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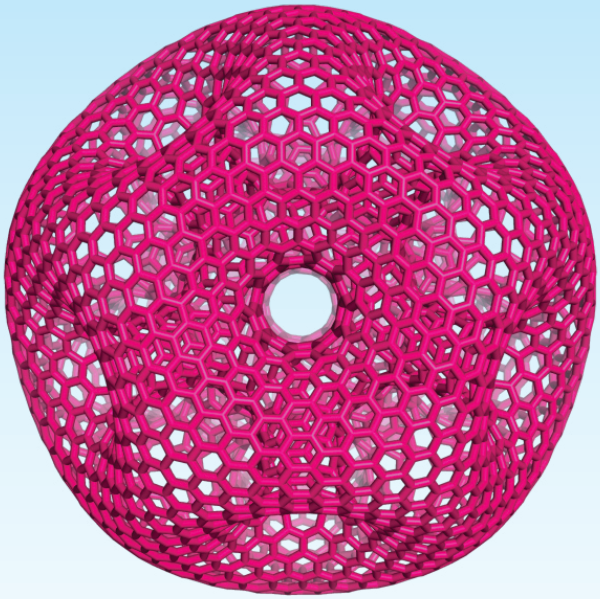
MATHEMATICAL METHODS AND MODELLING

FOR STUDENTS OF CHEMISTRY AND BIOLOGY



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Zagreb, December 2009

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Foreword

It is said that some discipline only then becomes a science when it is formulated and discussed in mathematical terms. A general consensus is established that this is true for physics. But this statement is still under dispute when one is concerned with chemistry and even more when one deals with biology. Chemistry is a field which, especially in the past, was not too worried about mathematics. Stoichometry, differential calculus to study chemical kinetics and a few extra ingredients were sufficient for a successful research in chemistry. But all that changed when in the thirties of the previous century it becomes clear that matter on the atomic and molecular scale has to be described by waves. We have witnessed then an advent of quantum mechamics and later of quantum chemistry. However, a tedious task of performing calculations of molecular structure and properties was limited to very small molecules until computers entered the field after the Second World War. Today computers and computing are broadly used in chemistry, both in its theoretical and experimental parts.

However, a series of researchers started to realize that there should be a more direct route to chemical reality based on intuition but formulated in mathematical terms. These voices intensified and the seventies of the previous century witnessed a rise of Chemical Graph Theory, CGT, a new field of chemistry where mathematics, especially discrete mathematics, is extensively used.

This new discipline is today in a full swing and besides chemistry is aplied in biology, drug design, environmental studies, material sciences, and other fields. However, it has not yet found a proper space, which it deserves, in students' curricula. In order to remedy this deficiency and to see what is a present status of the field and how to bring it to universities, an international group of professors and students met in September 2007 in the City of Split, Croatia, at the meeting *Mathematical Methods in Chemistry 2007* (*MMC 2007*). Due to limited resources only some twenty professors and assistants have been invited to Split, but all of them had some experience in teaching mathematical methods to students of chemistry and biology. Some of the lectures presented there, togeher with a few *in absentia* contributed papers, are collected in this book which is mostly concerned with applications of mathematics, especially discrete mathematics, to chemistry and biology.

The book contains altogether fourteen articles and they are organized as follows. The first one of Nenad Trinajstić is of a general interest and explains the importance of models and modelling in chemistry. The idea that the only way to learn about properties of enormously large number of realized and as well as of possible chemical species is to study them by mathematical models, especially those based on chemical graph theory, is advocated in the second paper written by Ivan Gutman. A model to study energy effects of cyclic conjugation is explaned there and further elaborated by himself and his co-workers Jelena Đurđević, Boris Furtula, Slavko Radenković and Sonja Stanković, in the third article which studies cyclic conjugation in tribenzoperylene isomers. The fourth contribution of Aleksander Vesel deals with Kekulé structures and resonance graphs in catacondensed benzenoid molecules. The papers 2-4 are related to Molecular Orbital (MO) and Valence Bond (VB) theories and most of students have acquired some knowledge of them during their studies. However, only rare among them have ever heard how these theories are closely related to graph theory and molecular topology. This relation is explained in a full depth (for the MO theory) by Roger B. Mallion in the fifth article.

Already in the seventies of the previous century an intensive research developed based on the idea that molecular graphs by themselves are a source of valuable informations on properties and activities of molecules without any reference to MO and VB theories. Such an approach is advocated and demonstrated by Milan Randić in the sixth paper with a special emphasis on Partial Ordering and its use in finding regularities in variation of physico-chemical properties of octane constitutional isomers. Numbers ascribed to molecular graphs are known as molecular descriptors (or topological indices) and have found wide applications in chemistry, biology, drug design and other fields. The most used ones are descriptors introduced by Wiener, Hosoya, Randić and Balaban. Weighted Wiener index of trees is studied in the seventh paper of Blaž Zmazek and Janez Žerovnik where methods to compute this index and related polynomial are outlined. The first and second Zagreb index belong to the oldest topological indices but the inequalities among them are only recently discovered what is a subject of the eighth article presented by Damir Vukičević and Ante Graovac. Whether two molecular graphs

represent the same connectivity, i.e. the same molecule, is and old, famous and difficult problem of graph isomorphism. The fastest algorithm known to date to solve this problem is presented in the ninth paper of Jelena Sedlar.

Chemical Graph Theory has also found its applications in nanosciences, especially in the study of novel carbon structures. In the tenth article written by István László it is shown how the well known Euler polyhedral formula is of great help in studying fullerenes, nanotubes and their junctions, nanotubes networks, and other novel carbon species. The following paper of Mircea V. Diudea shows how such an ancient human activity as coverings in art is becoming so important these days in order to understand and develop new nanostructures and nanomaterials based on them.

The last three papers should be besides chemists also of a considerable interest to students of biology and related fields. In the first of them, presented by Subhash C. Basak and Denise Mills, a broad overview of possibilities and future trends in chemobioinformatics is given together with discussion of problems appearing there and suggestions how to resolve them. Having in mind an enormous accumulation of data in the DNA databases, the next article of Igor Pesek and Janez Žerovnik demonstrates the advantage of using graphical representations of DNA sequences as they provide quick and useful visual insight into their local and global similarities/dissimilarities. The important problem of alignment of RNA sequences is elaborated in the last article contributed by Roman R. Stocsits and a novel software RNAsalsa is offered there as a tool to deal with the problem. It is also shown there how this novel concept can be of use in phylogeny reconstruction.

The present book covers only a fraction of topics which should be added to curricula of chemistry and biology students. However, we hope that some of articles presented here could be already of some use as a teaching material.

The organization of the MMC 2007 and printing of this book were possible due to the support of Universities of Dubrovnik and Split, and Ministry of Science, Education and Sports of the Republic of Croatia. Many thanks go to its State Secretary for Science and Higher Education, Professor Dražen Vikić-Topić, on his opening address and lecture delivered at the MMC 2007. We thank all the authors on their contributions and patience.

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Comparative Study of Cyclic Conjugation in Tribenzoperylene Isomers

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The energy-effects of the 255 different cyclic conjugation modes of three isomeric octacyclic benzenoid hydrocarbons, namely of tribenzo[*b,n,pqr*]perylene, tribenzo[*b,k,pqr*]perylene, and tribenzo[*b,ghi,n*]perylene, are calculated by means of a recently developed molecular-orbital-based method. From these energy-effects one can better understand which structural details are responsible for the thermodynamic stability of the underlying molecules. In particular, it is possible to rationalize (in a quantitative manner) the causes of differences in the thermodynamic stability of isomers. From this example we learn how perplexed are the actual interactions of the π-electrons in polycyclic conjugated molecules.

Keywords: *cyclic conjugation, energy effect of cyclic conjugation, tribenzoperylenes, chemical graph theory*

1. INTRODUCTION

In the preceding article[1] the conceptual and mathematical background of a molecular-orbital-based method for computing the energy-effect of cyclic conjugation is described in due detail. There it is explained how the energy-effect of an individual cycle in a polycyclic conjugated molecule can be evaluated. In a recent work[2] this procedure was extended to pairs, triplets, quartets, ... of cycles. The respective formula reads:

$$ef(Z_1 + Z_2 + \Lambda + Z_p) = ef(Z_1 + Z_2 + \Lambda + Z_p \mid G) = \frac{2}{\pi}\int_0^\infty \ln\left|\frac{\phi(G,ix) - (-2)^p \phi(G - Z_1 - Z_2 - \Lambda - Z_p}{\phi(G,ix)}\right| dx \quad (1)$$

where $Z_1,Z_2,...,Z_p$ are mutually disjoint cycles contained in a polycyclic conjugated molecule whose molecular graph is G. The meaning of other symbols is same as in the preceding article.[1] Recall that the formula given in the article[1] is the special case of Eq. (1) for p=1.

We now report the results of the application of Eq. (1) to all cyclic conjugation modes of three isomeric tribenzoperylenes, whose structure is depicted in Figure 1.

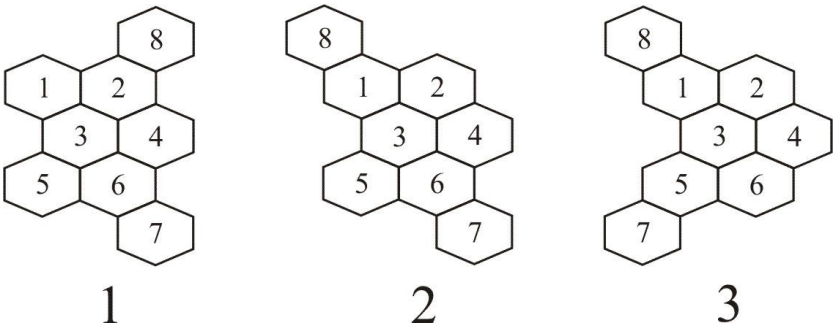

Figure 1. Tribenzo[b,n,pqr]perylene (**1**), tribenzo[b,k,pqr]perylene (**2**), and tribenzo[b,ghi,n]perylene (**3**), and the labelling of their rings. These isomeric benzenoid molecules have 8 rings, and therefore we have to distinguish between $2^8 - 1 = 255$ distinct conjugation modes in each of them.

The tribenzoperylenes studied in this work played an outstanding role in the formulation of the so-called *Clar aromatic sextet theory*. For more details along these lines the readers are referred to the books.[3-5] At this point it is important only that Clar theory predicts the stability order **1** > **2** > **3**, a conclusion that is corroborated by both the chemical behavior of the three isomers (for details see[3]), and by the calculated resonance energies. Thus, for instance, the Dewar resonance energies[6,7] of the compounds **1**, **2**, and **3** are equal to 1.6182, 1.5535, and 1.5075 β-units, respectively.

By separating the energy-effects of different conjugation modes, we can now see why **1** is the most stable and **3** the least stable isomer, and which structural features are responsible for this stability difference.

2. CYCLES IN TRIBENZOPERYLENES

In Figure 1 is indicated the labeling of the rings of the three tribenzoperylenes considered. In Figure 2 are provided examples clarifying the way in which their cycles, as well as pairs, triples, etc. of disjoint cycles are denoted. For instance, in **1**, Z_{135} denotes the 14-membered cycle embracing the rings 1, 3, and 5. The 26-membered cycle, embracing all the eight rings of **2**, is denoted by $Z_{12345678}$; thus $Z_{12345678}$ is the perimeter of **2**. By Z_{28}+Z_{56} (not shown in Figure 2) we would denote a pair of two disjoint 10-membered cycles of **1**, embracing the rings 2, 5, 6, and 8. On the other hand, the same four rings of **3** would induce a triple of mutually disjoint cycles, denoted by Z_2+Z_8+Z_{56}, consisting of two 6-membered and one 10-membered cycle.

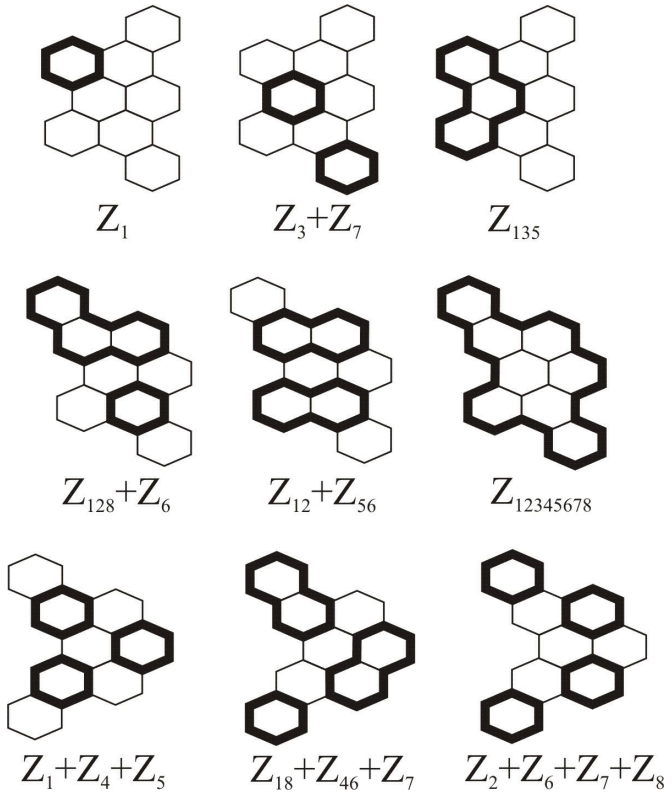

Figure 2. Examples showing the way in which the in the tribenzoperylenes considered, theircycles, pairs of disjoint cycles, triplets of mutually disjoint cycles, *etc.* are denoted. For the labeling of the rings of these tribenzoperylenes see Figure 1.

3. CYCLIC CONJUGATION IN TRIBENZOPERYLENES

As explained in the previous article,[1] in benzenoid hydrocarbons the energy-effect rapidly decreases when the size of the cycle increases. This means that the greatest energy effects have the six-membered cycles, the energy effects of 10-membered cycles are smaller, *etc*.

In benzenoid systems, all cycles of size 6, 10, 14, 18, ... (*i. e.*, $4k + 2$, $k = 1, 2, 3,...$), have stabilizing energy-effects (positive *ef*). The cycles of size 12, 16, 20, ... (*i.e.*, $4k$, $k = 3, 4, 5,...$), have a destabilizing energy-effect (negative *ef*).

The above facts can be directly checked from the data presented in Tables 1-4.

Using Eq. (1) we have computed all cyclic-conjugation energy-effects in the tribenzoperylene isomers **1**, **2**, and **3**. These results are given in Tables 1-4.

Table 1. Energy effects (in β-units) of cycles of tribenzoperylenes **1**, **2**, and **3** (see Figure 1).

cycle	size	**1**	**2**	**3**	cycle	size	**1**	**2**	**3**
Z_1	6	0.1462	0.0553	0.0548	Z_{138}	14	-	0.0019	0.0014
Z_2	6	0.0264	0.0757	0.0836	Z_{234}	12	-0.0004	-0.0010	-0.0007
Z_3	6	0.0255	0.0231	0.0217	Z_{235}	14	0.0004	0.0013	0.0005
Z_4	6	0.1124	0.0901	0.0714	Z_{236}	14	0.0001	0.0003	0.0010
Z_5	6	0.1462	0.1496	0.0548	Z_{238}	14	0.0005	-	-
Z_6	6	0.0264	0.0285	0.0836	Z_{246}	14	0.0005	0.0017	0.0066
Z_7	6	0.1886	0.1840	0.1427	Z_{248}	14	0.0044	-	-
Z_8	6	0.1886	0.1386	0.1427	Z_{345}	14	0.0042	0.0022	0.0008
Z_{12}	10	0.0096	0.0113	0.0128	Z_{346}	12	-0.0004	-0.0003	-0.0007
Z_{13}	10	0.0083	0.0033	0.0027	Z_{356}	12	-0.0005	-0.0005	-0.0006
Z_{18}	10	-	0.0311	0.0307	Z_{357}	14	-	-	0.0014
Z_{23}	10	0.0013	0.0034	0.0033	Z_{367}	14	0.0005	0.0005	-
Z_{24}	10	0.0066	0.0251	0.0191	Z_{456}	14	0.0040	0.0031	0.0037
Z_{28}	10	0.0111	-	-	Z_{467}	14	0.0044	0.0034	-
Z_{34}	10	0.0070	0.0044	0.0030	Z_{567}	14	0.0065	0.0079	0.0093
Z_{35}	10	0.0083	0.0064	0.0027	Z_{1234}	14	0.0012	0.0015	0.0008
Z_{36}	10	0.0013	0.0013	0.0033	Z_{1235}	16	-0.0002	-0.0002	-0.0001
Z_{46}	10	0.0066	0.0054	0.0191	Z_{1236}	16	0.0000	-0.0001	-0.0002
Z_{56}	10	0.0096	0.0111	0.0128	Z_{1238}	16	-0.0002	-0.0003	-0.0003
Z_{57}	10	-	-	0.0307	Z_{1246}	18	0.0003	0.0003	0.0013
Z_{67}	10	0.0111	0.0128	-	Z_{1248}	18	0.0032	0.0040	0.0029
Z_{123}	12	-0.0005	-0.0006	-0.0006	Z_{1345}	18	0.0031	0.0011	0.0004
Z_{124}	14	0.0040	0.0049	0.0037	Z_{1346}	16	-0.0001	-0.0001	-0.0002
Z_{128}	14	0.0065	0.0080	0.0093	Z_{1348}	18	-	0.0011	0.0005
Z_{134}	14	0.0042	0.0015	0.0008	Z_{1356}	16	-0.0002	-0.0001	-0.0001
Z_{135}	14	0.0046	0.0017	0.0006	Z_{1357}	18	-	-	0.0004
Z_{136}	14	0.0004	0.0002	0.0005	Z_{1358}	18	-	0.0013	0.0004

Table 1. (continued)

cycle	size	**1**	**2**	**3**
Z_{1367}	18	0.0002	0.0001	-
Z_{1368}	18	-	0.0001	0.0003
Z_{2345}	16	-0.0001	-0.0004	-0.0002
Z_{2346}	14	0.0001	0.0003	0.0010
Z_{2348}	16	-0.0002	-	-
Z_{2356}	16	0.0000	-0.0001	-0.0002
Z_{2357}	18	-	-	0.0003
Z_{2358}	18	0.0002	-	-
Z_{2367}	18	0.0001	0.0002	-
Z_{2368}	18	0.0001	-	-
Z_{2456}	18	0.0003	0.0011	0.0013
Z_{2467}	18	0.0003	0.0013	-
Z_{2468}	18	0.0003	-	-
Z_{3456}	14	0.0012	0.0007	0.0008
Z_{3457}	18	-	-	0.0005
Z_{3467}	16	-0.0002	-0.0001	-
Z_{3567}	16	-0.0002	-0.0002	-0.0003
Z_{4567}	18	0.0032	0.0025	0.0029
Z_{12345}	18	0.0009	0.0011	0.0004
Z_{12346}	16	-0.0001	-0.0001	-0.0003
Z_{12348}	18	0.0009	0.0011	0.0005
Z_{12356}	18	0.0000	0.0000	0.0000
Z_{12357}	20	-	-	0.0000
Z_{12358}	20	-0.0001	-0.0001	0.0000
Z_{12367}	20	0.0000	0.0000	-
Z_{12368}	20	0.0000	0.0000	-0.0001
Z_{12456}	22	0.0002	0.0003	0.0003
Z_{12467}	22	0.0002	0.0003	-
Z_{12468}	22	0.0002	0.0003	0.0011
Z_{13456}	18	0.0009	0.0003	0.0004
Z_{13457}	22	-	-	0.0003
Z_{13458}	22	-	0.0009	0.0003
Z_{13467}	20	-0.0001	0.0000	-
Z_{13468}	20	-	0.0000	-0.0001
Z_{13567}	20	-0.0001	0.0000	0.0000
Z_{13568}	20	-	0.0000	0.0000
Z_{13578}	22	-	-	0.0003
Z_{13678}	22	-	0.0001	-
Z_{23456}	16	-0.0001	-0.0003	-0.0003
Z_{23457}	20	-	-	-0.0001
Z_{23458}	20	-0.0001	-	-

cycle	size	**1**	**2**	**3**
Z_{23467}	18	0.0001	0.0002	-0.0001
Z_{23468}	18	0.0001	-	-
Z_{23567}	20	0.0000	-0.0001	-
Z_{23568}	20	0.0000	-	-
Z_{23678}	22	0.0000	-	-
Z_{24567}	22	0.0002	0.0009	0.0011
Z_{24568}	22	0.0002	-	-
Z_{24678}	22	0.0002	-	-
Z_{34567}	18	0.0009	0.0005	0.0005
Z_{123456}	18	0.0003	0.0003	0.0004
Z_{123457}	22	-	-	0.0003
Z_{123458}	22	0.0007	0.0009	0.0003
Z_{123467}	20	0.0000	-0.0001	-
Z_{123468}	20	0.0000	-0.0001	-0.0002
Z_{123567}	22	0.0000	0.0000	0.0000
Z_{123568}	22	0.0000	0.0000	0.0000
Z_{123578}	24	-	-	0.0000
Z_{123678}	24	0.0000	0.0000	-
Z_{124567}	26	0.0002	0.0002	0.0003
Z_{124568}	26	0.0002	0.0002	0.0003
Z_{124678}	26	0.0002	0.0002	-
Z_{134567}	22	0.0007	0.0002	0.0003
Z_{134568}	22	-	0.0002	0.0003
Z_{134578}	26	-	-	0.0003
Z_{134678}	24	-	0.0000	-
Z_{135678}	24	-	0.0000	0.0000
Z_{234567}	20	0.0000	-0.0002	-0.0002
Z_{234568}	20	0.0000	-	-
Z_{234678}	22	0.0000	-	-
Z_{235678}	24	0.0000	-	-
Z_{245678}	26	0.0002	-	-
$Z_{1234567}$	22	0.0002	0.0003	0.0003
$Z_{1234568}$	22	0.0002	0.0003	0.0003
$Z_{1234578}$	26	-	-	0.0003
$Z_{1234678}$	24	0.0000	0.0000	-
$Z_{1235678}$	26	0.0000	0.0000	0.0000
$Z_{1245678}$	30	0.0002	0.0002	0.0002
$Z_{1345678}$	26	-	0.0002	0.0003
$Z_{2345678}$	24	0.0000	-	-
$Z_{12345678}$	26	0.0002	0.0002	-0.0003

Table 2. Energy-effects (in β-units) of pairs of disjoint cycles of the tribenzoperylenes **1**, **2**, and **3** (see Figure 1).

cycles	size	**1**	**2**	**3**
$Z_1 + Z_4$	6+6	0.0324	0.0111	0.0084
$Z_1 + Z_5$	6+6	0.0339	0.0119	0.0042
$Z_1 + Z_6$	6+6	0.0031	0.0012	0.0042
$Z_1 + Z_7$	6+6	0.0337	0.0118	0.0090

cycles	size	**1**	**2**	**3**
$Z_1 + Z_8$	6+6	0.0433	-	-
$Z_2 + Z_5$	6+6	0.0031	0.0118	0.0042
$Z_2 + Z_6$	6+6	0.0012	0.0040	0.0150
$Z_2 + Z_7$	6+6	0.0037	0.0138	0.0151

Table 2. (continued)

cycles	size	**1**	**2**	**3**
Z_2+Z_8	6+6	-	0.0196	0.0225
Z_3+Z_7	6+6	0.0037	0.0028	0.0016
Z_3+Z_8	6+6	0.0037	0.0017	0.0016
Z_4+Z_5	6+6	0.0324	0.0249	0.0084
Z_4+Z_7	6+6	0.0337	0.0261	0.0100
Z_4+Z_8	6+6	0.0337	0.0131	0.0100
Z_5+Z_7	6+6	0.0433	0.0446	-
Z_5+Z_8	6+6	0.0337	0.0261	0.0090
Z_6+Z_7	6+6	-	-	0.0225
Z_6+Z_8	6+6	0.0037	0.0041	0.0151
Z_7+Z_8	6+6	0.0433	0.0287	0.0244
Z_1+Z_{46}	6+10	0.0020	0.0007	0.0029
Z_1+Z_{56}	6+10	0.0021	0.0008	0.0009
Z_1+Z_{57}	6+10	-	-	0.0030
Z_1+Z_{67}	6+10	0.0021	0.0008	-
Z_2+Z_{56}	6+10	0.0006	0.0024	0.0029
Z_2+Z_{57}	6+10	-	-	0.0030
Z_2+Z_{67}	6+10	0.0007	0.0028	-
Z_4+Z_{18}	6+10	-	0.0086	0.0063
Z_4+Z_{57}	6+10	-	-	0.0063
Z_5+Z_{12}	6+10	0.0021	0.0026	0.0009
Z_5+Z_{18}	6+10	-	0.0091	0.0030
Z_5+Z_{24}	6+10	0.0020	0.0087	0.0029
Z_5+Z_{28}	6+10	0.0021	-	-
Z_6+Z_{12}	6+10	0.0006	0.0007	0.0029
Z_6+Z_{18}	6+10	-	0.0008	0.0030
Z_6+Z_{28}	6+10	0.0007	-	-
Z_7+Z_{12}	6+10	0.0022	0.0026	0.0030
Z_7+Z_{13}	6+10	0.0022	0.0008	0.0003
Z_7+Z_{18}	6+10	-	0.0090	0.0067
Z_7+Z_{23}	6+10	0.0002	0.0005	0.0004
Z_7+Z_{24}	6+10	0.0022	0.0093	0.0034
Z_7+Z_{28}	6+10	0.0024	-	-
Z_7+Z_{34}	6+10	0.0022	0.0012	0.0003
Z_7+Z_{35}	6+10	0.0024	0.0016	-
Z_7+Z_{36}	6+10	-	-	0.0005
Z_7+Z_{46}	6+10	-	-	0.0066
Z_8+Z_{13}	6+10	0.0024	-	-
Z_8+Z_{23}	6+10	-	0.0005	0.0005
Z_8+Z_{24}	6+10	-	0.0090	0.0066
Z_8+Z_{34}	6+10	0.0022	0.0004	0.0003
Z_8+Z_{35}	6+10	0.0022	0.0007	0.0003
Z_8+Z_{36}	6+10	0.0002	0.0001	0.0004
Z_8+Z_{46}	6+10	0.0022	0.0009	0.0034
Z_8+Z_{56}	6+10	0.0022	0.0025	0.0030
Z_8+Z_{57}	6+10	-	-	0.0067
Z_8+Z_{67}	6+10	0.0024	0.0028	-
Z_1+Z_{456}	6+14	0.0016	0.0005	0.0007
Z_1+Z_{467}	6+14	0.0016	0.0005	-
Z_1+Z_{567}	6+14	0.0017	0.0006	0.0007
Z_2+Z_{567}	6+14	0.0004	0.0020	0.0024
Z_5+Z_{124}	6+14	0.0016	0.0020	0.0007
Z_5+Z_{128}	6+14	0.0017	0.0021	0.0007
Z_5+Z_{248}	6+14	0.0016	-	-

cycles	size	**1**	**2**	**3**
Z_6+Z_{128}	6+14	0.0004	0.0005	0.0024
Z_7+Z_{123}	6+12	-0.0001	-0.0001	-0.0001
Z_7+Z_{124}	6+14	0.0016	0.0020	0.0007
Z_7+Z_{128}	6+14	0.0017	0.0021	0.0024
Z_7+Z_{134}	6+14	0.0016	0.0005	0.0001
Z_7+Z_{135}	6+14	0.0017	0.0006	-
Z_7+Z_{136}	6+14	-	-	0.0001
Z_7+Z_{138}	6+14	-	0.0006	0.0002
Z_7+Z_{234}	6+12	-0.0001	-0.0002	-0.0001
Z_7+Z_{235}	6+14	0.0001	0.0003	-
Z_7+Z_{236}	6+14	-	-	0.0002
Z_7+Z_{238}	6+14	0.0001	-	-
Z_7+Z_{246}	6+14	-	-	0.0025
Z_7+Z_{248}	6+14	0.0017	-	-
Z_7+Z_{345}	6+14	0.0017	0.0008	-
Z_7+Z_{346}	6+12	-	-	-0.0001
Z_8+Z_{134}	6+14	0.0017	-	-
Z_8+Z_{135}	6+14	0.0017	-	-
Z_8+Z_{136}	6+14	0.0001	-	-
Z_8+Z_{234}	6+12	-	-0.0002	-0.0001
Z_8+Z_{235}	6+14	-	0.0003	0.0001
Z_8+Z_{236}	6+14	-	0.0001	0.0002
Z_8+Z_{246}	6+14	-	0.0006	0.0025
Z_8+Z_{345}	6+14	0.0016	0.0002	0.0001
Z_8+Z_{346}	6+12	-0.0001	0.0000	-0.0001
Z_8+Z_{356}	6+12	-0.0001	-0.0001	-0.0001
Z_8+Z_{357}	6+14	-	-	0.0002
Z_8+Z_{367}	6+14	0.0001	0.0001	-
Z_8+Z_{456}	6+14	0.0016	0.0006	0.0007
Z_8+Z_{467}	6+14	0.0017	0.0006	-
Z_8+Z_{567}	6+14	0.0017	0.0020	0.0024
Z_1+Z_{4567}	6+18	0.0014	0.0005	0.0006
Z_5+Z_{1248}	6+18	0.0014	0.0017	0.0006
Z_7+Z_{1234}	6+14	0.0004	0.0005	0.0001
Z_7+Z_{1235}	6+16	0.0000	0.0000	-
Z_7+Z_{1236}	6+16	-	-	0.0000
Z_7+Z_{1238}	6+16	0.0000	0.0000	0.0000
Z_7+Z_{1246}	6+18	-	-	0.0006
Z_7+Z_{1248}	6+18	0.0014	0.0017	0.0006
Z_7+Z_{1345}	6+18	0.0014	0.0005	-
Z_7+Z_{1346}	6+16	-	-	0.0000
Z_7+Z_{1348}	6+18	-	0.0005	0.0000
Z_7+Z_{1358}	6+18	-	0.0005	-
Z_7+Z_{1368}	6+18	-	-	0.0001
Z_7+Z_{2345}	6+16	0.0000	-0.0001	-
Z_7+Z_{2346}	6+14	-	-	0.0002
Z_7+Z_{2348}	6+16	0.0000	-	-
Z_7+Z_{2358}	6+18	0.0001	-	-
Z_8+Z_{1345}	6+16	0.0014	-	-
Z_8+Z_{1346}	6+16	0.0000	-	-
Z_8+Z_{1356}	6+16	0.0000	-	-
Z_8+Z_{1367}	6+18	0.0001	-	-
Z_8+Z_{2345}	6+16	-	-0.0001	0.0000
Z_8+Z_{2346}	6+14	-	0.0001	0.0002

Table 2. (continued)

cycles	size	**1**	**2**	**3**
Z_8+Z_{2356}	6+16	-	0.0000	0.0000
Z_8+Z_{2357}	6+18	-	-	0.0001
Z_8+Z_{2367}	6+18	-	0.0000	-
Z_8+Z_{2456}	6+18	-	0.0005	0.0006
Z_8+Z_{2467}	6+18	-	0.0005	-
Z_8+Z_{3456}	6+14	0.0004	0.0001	0.0001
Z_8+Z_{3457}	6+18	-	-	0.0000
Z_8+Z_{3467}	6+16	0.0000	0.0000	-
Z_8+Z_{3567}	6+16	0.0000	0.0000	0.0000
Z_8+Z_{4567}	6+18	0.0014	0.0005	0.0006
Z_7+Z_{12345}	6+18	0.0004	0.0005	-
Z_7+Z_{12346}	6+16	-	-	-0.0001
Z_7+Z_{12348}	6+18	0.0004	0.0005	0.0000
Z_7+Z_{12358}	6+20	0.0000	0.0000	-
Z_7+Z_{12368}	6+20	-	-	0.0000
Z_7+Z_{12468}	6+22	-	-	0.0005
Z_7+Z_{13458}	6+22	-	0.0004	-
Z_7+Z_{13468}	6+20	-	-	0.0000
Z_7+Z_{23458}	6+20	0.0000	-	-
Z_8+Z_{13456}	6+18	0.0004	-	-
Z_8+Z_{13467}	6+20	0.0000	-	-
Z_8+Z_{13567}	6+20	0.0000	-	-
Z_8+Z_{23456}	6+16	-	0.0000	-0.0001
Z_8+Z_{23457}	6+20	-	-	0.0000
Z_8+Z_{23467}	6+18	-	0.0000	-
Z_8+Z_{23567}	6+20	-	0.0000	0.0000
Z_8+Z_{24567}	6+22	-	0.0004	0.0005
Z_8+Z_{34567}	6+18	0.0004	0.0000	0.0000
Z_7+Z_{123458}	6+22	0.0003	0.0004	-
Z_7+Z_{123468}	6+20	-	-	0.0000
Z_8+Z_{134567}	6+22	0.0003	-	-
Z_8+Z_{234567}	6+20	-	0.0000	0.0000
$Z_{12}+Z_{56}$	10+10	0.0004	0.0005	0.0007
$Z_{12}+Z_{57}$	10+10	-	-	0.0007
$Z_{12}+Z_{67}$	10+10	0.0004	0.0005	-
$Z_{12}+Z_{567}$	10+14	0.0004	0.0005	0.0006
$Z_{18}+Z_{46}$	10+10	-	0.0005	0.0024
$Z_{18}+Z_{56}$	10+10	-	0.0006	0.0007
$Z_{18}+Z_{57}$	10+10	-	-	0.0025
$Z_{18}+Z_{67}$	10+10	-	0.0006	-
$Z_{18}+Z_{456}$	10+14	-	0.0005	0.0006
$Z_{18}+Z_{467}$	10+14	-	0.0005	-
$Z_{18}+Z_{567}$	10+14	-	0.0005	0.0006
$Z_{18}+Z_{4567}$	10+18	-	0.0004	0.0005
$Z_{24}+Z_{57}$	10+10	-	-	0.0024
$Z_{28}+Z_{56}$	10+10	0.0004	-	-
$Z_{28}+Z_{67}$	10+10	0.0005	-	-
$Z_{28}+Z_{567}$	10+14	0.0004	-	-
$Z_{56}+Z_{128}$	10+14	0.0004	0.0005	0.0006
$Z_{57}+Z_{124}$	10+14	-	-	0.0006
$Z_{57}+Z_{128}$	10+14	-	-	0.0006
$Z_{57}+Z_{1248}$	10+18	-	-	0.0005
$Z_{67}+Z_{128}$	10+14	0.0004	0.0005	-
$Z_{128}+Z_{567}$	14+14	0.0003	0.0004	0.0005

Table 3. Energy-effects (in β-units) of triplets of mutually disjoint cycles of the tribenzoperylenes **1**, **2**, and **3** (see Figure 1).

cycles	size	**1**	**2**	**3**
$Z_1+Z_4+Z_5$	6+6+6	0.0127	0.0043	0.0014
$Z_1+Z_4+Z_7$	6+6+6	0.0127	0.0043	0.0015
$Z_1+Z_4+Z_8$	6+6+6	0.0130	-	-
$Z_1+Z_5+Z_7$	6+6+6	0.0130	0.0045	-
$Z_1+Z_5+Z_8$	6+6+6	0.0130	-	-
$Z_1+Z_6+Z_7$	6+6+6	-	-	0.0015
$Z_1+Z_6+Z_8$	6+6+6	0.0010	-	-
$Z_1+Z_7+Z_8$	6+6+6	0.0130	-	-
$Z_2+Z_5+Z_7$	6+6+6	0.0010	0.0045	-
$Z_2+Z_5+Z_8$	6+6+6	-	0.0044	0.0015
$Z_2+Z_6+Z_7$	6+6+6	-	-	0.0054
$Z_2+Z_6+Z_8$	6+6+6	-	0.0013	0.0054
$Z_2+Z_7+Z_8$	6+6+6	-	0.0049	0.0055
$Z_3+Z_7+Z_8$	6+6+6	0.0010	0.0003	0.0002
$Z_4+Z_5+Z_7$	6+6+6	0.0130	0.0100	-
$Z_4+Z_5+Z_8$	6+6+6	0.0127	0.0047	0.0015
$Z_4+Z_7+Z_8$	6+6+6	0.0130	0.0048	0.0018
$Z_5+Z_7+Z_8$	6+6+6	0.0130	0.0100	-
$Z_6+Z_7+Z_8$	6+6+6	-	-	0.0055
$Z_1+Z_4+Z_{57}$	6+6+10	-	-	0.0012
$Z_1+Z_7+Z_{46}$	6+6+10	-	-	0.0012
$Z_1+Z_8+Z_{46}$	6+6+10	0.0008	-	-
$Z_1+Z_8+Z_{56}$	6+6+10	0.0008	-	-
$Z_1+Z_8+Z_{67}$	6+6+10	0.0008	-	-
$Z_2+Z_8+Z_{56}$	6+6+10	-	0.0010	0.0012
$Z_2+Z_8+Z_{57}$	6+6+10	-	-	0.0012
$Z_2+Z_8+Z_{67}$	6+6+10	-	0.0011	-
$Z_4+Z_5+Z_{18}$	6+6+10	-	0.0036	0.0012
$Z_4+Z_7+Z_{18}$	6+6+10	-	0.0036	0.0013
$Z_4+Z_8+Z_{57}$	6+6+10	-	-	0.0013
$Z_4+Z_8+Z_{67}$	6+6+10	-	-	0.0013
$Z_5+Z_7+Z_{12}$	6+6+10	0.0008	0.0010	-
$Z_5+Z_7+Z_{18}$	6+6+10	-	0.0038	-
$Z_5+Z_7+Z_{24}$	6+6+10	0.0008	0.0038	-
$Z_5+Z_7+Z_{28}$	6+6+10	0.0008	-	-
$Z_5+Z_8+Z_{24}$	6+6+10	-	0.0036	0.0012
$Z_6+Z_7+Z_{12}$	6+6+10	-	-	0.0012
$Z_6+Z_7+Z_{18}$	6+6+10	-	-	0.0012
$Z_7+Z_8+Z_{13}$	6+6+10	0.0008	-	-
$Z_7+Z_8+Z_{23}$	6+6+10	-	0.0001	0.0001
$Z_7+Z_8+Z_{24}$	6+6+10	-	0.0038	0.0013
$Z_7+Z_8+Z_{34}$	6+6+10	0.0008	0.0001	0.0000
$Z_7+Z_8+Z_{35}$	6+6+10	0.0008	0.0002	-
$Z_7+Z_8+Z_{36}$	6+6+10	-	-	0.0001
$Z_1+Z_8+Z_{456}$	6+6+14	0.0007	-	-
$Z_1+Z_8+Z_{467}$	6+6+14	0.0007	-	-
$Z_1+Z_8+Z_{567}$	6+6+14	0.0007	-	-
$Z_2+Z_8+Z_{567}$	6+6+14	-	0.0009	0.0010
$Z_4+Z_{18}+Z_{57}$	6+10+10	-	-	0.0010
$Z_5+Z_7+Z_{124}$	6+6+14	0.0007	0.0009	-
$Z_5+Z_7+Z_{128}$	6+6+14	0.0007	0.0009	-
$Z_5+Z_7+Z_{248}$	6+6+14	0.0007	-	-
$Z_6+Z_7+Z_{128}$	6+6+14	-	-	0.0010
$Z_7+Z_8+Z_{134}$	6+6+14	0.0007	-	-
$Z_7+Z_8+Z_{135}$	6+6+14	0.0007	-	-

Table 3. (continued)

cycles	size	**1**	**2**	**3**
$Z_7+Z_8+Z_{234}$	6+6+12	-	0.0000	0.0000
$Z_7+Z_8+Z_{235}$	6+6+14	-	0.0001	-
$Z_7+Z_8+Z_{236}$	6+6+14	-	-	0.0000
$Z_7+Z_8+Z_{246}$	6+6+14	-	-	0.0011
$Z_7+Z_8+Z_{345}$	6+6+14	0.0007	0.0001	-
$Z_7+Z_8+Z_{346}$	6+6+12	-	-	0.0000
$Z_7+Z_{18}+Z_{46}$	6+10+10	-	-	0.0010
$Z_1+Z_8+Z_{4567}$	6+6+18	0.0006	-	-
$Z_5+Z_7+Z_{1248}$	6+6+18	0.0006	0.0008	-
$Z_7+Z_8+Z_{1345}$	6+6+18	0.0006	-	-
$Z_7+Z_8+Z_{2345}$	6+6+16	-	0.0000	-
$Z_7+Z_8+Z_{2346}$	6+6+14	-	-	0.0000
$Z_8+Z_{24}+Z_{57}$	6+10+10	-	-	0.0010

Table 4. Energy-effects (in β-units) of quartets of mutually disjoint cycles of the tribenzoperylenes **1**, **2**, and **3** (see Figure 1); also the energy effect of the unique quintet of mutually disjoint cycles of **1** is included.

cycles	size	**1**	**2**	**3**
$Z_1+Z_4+Z_5+Z_7$	6+6+6+6	0.0055	0.0019	-
$Z_1+Z_4+Z_5+Z_8$	6+6+6+6	0.0055	-	-
$Z_1+Z_4+Z_7+Z_8$	6+6+6+6	0.0055	-	-
$Z_1+Z_5+Z_7+Z_8$	6+6+6+6	0.0055	-	-
$Z_2+Z_5+Z_7+Z_8$	6+6+6+6	-	0.0019	-
$Z_2+Z_6+Z_7+Z_8$	6+6+6+6	-	-	0.0022
$Z_4+Z_5+Z_7+Z_8$	6+6+6+6	0.0055	0.0020	-
$Z_4+Z_5+Z_7+Z_{18}$	6+6+6+10	-	0.0016	-
$Z_5+Z_7+Z_8+Z_{24}$	6+6+6+10	-	0.0016	-
$Z_1+Z_4+Z_5+Z_7+Z_8$	6+6+6+6+6	0.0025	-	-

By inspection of the data in Tables 1-4 we first conclude that the cyclic conjugation energy-effects of single six-membered and single ten-membered cycles are far the strongest. Some energy-effects of pairs of six-membered cycles are also not negligible (Table 2), but all other *ef*-values are two or more orders of magnitude smaller than those of single six-membered cycles.

Therefore, although in the tribenzoperylenes **1**, **2**, and **3** there are very many different modes of cyclic conjugation, the main cause of the difference in their thermodynamic stability are the energy-effects of their six-membered and (to a lesser extent) ten-membered cycles.

Some of these energy-effects are nearly equal in all three isomers considered. It is legitimate to compare the energy-effects only in structurally similar parts of the molecules. Such is the domain spanned by the rings 3 and 4. Now, whereas $ef(Z_3)$ is nearly equal in all three isomers (0.0255, 0.0231, and 0.0217 β-units for **1**, **2**, and **3**,

respectively), the effect of the ring 4 is significantly different (0.1124, 0.0901, and 0.0714 β-units for **1**, **2**, and **3**, respectively). This difference in the *ef*-values is one of the main reasons of the observed stability order **1** > **2** > **3**.

The domain spanned by the rings 1, 2, and 8 is structurally similar in **2** and **3**, but cannot be directly compared with that in **1**. Yet, if we add the *ef*-values of these three rings, namely, $ef(Z_1) + ef(Z_2) + ef(Z_8)$ we get values that clearly favour **1** over **2** and **3** (0.3612, 0.2696, and 0.2811 β-units for **1**, **2**, and **3**, respectively). Cyclic conjugation in the domain 1,2,8 slightly favours the isomer **3** over isomer **2**. However, if we perform an analogous comparison for the domain spanned by the rings 4,6,7, we see that $ef(Z_5) + ef(Z_6) + ef(Z_7)$ is equal to 0.3612, 0.3612, and 0.2811 β-units for **1**, **2**, and **3**, respectively. Thus, cyclic conjugation in this domain is much stronger in **1** and **2** than in **3**, also implying the stability order **2** > **3**.

Inspecting the Tables 1-4 in more detail (which we recommend to the readers of this article) we realize that only the above-specified energy-effects are those that determine the stability order. All other energy-effects (which sometimes favour the isomer **1**, sometimes **2**, sometimes **3**) are so small that cannot change the ordering caused by the effects of the ring 4 and the domains 1,2,8 and 5,6,7.

Thus, our considerations based on energy arguments yield the same conclusion as Clar theory: **1** is more stable than **2**, which in turn is more stable that **3**. However, the cause of this stability difference is seen in only a few cyclic conjugation energy-effects, involving only three regions of the molecules.

Our approach distinguishes and quantifies 255 cyclic conjugation energy-effects in **1**, **2**, and **3**, but only two or three of these differ significantly, and only these decide the stability order.

In Clar theory the fact that **1** has a quintet of mutually disjoint hexagons is considered to be crucial for its stability. This, indeed, may be the case, but the collective energy-effect of these five six-membered cycles is minor, only 0.0025 β-units. In **2** and **3** there are no such quintets, but there are quartets of mutually disjoint hexagons, each stabilizing **2** and **3** by some 0.020 β-units, roughly the same as the quintet in **1**.

In conclusion, the examples elaborated in this paper teach us that in polycyclic conjugated molecules the modes of cyclic conjugation follow a rather perplexed pattern; in an h-cyclic conjugated molecule there are 2^h-1 such modes, each with a

distinct (and calculable) energy-effect. However, most of these energy-effects are small and insignificant. Only very few energy-effects are large and may significantly differ between isomers, thus deciding their stability order.

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