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Pairwise energy effects of rings in benzo-annelated perylenes

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DFT calculations have been used to corroborate two regularities resulting from the analysis of cyclic conjugation in benzo-annelated perylenes reported earlier, viz., (a) the annelation of a benzene ring in angular position increases the extent of cyclic conjugation in the central ring, and, (b) the annelation of a benzene ring in linear position decreases the extent of cyclic conjugation in the central ring of benzo-annelated perylenes [Gutman *et al*., *Mon Chem,* 135 (2004) 1389]. In addition, a new method for assessing the pairwise energy effect is used to rationalize the obtained results. In the case of benzo-annelated perylenes, the pairwise energy effect is found to be related to the total π-electron energy of the two-ring-deleted conjugated fragment.

Keywords: Theoretical chemistry, Graph theory, Cyclic conjugation, Pairwise energy, Perylenes, Benzo-annelated perylenes

There are several methods for analyzing cyclic conjugation in polycyclic compounds. The effect of cyclic conjugation can be rationalized by its different manifestations, such as specific energetic, geometric and magnetic properties of polycyclic molecules[1-5]. An approach based on assessing the energy effect of cyclic conjugation was developed within the Hückel molecular orbital (HMO) theory by one of the present authors (for details see the review[6] and the recent papers[7-9]). Thus, by using chemical-graph-theoretical tools, the energy effect of a cycle Z in the molecule whose molecular graph is G can be computed by Eq. (1),

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

where $\phi(G,x)$ is the characteristic polynomial of G, $G - Z$ is the subgraph obtained by deleting Z from G and $i = \sqrt{-1}$. This and the energy effects described below are expressed in units of the HMO carbon-carbon resonance integral β. It is important to note that because β is negative-valued, positive values of *ef* and *pef* indicate a stabilizing effect caused by cyclic conjugation in the given cycle(s).

We have reported the cyclic conjugation in benzo-annelated perylenes by employing Eq. (1) earlier[10]. There exist two mono-, nine di-, eight tri-, and seven tetra-benzo-perylenes, a total of 26 distinct benzo-annelated derivatives (Fig. 1). If some ring in the given polycyclic molecule contains essentially single carbon-carbon bonds (i. e., the carbon-carbon bond that is single in all Kekulé structures), then such a ring is said to be "empty". Perylene is the simplest benzenoid hydrocarbon with an "empty" ring. According to the classical theories[1,4], in the "empty" rings of perylene derivatives there would be no cyclic conjugation. It has been shown that such a picture of cyclic conjugation is oversimplified and is not always true (for details see ref. 10).

Two regularities, which we want to emphasize here, were observed[10]. The first regularity was that the annelation of a ring in angular position increases the energy effect of the central ring of perylene derivatives. The increase of the extent of cyclic conjugation in the central ring is proportional to the number of such angular annelations. A characteristic example, illustrating these regularities is given in Fig. 2. While the *ef*(5) of perylene is 0.0218, the *ef*(5) values of the molecules a1, a1a2, a1a2a3, and a1a2a3a4 having one, two, three, and four angular annelations are 0.0263, 0.0325, 0.0407 and 0.0522, respectively.

The second regularity noticed was that annelation in linear position decreases the energy effect of the

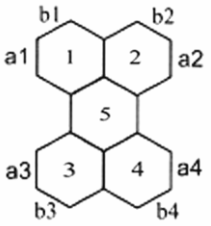

Fig. 1. — Labeling of the rings of perylene. From the viewpoint of the central ring 5, annelation may be either angular (in positions a1, a2, a3, and a4) or linear (in positions b1, b2, b3, and b4).

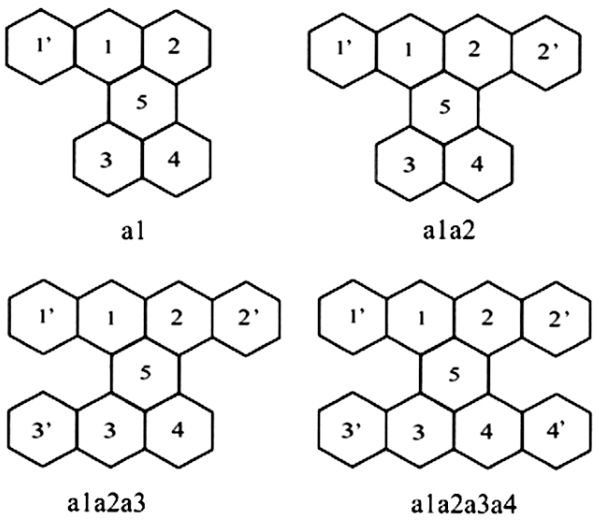

Fig. 2 — Some angularly annelated perylenes. Molecules a1, a1a2, a1a2a3 and a1a2a3a4 have one, two, three and four angular annelations, respectively.

central ring of perylene derivatives. For instance, we can compare *ef*(5) of perylene and *ef*(5) of the molecules b1, b1b2, b1b2b3 and b1b2b3b4 having one, two, three, and four linear annelations (Fig. 3). The corresponding *ef*(5) values are 0.0207, 0.0193, 0,0184 and 0.0173, respectively. It should be noted that the effect of the rings in angular position is significantly greater than the analogous effect of the rings in linear position.

Since these regularities were established by employing a method at the level of the simple HMO method, there could be doubts whether the observed results will remain valid at higher levels of theory or they are just caused by the simplicity of the HMO model. In order to eliminate these doubts we performed a DFT study which is outlined in the subsequent section.

There are several ways to measure the extent of cyclic conjugation in a polycyclic molecule by using DFT methods[5]. One way, based on molecular geometry, is to take into account the equalization of bond lengths. Among several indices aimed at measuring such "geometry" effect of cyclic conjugation, the *HOMA* index[11,12] appears to be the most popular. The *HOMA* index is calculated by Eq. (2),

$$HOMA = 1 - \frac{1}{m}\sum_{i=1}^{m} \alpha (R_{opt} - R_i)^2 \qquad \ldots(2)$$

where m is the number of bonds of the ring/cycle considered, $\alpha = 30.356 \times 10^{-3}$ is a normalization

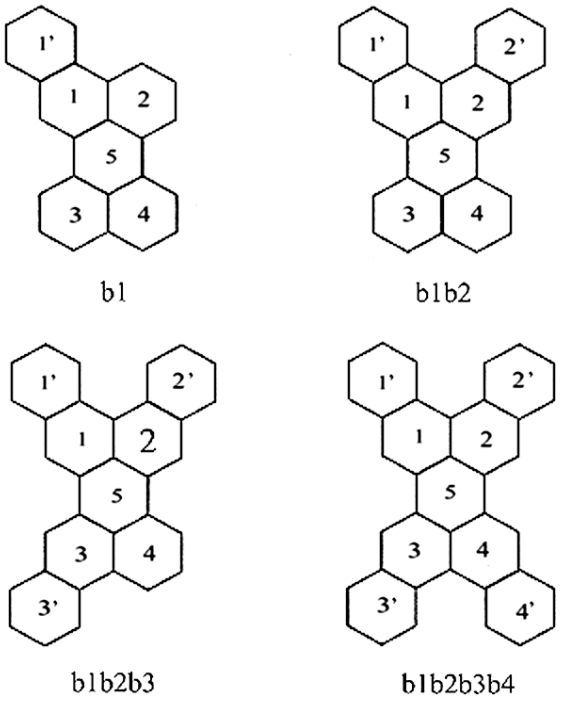

Fig. 3 — Some linearly annelated perylenes. Molecules b1, b1b2, b1b2b3 and b1b2b3b4 have one, two, three and four linear annelations, respectively.

constant, R_{opt} is the bond length for a fully delocalized π-electron system (R_{opt} is set equal to 140.4 pm) and R_i stands for an actual bond length. In this work, the parameters α and R_{opt} were determined in the same way as in the original work[11], except that we used the lengths of the essentially single bond of perylene and of the fixed double bond of zethrene, obtained at the B3LYP/6-31G(d) level of theory.

The *HOMA* index for the central rings of all benzo-annelated perylenes is given in Table 1. The required bond lengths were obtained by full geometry optimization of the given molecules at the B3LYP/6-31G(d) level of theory. All calculations were done by the GAUSSIAN 03 package[13].

By examining the calculated *HOMA* values (Table 1) it was found that both the above outlined regularities are confirmed without any exception. For instance, the molecules a1, a1a2, a1a2a3 and a1a2a3a4 (Fig. 2), with one, two, three, and four angular annelations, have *HOMA*(5) values of 0.3666, 0.4355, 0.4815 and 0.5498, respectively, while the *HOMA*(5) for perylene is 0.3052. On the other hand, the molecules b1, b1b2, b1b2b3 and b1b2b3b4, having one, two, three, and four linear annelations have the *HOMA*(5) values equal to 0.2427, 0.2222, 0.1879 and 0.1537, respectively.

Table 1 — *HOMA* values of the ring 5 in perylene and its benzo-annelated derivatives

Comp.[a]	*HOMA*	Comp.[a]	*HOMA*
perylene	0.3052	a1a3b2	0.3553
a1	0.3666	a1a4b2	0.3464
b1	0.2427	a1b2b3	0.2699
a1a2	0.4355	a1b2b4	0.2723
a1a3	0.4158	a1b3b4	0.2763
a1a4	0.4355	b1b2b3	0.1879
a1b2	0.3079	a1a2a3a4	0.5498
a1b3	0.3238	a1a2a3b4	0.4219
a1b4	0.3253	a1a2b3b4	0.3507
b1b2	0.2222	a1a3b2b4	0.2935
b1b3	0.1977	a1a4b2b3	0.2866
b1b4	0.2053	a1b2b3b4	0.2253
a1a2a3	0.4815	b1b2b3b4	0.1537
a1a2b3	0.3938		

[a]for notation see Figs 1 and 2.

Motivated by recent results in the investigation of cyclic conjugation of fluoranthene-type benzenoid hydrocarbons[8,14,15], it could be shown that these regularities can be extended to all benzenoid hydrocarbons[16,17].

From both the above specified regularities, one can see that the extent of cyclic conjugation in some rings of a polycyclic molecule strongly depends on the presence and positions of other rings. In order to quantify these results, a new method for describing the interaction of cyclic conjugation in the pairs of cycles was elaborated. This method, referred to as the pairwise energy effect (*pef*), will be briefly described here, while its mathematical details will be reported elsewhere[17].

By definition, *pef*(Z_1, Z_2) measures the influence of the cycle Z_2 on the energy effect of the cycle Z_1 in the polycyclic conjugated molecule. Recall that *ef(Z)* is defined[6] as the difference between the energy of the molecular graph, calculated from its characteristic polynomial, and the energy-like quantity, calculated from the reference polynomial that has no contribution from the cycle *Z*. Equation (1) is then deduced by applying the Coulson integral formula and the Sachs theorem. Using the analogous idea as in the original *ef*-method, the quantity *pef*(Z_1, Z_2) is conceived as the difference between the energy effect of the cycle Z_1 and a reference energy effect of the cycle Z_1 for which the contributions of the cycle Z_2 are not taken into account. This yields Eq. (3).

$$pef(Z_1,Z_2) = \frac{2}{\pi}\int_0^\infty \ln\left|\frac{\varphi(G,ix)}{\varphi(G,ix)+2\varphi(G-Z_1,ix)}\right| dx - \frac{2}{\pi}\int_0^\infty \ln\left|\frac{\varphi(G,ix)+2\varphi(G-Z_2,ix)}{\varphi(G,ix)+2\varphi(G-Z_1,ix)+2\varphi(G-Z_2,ix)+4\varphi(G-Z_1-Z_2,ix)}\right| dx \quad \ldots(3)$$

From the property given in Eq. (4), the *pef*(z_1,z_2) can be viewed as a measure of the interactions of cyclic conjugations in the pair of the cycles Z_1 and Z_2, a pairwise ring energy effect.

$$pef(Z_1,Z_2) = pef(Z_2,Z_1) \quad \ldots(4)$$

Values of *pef* were calculated for all pairs of the central ring 5 and the annelated benzo-rings, for all considered benzo-perylenes. The obtained *pef* values are in complete agreement with the previously found regularities. For example, for molecule a1 (Fig. 1) $pef(5,1') = 0.00185$ which indicates that because of the interaction of cyclic conjugations in the rings 5 and 1', the *ef*-value of the ring 5 is increased relative to *ef* of the respective ring of perylene. Similarly, for the molecule a1a2, $pef(5,1') = pef(5,2') = 0.00265$, for the molecule a1a2a3, $pef(5,1') = 0.00366$, $pef(5,2') = 0.00376$, $pef(5,3') = 0.00368$, and for the molecule a1a2a3a4, *pef*(5,1') = *pef*(5,2') = *pef*(5,3') = *pef*(5,4')=0.00526. This series shows that the *pef* value of two rings in angular position is proportional to the number of other angular arrangements present in the respective molecule. In all the 26 examined derivates of perylene, the *pef*-value for angular arrangements is positive, while for all linear constellations, *pef* is negative. For instance, for molecules in Fig. 2, the following results were obtained: $pef(5,1') = -0.00051$ in molecule b1, $pef(5,1') = pef(5,2') = -0.00050$ in molecule b1b2, $pef(5,1') = -0.00045$, $pef(5,2') = -0.00045$, $pef(5,3') = -0.00039$ in molecule b1b2b3, and $pef(5,1') = pef(5,2') = pef(5,3') = pef(5,4') = -0.00038$ in molecule b1b2b3b4. It is evident that the *pef* values for angular arrangements are significantly greater than those for linear arrangements.

In Fig. 4 are plotted the *ef*-values of the ring 5 of the benzo-annelated perylenes versus the sum of all *pef* values of the respective ring 5 and the annelated benzo-rings. This correlation is quite good, but evidently non-linear. It can be expressed by means of an expression of the form Eq. (5),

$$ef = c_1 + c_2 e^{c_3 \sum pef} \quad \ldots(5)$$

where $c_1 = (0.065 \pm 0.003)$, $c_2 = (-0.043 \pm 0.003)$, $c_3 = (-54 \pm 5)$. The respective correlation coefficient

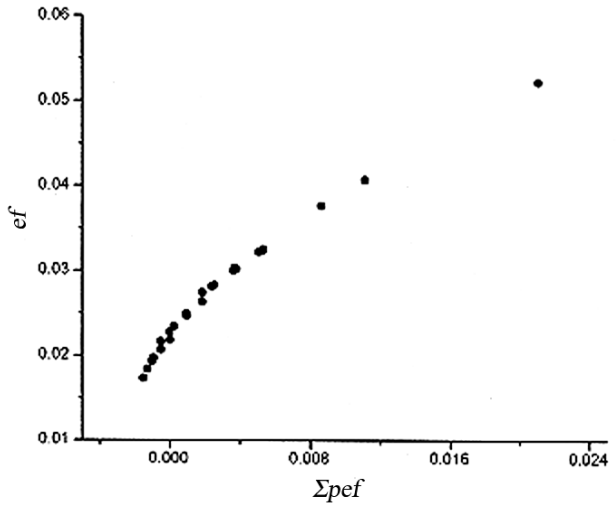

Fig. 4 — Energy effect of the central ring of benzo-annelated perylenes (*ef*) versus the sum of *pef* values of the central ring and the annelated benzo-rings (Σ*pef*).

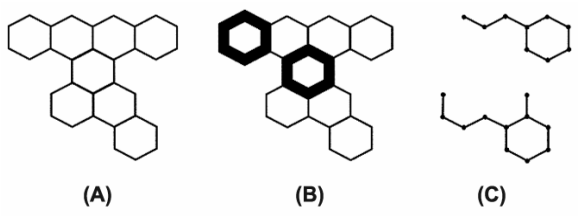

Fig. 5 — The tribenzoperylene isomer a1a2b4 (**A**), its two rings Z_5 and $Z_{1'}$ indicated (**B**), and the molecular graph representing the conjugated fragment obtained by deleting the rings Z_5 and $Z_{1'}$ (**C**). In Fig. 6 the energies of such two-ring-deleted fragments, e. g, $E(a1a2b4-Z_5-Z_{1'})$, are plotted versus the respective *pef* values, e. g., $pef\,(Z_5,Z_{1'})$, for all ring pairs involving the central ring Z_5 of all tribenzoperylene isomers.

is 0.9968. The existence of good correlation in Fig. 4 leads to two important conclusions. Firstly, the *ef* value, i. e., the extent of cyclic conjugation in the central ring of benzo-annelated perylenes can be assessed by means of its interaction with the annelated rings. Secondly, the interactions measured by *pef* are basically additive.

To understand the meaning of *pef* from the chemists' viewpoint, we have shown how it is related to the total π-electron energy of the respective two-ring-deleted conjugated fragment, cf. Fig. 5. Note that the total π-electron energy (*E*) is a much studied quantity, whose applications are well-known (details on *E* are found in the reviews[18,19] and the recent papers[20-27]). Figure 6 shows a characteristic plot of the total π-electron energy of the two-ring-deleted conjugated fragment versus the corresponding *pef*

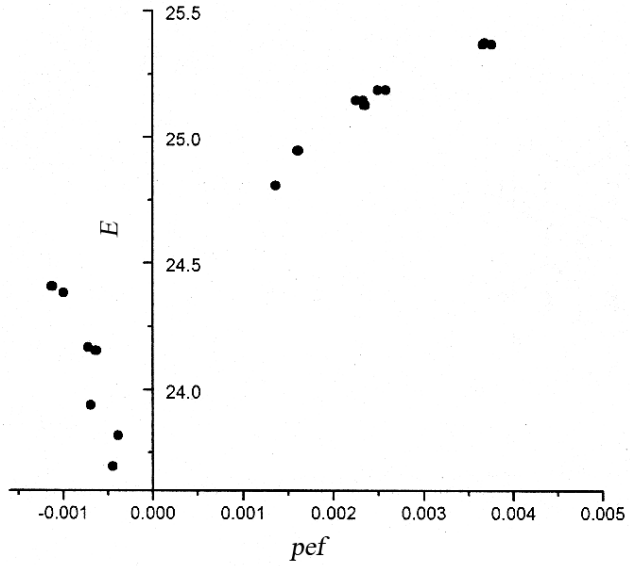

Fig. 6 — Total π-electron energy (*E*) of the two-ring-deleted conjugated fragment versus the respective *pef* values of the eight tribenzoperylene isomers; for details see Fig. 5 and text.

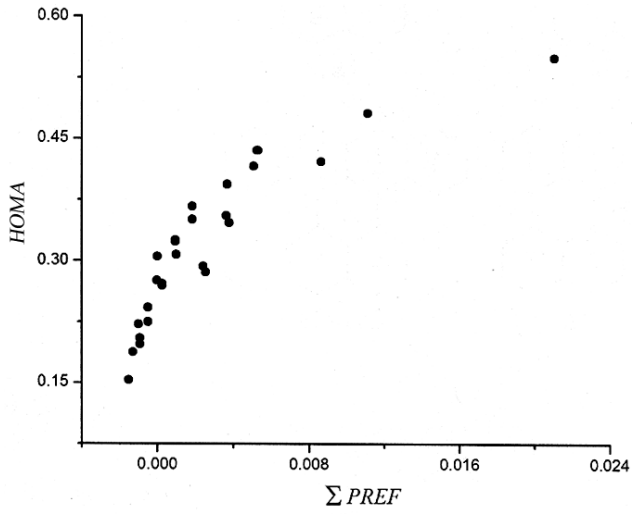

Fig. 7 — *HOMA* index of the central ring of benzo-annelated perylenes versus the sum of *pef* values of the central ring and the annelated benzo-rings (Σ*pef*).

value. Since *E* strongly depends on the molecule size, the data in Fig. 6 are restricted to isomeric tribenzoperylenes. From Fig. 6 it is seen that the positive *pef*-values increase with increasing *E*, and that the same holds good for the absolute value of the negative *pef* values also. Recall that positive *pef* values pertain to pairs consisting of the central ring Z_5 and a ring annelated in angular position (*a*), whereas the *pef* values of the ring pairs Z_5 and a ring in linear position (*b*) are negative.

Thus, from Fig. 6 we see that there is a positive correlation between E and $|pef|$. This may be understood as an indication that $pef(Z_1,Z_2)$ is a kind of measure of the energy-interaction between the rings Z_1 and Z_2.

Plots of *HOMA* values of the central ring versus the sum of *pef* values of the central ring and the annelated benzo-rings are shown in Fig. 7. The correlation is somewhat weaker than the one in Fig. 4 and can be expressed by Eq. (6),

$$HOMA = c_1 + c_2\, e^{c_3 \sum pef} \quad \ldots (6)$$

where c_1=(0.54±0.03), c_2=(−0.28±0.03), c3=(−150±30) and the correlation coefficient is 0.9547. The obtained correlation indicates that the predictions based on the *pef* approach agree with those obtained by using higher levels of theory.

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