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ON THE STRUCTURE OF "TETRAPHENYLDIPYRANYL ETHER"

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Abstract—The reaction product of 2,6-diphenylpyrylium perchlorate with water in presence of bases, which earlier was assigned the structure of $\alpha,\alpha',\alpha'',\alpha'''$-tetraphenyl-$\gamma,\gamma'$-dipyranyl ether, is identified now as 2,6-dipyranylidene-1,5-diphenylpentenedione-1,5 from its chemical and spectral properties and by X-ray analysis.

Crystals are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 24.088$, $b = 9.323$, $c = 11.289$ Å, $\beta = 95.30°$. The structure was solved by direct method and refined isotropically to $R = 0.126$ for 2423 reflections.

It was reported earlier[1] that interaction of 2,6-diphenylpyrylium perchlorate (1) with water in presence of bases gave moderate yields of the product "Z", which was assigned the structure of $\alpha,\alpha',\alpha'',\alpha'''$ - tetraphenyl - γ,γ' - dipyranyl ether (2). This assignment was done on the basis of elemental analysis and by analogy with similar derivatives of cyclopropenylium[2] and tropylium[3] formed under like conditions. These were the only arguments in favour of the proposed structure.*

However the ether formulation 2 is in poor agreement with the intense red colour of "Z" and the strong band at 1650 cm^{-1} in its IR spectrum hardly could be assigned to vibrations of double C–C bonds of the pyrane cycle. Moreover the treatment of dipyranyl ether 2 by perchloric acid would lead to the initial pyrylium salt 1. However this reaction gave rise to formation of a new perchlorate (3).[1]

The molecular weight of "Z" determined by measurement of condensation thermal effects ($CHCl_3$, 30°C) is equal to 466 ± 10 and in fact corresponds to a dimeric structure. The NMR spectrum of "Z" in $CDCl_3$ was rather complicated and we could not interpret it unequivocally.

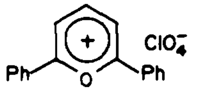
The NMR spectrum of perchlorate 3 in CF_3COOH has two one-proton doublets centered at $\delta = 8.82$ and 8.25 ppm ($J = 10$ Hz), i.e. in the same positions as signals of β,γ-protons in spectra of 2,3,6-trisubstituted pyrylium salts. The next two-proton singlet at $\delta = 8.00$ ppm resembles a singlet of two β-protons of 2,4,6-trisubstituted pyrylium cation.[5]

At $\delta = 7.75$–7.00 ppm the multiplet of 20 aromatic protons is situated. Thus on the basis of the NMR spectrum the structure of 3 was shown to be a combination of 2,3,6- and 2,4,6-trisubstituted pyrylium salts.

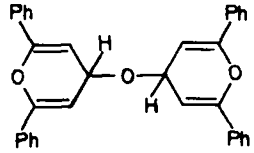
By treatment with water or bases the bisperchlorate 3 is transformed into "Z". If the structure 3 is correct then "Z" must have a C–C bond between two pyrane rings.

For elucidation the structure of "Z" it was necessary to determine a position of the third O atom, the presence of which followed from the results of elemental analysis. Taking into account an easiness of transformation "Z"$\rightleftarrows$3 at least two structures (4 as well as 5) could be proposed.

The structure 4 could be realized if an OH added to γ-position of a pyrylium ring with subsequent splitting-off of a proton. The structure 5 could be formed by an initial ring opening of the more electrophilic 2,3,6-trisubstituted pyrylium cation through a OH addition in an α-position.



1



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For a definite determination of the structure of "Z" we undertook its X-ray study.

Crystals of "Z" are monoclinic, $a = 24.088(2)$, $b = 9.323(5)$, $c = 11.289(1)$ Å, $\beta = 95.30(1)°$, $D_m = 1.257$, $D_c = 1.265$ g.cm^{-1}, $Z = 4$, space group $P2_1/n$. Intensities of reflections were measured with an automatic four-circle Hilger & Watts diffractometer (Cu radiation, graphite monochromator, ω scan, $\theta \leq 57°$). Experimental technique and programmes used for subsequent calculations were the same as described in Ref. 6. The structure was solved by the direct method using the programme[7] and refined by the least squares method in isotropic approximation to $R = 0.126$ for 2423 reflections.

The structure of the molecule found is shown in Fig. 1. bond lengths and angles are given in the Table. One of the pyranyl rings (A) enters into the molecule in its invariable form. However the other pyranyl residue is represented by acyclic diketo-form [O(3)–C(28)–C(18)–C(19)–C(20)–C(21)–O(2)] joined by its β-C atom C(18) to the γ-position of pyranyl cycle. Thus the compound studied has in fact the structure 5.

With the exception of the benzoyl group at C(18) the molecule is approximately planar. The phenyl rings B and C make with the plane of the pyranyl ring A angles equal to 6.8 and 2.9° respectively. The plane of the side chain C(3)–C(18)–C(19)–C(20)–C(21)–O(2)–C(22) forms with the ring A and the phenyl ring D angles of 5.0 and 3.4° respectively. This conformation causes a strong distortion of exocyclic angles at C(1) and C(5). It contains also a large number of intramolecular non-bonded distances which are shorter than corresponding sums of van-der-Waals radii: C...C 2.91–2.97, C...O 2.69–2.79 Å. The preservation of so considerable steric strains which

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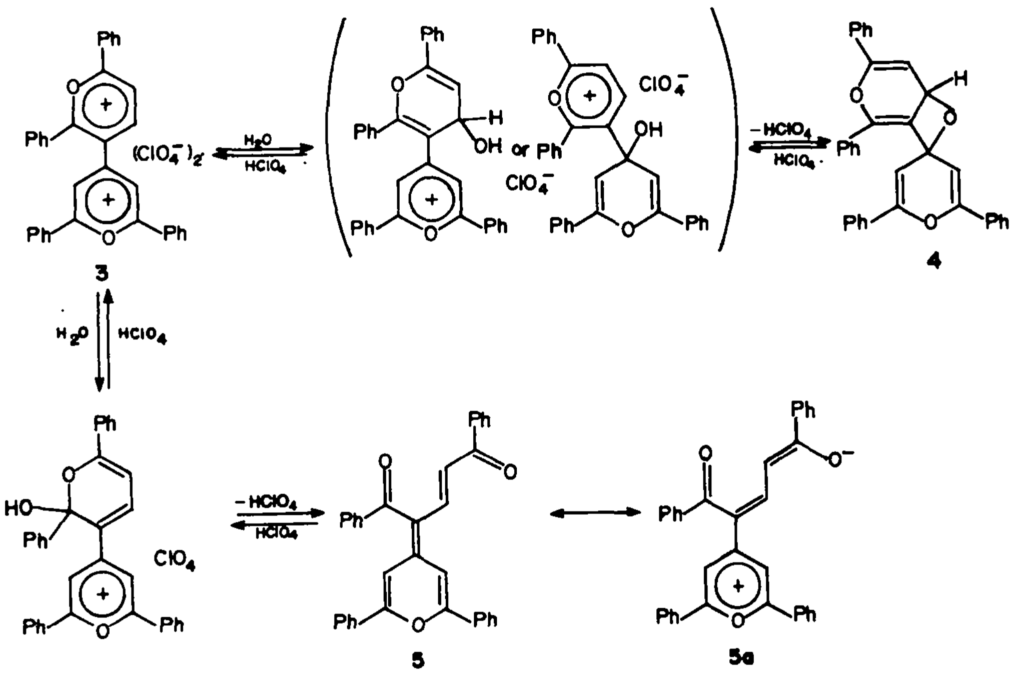
*The same compound was also described as 1,5,9 - triphenyl - 6 - benzoyl - 2,4,6 - triene - 1,9 - dione.[4] The reaction scheme proposed by these authors involves a crotonic condensation of two molecules of dibenzoylpropene.


Ph
$(ClO_4^-)_2$
H_2O
$HClO_4$
3
OH
H
or
ClO_4^-
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ClO_4
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O^-
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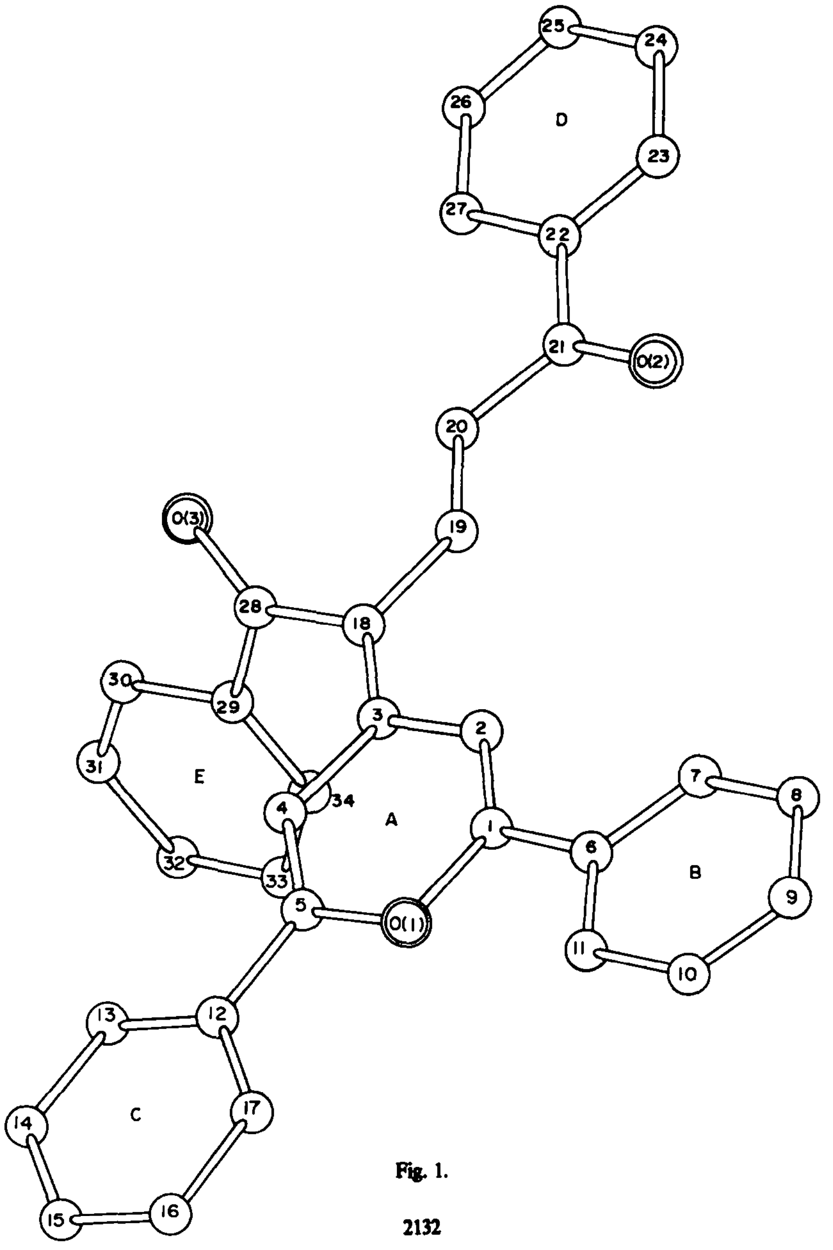
25
24
26
D
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27
22
21
O(2)
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O(3)
19
28
18
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29
3
2
31
E
34
4
A
7
8
1
6
B
32
33
9
5
O(1)
11
10
13
12
14
C
17
15
16

Fig. 1.

Table 1. Bond lengths (d, A) and bond angles (ω°)

Atoms	d	Atoms	d	Atoms	d	Atoms	d
O(1)–C(1)	1.364(8)	C(6)–C(7)	1.402(10)	C(16)–C(17)	1.401(11)	C(25)–C(26)	1.366(12)
O(1)–C(5)	1.370(8)	C(7)–C(8)	1.417(11)	C(17)–C(12)	1.407(9)	C(26)–C(27)	1.414(11)
O(2)–C(21)	1.228(8)	C(8)–C(9)	1.403(11)	C(3)–C(18)	1.388(8)	C(27)–C(22)	1.381(10)
O(3)–C(28)	1.218(8)	C(9)–C(10)	1.378(12)	C(18)–C(19)	1.432(9)	C(18)–C(28)	1.489(9)
C(1)–C(2)	1.344(9)	C(10)–C(11)	1.411(11)	C(19)–C(20)	1.371(9)	C(28)–C(29)	1.494(9)
C(2)–C(3)	1.442(9)	C(11)–C(6)	1.377(10)	C(20)–C(21)	1.486(9)	C(29)–C(30)	1.423(10)
C(3)–C(4)	1.452(9)	C(12)–C(13)	1.392(10)	C(21)–C(22)	1.491(9)	C(30)–C(31)	1.387(12)
C(4)–C(5)	1.356(9)	C(13)–C(14)	1.397(11)	C(22)–C(23)	1.386(10)	C(31)–C(32)	1.382(12)
C(1)–C(6)	1.471(9)	C(14)–C(15)	1.408(11)	C(23)–C(24)	1.425(11)	C(32)–C(33)	1.382(12)
C(5)–C(12)	1.471(9)	C(15)–C(16)	1.376(11)	C(24)–C(25)	1.340(12)	C(33)–C(34)	1.409(11)
						C(34)–C(29)	1.378(9)

Atoms	ω	Atoms	ω	Atoms	ω	Atoms	ω
C(5)–O(1)–C(1)	119.0(5)	C(7)–C(8)–C(9)	120.0(7)	C(3)–C(18)–C(19)	120.5(6)	C(25)–C(26)–C(27)	120.2(8)
O(1)–C(1)–C(2)	122.1(6)	C(8)–C(9)–C(10)	119.8(8)	C(3)–C(18)–C(28)	122.5(6)	C(26)–C(27)–C(22)	119.6(7)
O(1)–C(2)–C(3)	121.7(6)	C(9)–C(10)–C(11)	120.3(7)	C(28)–C(18)–C(19)	117.0(5)	C(18)–C(28)–O(3)	119.6(6)
C(2)–C(3)–C(4)	114.3(5)	C(10)–C(11)–C(6)	120.4(7)	C(18)–C(19)–C(20)	124.7(6)	C(29)–C(28)–O(3)	121.1(6)
C(3)–C(4)–C(5)	120.6(6)	C(5)–C(12)–C(13)	120.5(6)	C(19)–C(20)–C(21)	118.6(6)	C(18)–C(28)–C(29)	119.3(5)
C(4)–C(5)–O(1)	122.1(6)	C(5)–C(12)–C(17)	119.8(6)	C(20)–C(21)–O(2)	121.7(6)	C(28)–C(29)–C(30)	116.9(6)
O(1)–C(1)–C(6)	111.6(5)	C(17)–C(12)–C(13)	119.7(6)	C(22)–C(21)–O(2)	119.3(6)	C(28)–C(29)–C(34)	123.2(6)
C(2)–C(1)–C(6)	126.3(6)	C(12)–C(13)–C(14)	120.2(7)	C(20)–C(21)–C(22)	119.0(5)	C(34)–C(29)–C(30)	119.9(6)
O(1)–C(5)–C(12)	112.3(5)	C(13)–C(14)–C(15)	119.7(7)	C(21)–C(22)–C(23)	117.5(6)	C(29)–C(30)–C(31)	118.7(7)
C(4)–C(5)–C(12)	125.6(6)	C(14)–C(15)–C(16)	120.2(7)	C(21)–C(22)–C(27)	122.4(6)	C(30)–C(31)–C(32)	121.3(8)
C(1)–C(6)–C(7)	118.7(6)	C(15)–C(16)–C(17)	120.3(7)	C(27)–C(22)–C(23)	120.0(6)	C(31)–C(32)–C(33)	120.0(8)
C(1)–C(6)–C(11)	121.1(6)	C(16)–C(17)–C(12)	119.8(7)	C(22)–C(23)–C(24)	118.4(7)	C(32)–C(33)–C(34)	119.9(7)
C(11)–C(6)–C(7)	120.2(6)	C(2)–C(3)–C(18)	123.6(6)	C(23)–C(24)–C(25)	121.4(8)	C(33)–C(34)–C(29)	120.1(7)
C(6)–C(7)–C(8)	119.2(7)	C(4)–C(3)–C(18)	122.1(6)	C(24)–C(25)–C(26)	120.4(8)		

could be well diminished by mutual rotation of molecule fragments (phenyl groups in the first place) indicates a strong conjugation in the molecule.

The C(2)–C(3) 1.44 and C(3)–C(4) 1.45 Å bonds are shorter than the standard C(sp^2)–C(sp^2) bond length (1.48 Å[8]). The C(1)–O(1) and C(5)–O(1) bond lengths of 1.36 and 1.37 Å respectively are equal to the C–O bond distance in furan (1.37 Å[9]). These details of bond lengths distribution also testify to a considerable conjugation in a pyranyl cycle although lesser than in the completely delocalized system of 2,4,6-triphenylpyrylium cation.[10] Therefore the structure of the molecule "Z" is better described by the formula 5 with pyranyl cycle. However bond lengths both in this cycle and in the side chain indicate some contribution of the betaine structure 5a with a pyrylium cycle. An indirect confirmation of this conclusion is supplied by a molecular packing in crystals. The atom O(2) is situated approximately over the center of the pyranyl ring of the neighbouring molecule: distances from O(2) to O(1), C(1)...C(5) are equal to 3.37, 3.40, 3.51, 3.59, 3.58 and 3.44 Å respectively.

Thus the X-ray structural study has shown that contrary to cyclopropenylium and tropilium derivatives the perchlorate of 2,6-diphenylpyrylium interacts with water in presence of bases with formation of 2,6-diphenylpyranylidene - 1,5 - diphenylpentenedione - 1,5. Earlier such transformations were not known among oxonium compounds.

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