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Cyclic conjugation in benzo-annelated triphenylenes

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Abstract: Cyclic conjugation in benzo-annelated triphenylenes was studied by means of the energy effect (*ef*) and the π -electron content (*EC*) of the six-membered rings. A regularity that was earlier discovered in the case of acenaphthylene and fluoranthene congeners is now shown to hold also for benzo-annelated triphenylenes: Benzenoid rings that are annelated angularly with regard to the central six-membered ring Z_0 of triphenylene increase the intensity of the cyclic conjugation in Z_0 , whereas linearly annelated benzenoid rings decrease the cyclic conjugation in Z_0 . The *ef*- and *EC*-values are strongly correlated, yet in a non-linear manner.

Keywords: cyclic conjugation; energy effect of cyclic conjugation; triphenylene; benzo-annelated triphenylene.

INTRODUCTION

Whereas benzenoid hydrocarbons have been in the focus of interest of theoretical organic chemistry for almost a whole century,^{1–3} a systematic study of the structurally closely related acenaphthylene and fluoranthene congeners have only started quite recently.⁴ (Recall that these latter polycyclic conjugated molecules differ from benzenoids by possessing one five-membered ring). In a series of recent works^{4–14} various structure-property relations for acenaphthylenes and fluoranthenes were established. The most remarkable of these seem to be the regularities found for the intensity of cyclic conjugation in the five-membered ring: benzenoid rings that are annelated angularly (resp. linearly) with regard to the five-membered ring increase (resp. decrease) the intensity of the cyclic conjugation in it. These, so-called PCP- and linear rules, were first recognized within studies of the energy effects (*ef*) of the individual rings,^{6–8,10} but were eventually corroborated by several independent theoretical approaches.^{9,12–14} It was shown that fully analogous regularities hold for acenaphthylene and fluoranthene analogs, in which instead of a 5-membered ring, there is some other odd-membered ring.¹⁵

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Bearing the above in mind, the obvious question that emerges is whether there similar regularities exist also for ordinary benzenoid hydrocarbons. The aim of this work was to provide an answer. In order to arrive at clear and conclusive results, the class of benzo-annelated triphenylenes (*cf.* Fig. 1) was chosen for study.

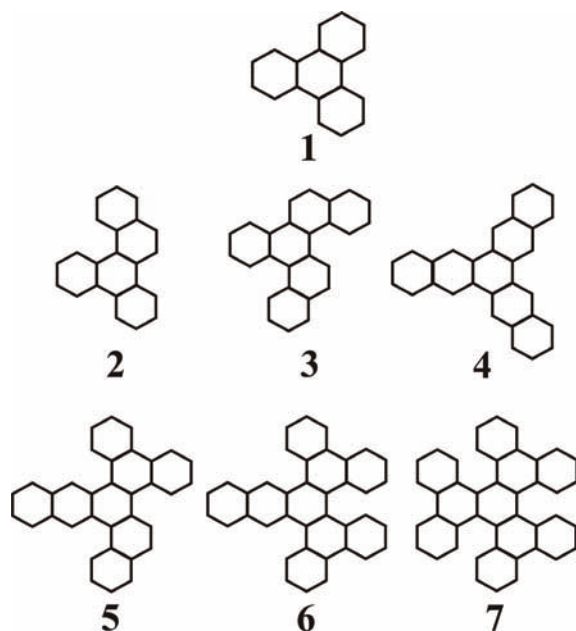


Fig 1. Triphenylene (**1**) and some of its benzo-annelated derivatives: **2–7** are examples of mono-, di-, tri-, tetra-, penta-, and hexa-benzo annelated species. There are 2, 7, 10, 7, 2, and 1 distinct, symmetry-non-equivalent, mono-, di-, tri-, tetra-, penta-, and hexa-benzo-triphenylene isomers, *cf.* Table 1.

TRIPHENYLENE AND ITS BENZO-ANNELATED DERIVATIVES

The reason for considering cyclic conjugation in triphenylene and its benzo-annelated derivatives is the following. First of all, the members of this class of benzenoid hydrocarbons are stable, easy-to-synthesize compounds, most of which have been known for a long time.^{16,17} All members of this class have a central six-membered ring (denoted by Z_0), surrounded by three disjoint six-membered rings. To these latter rings, one or more benzene rings are annelated, each either in an angular or in a linear constellation with regard to Z_0 (*cf.* Fig. 2). In all benzo-annelated triphenylenes, the manner in which the central ring Z_0 is attached to its neighbors is exactly the same. Therefore, the very strong first-neighbor effects^{18,19} on the cyclic conjugation in Z_0 are equal in all members of the class considered, and thus may be disregarded.

Throughout this paper, an abbreviated naming of the benzo-annelated triphenylenes is employed. In Fig. 3, it is shown how the carbon-carbon bonds of triphenylene are labeled by a_1 – a_6 (for angular annelation), and by l_1 – l_3 (for linear annelation). Then, the structure of a benzo-annelated triphenylene is determined by indicating the sites of annelation. For instance, compounds **2–7**, depicted in

Fig. 1, are coded as a_1 , a_2a_4 , $l_1l_2l_3$, $a_1a_2a_4l_3$, $a_1a_2a_3a_4l_3$ and $a_1a_2a_3a_4a_5a_6$, respectively.

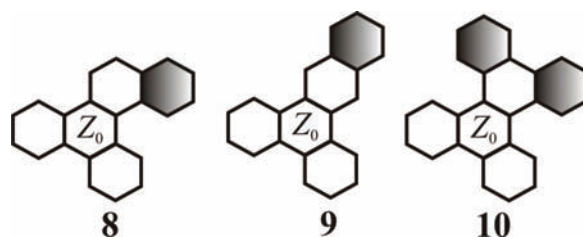


Fig. 2. Types of benzo-annulation: angular (8), linear (9), and geminal (10).

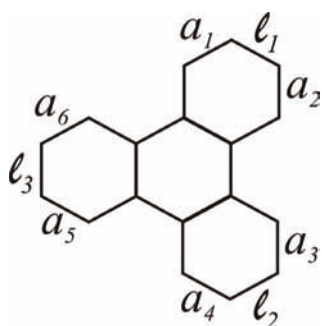


Fig. 3. Labeling of the sites of triphenylene used for denoting its benzo-annulated derivatives; for details, see text.

QUANTIFYING THE CYCLIC CONJUGATION IN A RING

A variety of theoretical methods has been proposed for assessing the intensity of cyclic conjugation in individual rings of a polycyclic conjugated molecule.^{1,2} In this work, the molecular-orbital-based energy effect (ef) and the Kekulé-structure-based π -electron content (EC) are applied. The former method was conceived already in the 1970s^{20–22} and eventually much applied. For details of the ef -method, see the review²³ and the recent works.^{6–8,10,14,15,24–28} The idea of using Kekulé structures for distributing the π -electrons of a polycyclic conjugated molecule into its rings was suggested by Randić and Balaban²⁹ in 2004, and then elaborated and applied in numerous papers.^{30–38} As will be seen in the subsequent section, in the case of benzo-annulated triphenylenes, the ef - and EC -values are strongly correlated, which confirms that they measure one and the same physico-chemical property of the underlying rings.

NUMERICAL WORK

Using in-house software, the energy effects and π -electron contents of all six-membered rings of triphenylene and all its benzo-annulated congeners were calculated. In Table I are given the (for this study most important) ef - and EC -values of the central ring Z_0 . The numerical values of the other energy effects and π -electron contents can be obtained from the authors upon request.

TABLE I. Energy effects (ef) and π -electron contents (EC) of the central ring Z_0 of triphenylene (**1**) and its benzo-annelated derivatives. The benzo-annelated species are labeled according to Fig. 3

Molecule	$ef(Z_0)$	$EC(Z_0)$
1	0.0242	2.0000
a_1	0.0304	2.2857
l_1	0.0204	1.6923
a_1a_2	0.0360	2.5000
a_1a_3	0.0390	2.5909
a_1a_4	0.0390	2.5909
a_2a_3	0.0389	2.5909
l_1a_3	0.0249	1.9500
l_1a_4	0.0249	1.9500
l_1l_2	0.0179	1.4211
$a_1a_2a_3$	0.0466	2.8158
$a_1a_2a_4$	0.0467	2.8158
$a_1a_3a_5$	0.0511	2.9143
$a_1a_3a_6$	0.0510	2.9143
$a_1a_2l_2$	0.0289	2.1471
$a_1a_3l_3$	0.0310	2.2258
$a_1a_4l_3$	0.0310	2.2258
$a_2a_3l_3$	0.0309	2.2258
$a_1l_2l_3$	0.0212	1.6552
$l_1l_2l_3$	0.0161	1.1786
$a_1a_2a_3a_4$	0.0562	3.0455
$a_1a_2a_3a_5$	0.0616	3.1475
$a_1a_2a_3a_6$	0.0615	3.1475
$a_1a_2a_4a_5$	0.0617	3.1475
$a_1a_2a_3l_3$	0.0364	2.4340
$a_1a_2l_2a_5$	0.0365	2.4340
$a_1a_2l_2l_3$	0.0242	1.8367
$a_1a_2a_3a_4a_5$	0.0748	3.3832
$a_1a_2a_3a_4l_3$	0.0432	2.6484
$a_1a_2a_3a_4a_5a_6$	0.0910	3.6190

What first requires checking is whether the ef - and EC -values yield consistent results. That this is indeed the case can be seen from Fig. 4; although not linear, the correlation between ef and EC is remarkably good and, of course, positive. This means that the (stabilizing) energy effect of the cyclic conjugation is proportional to the amount of π -electrons in the underlying ring. In other words, both ef and EC indicate to the same regularities for the structure-dependency of cyclic conjugation in the central ring of triphenylene congeners; these regularities are discussed in due detail in the subsequent section.

The correlation between the ef - and EC -values of the annelated benzenoid rings is shown in Fig. 5. Here the data points lie on three nearly parallel lines, each line pertaining to one of the three annelation modes shown in Fig. 2. Such a clustering of the data-points was expected, in view of the results of earlier investigations.^{35,36}

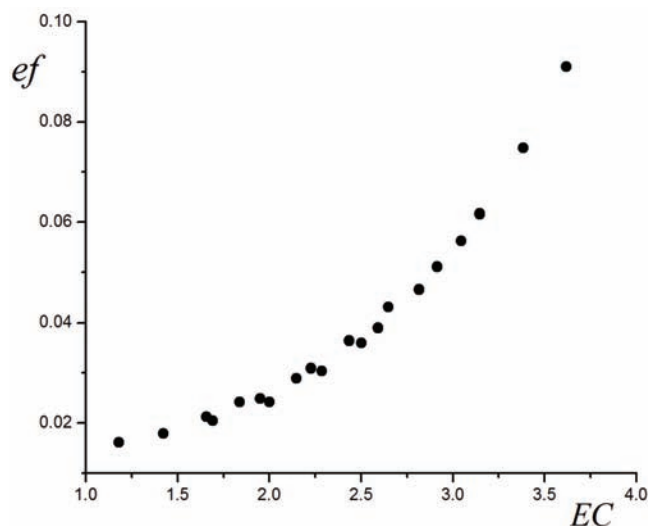


Fig. 4. The energy effect (ef) of the central ring Z_0 of triphenylene congeners vs. its π -electron content (EC).

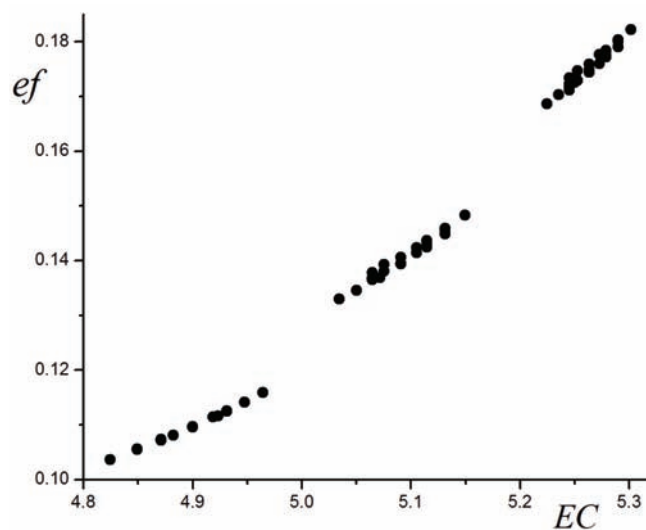


Figure 5. The energy effects (ef) of the annelated marginal rings of triphenylene congeners vs. their electron contents (EC). The clustering of the data points reflects the three modes of annelation (*cf.* Fig. 2): linear (lower line), angular (middle line), and geminal (upper line).

RESULTS AND DISCUSSION

The data collected in Table I clearly, and without a single exception, confirm the validity of the following regularities.

Rule 1 (angular effect)

Six-membered rings annelated in an angular mode (*cf.* Fig. 2) increase both the energy effect and the π -electron content of the central ring. The larger the number of angularly annelated six-membered rings is, the greater are the *ef*- and *EC*-values.

Examples. The *ef*-values of triphenylene and its a_1 , a_1a_3 , and $a_1a_3a_5$ derivatives are 0.0242, 0.0304, 0.0390, and 0.0511, respectively; the *EC*-values of the same species are 2.0000, 2.2857, 2.5909, and 2.9143, respectively.

Rule 2 (linear effect)

Six-membered rings annelated in a linear mode (*cf.* Fig. 2) decrease both the energy effect and the π -electron content of the central ring. The larger the number of linearly annelated six-membered rings is, the smaller are the *ef*- and *EC*-values.

Examples. The *ef*-values of triphenylene and its l_1 , l_1l_2 , and $l_1l_2l_3$ derivatives are 0.0242, 0.0204, 0.0179, and 0.0161, respectively; the *EC*-values of the same species are 2.0000, 1.6923, 1.4211, and 1.1786, respectively.

As a consequence of Rules 1 and 2, the minimal and maximal *ef*-values are found for the $l_1l_2l_3$ and $a_1a_2a_3a_4a_5a_6$ species, equal to 0.0161 and 0.0910, respectively. The corresponding *EC*-values are 1.1786 and 3.6190, also minimal and maximal.

Rule 3

The effect of a geminally annelation (*cf.* Fig. 2) is slightly weaker than the effect of two six-membered rings attached to different hexagons.

Examples. $ef(a_1a_2) = 0.0360$ whereas $ef(a_1a_3) = 0.0390$; $EC(a_1a_2) = 2.5000$ whereas $EC(a_1a_3) = 2.5909$, $ef(a_1a_2l_3) = 0.0289$ whereas $ef(a_1a_3l_3) = 0.0310$; $EC(a_1a_2l_3) = 2.1471$ whereas $EC(a_1a_3l_3) = 2.2258$.

If an equal number of angularly and linearly annelated marginal benzenoid rings are present, then their effect on the cyclic conjugation roughly cancels out. For example, $ef(a_2l_2) = 0.0249$ and $ef(a_1a_2l_2l_3) = 0.0242$, as compared with $ef = 0.0242$ for the parent triphenylene. Similarly, $EC(a_2l_2) = 1.9500$ and $EC(a_1a_2l_2l_3) = 1.8367$, which are nearly equal to $EC = 2.0000$ for triphenylene.

Rule 4 (isoarithmicity)

The energy effect and the π -electron content depend on the number of angularly and linearly annelated benzenoid rings, but are insensitive to their actual position. The respective *ef*-values are nearly equal, whereas the *EC*-values are strictly equal.

Examples. $ef(a_1a_3) = 0.0390$, $ef(a_1a_4) = 0.0390$, $ef(a_2a_3) = 0.0389$, and $EC(a_1a_3) = EC(a_1a_4) = EC(a_2a_3) = 2.5909$. Similarly, $ef(a_1a_3l_3) = 0.0310$,

$ef(a_1a_4l_3) = 0.0310$, $ef(a_2a_3l_3) = 0.0309$, and $EC(a_1a_3l_3) = EC(a_1a_4l_3) = EC(a_2a_3l_3) = 2.2258$.

Additional examples illustrating the above Rules 1–4 can be envisaged by inspecting the data in Table I. For more details on the concept of isoarithmeticity,³⁹ see a recent article.⁸

As a final remark, it should be mentioned that with present-day knowledge, it can be seen that the results obtained in an earlier work,⁴⁰ in which benzo-derivatives of perylene were examined, are tantamount to Rule 1. In the time when the work⁴⁰ was created, this fact was been recognized.

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ИЗВОД

ЦИКЛИЧНА КОНЈУГАЦИЈА У БЕНЗО-АНЕЛИРАНИМ ТРИФЕНИЛЕНИМА

СВЕТЛАНА ЈЕРЕМИЋ, СЛАВКО РАДЕНКОВИЋ И ИВАН ГУТМАН

Природно–математички факултет Универзитета у Крагујевцу

Циклична конјугација у бензо-анелираним трифениленима проучавана је помоћу енергетског ефекта (ef) и π -електронског садржаја (EC) шесточланих прстенова. Показано је да једна правилност, раније откривена код једињења аценафтиленског и флуорантенског типа, важи и у случају анелираних трифенилена: Бензеноидни прстен који је анелиран ангуларно у односу на централни шесточлани прстен Z_0 трифенилена, појачава интензитет цикличне конјугације у Z_0 , док линеарно анелирани бензеноидни прстен умањује цикличну конјугацију у Z_0 . Нађено је да постоји добра корелација између ef и EC , иако корелација није линеарна.

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