,6} is an important topic in chemical graph theory. Randić⁷ wrote an extensive review on aromaticity of polycyclic conjugated hydrocarbons. How impor-

tant this subject is can be demonstrated by the fact that more than one thousand (!) references were cited in Randić's compilation. There are currently three approaches that can be used to obtain K : (i) Constructive enumeration;⁸ (ii) Kasteleyn's formula;⁹ and (iii) Various algorithms and formulas for special classes of structures. Details concerning the enumeration by using algorithms and formulas were reviewed by Trinajstić¹⁰ and by Cyvin and Gutman in the 1980s.³ Methods of enumerating Kekulé structures of rectangle-shaped benzenoids were discussed by Rongsi *et al.*¹¹ General explicit formulas were obtained by Klein *et al.*¹² for benzenoid polymers with armchair edges. It has to be noted that the semi-empirical graph theoretical approaches used to estimate the aromatic character of conjugated molecules, so the enumeration of Kekulé structures and of conjugated circuits in most cases cannot be replaced by quantum chemical calculations because the size of these structures is prohibitively large.

Carbon nanotubes (CNTs) are a special subclass of benzenoids, in which the graphite sheets are rolled up

along certain vectors. The properties of CNTs can be approximated by taking graphite into account.¹³ This assumption remains valid if CNTs are functionalized: functionalization may affect the π -electron system in the molecules. Therefore, incomplete (see next section) and defective (see next section) hexagon sheets might account adequately for the properties of the functionalized CNTs.

The aim of this work was to devise an effective algorithm for the enumeration of Kekulé structures in rectangular and also in incomplete, defective graphite sheets. It was found that moderate functionalization may slightly increase the aromatic character.

ALGORITHM

Figure 1a depicts a rectangular structure containing five »rows« and three »columns«, and incomplete rectangular structures with a double bond (Figure 1b) and a single bond (Figure 1c) at the specified site. A specified edge must be either a double bond or a single bond. If the bond is a double bond (Figure 1b), the neighbouring bonds must be single bonds and the number of Kekulé structures is equal to the number of Kekulé structures of an incomplete pattern, containing one hexagon less in this case. Similarly, if the specified bond is a single bond (Figure 1c), then the bonds designated by numerals 1, must be double bonds. If the bonds designated by 1 are double bonds, then the bonds designated by 2 must also be double bonds, *etc.* Finally, if bonds 1–6 are double bonds, then all neighbouring bonds must be single bonds, including those which were dissected by a thin line. This means that we can express the number of Kekulé structures in terms of the number of Kekulé structures of two reduced incomplete structures. In algebraic form:

$$(3)_{5,2} = (2)_{5,2} + (2)_{5,1} \quad (1)$$

where $(3)_{5,2}$ denotes the number of Kekulé structures in an incomplete structure consisting of five rows, two columns and containing three additional hexagons. Eq. (1) can easily be generalized:

$$(k)_{m,n} = (k-1)_{m,n} + (m-k)_{m,n-1} \quad (2)$$

The position of additional hexagons needs some more explanation. Let us denote columns by letters »u« (for upper) and »l« (for lower); the first structure in Figure 1 contains two »u« columns and one »l« column. From this explanation, the meaning of the letters is clear: in a complete pattern, the topmost hexagon is higher than the topmost hexagon in the »l« column. If the additional hexagons belong to a »u« column, they must be attached to the upper part of the original struc-

ture (G); if the additional hexagons belong to a »l« column they must be attached to the bottom of G.

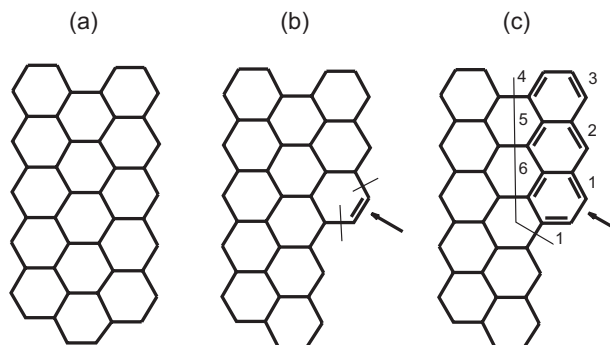


Figure 1. Rectangular graphite (a), and incomplete rectangular structures with a double bond (b) and a single bond (c) at the specified (arrow) site. Numbers in (c) indicate the order of inference: if i is a double bond, then $i+1$ must also be a double bond. Thin lines dissecting an edge indicate that it is a single bond.

The procedure of enumeration is illustrated in Figure 2. The process starts with the first complete column from top to bottom in »u« columns (and from bottom to top in »l« columns). Write number »1« on top of the first column and proceed from top to bottom by attaching consecutive numbers to the next unlabeled hexagon. If the pattern contains just a single column (*i.e.*, it is a polyacene), the enumeration will be in accordance with the rule that $K_{\text{polyacene}} = h + 1$, where h denotes the number of hexagons. (Note that the ring labelling in the benzenoid was first used by Gordon and Davison.¹⁴) Write the last number (in our example 6) below the next column, which is an »l« column. Now add this and the number in the second hexagon from the bot-

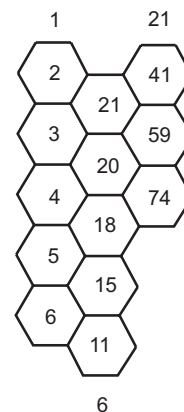


Figure 2. Enumeration scheme for an incomplete rectangular pattern. Counting starts from the top of the left column; the numbers in hexagons indicate the total number of Kekulé structures up to that hexagon.

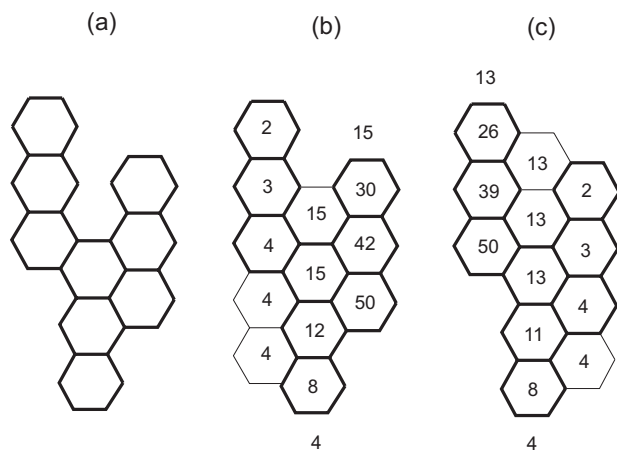


Figure 3. A defective rectangular pattern (a) and the enumeration schemes used to obtain the Kekulé count. (b) Enumeration starts from the top of the left hand column. (c) Enumeration starts from the top of the right hand column.

tom of the previous »u« column (in our example 5) and write it into the first hexagon from the bottom. Continue this procedure until the last hexagon has been considered and write the last number on the top of the next »u« column, and continue the process. The procedure will eventually yield $K = 74$, which is the total number of Kekulé structures in the incomplete pattern depicted in Figure 2. Continuation of this procedure will yield $K = 91$ for the structure depicted in Figure 1a.

Figure 3a depicts a defective pattern, having more than one incomplete column. First the pattern must be completed by »virtual hexagons« indicated by thin lines (Figures 3b and 3c). Figure 3b illustrates the enumeration procedure starting at the left column, while Figure 3c illustrates the procedure starting at the right column of the defective pattern. In both cases, we obtain an identical result ($K = 50$). Virtual hexagons should not change the type of the column with respect to the subsequent column to be considered. This rule was observed in Figure 3c: the second column is an »l« column with respect to the left hand column. With these amendments, the enumeration procedure is similar to that shown in the previous section.

The validity of this procedure can be proved as follows:

- (i) The number of virtual hexagons plus one ($2 + 1 = 3$) will indicate the number by which the count in the upper left part (4) has to be multiplied (Figure 4a). The multiplication factor is equal to the number of Kekulé structures in the detached lower right part.
- (ii) The specified edge (indicated by a bold arrow) of the connecting hexagon can again be a double bond (Figure 4b) or a single bond (Figure 4c). If it is a double bond, then the opposite bond in the same hexagon must be a single bond (denoted by a thin arrow) and so the contribution is equal to the number

obtained for the previous hexagon (in our case 12) or formally $(k-1)_{m,n}$.

- (iii) If the specified bond is a single bond (Figure 4c), the lower column has just a single Kekulé structure, while the free part of the upper column has 3, or formally $(m-k)_{m,n-1}$. The sum of these contributions is equal to K .
- (iv) The enumeration proceeds in the same way as with other incomplete patterns. Figure 5 illustrates a case in which the upper left part contains more than one column contributing $(m-k)_{m,n-1}$. The argumentation remains valid for any rectangular defective pattern made up by alternating »u« and »l« columns.

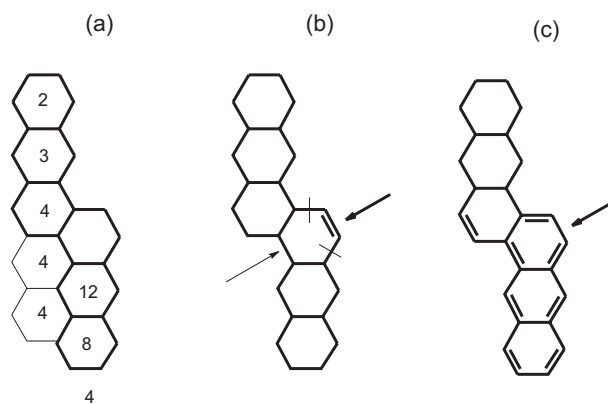


Figure 4. Enumeration of isolated sub-patterns and the effect of bridge-hexagon. Bold arrows point to an edge, the type of which has been predefined. The thin arrow points to an edge that must be a single bond.

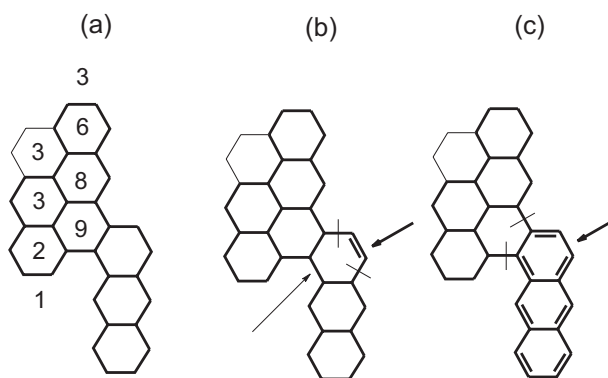


Figure 5. Extension of the enumeration scheme.

DISCUSSION

In the series of rectangular graphite sheets patterns made up of three columns and n rows, the Kekulé count grows polynomially in terms of the number of rows (Figure 6), and as a consequence $\ln K/\#_C$ (and $\log_2 K/h$) converges to zero. This conclusion is in accordance with that obtained for the reactivity of zigzag boundaries,¹⁷ whereas it is in

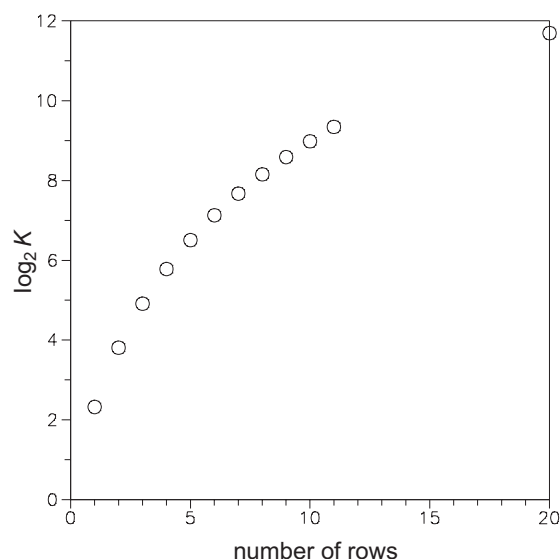


Figure 6. $\log_2 K$ in terms of the number of rows (n) in n by 3, rectangular patterns.

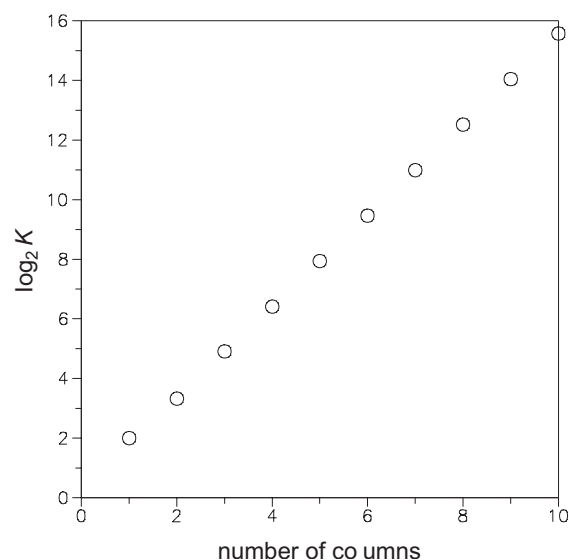


Figure 7. $\log_2 K$ in terms of the number of columns (n) in 3 by n , rectangular patterns.

contrast to that observed in the series made up of three rows and n columns, in which K grows exponentially in terms of n (Figure 7), meaning that armchair boundaries are less reactive than their zigzag counterparts.

The present method of enumeration might be viewed as a sort of generalization of that of Gordon and Davison for cata-condensed chains.¹⁴ The present method allows to take into account peri-condensed systems, while the Gordon-Davison method is capable of dealing with more general cata-fused chains. (A different extension of the Gordon-Davison method allows the treatment of all cata-condensed benzenoids with arbitrary branching.¹⁵)

Incomplete and defective graphite patterns were assumed to model the functionalized graphite sheets. The chemical formulas of the patterns depicted in Figures 1a, 2, and 3a are $C_{46}H_{18}$, $C_{42}H_{18}$, and $C_{36}H_{20}$, respectively. Functionalization means that the conjugated electron system is disrupted by addition of electrophilic atoms, functional groups, or molecules. $C_{36}H_{20}$ represents a functionalized structure. Table I lists the main results; aromaticity was taken into account by using the »Kekulé index«¹⁶ $k = \log_2 K/h$, where \log_2 indicates that the logarithm is to the base 2. Aromaticity of benzene is equal to 1 in this scheme. Several variants^{16,17,18} of the Kekulé index are known; one of these¹⁶ expresses the resonance

energy/electron (REPE) in terms of the Kekulé counts $Re = 1.185 \times \ln K/\#_C$, where $\#_C$ denotes the number of carbon atoms in the structure. The Kekulé index and the REPE should preferably be used in connection with benzenoids only. For other species containing pentagons, heptagons, etc. (like buckminsterfullerene) these formulas may overestimate the resonance energy, and therefore in these cases the more adequate conjugated circuit model should be used.¹⁹

In this approach, $(REPE)_{benzene} = 0.137$ eV, while $(REPE)_{buckminsterfullerene} = 0.186$ eV.²⁰ It has to be noted that the resonance energy of (1,1) CNTs consisting of ten naphthalene units²¹ is equal to $(REPE)_{CNT} = 0.270$ eV, while the corresponding value of the Kekulé index as calculated from the Kekulé count¹³ is $k_{CNT} = 0.740$.

As can be seen, »functionalization« slightly increases aromaticity in rectangular graphite sheets. This effect is mainly due to the increase of the number of peripheral C–C bonds, which encompasses the (relative) increase in the logarithm of the Kekulé count, even if the absolute value of $\ln K$ decreases. According to the present calculations of the values of REPE, the aromatic character of rectangular patterns is slightly less than in benzene. How functionalization affects carbon CNTs remains to be investigated.

TABLE I. Relationship between functionalization and aromaticity

Molecule	Number of hexagons (h)	Number of Kekulé structures (K)	$k = \log_2 K/h$ (Ref. 3)	REPE = $1.185 \times \ln K/\#_C$ (Ref. 13)
$C_{46}H_{18}$ (Fig. 1a)	15	91	0.434	0.116
$C_{42}H_{18}$ (Fig. 2)	13	74	0.478	0.121
$C_{36}H_{20}$ (Fig. 3a)	9	50	0.627	0.129

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REFERENCES

1. J. A. N. F. Gomes and R. B. Mallion, *Chem. Rev.* **101** (2001) 1349–1383.
2. R. B. King, *Chem. Rev.* **101** (2001) 1119–1152.
3. S. J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer Verlag, Berlin, 1988.
4. D. Vukičević, H. W. Kroto, and M. Randić, *Croat. Chem. Acta* **78** (2005) 223–234.
5. M. Randić, *Chem. Phys. Lett.* **38** (1976) 68–70.
6. S. Nikolić, N. Trinajstić, and D. J. Klein, *Comput. Chem.* **14** (1990) 313–322.
7. M. Randić, *Chem. Rev.* **103** (2003) 3449–3605.
8. L. Pauling, *Acta Crystallogr., Sect. B* **36** (1980) 1898–1901.
9. P. W. Kasteleyn, *J. Math. Phys.* **4** (1963) 287–295.
10. N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, 1983, Vol. II, Chapter 2.
11. C. Rongsi, S. J. Cyvin, B. N. Cyvin, J. Brunvoll, and D. J. Klein, *Top. Curr. Chem.* **153** (1990) 227–253.
12. D. J. Klein, G. E. Hite, W. A. Seitz, and T. G. Schmalz, *Theor. Chim. Acta* **69** (1986) 409–423.
13. I. Lukovits and D. Janežič, *J. Chem. Inf. Comput. Sci.* **44** (2004) 410–414.
14. M. Gordon and W. H. T. Davison, *J. Chem. Phys.* **20** (1952) 428–435.
15. D. J. Klein and W. A. Seitz, *J. Mol. Struct. (Theochem.)* **169** (1988) 167–181.
16. R. Swinborne-Sheldrake, W. C. Herndon, and I. Gutman, *Tetrahedron Lett.* **10** (1975) 755–758.
17. W. A. Seitz, D. J. Klein, T. G. Schmalz, and M. A. Garcia-Bach, *Chem. Phys. Lett.* **115** (1985) 139–143.
18. H. Sachs, P. Hansen, and M. Zheng, *MATCH. Commun. Math. Comput. Chem.* **33** (1996) 169–241.
19. D. J. Klein, T. G. Schmalz, G. E. Hite, and W. A. Seitz, *J. Am. Chem. Soc.* **108** (1986) 1301–1302.
20. N. Trinajstić, M. Randić, D. J. Klein, D. Babić, and Z. Mihalić, *Croat. Chem. Acta* **68** (1995) 241–267.
21. I. Lukovits, A. Graovac, E. Kálmán, Gy. Kaptay, P. Nagy, S. Nikolić, J. Sytchev, and N. Trinajstić, *J. Chem. Inf. Comput. Sci.* **43** (2003) 609–614.

SAŽETAK

Prebrojavanje Kekuléovih struktura u pravokutnim benzenoidima s defektima

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Aromatski karakter grafita i drugih polibenzenoida ovisi o pripadnom broju Kekuléovih struktura. U radu je predložen algoritam za prebrojavanje Kekuléovih struktura u potpunom i nepotpunom grafitu i grafitu s defektima koji modelira funkcionalizirani grafit. Pokazano je da umjerena funkcionalizacija dovodi do blagog porasta aromatičnosti.