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 acenaphthylene 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.\textsuperscript{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\textsuperscript{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 \( a_1, a_2a_4, l_1l_3, a_1a_2a_4l_3, a_1a_2a_3a_4l_3 \) and \( a_1a_2a_3a_4a_5a_6 \), respectively.

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

Fig. 3. Labeling of the sites of triphenylene used for denoting its benzo-annelated 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 \( \pi \)-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 review\(^ {23} \) and the recent works.\(^ {6–8,10,14,15,24–28} \) The idea of using Kekulé structures for distributing the \( \pi \)-electrons of a polycyclic conjugated molecule into its rings was suggested by Randić and Balaban\(^ {29} \) 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-annelated 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 \( \pi \)-electron contents of all six-membered rings of triphenylene and all its benzo-annelated 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 \( \pi \)-electron contents can be obtained from the authors upon request.
TABLE I. Energy effects ($\textit{ef}$) and $\pi$-electron contents ($\textit{EC}$) of the central ring $Z_0$ of triphenylene (1) and its benzo-annelated derivatives. The benzo-annelated species are labeled according to Fig. 3.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\textit{ef}(Z_0)$</th>
<th>$\textit{EC}(Z_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0242</td>
<td>2.0000</td>
</tr>
<tr>
<td>$a_1$</td>
<td>0.0304</td>
<td>2.2857</td>
</tr>
<tr>
<td>$l_1$</td>
<td>0.0204</td>
<td>1.6923</td>
</tr>
<tr>
<td>$a_1a_2$</td>
<td>0.0360</td>
<td>2.5000</td>
</tr>
<tr>
<td>$a_1a_3$</td>
<td>0.0390</td>
<td>2.5909</td>
</tr>
<tr>
<td>$a_1a_4$</td>
<td>0.0390</td>
<td>2.5909</td>
</tr>
<tr>
<td>$a_2a_3$</td>
<td>0.0389</td>
<td>2.5909</td>
</tr>
<tr>
<td>$l_1a_3$</td>
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<td>1.9500</td>
</tr>
<tr>
<td>$l_1a_4$</td>
<td>0.0249</td>
<td>1.9500</td>
</tr>
<tr>
<td>$l_1l_2$</td>
<td>0.0179</td>
<td>1.4211</td>
</tr>
<tr>
<td>$a_1a_2a_3$</td>
<td>0.0466</td>
<td>2.8158</td>
</tr>
<tr>
<td>$a_1a_2a_4$</td>
<td>0.0467</td>
<td>2.8158</td>
</tr>
<tr>
<td>$a_1a_3a_5$</td>
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<td>2.9143</td>
</tr>
<tr>
<td>$a_1a_4a_6$</td>
<td>0.0510</td>
<td>2.9143</td>
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<tr>
<td>$a_1a_2l_2$</td>
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<td>2.1471</td>
</tr>
<tr>
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<td>2.2258</td>
</tr>
<tr>
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<td>2.2258</td>
</tr>
<tr>
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<td>2.2258</td>
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<tr>
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<td>1.1786</td>
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</tr>
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<td>$a_1a_2a_4a_5a_6$</td>
<td>0.0910</td>
<td>3.6190</td>
</tr>
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</table>

What first requires checking is whether the $\textit{ef}$- and $\textit{EC}$-values yield consistent results. That this is indeed the case can be seen from Fig. 4; although not linear, the correlation between $\textit{ef}$ and $\textit{EC}$ is remarkably good and, of course, positive. This means that the (stabilizing) energy effect of the cyclic conjugation is proportional to the amount of $\pi$-electrons in the underlying ring. In other words, both $\textit{ef}$ and $\textit{EC}$ 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 $\textit{ef}$- and $\textit{EC}$-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.\textsuperscript{35,36}
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 \(\pi\)-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 \(\pi\)-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 \(a_1a_3a_5a_7\) 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 (isarithmicity)
The energy effect and the \(\pi\)-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(\(a1a4l3\)) = 0.0310, ef(\(a2a3l3\)) = 0.0309, and \(EC(a1a3l3) = EC(a1a4l3) = EC(a2a3l3) = 2.2258\).

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 isoarithmicity, see a recent article. 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, in which benzo-derivatives of perylene were examined, are tantamount to Rule 1. In the time when the work was created, this fact was been recognized.

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