

Dedicated to Professor Victor Emanuel Sahini
on the occasion of his 75th anniversary

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

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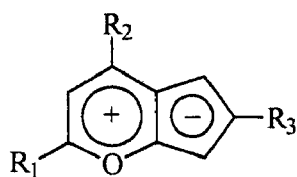
The reaction of 1,2-diphenylethanedione (benzil) with cyclopentadiene in the presence of sodium methoxide unexpectedly afforded the novel fully conjugated 2,3,7-triphenyl derivative of cyclopenta[*c*]pyran, a pyranic pseudoazulene. The structure was proved by physical methods (IR, UV/VIS; ¹H-NMR, ¹³C-NMR; 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

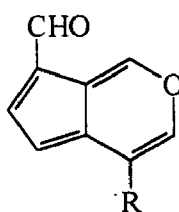
Pseudoazulenic iridoids with cyclopenta[*c*]pyranic structure

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 π -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. Boyd¹ described in 1958 the first synthesis of 2,4,6-trisubstituted derivatives **1** of cyclopenta[*b*]pyran (oxalenes), which are isoelectronic with azulene. The literature data about these derivatives are fairly scarce so far.^{2,3}

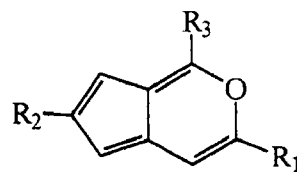
On the other hand, naturally occurring iridoids with cyclopenta[*c*]pyran skeleton, usually bearing formyl substituents *e.g.*: novburtinal **2a**,⁴ viburtinal **2b**,⁵ cerbinal **2c**,⁶ baldrinal **2d**,⁷ etc. are actively investigated due to their various biological activities.^{8,9} Until recently only three pseudoazulenes with cyclopenta[*c*]pyran skeleton not bearing electron-acceptor groups were synthesized: the parent compound **3a** (in four steps from BrCH₂CH(OMe)₂ and 5-(trimethylsilyl)-1,3-cyclopentadiene¹⁰), and the substituted derivatives **3b**¹⁰ and **3c**.¹¹ A major breakthrough in this domain was brought about in 1998 by Christl 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 α -pyrones. Compounds **4** undergo electrophilic substitution (*e.g.* nitration, formylation, etc.).¹² 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.



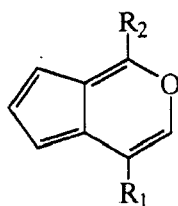
1 a ; $R_1 = R_2 = R_3 = \text{Ph}$
b ; $R_1 = t\text{-Bu}$; $R_2 = R_3 = \text{Ph}$



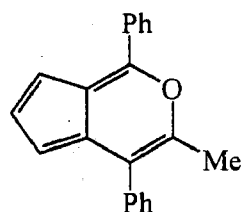
2 a ; $R = \text{H}$
b ; $R = \text{Me}$
c ; $R = \text{COOMe}$
d ; $R = \text{CH}_2\text{OAc}$



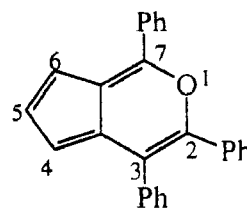
3 a ; $R_1 = R_2 = R_3 = \text{H}$
b ; $R_1 = R_3 = \text{H}$; $R_2 = t\text{-Bu}$
c ; $R_1 = R_3 = \text{Ph}$; $R_2 = t\text{-Bu}$



4 a ; $R_1 = R_2 = \text{Ph}$
b ; $R_1 = \text{Ph}$; $R_2 = p\text{-MeOC}_6\text{H}_4$
c ; $R_1 = \text{Ph}$; $R_2 = \text{COOMe}$
d ; $R_1 = i\text{-Pr}$; $R_2 = \text{Ph}$
e ; $R_1 = i\text{-Pr}$; $R_2 = p\text{-MeOC}_6\text{H}_4$



5



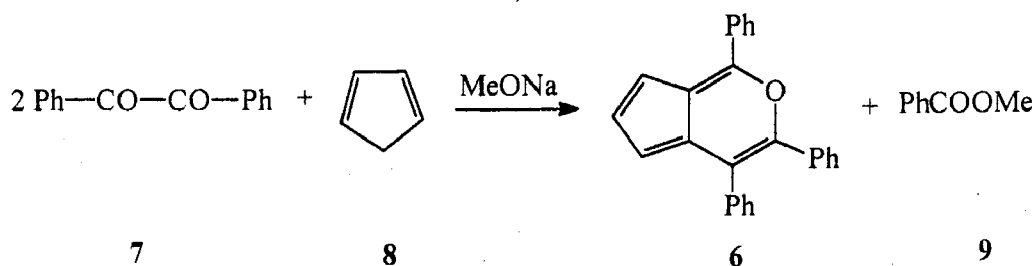
6

RESULTS

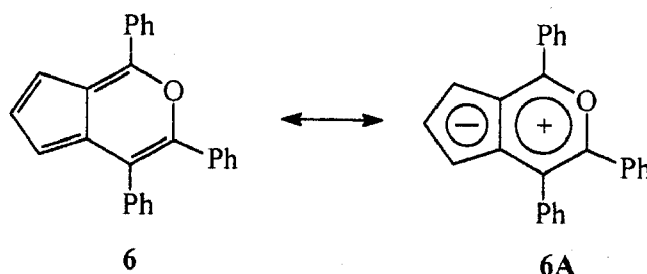
Synthesis of 2,3,7-triphenylcyclopenta[c]pyran

In a preliminary communication¹⁹ 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. $140\text{-}2^\circ\text{C}$), 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,¹⁹ and corresponds to a fully conjugated 2,3,7-triphenylcyclopenta[c]pyran. The stoichiometric equation involves two moles of benzil (**7**) and one mole of cyclopentadiene (**8**), and yields **6** and **9**.



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 $1600 - 2000\text{ cm}^{-1}$. 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**¹ [247 nm ($\lg\epsilon = 4.49$); 290 nm ($\lg\epsilon = 4.61$); 418 ($\lg\epsilon = 4.56$) and approx. 508 ($\lg\epsilon = 3.07$) shoulder] due to the different annulation respectively conjugation between the 7- and 5- membered rings.

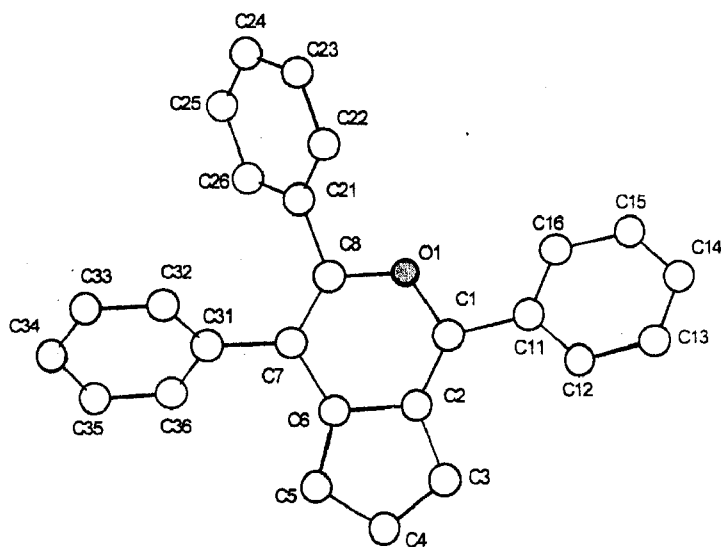
The mass spectrum of **6** presents the molecular peak (which is also the base peak) at $m/z = 346$ and the fragmentation pattern in agreement with the structure.

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

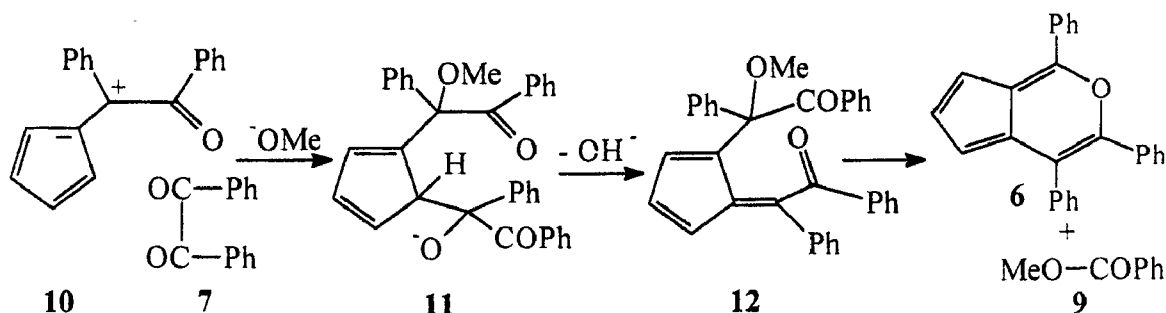
The $^{13}\text{C-NMR}$ spectrum allowed the assignment of carbon atoms signals in agreement with the proposed structure.

The molecular structure of **6** determined by single crystal X-ray analysis¹⁹ 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 \AA] and six-membered rings [C1-C2 1.361 , C7-C8 1.359 , C2-C6 1.464 , C6-C7 1.431 \AA] 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 $1.381(2)\text{ \AA}$].

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 *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. *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.

Table 1

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**

		13	14	15	6	16	17
heats of formation	AM1	40.23	188.12	185.36	127.56	259.75	260.91
total energies	AM1	-52.35604	-52.62219	-52.62658	-143.05888	-143.35005	-143.34821
	HF 3-21G	-379.11269	-379.49026	-379.49929			

Table 2

Computed net atomic charges for compounds **6**, **13-17**

Method	AM1	AM1	AM1	AM1	AM1	AM1	3-21G	3-21G	3-21G
Compound	6	13	14	15	16	17	13	14	15
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	0.319	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

Table 3

Comparison between experimental (X-ray)* and computed bond lengths

Method Compound	X-Ray 6	AM1 6	AM1 13	AM1 14	AM1 15	3-21G 13	3-21G 14	3-21G 15
Bond								
C1-O1	1.395(2)	1.381	1.373	1.362	1.366	1.329	1.347	1.352
O1-C8	1.381(2)	1.393	1.384	1.355	1.360	1.382	1.333	1.342
C7-C8	1.359(2)	1.368	1.356	1.389	1.381	1.329	1.363	1.353
C6-C7	1.431(2)	1.430	1.424	1.391	1.401	1.438	1.387	1.401
C2-C6	1.464(2)	1.486	1.490	1.441	1.446	1.478	1.414	1.421
C1-C2	1.361(2)	1.357	1.350	1.376	1.366	1.329	1.352	1.340
C2-C3	1.428(2)	1.454	1.454	1.463	1.500	1.450	1.472	1.512
C3-C4	1.360(3)	1.379	1.378	1.360	1.507	1.352	1.328	1.515
C4-C5	1.421(3)	1.456	1.459	1.510	1.370	1.461	1.521	1.341
C5-C6	1.375(2)	1.378	1.376	1.495	1.445	1.350	1.508	1.445
C1-C11	1.471(2)	1.462	1.101	1.108	1.107	1.067	1.066	1.066
C8-C21	1.475(2)	1.465	1.100	1.110	1.110	1.065	1.066	1.066
C7-C31	1.488(2)	1.466	1.099	1.104	1.104	1.070	1.069	1.068

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/bl/b105878a> in CIF format.

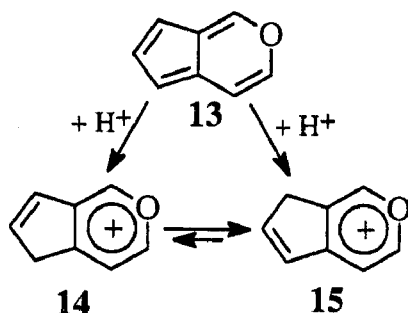
Table 4

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

Method Compound	X-ray 6	AM1 6	AM1 13	AM1 14	AM1 15	3-21G 13	3-21G 14	3-21G 15
Angle								
C1-O1-C8	122.62(12)	119.55	118.30	120.39	119.98	120.55	123.81	122.88
O1-C1-C2	119.69(15)	121.05	122.01	120.26	120.45	121.31	118.73	119.23
O1-C1-C11	111.01(13)	111.43	109.87	110.86	110.50	112.15	113.17	112.83
C2-C1-C11	129.24(15)	127.52	128.12	128.88	129.05	126.55	128.10	127.94
C1-C2-C3	133.57(16)	133.76	133.79	132.10	131.72	133.71	132.61	132.04
C1-C2-C6	119.13(15)	120.20	120.13	119.58	120.02	119.68	118.59	119.16
C3-C2-C6	107.29(15)	106.03	106.08	108.33	108.27	106.62	108.80	108.90
C2-C3-C4	106.85(17)	108.07	107.95	108.77	102.84	107.13	108.80	101.12
C3-C4-C5	111.00(17)	109.66	109.82	111.33	111.42	110.41	111.89	112.39
C4-C5-C6	107.78(17)	108.11	108.06	103.20	108.82	107.90	102.16	108.86
C5-C6-C7	133.75(16)	134.57	135.68	132.48	132.84	135.15	130.56	130.99
C2-C6-C5	107.06(15)	108.13	108.11	108.37	108.66	107.95	108.35	108.83
C2-C6-C7	119.20(14)	117.30	116.21	119.16	118.50	116.91	121.09	120.18
C6-C7-C8	117.71(15)	118.59	119.09	117.76	117.91	119.00	117.17	117.28
O1-C8-C7	121.54(15)	123.28	124.25	122.86	123.14	122.56	120.62	121.26
O1-C8-C21	109.23(13)	109.34	108.68	110.37	110.02	111.26	113.09	112.67
C7-C8-C21	129.22(15)	127.38	127.07	126.77	126.84	126.18	126.29	126.07
C8-C7-C31	121.69(15)	122.79	120.94	120.06	120.51	119.73	120.09	120.35
C6-C7-C31	120.60(14)	118.62	119.97	122.18	121.58	121.27	122.75	122.37

* Data published in ref. ¹⁹ and deposited at <http://www.rsc.org/suppdata/nj/bl/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.

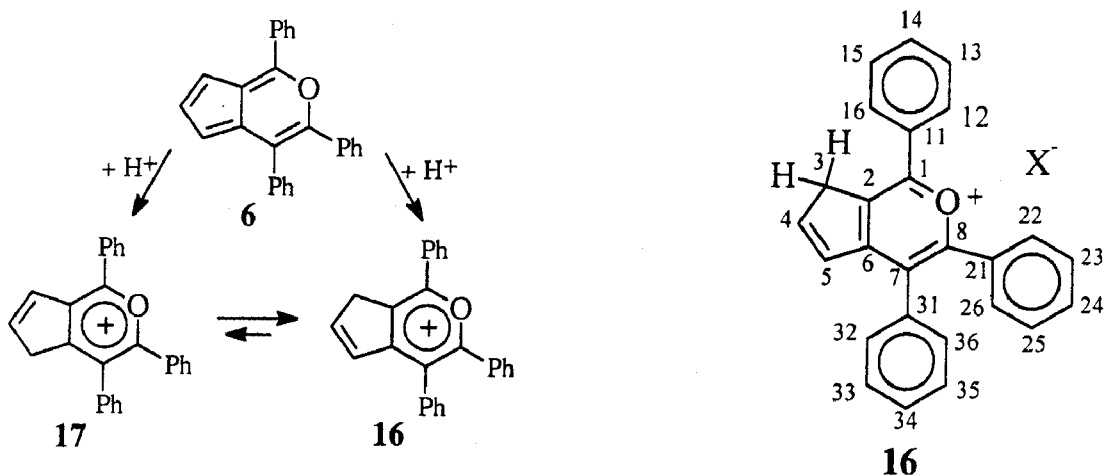


In compounds **6** and **16** (*vide infra*), atoms C11, C21, and C31 are carbon atoms included in phenyl groups whereas in compounds **13**, **14**, **15**, these positions are occupied by hydrogen atoms.

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 pyrylium salts. As expected, in the pyrylium 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.

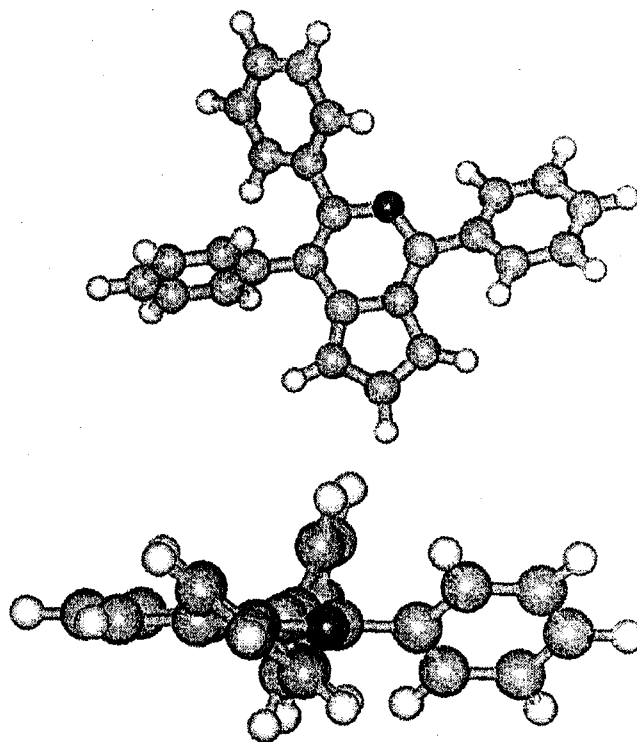
Although the negative charge in position 5 of the unsubstituted system **13** is higher than in position 3, on substitution with phenyl groups the difference in negative charge between these two positions becomes negligible. Therefore the regioselectivity of protonation will be controlled by the thermodynamic stability of the protonated systems. A comparison of the computed 3-21 G total energies (in a.u.) for the protonated isomeric pyrylium 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 3 position has a definitely lower energy than its isomer **14** protonated in the 5 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 3 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 AM 1 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 5

List of torsion angles [$^\circ$] for compound 6

	Experimental	Computed (AM1)
O(1)-C(1)-C(11)-C(12)	149.45(16)	143.87
C(2)-C(1)-C(11)-C(12)	-33.2(3)	-36.56
O(1)-C(1)-C(11)-C(16)	-31.3(2)	-36.15
C(2)-C(1)-C(11)-C(16)	146.05(18)	143.43
C(7)-C(8)-C(21)-C(26)	-48.9(3)	-43.16
O(1)-C(8)-C(21)-C(26)	131.96(16)	137.25
C(7)-C(8)-C(21)-C(22)	132.6(2)	137.65
O(1)-C(8)-C(21)-C(22)	-46.6(2)	-41.95
C(8)-C(7)-C(31)-C(32)	-50.1(2)	-76.68
C(6)-C(7)-C(31)-C(32)	129.02(18)	102.71
C(8)-C(7)-C(31)-C(36)	131.29(18)	105.30
C(6)-C(7)-C(31)-C(36)	-49.6(2)	-75.30

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 ^1H 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 mmol) 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 mmol) 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 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 MgSO_4 , filtered and evaporated *in vacuo*. The resulting red oily 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 $\text{C}_{26}\text{H}_{18}\text{O}$: 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; λ_{max} in nm, lg ϵ_{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).

$^1\text{H-NMR}$ spectrum (CDCl_3 ; δ ppm; J, Hz): 6.40 (dd; 2.9; 1.3; 1H; H^4); 7.13 (dd; 4.7; 1.3; 1H; H^6); 7.33 (dd; 4.7; 2.9; 1H; H^5); 7.22 - 7.48 (m; 10H; H_{arom}); 7.61 (m; 3H; $\text{H}^{\text{meta/para of Ph}}$); 8.19 (dd; 8.1; 2.1; 2H; $\text{H}^{\text{ortho of Ph}}$) (numbering cf. formula **6**).

$^{13}\text{C-NMR}$ spectrum (CDCl_3 ; δ ppm): 110.43 (C^6); 110.54 (C^4); 121.26 (Cq); 121.36 (Cq); 127.63 (CH); 127.87 (CH); 127.99 (2CH); 128.60 (2CH); 128.83 (2CH); 128.98 (2CH); 129.17 (2CH); 130.19 (2CH); 130.56 (CH); 131.06 (Cq); 133.67 (Cq); 134.12 (Cq); 135.52 (C^3); 136.32 (Cq); 144.55 (Cq); 155.05 (Cq) (numbering cf. formula **6**).

The pyrylium salt **16** is formed in solution on 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.

$^1\text{H-NMR}$ spectrum (CDCl_3 + TFA); (δ ppm; J Hz): 4.40 (t; 1.8; 2H; $\text{H}^{3,3'}$); 7.16 (dt; 5.4; 1.7; 1H; $\text{H}^{4(5)}$); 7.35 (dd; 8.0; 1.6; 2H; $\text{H}^{32,36}$); 7.49 (dd; 8.3; 7.3; 2H; $\text{H}^{23,25}$); 7.51-7.65 (m; 6H; $\text{H}^{22,24,26,33,34,35}$); 7.77 (t; 7.5; 2H; $\text{H}^{13,15}$); 7.85 (tt; 7.5; 1.4; 1H; H^{14}); 7.94 (dt; 5.4; 1.9; 1H; $\text{H}^{5(4)}$); 8.22 (dd; 7.5; 2.4; 2H; $\text{H}^{12,16}$).

$^{13}\text{C-NMR}$ spectrum (CDCl_3 + TFA); (δ ppm): 41.64 (C^3); 128.22 (Cq); 128.55 (Cq); 129.11 (C^{12} , C^{16}); 129.20 (Cq); 129.37 (C^{32} , C^{36}); 129.60 (C^{23} , C^{25}); 130.22 (C^{33} , C^{35}); 130.39 (C^{22} , C^{26}); 130.53 (C^{13} , C^{15}); 130.73 (C^{34}); 131.77 (C^4); 132.50 (Cq); 134.07 (C^{24}); 135.44 (C^{14}); 159.37 (C^5); 164.27 (C^6); 169.12 (C^8); 172.49 (C^1). One quaternary carbon atom could not be localized.

UV spectrum (MeOH; λ_{max} nm): 217.3; 245.1; 333.3.

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