UNEXPECTED FORMATION OF 2,3,7-TRIPHENYLCYCLOPENTA[c]PYRAN FROM THE REACTION OF 1,2-DIPHENYLETHANEDIONE (BENZIL) WITH CYCLOPENTADIENE

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The reaction of 1,2-diphenylethanedione (benzil) with cyclopentadiene in the presence of sodium methoxide unexpectedly afforded the novel fully conjugated 2,3,7-triphenyl derivative of cyclopenta[c]pyran, a pyranic pseudoazulene. The structure was proved by physical methods (IR, UV/VIS; 1H-NMR, 13C-NMR; MS), and confirmed by X-ray crystallography. Protonation affords a pyrylium salt with a structure that agrees with the results of semiempirical and ab-initio methods, which also agree fairly well with experimentally-determined bond lengths.

INTRODUCTION

Pseudoazulenic iridoids with cyclopenta[c]pyranic structure

Cyclopenta[c]pyran derivatives (1, R = H) belong to the class of pseudoazulenes: like azulenes, they possess a cyclopentadiene ring fused to another ring, and the total number of conjugated \(\pi\)-electrons is 10 as in azulene. Also as in azulene, a dipolar resonance structure contributes to the description of the electronic distribution. Unlike azulene, which has a 7-membered ring, in 1 this ring is replaced by a pyranic ring. Boyd described in 1958 the first synthesis of 2,4,6-trisubstituted derivatives 1 of cyclopenta[c]pyran (oxalenes), which are isoelctronic with azulene. The literature data about these derivatives are fairly scarce so far.2

On the other hand, naturally occurring iridoids with cyclopenta[c]pyran skeleton, usually bearing formyl substituents e.g.: novburtilinal 2a,4 viburtinal 2b,5 cerbinal 2c,6 baldrinal 2d,7 etc. are activelly investigated due to their various biological activities.8,9 Until recently only three pseudoazulenes with cyclopenta[c]pyran skeleton not bearing electron-acceptor groups were synthesized: the parent compound 3a (in four steps from BrCH2CH(OH)2 and 5-(trimethylsilyl)-1,3-cyclopentadiene 10), and the substituted derivatives 3b 10 and 3c.11 A major breakthrough in this domain was brought about in 1998 by Christi and co-workers12 who designed a very interesting general method for synthesis of di- and three-substituted cyclopenta[c]pyrans 4 and 5. His reaction sequence included cycloaddition of cyclopentadiene to 6-oxo-6H-1,3,4-oxadiazines, dehydrogenation with dichloro-dicyano-p-benzoquinone, and finally the reduction of the resulting \(\alpha\)-pyrones. Compounds 4 undergo electrophilic substitution (e.g. nitration, formylation, etc.).13 Other such natural and/or synthetic iridoids have been described.13-18 In spite of these notable achievements, the 2,3,7-triphenyl-substituted derivative 6 of 3a had not been synthesized until now.
RESULTS

Synthesis of 2,3,7-triphenylcyclopenta[c]pyran

In a preliminary communication, we reported the unexpected formation of compound 6 (isomeric with 1a) during an attempt to obtain fulvenes from α-dicarbonyl compounds. Thus, the treatment of 1,2-diphenylethanedione (benzil) 7 with excess cyclopentadiene 8 in a strongly basic medium (MeO'Na⁺, KOH) leads to the formation of a red compound (m.p. 140-2°C), which could be isolated in small yields and purified by liquid chromatography on neutral alumina. Along with large amounts of polymeric materials, methyl benzoate 9 was identified among the reaction products when sodium methoxide was used as condensation agent. Single crystal X-ray analysis confirmed the structure of compound 6. In the present paper we give experimental details, and report the results of protonation experiments and of theoretical calculations using both semiempirical and ab-initio methods.

The structure of the new compound 6 was established on the basis of physico-chemical data including X-ray analysis, and corresponds to a fully conjugated 2,3,7-triphenylcyclopenta[c]pyran. The stoechiometric equation involves two moles of benzil 7 and one mole of cyclopentadiene 8, and yields 6 and 9.

\[
2 \text{Ph} = \text{CO} = \text{CO} = \text{Ph} \quad + \quad \text{MeONa} \quad \rightarrow \quad \text{Ph} \quad + \quad \text{PhCOOMe}
\]
The IR spectrum confirms the presence of cyclopentadienic C=C bonds by their stretching frequency from 1619 cm\(^{-1}\), of the monosubstituted benzenic rings by their characteristic absorptions from 694; 746 and 912 cm\(^{-1}\) as well as by those between 1600 - 2000 cm\(^{-1}\). The presence of absorption bands at 659, 848, 942, 1027, 1054 and 1174 cm\(^{-1}\) could be attributed to a pyrylium ring that is evident in the mesomeric form 6A.

The electronic spectrum of the deep red 6 presents absorptions at: 257 nm, 301.2 nm, 349.5 nm and a large one centered at 471.5 nm. This spectrum differs from that of 1A\(^{11}\) [247 nm (lge = 4.49); 290 nm (lge = 4.61); 418 (lge = 4.56) and approx. 508 (lge = 3.07) shoulder] due to the different annulation respectively conjugation between the 7- and 5- membered rings.

The mass spectrum of 6 presents the molecular peak (which is also the base peak) at m/z = 346 and the fragmentation pattern in agreement with the structure.

The \(^1\)H-NMR spectrum clearly proves the presence of the cyclopentadienic ring by the signals at \(\delta\) 6.40; 7.13 and 7.33 ppm (all of them as double doublets with the corresponding couplings).

The \(^13\)C-NMR spectrum allowed the assignment of carbon atoms signals in agreement with the proposed structure.

The molecular structure of 6 determined by single crystal X-ray analysis\(^{19}\) is shown in Fig. 1 (including the crystallographic numbering); the corresponding experimental bond lengths and bond angles (with the last digits in brackets) are presented in Tables 3 and 4. The skeleton of cyclopenta[c]pyran is nearly planar. The carbon-carbon bond lengths in the five-membered [C2-C3 1.428, C4-C5 1.421, C3-C4 1.360 and C5-C6 1.375 Å] and six-membered rings [C1-C2 1.361, C7-C8 1.359, C2-C6 1.464, C6-C7 1.431 Å] indicate variations in agreement with structure 6 (distinct double and single bonds). There is an unexplained difference in the carbon-oxygen bond lengths in the six-membered ring [C1-O1 1.395(2) and C8-O1 1.381(2) Å].

Fig. 1 - Molecular structure of 2,3,7-triphenylcyclopenta[c]pyran (6).

The unexpected formation of 6 in the reaction of benzil with cyclopentadiene can be rationalized by the mechanism suggested in the following Scheme: the initially formed benzil monofulvene 10 reacts with the second molecule of benzil by a catalytic addition of the methoxide anion affording 11. This eliminates a hydroxyl anion after a prototropic migration (having as driving force an increase of conjugation) generating 12 which undergoes cyclization to 6 accompanied by the loss of methyl benzoate.
Semiempirical (AM1) and \textit{ab-initio} calculations (3-21G).
Protonation yielding a pyrylium salt

Pyranic pseudoazulenes are protonated to pyrylium cations. In the case of 6, there are two non-equivalent sites on the cyclopentadienic ring where protonation can take place, yielding two isomeric pyrylium cations, of the type 14 and 15. Calculations were carried out in order to predict the structure of the cation, and to see whether the experimental bond lengths in the neutral unsubstituted pseudoazulene 13 and in the triphenyl derivative 6 will agree with the predicted ones. \textit{Ab-initio} methods could not be used for the larger system 6 with three phenyl groups, and therefore we present 3-21 G results only for unsubstituted compounds 13, 14, 15. Semiempirical methods do not require powerful computers, and therefore we present AM1 results for compounds 6, 13, 14, 15.

A vibrational analysis was carried out in order to ensure that all geometries represent equilibrium structures, with no negative values in the vibrational spectrum. Table 1 presents the results of the computations for energies, and Table 2 for electrical charges. The atom numbering in these tables and in the following discussion of the structure and NMR spectra is the crystallographic numbering used in reference 19 and in the deposited material and differs from the IUPAC numbering used in the title and introduction of this paper.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
heats of formation & AM1 & 40.23 & 188.12 & 185.36 & 127.56 & 259.75 & 260.91 \\
\hline
total energies & AM1 & -52.35604 & -52.62219 & -52.62658 & -143.05888 & -143.35005 & -143.34821 \\
\hline
\hline
\end{tabular}
\caption{Calculated total energies (in atomic units) and heats of formation (in kcal/mol) for unsubstituted compounds 13-15 and triphenyl derivatives 6, 16, and 17}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
Method & AM1 & AM1 & AM1 & AM1 & AM1 & AM1 & 3-21G & 3-21G & 3-21G \\
Compound & 6 & 13 & 14 & 15 & 16 & 17 & 13 & 14 & 15 \\
\hline
Atom & & & & & & & & & \\
C1 & 0.158 & 0.052 & 0.087 & 0.097 & 0.215 & 0.211 & 0.266 & 0.331 & 0.314 \\
O1 & -0.124 & -0.127 & -0.019 & -0.040 & -0.073 & -0.062 & -0.711 & -0.659 & -0.669 \\
C8 & 0.063 & -0.054 & 0.087 & -0.092 & 0.221 & 0.219 & 0.189 & 0.309 & 0.312 \\
C7 & -0.044 & -0.147 & -0.180 & -0.193 & -0.088 & -0.081 & -0.338 & -0.384 & -0.368 \\
C6 & -0.059 & -0.065 & 0.084 & 0.141 & 0.128 & 0.077 & 0.017 & 0.135 & 0.091 \\
C2 & -0.141 & -0.153 & -0.112 & -0.187 & -0.195 & -0.135 & -0.226 & -0.234 & -0.193 \\
C3 & -0.159 & -0.157 & -0.141 & -0.133 & -0.118 & -0.134 & -0.220 & -0.171 & -0.476 \\
C4 & -0.124 & -0.121 & -0.090 & -0.010 & -0.054 & -0.117 & -0.228 & -0.175 & -0.125 \\
C5 & -0.161 & -0.165 & -0.153 & -0.187 & -0.173 & -0.140 & -0.267 & -0.492 & -0.215 \\
C11 & -0.063 & 0.180 & 0.246 & 0.240 & -0.121 & -0.121 & 0.288 & 0.373 & 0.366 \\
C21 & -0.046 & 0.178 & 0.244 & 0.240 & -0.128 & -0.130 & 0.278 & 0.374 & 0.368 \\
C31 & -0.031 & 0.152 & 0.212 & 0.212 & -0.087 & -0.091 & 0.259 & 0.339 & 0.335 \\
\hline
\end{tabular}
\caption{Computed net atomic charges for compounds 6, 13-17}
\end{table}
Table 3
Comparison between experimental (X-ray)* and computed bond lengths

<table>
<thead>
<tr>
<th>Method Compound</th>
<th>X-Ray Bond</th>
<th>AM1 6</th>
<th>AM1 13</th>
<th>AM1 14</th>
<th>AM1 15</th>
<th>3-21G 13</th>
<th>3-21G 14</th>
<th>3-21G 15</th>
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</thead>
<tbody>
<tr>
<td>C1-O1</td>
<td>1.395(2)</td>
<td>1.381</td>
<td>1.373</td>
<td>1.362</td>
<td>1.366</td>
<td>1.329</td>
<td>1.347</td>
<td>1.352</td>
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<tr>
<td>O1-C8</td>
<td>1.381(2)</td>
<td>1.393</td>
<td>1.384</td>
<td>1.355</td>
<td>1.360</td>
<td>1.382</td>
<td>1.333</td>
<td>1.342</td>
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<td>O1-C7</td>
<td>1.359(2)</td>
<td>1.368</td>
<td>1.356</td>
<td>1.389</td>
<td>1.381</td>
<td>1.329</td>
<td>1.363</td>
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<td>C2-C6</td>
<td>1.431(2)</td>
<td>1.430</td>
<td>1.424</td>
<td>1.391</td>
<td>1.401</td>
<td>1.438</td>
<td>1.387</td>
<td>1.401</td>
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<tr>
<td>C2-C7</td>
<td>1.464(2)</td>
<td>1.486</td>
<td>1.490</td>
<td>1.441</td>
<td>1.446</td>
<td>1.478</td>
<td>1.414</td>
<td>1.421</td>
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<td>1.361(2)</td>
<td>1.357</td>
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<td>1.366</td>
<td>1.329</td>
<td>1.352</td>
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<td>1.454</td>
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<td>1.500</td>
<td>1.450</td>
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<td>1.360(3)</td>
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<td>1.378</td>
<td>1.360</td>
<td>1.507</td>
<td>1.352</td>
<td>1.328</td>
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<td>C4-C5</td>
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<td>1.459</td>
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<td>1.461</td>
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<td>C5-C6</td>
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<td>1.378</td>
<td>1.376</td>
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<td>1.445</td>
<td>1.350</td>
<td>1.508</td>
<td>1.445</td>
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<td>C1-C11</td>
<td>1.471(2)</td>
<td>1.462</td>
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<td>C8-C21</td>
<td>1.475(2)</td>
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<tr>
<td>C7-C31</td>
<td>1.488(2)</td>
<td>1.466</td>
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<td>1.104</td>
<td>1.104</td>
<td>1.070</td>
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<td>1.068</td>
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</table>

Note: the last three bonds in 6 are C–C bonds, but C–H bonds for all other compounds.

* Data published in ref. 19 and deposited at http://www.rsc.org/suppdata/nj/b1/b105878a in CIF format.

Table 4
Comparison between experimental (X-ray)* and computed bond angles

<table>
<thead>
<tr>
<th>Method Compound</th>
<th>X-ray Angle</th>
<th>AM1 6</th>
<th>AM1 13</th>
<th>AM1 14</th>
<th>AM1 15</th>
<th>3-21G 13</th>
<th>3-21G 14</th>
<th>3-21G 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-O1-C8</td>
<td>122.62(12)</td>
<td>119.55</td>
<td>118.30</td>
<td>120.39</td>
<td>119.98</td>
<td>120.55</td>
<td>123.81</td>
<td>122.88</td>
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<tr>
<td>O1-C1-C2</td>
<td>119.69(15)</td>
<td>121.05</td>
<td>122.01</td>
<td>120.26</td>
<td>120.45</td>
<td>121.31</td>
<td>118.73</td>
<td>119.23</td>
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<tr>
<td>O1-C1-C11</td>
<td>111.01(13)</td>
<td>111.43</td>
<td>109.87</td>
<td>110.86</td>
<td>110.50</td>
<td>112.15</td>
<td>113.17</td>
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<tr>
<td>C2-C1-C11</td>
<td>129.24(15)</td>
<td>127.52</td>
<td>128.12</td>
<td>128.88</td>
<td>129.05</td>
<td>126.55</td>
<td>128.10</td>
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<tr>
<td>C1-C2-C3</td>
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<td>133.76</td>
<td>133.79</td>
<td>132.10</td>
<td>131.72</td>
<td>133.71</td>
<td>132.61</td>
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<td>C2-C6-C7</td>
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<td>116.21</td>
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<td>116.91</td>
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<td>118.59</td>
<td>119.09</td>
<td>117.76</td>
<td>117.91</td>
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<td>123.28</td>
<td>124.25</td>
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<td>123.56</td>
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<td>C7-C8-C21</td>
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<td>C6-C7-C31</td>
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<td>121.58</td>
<td>121.27</td>
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<td>122.37</td>
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</table>

* Data published in ref. 19 and deposited at http://www.rsc.org/suppdata/nj/b1/b105878a in CIF format.

The agreement between observed (X-ray) and calculated data (Table 3) is satisfactory for bond lengths (generally within 0.01-0.02 Å) and reflects the major features of the structure. For the bond angles the agreement (Table 4) is also good. Both experimental and calculated values support formulation 13 of the molecular backbone.
In compounds 6 and 16 (vide infra), atoms C11, C21, and C31 are carbon atoms included in phenyl groups whereas in compounds 13, 14, 15, these positions are occupied by hydrogen atoms.

One may observe that both methods agree for the most part. Differences are noted when using method AM1 in the sign change of charges (i) for atom 8 from the unsubstituted (13) to the triphenyl-substituted pyran (6), and (ii) for atom 6 on passing from pyrans to pyrylum salts. As expected, in the pyrylum salts 16 and 17 the α (C1 and C8) and γ carbon atoms (C6) are positively charged, and so are also the substituents attached to them (hydrogen or carbon atoms C11 and C21). The positive charges of these substituents are higher, owing to conjugation, than the positive charge of the substituent C31 attached to the β-carbon atom C7, which is negatively charged.

The course of the protonation can be predicted both from the electrical charges in the pyrans 6 and 13, and from the stability of the two isomers 14 and 15. Both the semiempirical and the ab-initio methods predict a higher negative charge for atom C5 than for atom C3 in the pyrans 6 and 13. The calculated difference between the charges is smaller in the AM1 method.

Although the negative charge in position 5 of the unsubstituted system 13 is higher than in position 3, on substitution with phenyl groups the difference in negative charge between these two positions becomes negligible. Therefore the regioselectivity of protonation will be controlled by the thermodynamic stability of the protonated systems. A comparison of the computed 3-21 G total energies (in a.u.) for the protonated isomeric pyrylum cations 14 (-379.49026) and 15 (-379.49929) indicates that the latter is thermodynamically more stable. The same conclusion is obtained from the AM1 total energies (in a.u.) (14, -52.62219, and 15, -52.62658) and heat of formation (in kcal/mol) (for 14, 188.12, and for 15, 185.36). Thus the unsubstituted system 15 protonated in the 5 position has a definitely lower energy than its isomer 14 protonated in the 3 position as calculated with all methods. The same trend in stabilities is observed for the protonated triphenyl derivative from the semiempirical results. Experimental data confirm that the triphenyl derivative is protonated in the 5 position affording 16, and not in the 5 position when the result would have been 17.

The geometry of compound 6 calculated with the AM1 method can be seen in Fig. 2. A remarkable similarity can be observed between the experimentally observed geometry and the upper view of Fig. 1 for the calculated geometry. It is evident that the cyclopenta[c]pyran system is practically planar, as are also the three phenyl rings that have various dihedral angles with the central cyclopenta[c]pyran system, as can be
seen from the lower view in Fig 2. The largest dihedral angle is observed and calculated for the less
conjugated 6-phenyl ring (a β-substituent relative to the pyranic oxygen). Bond lengths between rings
calculated with the ab-initio method are in agreement with this observation, as the inter-ring bonds of the
two α-phenyl substituents attached to carbon atoms 1 and 8 have somewhat lower bond lengths than for the
bond to the less conjugated β-phenyl ring attached to carbon 7. Bond angles in the 5- and 6-membered rings
are close to 108° and 120° degrees, respectively, but bond angles involving pyranic ring atoms and exocyclic
atoms have values higher than 120°.

![Fig. 2 - The geometry of 2,3,7-triphenylcyclopenta[c]pyran (6) calculated with the AM1 method.]

The experimentally determined and semiempirically calculated dihedral angles (Table 5) between the
cyclopentapyran main scaffold and the three phenyl groups present notable differences: the least tilted is the
group connected via C(11) to position 1 (dihedral angle: calculated 36°, found 33°); the most tilted is the
phenyl group connected via C(31) to position 7 (dihedral angle: calculated 75°, found 50°); the group
connected to position 8 via C(21) has an intermediate dihedral angle (calculated 43°, found 49°). It is
reasonable to expect that the two vicinal phenyl groups will be more deviated from coplanarity with the main
scaffold than the isolated phenyl group. The larger difference for the most tilted phenyl group between the
calculated and the experimental values may be due to intermolecular packing forces that are ignored in the
quantum-chemical computations.

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Computed (AM1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-C(1)-C(11)-C(12)</td>
<td>149.45(16)</td>
<td>143.87</td>
</tr>
<tr>
<td>C(2)-C(1)-C(11)-C(12)</td>
<td>-33.2(3)</td>
<td>-36.56</td>
</tr>
<tr>
<td>O(1)-C(1)-C(11)-C(16)</td>
<td>-31.3(2)</td>
<td>-36.15</td>
</tr>
<tr>
<td>C(2)-C(1)-C(11)-C(16)</td>
<td>146.05(18)</td>
<td>143.43</td>
</tr>
<tr>
<td>C(7)-C(8)-C(21)-C(26)</td>
<td>-48.9(3)</td>
<td>-43.16</td>
</tr>
<tr>
<td>O(1)-C(8)-C(21)-C(26)</td>
<td>131.96(16)</td>
<td>137.25</td>
</tr>
<tr>
<td>C(7)-C(8)-C(21)-C(22)</td>
<td>132.6(2)</td>
<td>137.65</td>
</tr>
<tr>
<td>O(1)-C(8)-C(21)-C(22)</td>
<td>-46.6(2)</td>
<td>-41.95</td>
</tr>
<tr>
<td>C(8)-C(7)-C(31)-C(32)</td>
<td>-50.1(2)</td>
<td>-76.68</td>
</tr>
<tr>
<td>C(6)-C(7)-C(31)-C(32)</td>
<td>129.02(18)</td>
<td>102.71</td>
</tr>
<tr>
<td>C(8)-C(7)-C(31)-C(36)</td>
<td>131.29(18)</td>
<td>105.30</td>
</tr>
<tr>
<td>C(6)-C(7)-C(31)-C(36)</td>
<td>-49.6(2)</td>
<td>-75.30</td>
</tr>
</tbody>
</table>
One has also to expect the conjugation (hence the tendency for coplanarity) to be strongest at phenyl groups connected to positions with the highest positive charge, namely 2 and 7. The interatomic bond distances (Table 3) also reflect the parallelism between decreased bond length and increased conjugation/coplanarity.

**EXPERIMENTAL**

NMR Spectra were recorded with a VARIAN GEMINI 300 apparatus (300 MHz for $^1$H and 75 MHz for $^{13}$C) using TMS as internal standard. Standard AM1 and ab initio molecular orbital calculations were carried out with the HyperChem 5 program. The geometry of 6 was optimized only at the AM1 level due to the too large number of atoms in this molecule. Optimized geometries of compounds 13, 14, and 15 were obtained with the 3-21 G basis set.

2,3,7-Triphenylcyclopenta[c]pyran (6): Over a cooled solution of sodium methoxide prepared from 4.5 g (195.5 mg atoms) Na in 50 mL anhydrous methanol a solution of freshly distilled cyclopentadiene 17 mL (206 mmole) in 10 mL anhydrous methanol was added dropwise with stirring under argon atmosphere. The solution became red-colored due to the formation of cyclopentadienylsodium. Then a solution of benzil (20 g: 95.2 mmole) in 500 mL anhydrous methanol was dropped with stirring during two hours. The red-brown reaction mixture was stirred at 50°C for additional 3 hrs maintaining the inert atmosphere. After cooling at room temperature, the reaction mixture was decomposed by adding of 150 mL cold water, when formation of a black tarry material was observed. The red-brown reaction solution was extracted with petroleum ether (b.p. 30 - 40°C); 4 x 125 mL. The combined red solutions thus obtained were washed with water until pH = 7, dried on anhydrous MgSO₄, filtered and evaporated in vacuo. The resulting red oil solution was subjected to liquid chromatography on neutral alumina using petroleum ether (b.p. 30 - 40°C) as eluent. The red zone of chromatographic column was collected as an eluate which, after evaporation of the solvent afforded a deep-red oily solution which was left overnight at 0°C. The crystals obtained were filtered from an oily red liquid (methylbenzoate impurified with 6) then recrystallized from petroleum ether or from methanol affording red crystals of 6 (1.6 g; 9.7%) with m.p. 140-2°C. Found: C, 89.91; H, 5.35. Calculated for C₃₅H₃₈O: C, 90.20, H, 5.20%.

**IR spectrum (KBr, cm⁻¹)**: 659 m, 694 vs, 746 m, 768 s, 800 w, 848 w, 912 m, 942 w, 1027 m, 1054 m, 1080 w, 1120 w, 1174 m, 1211 w, 1252 w, 1330 m, 1379 s, 1445 m, 1496 m, 1539 w, 1574 w, 1619 m, 3020 w, 3060 w.

**UV/VIS spectrum (dioxane; $\lambda_{\text{max}}$ nm, lg $\epsilon_{\text{max}}$)**: 257 (4.27); 301.2 (4.39); 349.5 (3.96); 471.5 (3.06).

**Mass spectrum (m/z; relative abundance %)**: 51 (11); 63 (3); 76 (2); 77 (26); 78 (3); 105 (15); 151 (3); 165 (3); 213 (3); 237 (3); 238 (2); 239 (15); 240 (6); 241 (8); 302 (3); 315 (3); 317 (7); 345 (16); 346 (molecular and base peak); 100 (347); M+1 (27); 348 (M+2; 4).

$^1$H-NMR spectrum (CDCl₃; 6 ppm; J Hz): 6.40 (dd; 2.9; 1.3; 1H; H₁); 7.13 (dd; 4.7; 1.3; 1H; H₃); 7.33 (dd; 4.7; 2.9; 1H; H₅); 7.22 - 7.48 (m; 10H; H_{mon}; 7.61 (m; 3H; H_{meta} of Ph); 8.19 (dd; 8.1; 2.1; 2H; H_{meta} of Ph) (numbering cf. formula 6).

$^1$C-NMR spectrum (CDCl₃; 6 ppm): 110.43 (C₂); 110.54 (C); 121.26 (Cq); 121.36 (Cq); 127.63 (CH); 127.87 (CH); 127.99 (2CH); 128.60 (2CH); 128.83 (2CH); 128.98 (2CH); 130.19 (2CH); 130.56 (CH); 131.06 (Cq); 133.67 (Cq); 134.12 (Cq); 135.52 (C); 143.32 (Cq); 144.55 (Cq); 155.05 (Cq) (numbering cf. formula 6).

The pyrillon salt 16 is formed in solution by protonation in position 3 from 6 and trifluoro-acetic acid, as seen from the NMR spectra (vide infra; numbering cf. formula 16). The solution is stable at room temperature only for a few days.

$^1$H-NMR spectrum (CDCl₃ + TFA; 6 ppm; J Hz): 4.40 (t; 1.8; 2H; H_{18}); 7.16 (d; 5.4; 1.7; 1H; H_{12}); 7.35 (dd; 8.0; 1.6; 2H; H_{16}; 7.49 (dd; 8.3; 7.3; 2H; H_{13, 15}); 7.51 - 7.65 (m; 6H; H_{1, 2, 3, 4, 5, 6}); 7.77 (t; 7.5; 2H; H_{15, 16}); 7.85 (t; 7.5; 1.4; 1H; H_{10}); 7.94 (dt; 5.4; 1.9; 1H; H_{11}); 8.22 (dd; 7.5; 2.4; 2H; H_{12, 16}).

$^1$C-NMR spectrum (CDCl₃ + TFA; 6 ppm): 41.64 (C₂); 128.22 (Cq); 128.55 (Cq); 129.11 (C_{12}; C_{16}); 129.20 (Cq); 139.17 (C_{16}; C_{18}; 129.60 (C_{12}; C_{16}); 130.22 (C_{12}; C_{18}; 130.39 (C_{12}; C_{16}); 130.53 (C_{13}; C_{15}); 130.73 (C_{18}; 131.77 (C_{18}; 132.50 (Cq); 134.07 (C_{12}); 135.44 (C_{16}); 159.37 (C); 164.27 (C); 169.12 (C); 172.49 (C). One quaternary carbon atom could not be localized.

**UV spectrum (MeOH; $\lambda_{\text{max}}$ nm)**: 217.3; 245.1; 333.3.

**REFERENCES**