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# Comparing the stability of tribenzo[*b*,*n*,*pqr*]perylene and tribenzo[*b*,*k*,*pqr*]perylene

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**Abstract** Two isomeric benzenoid hydrocarbons – tribenzo[*b*,*n*,*pqr*]perylene and tribenzo[*b*,*k*,*pqr*]perylene played a crucial role in the formulation of the *Clar* aromatic sextet theory. The basic assumption of this theory is that tribenzo[*b*,*n*,*pqr*]perylene is more stable than tribenzo[*b*,*k*,*pqr*]perylene because the former has five, whereas the latter only four aromatic sextets. We now approach this stability problem from a different direction. By means of a recently developed molecular-orbital-based method it is possible to estimate the energy effects of individual cycles, as well as pairs, triplets, *etc*. of cycles in polycyclic conjugated molecules. From these energy-effects one can better understand which structural details are responsible for the thermodynamic stability of the underlying molecule. In particular, it is possible to rationalize (in a quantitative manner) the causes of differences in the thermodynamic stability of isomers. Our analysis corroborates the conclusion of *Clar* theory, but points out a number of hitherto overlooked structure-stability connections.

**Keywords** *Clar* theory; Cyclic conjugation; Energy effect of cyclic conjugation; Tribenzoperylene.

## Introduction

The comparison of two isomeric tribenzoperylenes (**1** and **2**, see Fig. 1) played a crucial role in the discovery of the *Clar aromatic sextet theory.*

In the 1950s *Eric Clar* together with his student *Maximilian Zander* [1] synthesized two isomeric tribenzoperylenes and found that tribenzo[*b*,*k*,*pqr*]-perylene (**2**) is significantly more reactive than tribenzo[*b*,*n*,*pqr*]perylene (**1**). *Clar* connected these experimental observations with the fact that the 30 $\pi$-electrons of **1** can be divided into five groups of six, and each such group (referred to as an "*aromatic sextet*") can be formally located in one of the five mutually disjoint six-membered rings of **1**. In the case of **2** no such partitioning of $\pi$-electrons is possible: of the 30$\pi$-electrons of **2** only 24 can be grouped into aromatic sextets whereas the remaining 6 must belong to ordinary double bonds. When the aromatic sextets are represented by circles, we arrive at the diagrams that nowadays are known as *Clar aromatic sextet formulas*, see Fig. 1. In *Clar*'s opinion [1, 2], the isomer **1** is more stable than **2** because the *Clar* formula of **1** has five, whereas any of the *Clar* formulas of **2** has only four aromatic sextets.

Generalizing this way of looking at the electronic structure of benzenoid hydrocarbons, *Clar* arrived at what nowadays is called the *Clar aromatic sextet theory* [2, 3]. Eventually, this theory became one of the standard approaches by means of which the

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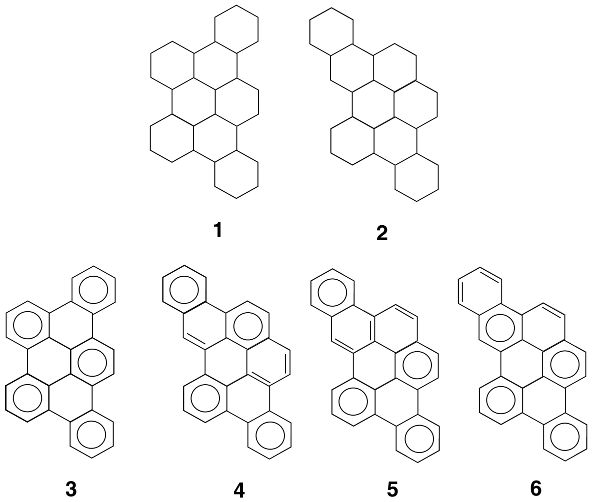

**Fig. 1** Tribenzo[*b*, *n*, *pqr*]perylene (**1**), tribenzo[*b*, *k*, *pqr*]-perylene (**2**), and their *Clar* aromatic sextet formulas. Whereas **1** has a unique sextet formula with five aromatic sextets (**3**), its isomer **2** is represented by three such formulas (**4**, **5**, **6**), each with 4 aromatic sextets

peculiar physico-chemical properties of benzenoid molecules can be rationalized [2–4]. Research along these lines is currently very active, see the reviews [4, 5], the papers [6–8], and the references cited therein.

A critical-minded chemist may argue that *Clar*'s reasoning [1, 2] is no *explanation* whatsoever why tribenzo[*b*,*n*,*pqr*]perylene is more stable than tribenzo[*b*,*k*,*pqr*]perylene. Namely, there is no physical argument (especially, no such argument coming from quantum theory) that would relate the number of aromatic sextets with the stability (especially, thermodynamic stability) of a benzenoid molecule. The only reason why we may *believe* in *Clar* theory is that there exist numerous examples that the stability of isomeric benzenoid compounds increases with the number of their aromatic sextets. There, however, exist exceptions of this rule [8–10].

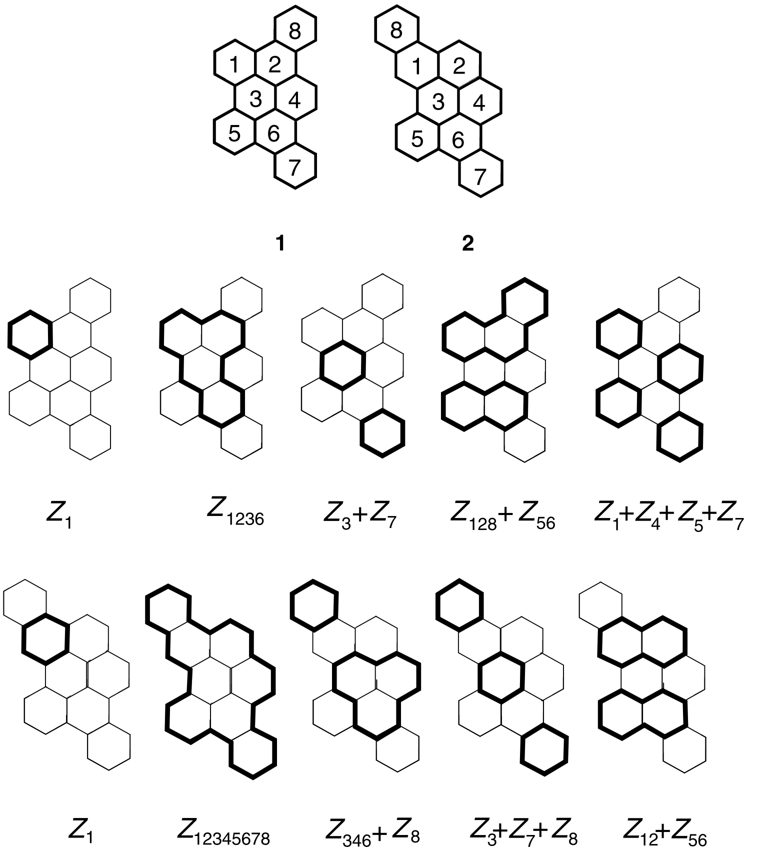

**Fig. 2** The numbering of the six-membered rings of the tribenzoperylenes **1** and **2**, and examples showing the way in which their cycles, pairs of disjoint cycles, triplets of mutually disjoint cycles, *etc.* are denoted. Tribenzo[*b*,*n*,*pqr*]perylene (**1**) has a total of 109 cycles, 106 pairs of disjoint cycles, as well as 34 triples, 5 quartets, and 1 quintet of mutually disjoint cycles. Tribenzo[*b*,*k*,*pqr*]perylene (**2**) has a total of 104 cycles, 114 pairs of disjoint cycles, as well as 32 triples and 5 quartets of mutually disjoint cycles

In this paper we show how the stability order of the tribenzoperylene isomers could be explained by using a completely different way of reasoning, namely by comparing the energy-effects of their various cycles.

There are several possible ways to quantify cyclic conjugation of polycyclic conjugated molecules. Details of these approaches can be found in the books [2, 3] and reviews [4, 5]. Another, conceptually different approach is the (molecular-orbital-based) calculation of the energy-effect that results from conjugation in a particular cycle, or pairs of cycles, or triplets of cycles, *etc*. A pioneering work along these lines was published already in the 1960s [11], but the complete theory could be formulated only after appropriate graph-theoretical methods were developed. The energy-effects of individual cycles in polycyclic conjugated molecules were first calculated by one of the present authors [12, 13], and independently (in a somewhat different manner) by *Aihara* [14]. Details of this theory of cyclic conjugation are found in the review [15] and the recent paper [16].

Let $G$ be the molecular graph [17], representing a polycyclic conjugated molecule, and $Z$ a cycle contained in it. Then the energy-effect resulting from the cyclic interaction of the $\pi$-electrons along $Z$ is expressed as

$$ef(Z) = ef(Z\,|\,G) = \frac{2}{\pi}\int_0^\infty \ln\left|\frac{\phi(G,ix)+2\phi(G-Z,ix)}{\phi(G,ix)}\right| dx \qquad (1)$$

where $\phi(G,x)$ is the characteristic polynomial of $G$, and $\phi(G-Z,x)$ is the characteristic polynomial of the subgraph $G-Z$, obtained by deleting the cycle $Z$ from $G$. Further, $i=\sqrt{-1}$.

The analogous energy-effect of two disjoint cycles $Z_1$ and $Z_2$ is

$$ef(Z_1,Z_2) = ef(Z_1,Z_2\,|\,G) = \frac{2}{\pi}\int_0^\infty \ln\left|\frac{\phi(G,ix)-4\phi(G-Z_1-Z_2,ix)}{\phi(G,ix)}\right| dx$$

of three mutually disjoint cycles $Z_1$, $Z_2$, and $Z_3$ is

$$ef(Z_1,Z_2,Z_3) = ef(Z_1,Z_2,Z_3\,|\,G) = \frac{2}{\pi}\int_0^\infty \ln\left|\frac{\phi(G,ix)+8\phi(G-Z_1-Z_2-Z_3,ix)}{\phi(G,ix)}\right| dx$$

and in the general case,

$$ef(Z_1,\ldots,Z_n) = ef(Z_1,\ldots,Z_n|G) = \frac{2}{\pi}\int_0^\infty \ln\left|\frac{\phi(G,ix)-(-2)^n\phi(G-Z_1-\cdots-Z_n,ix)}{\phi(G,ix)}\right| dx. \qquad (2)$$

If the cycles are not disjoint, then their collective energy effect is zero. For more details on the quantity *ef* see Refs. [15, 16] and the references cited therein.

The above-specified energy-effects are expressed in the units of the HMO carbon–carbon resonance integral $\beta$, whose value is negative. Therefore, if $ef>0$, then the respective interaction of $\pi$-electrons causes thermodynamic stabilization. Otherwise, $ef<0$ implies thermodynamic destabilization.

## Results and discussion

### *Cycles in tribenzoperylenes*

In Fig. 2 is indicated the labelling of the rings of the two tribenzoperylenes considered, and examples are provided clarifying the way in which their

**Table 1** The energy-effects (in $\beta$-units) of the six- and ten-membered cycles of tribenzoperylenes **1** and **2**, *cf.* Fig. 1. The labelling of the cycles is indicated in Fig. 2

| Cycle | Size | **1** | **2** |
|---|---|---|---|
| $Z_1$ | 6 | 0.1462 | 0.0553 |
| $Z_2$ | 6 | 0.0264 | 0.0757 |
| $Z_3$ | 6 | 0.0255 | 0.0231 |
| $Z_4$ | 6 | 0.1124 | 0.0901 |
| $Z_5$ | 6 | 0.1462 | 0.1496 |
| $Z_6$ | 6 | 0.0264 | 0.0285 |
| $Z_7$ | 6 | 0.1886 | 0.1840 |
| $Z_8$ | 6 | 0.1886 | 0.1386 |
| $Z_{12}$ | 10 | 0.0096 | 0.0113 |
| $Z_{13}$ | 10 | 0.0083 | 0.0033 |
| $Z_{18}$ | 10 | – | 0.0311 |
| $Z_{23}$ | 10 | 0.0013 | 0.0034 |
| $Z_{24}$ | 10 | 0.0066 | 0.0251 |
| $Z_{28}$ | 10 | 0.0111 | – |
| $Z_{34}$ | 10 | 0.0070 | 0.0044 |
| $Z_{35}$ | 10 | 0.0083 | 0.0064 |
| $Z_{36}$ | 10 | 0.0013 | 0.0013 |
| $Z_{46}$ | 10 | 0.0066 | 0.0054 |
| $Z_{56}$ | 10 | 0.0096 | 0.0111 |
| $Z_{67}$ | 10 | 0.0111 | 0.0128 |

**Table 2** Same data as in Table 1 for pairs of disjoint six- and ten-membered cycles

| Cycle | Size | **1** | **2** | Cycle | Size | **1** | **2** |
|---|---|---|---|---|---|---|---|
| $Z_1 + Z_4$ | $6+6$ | 0.0324 | 0.0111 | $Z_6 + Z_{12}$ | $6+10$ | 0.0006 | 0.0007 |
| $Z_1 + Z_5$ | $6+6$ | 0.0339 | 0.0119 | $Z_6 + Z_{18}$ | $6+10$ | – | 0.0008 |
| $Z_1 + Z_6$ | $6+6$ | 0.0031 | 0.0012 | $Z_6 + Z_{28}$ | $6+10$ | 0.0007 | – |
| $Z_1 + Z_7$ | $6+6$ | 0.0337 | 0.0118 | $Z_7 + Z_{12}$ | $6+10$ | 0.0022 | 0.0026 |
| $Z_1 + Z_8$ | $6+6$ | 0.0433 | – | $Z_7 + Z_{13}$ | $6+10$ | 0.0022 | 0.0008 |
| $Z_2 + Z_5$ | $6+6$ | 0.0031 | 0.0118 | $Z_7 + Z_{18}$ | $6+10$ | – | 0.0090 |
| $Z_2 + Z_6$ | $6+6$ | 0.0012 | 0.0040 | $Z_7 + Z_{23}$ | $6+10$ | 0.0002 | 0.0005 |
| $Z_2 + Z_7$ | $6+6$ | 0.0037 | 0.0138 | $Z_7 + Z_{24}$ | $6+10$ | 0.0022 | 0.0093 |
| $Z_2 + Z_8$ | $6+6$ | – | 0.0196 | $Z_7 + Z_{28}$ | $6+10$ | 0.0024 | – |
| $Z_3 + Z_7$ | $6+6$ | 0.0037 | 0.0028 | $Z_7 + Z_{34}$ | $6+10$ | 0.0022 | 0.0012 |
| $Z_3 + Z_8$ | $6+6$ | 0.0037 | 0.0017 | $Z_7 + Z_{35}$ | $6+10$ | 0.0024 | 0.0016 |
| $Z_4 + Z_5$ | $6+6$ | 0.0324 | 0.0249 | $Z_8 + Z_{13}$ | $6+10$ | 0.0024 | – |
| $Z_4 + Z_7$ | $6+6$ | 0.0337 | 0.0261 | $Z_8 + Z_{23}$ | $6+10$ | – | 0.0005 |
| $Z_4 + Z_8$ | $6+6$ | 0.0337 | 0.0131 | $Z_8 + Z_{24}$ | $6+10$ | – | 0.0090 |
| $Z_5 + Z_7$ | $6+6$ | 0.0433 | 0.0446 | $Z_8 + Z_{34}$ | $6+10$ | 0.0022 | 0.0004 |
| $Z_5 + Z_8$ | $6+6$ | 0.0337 | 0.0261 | $Z_8 + Z_{35}$ | $6+10$ | 0.0022 | 0.0007 |
| $Z_6 + Z_8$ | $6+6$ | 0.0037 | 0.0041 | $Z_8 + Z_{36}$ | $6+10$ | 0.0002 | 0.0001 |
| $Z_7 + Z_8$ | $6+6$ | 0.0433 | 0.0287 | $Z_8 + Z_{46}$ | $6+10$ | 0.0022 | 0.0009 |
| $Z_1 + Z_{46}$ | $6+10$ | 0.0020 | 0.0007 | $Z_8 + Z_{56}$ | $6+10$ | 0.0022 | 0.0025 |
| $Z_1 + Z_{56}$ | $6+10$ | 0.0021 | 0.0008 | $Z_8 + Z_{67}$ | $6+10$ | 0.0024 | 0.0028 |
| $Z_1 + Z_{67}$ | $6+10$ | 0.0021 | 0.0008 | $Z_{12} + Z_{56}$ | $10+10$ | 0.0004 | 0.0005 |
| $Z_2 + Z_{56}$ | $6+10$ | 0.0006 | 0.0024 | $Z_{12} + Z_{67}$ | $10+10$ | 0.0004 | 0.0005 |
| $Z_2 + Z_{67}$ | $6+10$ | 0.0007 | 0.0028 | $Z_{18} + Z_{46}$ | $10+10$ | – | 0.0005 |
| $Z_4 + Z_{18}$ | $6+10$ | – | 0.0086 | $Z_{18} + Z_{56}$ | $10+10$ | – | 0.0006 |
| $Z_5 + Z_{12}$ | $6+10$ | 0.0021 | 0.0026 | $Z_{18} + Z_{67}$ | $10+10$ | – | 0.0006 |
| $Z_5 + Z_{18}$ | $6+10$ | – | 0.0091 | $Z_{28} + Z_{56}$ | $10+10$ | 0.0004 | – |
| $Z_5 + Z_{24}$ | $6+10$ | 0.0020 | 0.0087 | $Z_{28} + Z_{67}$ | $10+10$ | 0.0005 | – |
| $Z_5 + Z_{28}$ | $6+10$ | 0.0021 | – | | | | |

cycles, as well as pairs, triples, *etc.* of disjoint cycles are denoted. For instance, in **1**, $Z_{1236}$ denotes the 17-membered cycle embracing the rings 1, 2, 3, and 6. The 26-membered cycle, embracing all the eight rings of **8**, is denoted by $Z_{12345678}$; thus $Z_{12345678}$ is the perimeter of **2**. By $Z_{28} + Z_{56}$ (not shown in Fig. 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 **2** would induce a triple of mutually disjoint cycles – $Z_2 + Z_8 + Z_{56}$, consisting of two 6-membered and one 10-membered cycle.

The examination of cyclic conjugation of a large number of benzenoid hydrocarbons [15] showed that in the majority of cases, 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.* For this reason, as well as because of the very large number of cycles in the tribenzoperylenes (*cf.* Fig. 2), in what follows we consider and discuss only the $ef$-values of 6- and 10-membered cycles, and of their disjoint combinations.[1]

At this point we mention that in benzenoid systems, all cycles of size $4k+2$, $k = 1, 2, 3, \ldots$, have a stabilizing energy-effect (positive $ef$) [15, 18]. The cycles of size $4k, k = 3, 4, 5, \ldots$, have a destabilizing energy-effect (negative $ef$) [15, 18]. The energy-effects of the $(4k)$-membered cycles in tribenzoperylenes are very small, and therefore their neglect is fully justified. For instance, for the 12-membered cycles $Z_{123}$ and $Z_{346}$ we have $ef(Z_{123}\,|\,\mathbf{1}) = -0.0005$, $ef(Z_{123}\,|\,\mathbf{2}) = -0.0006$, $ef(Z_{346}\,|\,\mathbf{1}) = -0.0004$, and $ef(Z_{346}\,|\,\mathbf{2}) = -0.0003$, values that should be compared with those in Tables 1 and 2. The energy-effects of $(4k)$-membered cycles whose size is greater than 12 are practically equal to zero.

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[1] The $ef$-values of all cycles and disjoint combinations thereof of **1** and **2** are available from the authors, upon request.

**Table 3** Same data as in Table 1 for triplets of mutually disjoint six- and ten-membered cycles

| Cycle | Size | **1** | **2** |
|---|---|---|---|
| $Z_1 + Z_4 + Z_5$ | 6 + 6 + 6 | 0.0127 | 0.0043 |
| $Z_1 + Z_4 + Z_7$ | 6 + 6 + 6 | 0.0127 | 0.0043 |
| $Z_1 + Z_4 + Z_8$ | 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 | – |
| $Z_1 + Z_6 + Z_8$ | 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 |
| $Z_2 + Z_6 + Z_8$ | 6 + 6 + 6 | – | 0.0013 |
| $Z_2 + Z_7 + Z_8$ | 6 + 6 + 6 | – | 0.0049 |
| $Z_3 + Z_7 + Z_8$ | 6 + 6 + 6 | 0.0010 | 0.0003 |
| $Z_4 + Z_5 + Z_7$ | 6 + 6 + 6 | 0.0130 | 0.0100 |
| $Z_4 + Z_5 + Z_8$ | 6 + 6 + 6 | 0.0127 | 0.0047 |
| $Z_4 + Z_7 + Z_8$ | 6 + 6 + 6 | 0.0130 | 0.0048 |
| $Z_5 + Z_7 + Z_8$ | 6 + 6 + 6 | 0.0130 | 0.0100 |
| $Z_1 + Z_8 + Z_{46}$ | 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 |
| $Z_2 + Z_8 + Z_{67}$ | 6 + 6 + 10 | – | 0.0011 |
| $Z_4 + Z_5 + Z_{18}$ | 6 + 6 + 10 | – | 0.0036 |
| $Z_4 + Z_7 + Z_{18}$ | 6 + 6 + 10 | – | 0.0036 |
| $Z_5 + Z_7 + Z_{12}$ | 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 | – | 0.0038 |
| $Z_5 + Z_7 + Z_{28}$ | 6 + 6 + 10 | 0.0008 | – |
| $Z_5 + Z_8 + Z_{24}$ | 6 + 6 + 10 | – | 0.0036 |
| $Z_7 + Z_8 + Z_{13}$ | 6 + 6 + 10 | 0.0008 | – |
| $Z_7 + Z_8 + Z_{23}$ | 6 + 6 + 10 | – | 0.0001 |
| $Z_7 + Z_8 + Z_{24}$ | 6 + 6 + 10 | – | 0.0038 |
| $Z_7 + Z_8 + Z_{34}$ | 6 + 6 + 10 | 0.0008 | 0.0001 |
| $Z_7 + Z_8 + Z_{35}$ | 6 + 6 + 10 | 0.0008 | 0.0002 |

**Table 4** Same data as in Table 1 for quartets of mutually disjoint six- and ten-membered cycles. Also the energy-effect of the five mutually disjoint six-membered cycles of **1** is included

| Cycle | Size | **1** | **2** |
|---|---|---|---|
| $Z_1 + Z_4 + Z_5 + Z_7$ | 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 |
| $Z_4 + Z_5 + Z_7 + Z_8$ | 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 | – |

## *Cyclic conjugation in tribenzoperylenes*

Using Eqs. (1) and (2) we have computed all cyclic-conjugation energy-effects in the tribenzoperylenes **1** and **2**. The respective results, pertaining to their six- and ten-membered cycles, are given in Tables 1–4.

By inspection of the 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. (Equally small, or even smaller, are the *ef*-values pertaining to cycles greater than 10, not shown in Tables 1–4.)

Therefore, although in the tribenzoperylenes **1** and **2** 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.

From Figs. 1 and 2 we see that in the isomers **1** and **2** one may directly compare the energy-effects resulting from cyclic conjugation in the rings 3, 4, 5, 6, and 7. Some of these are nearly equal, in particular $ef(Z_3)$, $ef(Z_5)$, $ef(Z_6)$, $ef(Z_7)$, $ef(Z_{36})$, and $ef(Z_5 + Z_7)$. Some energy-effects slightly favor the isomer **1**, in particular, $ef(Z_{34})$, $ef(Z_{35})$, $ef(Z_{46})$, $ef(Z_3 + Z_7)$, $ef(Z_4 + Z_5)$, and $ef(Z_4 + Z_5)$, whereas a few slightly favor the isomer **2**, in particular $ef(Z_{56})$ and $ef(Z_{67})$. However, only one of these energy-effects, namely of $Z_4$, is much stronger in **1** than in **2**. Indeed,

$$ef(Z_4\,|\,\mathbf{1}) = 0.112$$
$$ef(Z_4\,|\,\mathbf{2}) = 0.090.$$

The effects of cyclic conjugation resulting from the rings 1, 2, and 8 cannot be directly compared. However, these again favor the isomer **1**. To see this observe that

$$ef(Z_1\,|\,\mathbf{1}) + ef(Z_2\,|\,\mathbf{1}) + ef(Z_8\,|\,\mathbf{1}) = 0.361$$
$$ef(Z_1\,|\,\mathbf{2}) + ef(Z_2\,|\,\mathbf{2}) + ef(Z_8\,|\,\mathbf{2}) = 0.270$$

as well as

$$ef(Z_1 + Z_8\,|\,\mathbf{1}) = 0.043$$
$$ef(Z_2 + Z_8\,|\,\mathbf{2}) = 0.020.$$

It turns out that only the two above specified cyclic conjugation effects are responsible for the increased stability of the tribenzoperylene **1** relative to its isomer **2**. These pertain to the ring 4 and to the domain spanned by the rings 1, 2, and 8.

Thus, our considerations based on energy arguments yield the same conclusion as *Clar* theory: tribenzo[*b*,*n*,*pqr*]perylene (**1**) is more stable than tribenzo[*b*,*k*,*pqr*]perylene (**2**). However, the cause of this stability difference is seen in only a few cyclic conjugation energy-effects, involving only two regions of the two molecules. Our approach distinguishes and quantifies 255 cyclic conjugation energy-effects in **1** and **2**, 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 $\beta$-units. In **2** there is no such quintet, but there are three quartets of mutually disjoint hexagons, each stabilizing **2** by some 0.020 $\beta$-units, roughly the same as the quintet in **1**.

In conclusion, the analysis performed in this paper shows that the success of *Clar* theory cannot be explained on the basis of energy-effects caused by cyclic conjugation of $\pi$-electrons (and therefore remains to be a mystery of theoretical chemistry). 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 a very few energy-effects are large and may significantly differ between isomers, thus deciding their stability order.

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