Reactions of trimethinecyanines of the 1,3-dioxenium series with nucleophiles. The structures of the parent carbocation and of a product of its reaction with methanol

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The chemistry and the regioselectivity of alcoholysis, aminolysis, and hydrolysis of symmetrical trimethinecyanine carbenium ions in 4-[3-(2,2-diorganyl-6-phenyl-4*H*-1,3-dioxen-4-ylidene)prop-1-enyl]-2,2-diorganyl-6-phenyl-1,3-dioxenium perchlorates (**4a,b**) were investigated. The structures of trimethinecyanine 4,5:4',5'-bisannelated at the methine chain (**3**) and of a product of the reaction of nonannelated trimethinecyanine with the methoxide anion were established by X-ray diffraction analysis, ¹H NMR spectroscopy, and quantum-chemical calculations (PM3). The nucleophile attacks the mesomeric π-conjugated system of the trimethinecyanine cation selectively at the C(6) atom of one of the dioxenium fragments, the second dioxenium ring being deactivated. Alcoholysis affords products of addition of the methoxy group to trimethinecyanines. In the course of aminolysis and hydrolysis, the dioxenium ring that is subjected to the attack eliminates acetone to form 1,3-dioxenylidenepropenylic derivatives of 1,3-enaminoketones and 1,3-ketoenols, respectively.

Key words: 2,2-dimethyl-6-[3-(2,2-dimethyl-6-phenyl-4*H*-1,3-dioxen-4-ylidene)prop-1-enyl]-4-methoxy-4-phenyl-4*H*-1,3-dioxene; 4-methoxy-4-phenyl-2-[3-(4-phenyl-1,5-dioxaspiro[5.5]undec-3-en-2-ylidene)prop-1-enyl]-1,5-dioxaspiro[5.5]undec-2-ene; 1-amino-6-(2,2-dimethyl-6-phenyl-4*H*-1,3-dioxen-4-ylidene)-1-phenylhexa-1,4-dien-3-one; 6-(2,2-dimethyl-6-phenyl-4*H*-1,3-dioxen-4-ylidene)-1-morpholino-1-phenylhexa-1,4-dien-3-one; 6-(2,2-dimethyl-6-phenyl-4*H*-1,4-dioxen-4-ylidene)-1-hydroxy-1-phenylhexa-1,4-dien-3-one; X-ray diffraction study, molecular structure.

Over the last decades, the necessity of studying the relationship between the structures of the carboxonium cations and their reactivity in interactions with nucleophiles, as well as of revealing preferential directions of these reactions, was repeatedly confirmed by detection of useful conversions and valuable products, for example, the salts of pyrylium,[1] 1-benzopyrylium,[2] 2-benzopyrylium,[3] etc. In this connection, perchlorates of previously unknown carboxonium cations, viz., of 1,3-dioxenium, which we have prepared recently,[4] are of particular interest because they are highly efficient in condensations at active methyl (methylene) groups to form cations of trimethinecyanine bis-dioxenium dyes

containing several equivalent electrophilic centers, which can be subjected to nucleophilic attack, due to the symmetrical structure and delocalization of the positive charge.

Previously,[5] we have found configurational *Z,E* isomerism in a series of trimethinecyanine perchlorates **1**, which have been prepared from the 4-methyl-6-phenyl-1,3-dioxenium carbocation, by the dynamic ¹H NMR method. We established that cyanines of type **1** that are not annelated with carbocycles at positions 4, 5 and 4', 5' exist in solutions (CDCl₃ or C₆D₅NO₂) as an equilibrium mixture of three configurational *Z,E* isomers, namely, two symmetrical isomers (**L** and **U**) and one

Scheme 1

1L

1U

1G

2

3
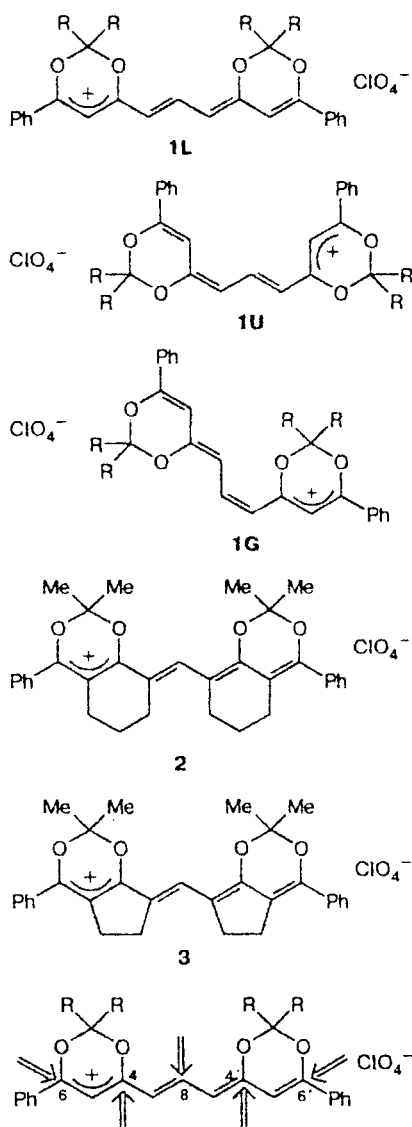
unsymmetrical isomer (**G**) relative to the methine chain. The insertion of the C=C bonds of the cyanine fragment adjacent to the central methine unit into the five- and six-membered rings results in reduction of the Z,E stereo-dynamics, and hence, the corresponding derivatives **2** and **3** are stable as the single configurational isomers (Scheme 1).

The reactions of carbenium ions **1—3** with nucleophiles (hydrolysis, alcoholysis, and aminolysis) can afford new heterocycles, homologs of ketoenols, their functionally substituted derivatives, and other products in which one of two oxygen-containing heterocycles is retained as the 1,3-dioxenylidene fragment. The latter is of interest in connection with extensive studies[6] of conversions of related 1,3-dioxin-4-ones into chiral synthons and physiologically active compounds.

It is known[7] that the reactions of heterocyclic cations with nucleophiles either afford addition products or are accompanied by subsequent transformations, for example, by recyclization. The specificity of the trimethinecyanines under study results from the symmetry of their structures and delocalization of the positive charge over the π-conjugation chain. Hence, their reactions with nucleophiles would be expected to give several products.

The standard references for the resonance structures of cyanines **1—3** with consideration of their symmetry revealed three alternative directions of the nucleophilic attack, namely, on positions 4 and 6 of the dioxenium heterocycles and on the central methine C(8) atom. With the aim of predicting the most probable direction of interaction, we studied the structure of cyanine **3** by X-ray diffraction analysis and by semiempirical quantum-chemical PM3 calculations.

On the structures of 1,3-dioxenium salts

X-ray diffraction analysis of carbocation perchlorate **3** (Fig. 1; Tables 1—3) demonstrated that compound **3** exists in the crystal as a solvate with chloroform of 1 : 1 composition.
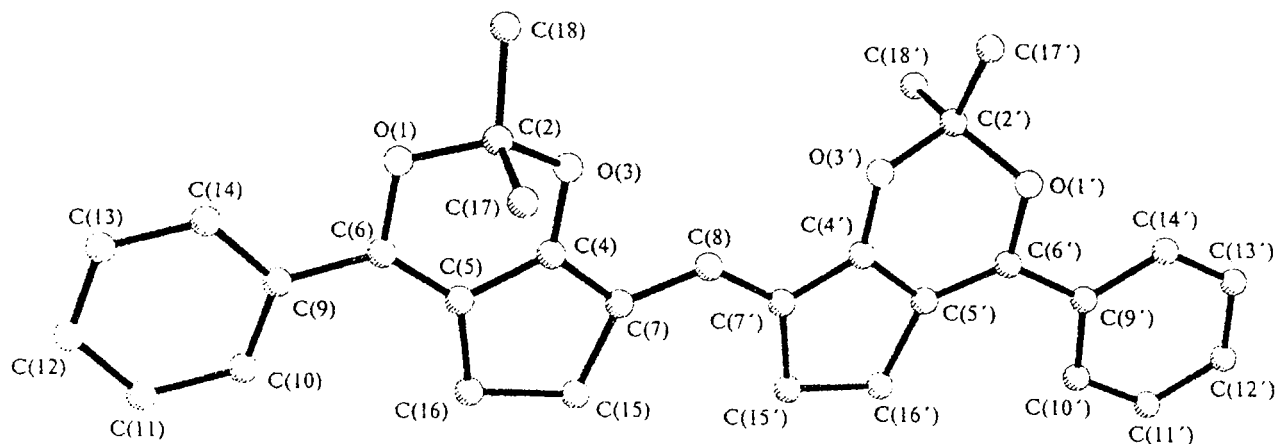

Fig. 1. Structure of cation **3** (hydrogen atoms are omitted).

Table 1. Coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) and their equivalent isotropic thermal parameters ($\times 10^3/\text{Å}^2$) in the structure of **3**

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Cl(1)	1191(1)	1363(1)	2456(1)	32(1)	C(18')	1260(4)	−85(1)	6427(2)	36(1)
O(1A)	−338(2)	1361(1)	2397(2)	56(1)	C(18)	8502(3)	781(1)	9823(2)	37(1)
O(2A)	1858(3)	1788(1)	3086(2)	46(1)	Cl(1S)	4570(1)	47(1)	11935(1)	70(1)
O(3A)	1480(3)	1446(1)	1497(2)	53(1)	Cl(2S)	3675(2)	597(1)	10103(1)	98(1)
O(4A)	1790(2)	856(1)	2823(2)	57(1)	Cl(3S)	5821(2)	1060(1)	11633(1)	87(1)
O(1)	9557(2)	1405(1)	8917(1)	29(1)	C(1S)	4225(4)	671(1)	11359(3)	48(1)
O(1')	−461(2)	561(1)	6809(1)	29(1)	H(8)	450(3)	113(1)	757(2)	21(7)
C(2)	8274(3)	1302(1)	9277(2)	29(1)	H(10)	1033(3)	255(1)	707(2)	28(7)
C(2')	935(3)	316(1)	7155(2)	28(1)	H(10')	−176(4)	150(2)	448(3)	60(11)
O(3)	7055(2)	1211(1)	8456(1)	29(1)	H(11)	1263(4)	292(2)	718(3)	54(10)
O(3')	2052(2)	736(1)	7325(1)	27(1)	H(11')	−416(5)	156(2)	367(3)	68(12)
C(4)	6961(3)	1575(1)	7747(2)	24(1)	H(12)	1460(3)	264(1)	837(2)	32(8)
C(4')	1931(3)	1094(1)	6606(2)	23(1)	H(12')	−599(4)	96(2)	413(3)	54(10)
C(5)	8169(3)	1885(1)	7613(2)	24(1)	H(13)	1428(5)	200(2)	950(3)	74(13)
C(5')	609(3)	1177(1)	5919(2)	24(1)	H(13')	−533(4)	45(1)	549(3)	45(9)
C(6)	9488(3)	1792(1)	8215(2)	24(1)	H(14)	1196(4)	166(2)	942(3)	45(9)
C(6')	−601(3)	909(1)	6044(2)	24(1)	H(14')	−294(4)	38(2)	632(3)	47(9)
C(7)	5696(3)	1676(1)	7064(2)	25(1)	H(15B)	549(3)	243(1)	648(2)	29(7)
C(7')	3062(3)	1423(1)	6471(2)	25(1)	H(15A)	577(3)	201(1)	575(2)	28(7)
C(8)	4428(3)	1394(1)	7083(2)	25(1)	H(15D)	256(3)	214(1)	574(2)	32(8)
C(9)	10907(3)	2037(1)	8239(2)	27(1)	H(15C)	313(3)	172(1)	511(2)	29(7)
C(9')	−2103(3)	946(1)	5494(2)	28(1)	H(16B)	776(3)	261(1)	687(2)	31(7)
C(10)	11118(3)	2420(1)	7551(2)	31(1)	H(16A)	818(3)	215(1)	624(2)	27(7)
C(10')	−2495(3)	1279(1)	4677(2)	35(1)	H(16D)	27(4)	194(1)	524(2)	40(8)
C(11)	12480(3)	2652(1)	7613(2)	34(1)	H(16C)	76(4)	147(2)	456(3)	48(9)
C(11')	−3938(3)	1294(2)	4165(2)	44(1)	H(17C)	880(3)	184(1)	1040(2)	34(8)
C(12)	13650(3)	2500(1)	8337(2)	35(1)	H(17B)	701(4)	171(1)	1003(2)	35(8)
C(12')	−4985(3)	986(1)	4451(2)	46(1)	H(17A)	779(4)	210(1)	948(3)	43(9)
C(13)	13449(3)	2122(1)	9018(2)	41(1)	H(17F)	186(3)	−7(1)	840(2)	23(7)
C(13')	−4611(3)	656(1)	5258(3)	42(1)	H(17E)	73(4)	36(2)	856(3)	49(10)
C(14)	12097(3)	1894(1)	8974(2)	36(1)	H(17D)	18(4)	−16(2)	807(2)	43(9)
C(14')	−3188(3)	631(1)	5779(2)	34(1)	H(18F)	51(4)	−39(1)	632(2)	43(9)
C(15)	6005(3)	2118(1)	6398(2)	29(1)	H(18E)	219(4)	−25(2)	669(3)	52(10)
C(15')	2504(3)	1773(1)	5594(2)	30(1)	H(18D)	126(3)	8(1)	578(3)	39(8)
C(16)	7660(3)	2242(1)	6732(2)	26(1)	H(18C)	862(3)	50(1)	941(2)	35(8)
C(16')	890(3)	1605(1)	5222(2)	31(1)	H(18B)	932(4)	81(1)	1039(3)	49(9)
C(17)	7926(3)	1774(1)	9861(2)	36(1)	H(18A)	764(4)	71(1)	1005(3)	45(9)
C(17')	915(3)	83(1)	8133(2)	35(1)	H(1S)	350(4)	83(1)	1164(3)	42(9)

Table 2. Bond lengths (*d*) in the structure of **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Cl(1)—O(1A)	1.423(2)	C(2')—C(17')	1.500(4)	C(6)—C(9)	1.461(4)	C(11)—C(12)	1.384(4)
Cl(1)—O(4A)	1.432(2)	C(2')—C(18')	1.508(4)	C(6')—C(9')	1.462(3)	C(11')—C(12')	1.375(5)
Cl(1)—O(2A)	1.438(2)	O(3)—C(4)	1.338(3)	C(7)—C(8)	1.389(4)	C(12)—C(13)	1.387(5)
Cl(1)—O(3A)	1.450(2)	O(3')—C(4')	1.336(3)	C(7)—C(15)	1.513(4)	C(12')—C(13')	1.387(5)
O(1)—C(6)	1.374(3)	C(4)—C(7)	1.385(4)	C(7')—C(8)	1.389(4)	C(13)—C(14)	1.382(4)
O(1)—C(2)	1.428(3)	C(4)—C(5)	1.418(4)	C(7')—C(15')	1.513(4)	C(13')—C(14')	1.384(4)
O(1')—C(6')	1.368(3)	C(4')—C(7')	1.387(4)	C(9)—C(14)	1.400(4)	C(15)—C(16)	1.558(4)
O(1')—C(2')	1.436(3)	C(4')—C(5')	1.420(3)	C(9)—C(10)	1.404(4)	C(15')—C(16')	1.554(4)
C(2)—O(3)	1.463(3)	C(5)—C(6)	1.366(4)	C(9')—C(10')	1.404(4)	Cl(1S)—C(1S)	1.752(4)
C(2)—C(18)	1.503(4)	C(5)—C(16)	1.520(4)	C(9')—C(14')	1.412(4)	Cl(2S)—C(1S)	1.747(4)
C(2)—C(17)	1.508(4)	C(5')—C(6')	1.363(4)	C(10)—C(11)	1.390(4)	Cl(3S)—C(1S)	1.758(4)
C(2')—O(3')	1.465(3)	C(5')—C(16')	1.511(4)	C(10')—C(11')	1.395(4)		

In cation **3**, the C(4)...C(8) and C(4')...C(8') atoms are in a single plane to within 0.03 Å. The bonds between these atoms are to a large extent equalized and their lengths are close to the C(Ar)—C(Ar) bond length,[8] which is indicative of substantial delocalization of the electron density in this fragment. The C(9)...C(14) and

Table 3. Bond angles (ω) in the structure of 3

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(1A)—Cl(1)—O(4A)	109.5(2)	O(3)—C(4)—C(5)	122.7(2)	C(7')—C(8)—C(7)	130.3(2)
O(1A)—Cl(1)—O(2A)	109.9(2)	C(7)—C(4)—C(5)	113.8(2)	C(14)—C(9)—C(10)	118.5(2)
O(4A)—Cl(1)—O(2A)	109.8(2)	O(3')—C(4')—C(7')	123.7(2)	C(14)—C(9)—C(6)	119.5(2)
O(1A)—Cl(1)—O(3A)	109.5(2)	O(3')—C(4')—C(5')	122.4(2)	C(10)—C(9)—C(6)	122.0(2)
O(4A)—Cl(1)—O(3A)	109.1(2)	C(7')—C(4')—C(5')	113.9(2)	C(10')—C(9')—C(14')	118.8(3)
O(2A)—Cl(1)—O(3A)	109.12(14)	C(6)—C(5)—C(4)	118.2(2)	C(10')—C(9')—C(6')	121.9(2)
C(6)—O(1)—C(2)	117.8(2)	C(6)—C(5)—C(16)	133.9(2)	C(14')—C(9')—C(6')	119.3(2)
C(6')—O(1')—C(2')	117.7(2)	C(4)—C(5)—C(16)	107.7(2)	C(11)—C(10)—C(9)	120.1(3)
O(1)—C(2)—O(3)	109.0(2)	C(6')—C(5')—C(4')	118.3(2)	C(11')—C(10')—C(9')	119.9(3)
O(1)—C(2)—C(18)	107.3(2)	C(6')—C(5')—C(16')	134.1(2)	C(12)—C(11)—C(10)	120.7(3)
O(3)—C(2)—C(18)	105.9(2)	C(4')—C(5')—C(16')	107.4(2)	C(12')—C(11')—C(10')	120.8(3)
O(1)—C(2)—C(17)	110.6(2)	C(5)—C(6)—O(1)	117.7(2)	C(11)—C(12)—C(13)	119.5(3)
O(3)—C(2)—C(17)	109.2(2)	C(5)—C(6)—C(9)	130.4(2)	C(11')—C(12')—C(13')	119.9(3)
C(18)—C(2)—C(17)	114.6(2)	O(1)—C(6)—C(9)	111.9(2)	C(14)—C(13)—C(12)	120.5(3)
O(1')—C(2')—O(3')	109.0(2)	C(5')—C(6')—O(1')	118.0(2)	C(14')—C(13')—C(12')	120.7(3)
O(1')—C(2')—C(17')	106.7(2)	C(5')—C(6')—C(9')	129.7(2)	C(13)—C(14)—C(9)	120.8(3)
O(3')—C(2')—C(17')	105.9(2)	O(1')—C(6')—C(9')	112.3(2)	C(13')—C(14')—C(9')	120.0(3)
O(1')—C(2')—C(18')	110.7(2)	C(4)—C(7)—C(8)	120.6(2)	C(7)—C(15)—C(16)	105.5(2)
O(3')—C(2')—C(18')	110.0(2)	C(4)—C(7)—C(15)	108.2(2)	C(7')—C(15')—C(16')	105.4(2)
C(17')—C(2')—C(18')	114.4(2)	C(8)—C(7)—C(15)	131.2(2)	C(5)—C(16)—C(15)	104.6(2)
C(4)—O(3)—C(2)	113.7(2)	C(4')—C(7')—C(8)	121.2(2)	C(5')—C(16')—C(15')	105.3(2)
C(4')—O(3')—C(2')	114.2(2)	C(4')—C(7')—C(15')	108.1(2)	Cl(2S)—C(1S)—Cl(1S)	111.2(2)
O(3)—C(4)—C(7)	123.6(2)	C(8)—C(7')—C(15')	130.7(2)	Cl(2S)—C(1S)—Cl(3S)	109.6(2)
				Cl(1S)—C(1S)—Cl(3S)	108.7(2)

C(9')...C(14') benzene rings are virtually coplanar with the above-mentioned plane (the C(5)—C(6)—C(9)—C(10) and C(5')—C(6')—C(9')—C(10') torsion angles are −2.9(4)° and −2.6(4)°, respectively) in spite of the presence of the following shortened intramolecular contacts: O(1)...H(14), 2.31 Å (the sum of the van der Waals radii[9] is 2.45 Å); C(5)...H(10), 2.84 Å (2.87 Å); C(16)...C(10), 3.24 Å (3.42 Å); C(16)...H(10), 2.57 Å; O(1')...H(14'), 2.33 Å; C(5')...H(10'), 2.80 Å; C(16')...C(10'), 3.22 Å; C(16')...H(10'), 2.51 Å; and H(16D)...H(10'), 2.27 Å (2.32 Å). This arrangement of the substituents suggests that the positive charge is delocalized over the π-electron system of the above-mentioned fragment and the benzene rings.

The six-membered O(1)...C(6) and O(1')...C(6') rings adopt a sofa conformation. The deviations of the C(2) and C(2') atoms from the planes through the remaining atoms of these rings are 0.575 Å and −0.578 Å, respectively. The O(1)—C(6) and O(1')—C(6') bonds (1.374(3) and 1.368(3) Å, respectively) are somewhat elongated and the O(1)—C(2) and O(1')—C(2') bonds (1.428(3) and 1.436(3) Å, respectively) are shortened compared to those observed previously[10] in the distyryl derivative of the 1,3-dioxenium cation (1.348 and 1.450 Å, respectively).

The five-membered C(4)—C(7)—C(15)—C(16)—C(5) ring has a highly flattened envelope conformation (the deviation of the C(4) atom from the plane through the other atoms of the ring is 0.06 Å). The C(4')—C(7')—C(15')—C(16')—C(5') ring is planar to within 0.006 Å.

The C(18) and C(17') methyl groups are in equatorial positions (the C(18)—C(2)—O(1)—C(6) and C(17')—C(2')—O(1')—C(6') torsion angles are 165.6(2)° and 164.9(2)°, respectively). The C(17) and C(18') methyl groups are in axial positions (the C(17)—C(2)—O(3)—C(4) and C(18')—C(2')—O(3')—C(4') torsion angles are 74.0(3)° and 75.3(3)°, respectively). These conformations of the methyl substituents are apparently responsible for the following shortened intramolecular contacts: C(5)...C(17), 3.24 Å; C(5)...H(17A), 2.77 Å; C(4)...H(17A), 2.72 Å; C(6)...H(17A), 2.73 Å; C(6')...H(18D), 2.79 Å; C(4')...H(18D), 2.80 Å; C(5')...C(18'), 3.25 Å; and C(5')...H(18D), 2.83 Å.

The geometric parameters of cation 3 calculated by the semiempirical method agree on the whole rather well with those determined experimentally. Thus, according to the results of semiempirical PM3 calculations, the bonds in the central 1,5-dioxypentadienyl chain are virtually equalized and their lengths are approximately equal to the average C(Ar)—C(Ar) bond length.[8] However, the C(4)—C(5) and C(4')—C(5') bond lengths (1.440 and 1.440 Å, respectively) are somewhat larger than the experimental values and are close to the C(sp²)—C(sp²) bond length in conjugated systems.[8] The molecular fragment containing the C(6), C(5), C(4), C(7), C(8), C(7'), C(4'), C(5'), and C(6') atoms is flattened to a substantially lesser degree (the root-mean-square deviation of the atoms from this plane is 0.07 Å) than that determined by X-ray diffraction

Table 4. Charges on selected carbon atoms in cyanine **3** and in the configurational isomers of cyanine **4** calculated by the PM3 method

Compound	C(6)	C(4)	C(4')	C(6')	C(8)
3	0.28	0.31	0.31	0.28	0.21
4L	0.27	0.32	0.32	0.26	0.20
4U	0.30	0.33	0.33	0.30	0.19
4G	0.30	0.37	0.30	0.25	0.20

analysis. The phenyl substituents are noticeably rotated with respect to the plane of this fragment (the C(5)—C(6)—C(9)—C(10) and C(5')—C(6')—C(9')—C(10') torsion angles are −30.6° and −30.8°, respectively).

Analysis of the charge distribution in cation **3** revealed the alternation of the positive and negative charges, which are approximately equal in magnitude, on the atoms of the above-mentioned fragment, the positive charges being localized on the C(4), C(6), C(4'), and C(6') atoms and the somewhat smaller positive charge being localized on the C(8) atom (Table 4).

Therefore, positions 4 and 6 of the heterocycles in cation **3** are the most electron-deficient and the nucleophilic attack is most likely to occur at one of these positions. The predicted nucleophilic reactivity was verified experimentally using an analog of compound **3**, namely, nonannelated cyanine **4**, as an example.

On the regioselectivity of the nucleophilic attack on 1,3-dioxenium cations
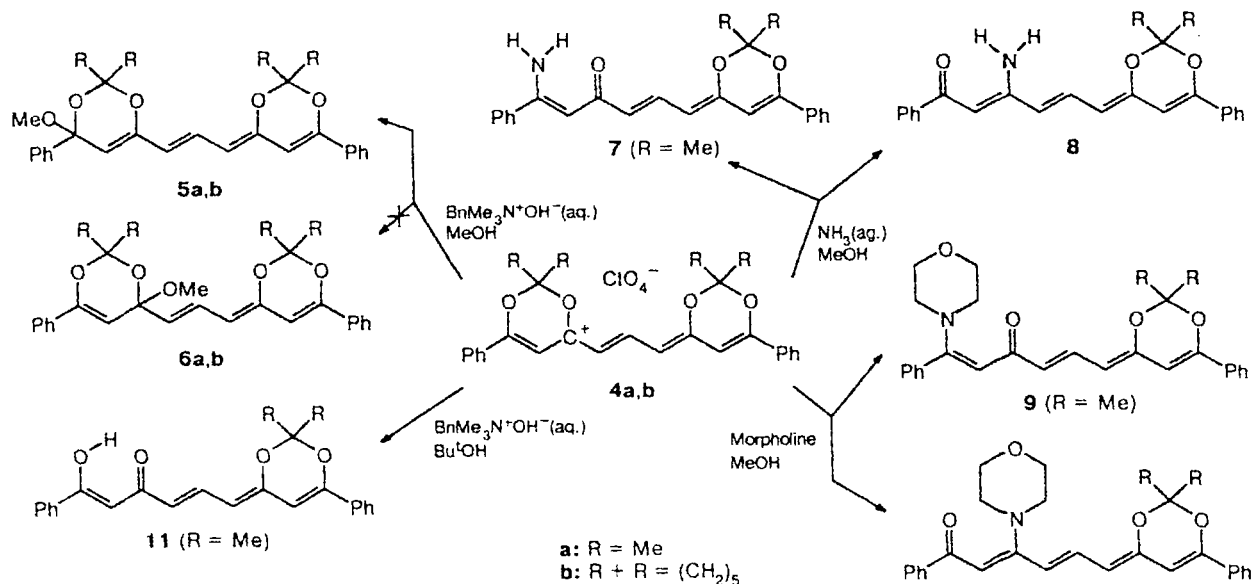
Carbocation perchlorate **4** reacts with an aqueous-methanolic solution of benzyltrimethylammonium hydroxide to form a single compound. Based on the data

of ¹H NMR spectroscopy and elemental analysis, the structures of methoxy derivatives **5** or **6**, which resulted from the attack of the methoxide anion on positions 4 or 6, respectively, of the dioxenium rings (Scheme 2), can be assigned to the compound obtained. X-ray diffraction analysis (Fig. 2, Tables 5—7) demonstrated that the product of this reaction is methoxy derivative **5b**.

In this structure, the O(1)...C(6) and O(1')...C(6') six-membered rings adopt a sofa conformation. The deviations of the C(2) and C(2') atoms from the mean planes through the remaining atoms of the rings are −0.60 and 0.58 Å, respectively. These rings are spiro-fused with the saturated C(2),C(15)...C(19) and C(2'),C(15')—C(19') six-membered rings, which have a chair conformation. The deviations of the C(2), C(17), C(2'), and C(17') atoms from the corresponding mean planes through the remaining atoms of the rings are 0.65, −0.64, 0.63, and −0.67 Å, respectively. These conformations of the rings under consideration are apparently responsible for the following shortened intramolecular contacts: C(6)...H(19A), 2.80 Å (the sum of the van der Waals radii[9] is 2.87 Å); C(5)...C(19), 3.25 Å (3.42 Å); C(4)... H(19A), 2.74 Å; C(5)...H(19A), 2.78 Å; C(4')...H(15C), 2.74 Å; C(5')...C(15'), 3.23 Å; C(6')...H(15C), 2.79 Å; and C(5')...H(15C), 2.80 Å.

The polyene fragment in molecule **5b** is substantially flattened (the deviations of the atoms from the mean plane are no more than 0.04 Å) and there is the distinct alternation of single and double bonds in this ring (Table 6).

The methoxy group at the saturated C(6) atom is in the pseudoaxial orientation and the phenyl group is in the pseudoequatorial orientation (the O(20)—C(6)—O(1)—C(2) and C(9)—C(6)—C(5)—C(4) torsion angles
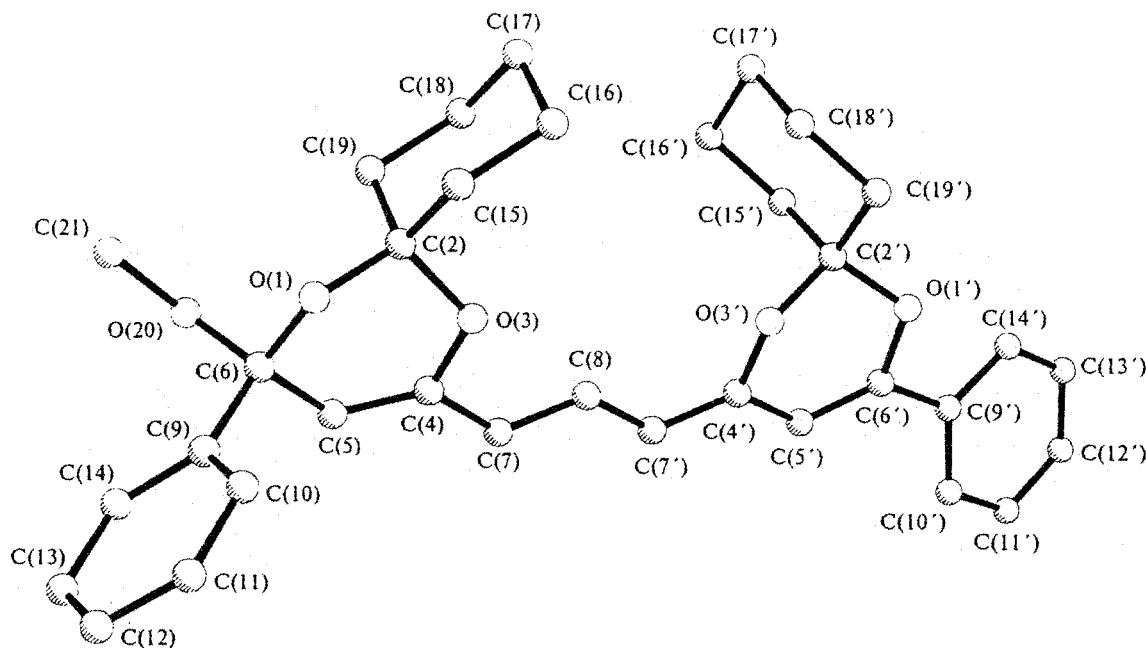
Scheme 2

7 (R = Me)

8

5a,b

6a,b

BnMe₃N⁺OH⁻(aq.)
MeOH

ClO₄⁻

NH₃(aq.)
MeOH

9 (R = Me)

4a,b

BnMe₃N⁺OH⁻(aq.)
BuᵗOH

Morpholine
MeOH

11 (R = Me)

a: R = Me
b: R + R = (CH₂)₅

10

Fig. 2. Structure of compound **5b** (hydrogen atoms are omitted).

are −84.3(2)° and −122.3(3)°, respectively). This arrangement of the substituents results in the following shortened intramolecular contacts: O(1)...H(10), 2.40 Å (2.45 Å); O(1)...H(21B), 2.42 Å; C(9)...H(21A), 2.75 Å; C(14)...C(21), 3.22 Å; and C(14)...H(21A), 2.73 Å. The C(21) methyl group is in a synclinal conformation with respect to the C(6)—O(1) bond (the C(21)—O(20)—C(6)—O(1) torsion angle is −55.1(3)°). The benzene ring is virtually perpendicular to the C(6)—C(5) bond (the C(10)—C(9)—C(6)—C(5) torsion angle is 92.5(3)°).

The C(9′)...C(14′) benzene ring is noticeably rotated with respect to the C(5′)—C(6′) bond (the C(10′)—C(9′)—C(6′)—C(5′) torsion angle is −23.4(4)°). Probably, such conformation of this substituent is realized due to the presence of the shortened intramolecular contacts: C(10′)...H(5′), 2.77 Å; C(5′)...H(10′),'2.75 Å; O(1′)...H(14′), 2.37 Å; and H(5′)...H(10′), 2.28 Å (2.32 Å).

From the results obtained it follows that the charge (kinetic) control apparently plays a decisive role in the direction of the attack of the methoxide anion, which occurs preferentially on the C(4) and C(6) atoms of the dioxenium ring rather that on the central C(8) atom of the methine chain. However, the selective formation of methoxy derivative **5** is inconsistent either with an insignificant difference in the values of the positive charges on the C(4) and C(6) atoms of the dioxenium fragments (Table 1) or with the close values of the calculated (PM3) heats of formation of the corresponding isomers (ΔH_f is −91.01 and −91.39 kcal mol^{-1} for **5** and **6**, respectively) because in accordance with the above-mentioned two facts one would expect the formation of a mixture of methoxy derivatives **5** and **6** (Scheme 2) in which isomer **6** should prevail.

The inverse ratio of the charges on the C(4) and C(6) atoms in one of the dioxenium fragments of the unsymmetrical configurational **G** isomer of cyanine **4** cannot be responsible for the above-described selective interaction between the methoxide anion and carbocation **4** because the charge distribution (Table 1) in this isomer is similar to those observed in the symmetrical linear (**L**) or U-shaped Z,E configurations, which exist in dynamic equilibrium with the **G** topomer.[5] Nevertheless, the possibility that the reverse electron deficiency on the C(4) and C(6) atoms does occur in the intermediate states of the stereoconversions **L**↔**G**↔**U** must not *a priori* be ruled out. Second, at the stage preceding the formation of the C—O bond, the methoxide anion forms a "tight" ionic pair or the π-complex with only one of the dioxenium fragments of the cyanine, and hence, the methoxide anion can apparently initiate polarization in the mesomeric both symmetrical (**L** and **U**) and unsymmetrical (**G**) carbocations such that the positive charge is localized preferentially on the C(6) atom of the heterocycle. As a result, the Z,E stereodynamics and the charge polarization of the cyanine substrate are apparently responsible for particular results of its interaction with nucleophilic reagents.

For example, carbocation **4** in methanol reacts with an aqueous solution of ammonia to form a single product. However, according to the data of ¹H NMR spectroscopy and elemental analysis, in this case one of the dioxenium rings opens and eliminates acetone and the reaction affords enaminoketone **7** or **8**. It is more probable that (as in the case of addition of the methoxy group to form product **5**) ammonia attacks one of the dioxenium rings of cyanine **4** at position 6 to form isomeric product **7**. Analogously, the reaction of cyanine

Table 5. Coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) and their equivalent isotropic thermal parameters ($\times 10^3/\text{Å}^2$) in the structure of **5b**

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
O(1)	2013(1)	3535(2)	3997(1)	51(1)	H(5)	306(1)	583(3)	492(1)	43(6)
O(1′)	7268(1)	1591(2)	2969(1)	57(1)	H(5′)	731(1)	459(3)	393(1)	57(7)
C(2)	2641(1)	2443(3)	3886(1)	50(1)	H(7)	447(1)	577(3)	455(1)	48(7)
C(2′)	6515(1)	1017(3)	3171(1)	50(1)	H(7′)	590(1)	525(3)	426(1)	44(6)
O(3)	3352(1)	3325(2)	3786(1)	47(1)	H(8)	474(1)	316(3)	371(1)	54(7)
O(3′)	5996(1)	2339(2)	3268(1)	48(1)	H(10′)	848(2)	539(4)	351(1)	85(10)
C(4)	3511(1)	4470(3)	4242(1)	42(1)	H(10)	162(2)	590(3)	342(1)	67(9)
C(4′)	6261(1)	3513(3)	3678(1)	42(1)	H(11′)	983(2)	546(5)	349(2)	131(16)
C(5)	2939(1)	5082(3)	4598(1)	46(1)	H(11)	88(2)	823(4)	324(2)	83(10)
C(5′)	7096(1)	3749(3)	3682(1)	47(1)	H(12)	43(2)	976(4)	407(1)	78(9)
C(6)	2101(1)	4616(3)	4520(1)	48(1)	H(12′)	1059(2)	329(4)	320(1)	90(10)
C(6′)	7564(1)	2836(3)	3324(1)	48(1)	H(13)	74(2)	897(4)	514(2)	98(11)
C(7)	4333(1)	4883(3)	4274(1)	44(1)	H(13′)	993(2)	92(4)	294(2)	94(12)
C(7′)	5723(1)	4370(3)	4004(1)	46(1)	H(14)	147(2)	668(3)	529(1)	71(9)
C(8)	4897(1)	4052(3)	3979(1)	44(1)	H(14′)	858(2)	67(4)	302(1)	80(10)
C(9)	1597(1)	6078(3)	4375(1)	49(1)	H(15B)	238(1)	248(3)	293(1)	49(7)
C(9′)	8420(1)	2985(3)	3266(1)	52(1)	H(15A)	192(2)	101(3)	334(1)	74(8)
C(10′)	8792(2)	4418(4)	3397(2)	73(1)	H(15C)	682(1)	64(3)	413(1)	60(8)
C(10)	1427(2)	6566(4)	3758(2)	59(1)	H(15D)	702(2)	−76(4)	367(1)	87(10)
C(11′)	9603(2)	4520(6)	3375(2)	93(1)	H(16B)	295(2)	−14(4)	266(2)	116(12)
C(11)	996(2)	7940(4)	3650(2)	69(1)	H(16A)	356(2)	97(4)	300(1)	82(9)
C(12)	735(2)	8845(4)	4150(2)	71(1)	H(16C)	591(2)	−144(4)	431(2)	104(12)
C(12′)	10040(2)	3221(6)	3219(2)	92(1)	H(16D)	546(2)	3(5)	409(2)	109(14)
C(13)	907(2)	8406(4)	4766(2)	70(1)	H(17B)	274(2)	−150(4)	368(2)	118(13)
C(13′)	9681(2)	1817(6)	3075(2)	84(1)	H(17A)	365(2)	−164(4)	353(2)	102(11)
C(14)	1339(2)	7032(4)	4877(2)	63(1)	H(17C)	587(2)	−270(5)	328(2)	101(11)
C(14′)	8876(2)	1670(4)	3099(2)	68(1)	H(17D)	499(2)	−219(4)	351(2)	104(12)
C(15)	2460(2)	1626(4)	3259(2)	66(1)	H(18B)	395(2)	50(4)	419(1)	95(10)
C(15′)	6599(2)	22(4)	3774(2)	64(1)	H(18A)	343(2)	−89(4)	457(2)	98(11)
C(16)	3082(2)	408(5)	3076(2)	88(1)	H(18C)	499(2)	16(4)	288(1)	85(10)
C(16′)	5820(2)	−775(5)	3949(2)	78(1)	H(18D)	525(2)	−130(4)	246(2)	85(10)
C(17)	3208(3)	−810(5)	3606(2)	97(1)	H(19B)	223(2)	66(4)	449(1)	86(9)
C(17′)	5502(3)	−1736(4)	3389(2)	86(1)	H(19A)	292(1)	181(3)	484(1)	61(8)
C(18)	3389(2)	−5(4)	4240(2)	78(1)	H(19C)	656(2)	−72(4)	251(1)	89(10)
C(18′)	5404(2)	−696(4)	2804(2)	74(1)	H(19D)	611(2)	85(4)	225(1)	82(10)
C(19)	2764(2)	1226(3)	4423(2)	63(1)	H(21C)	102(2)	276(5)	551(2)	118(14)
C(19′)	6172(2)	84(4)	2617(2)	63(1)	H(21B)	98(2)	266(4)	471(2)	110(13)
O(20)	1865(1)	3879(2)	5108(1)	56(1)	H(21A)	70(2)	411(5)	514(2)	129(15)
C(21)	1085(2)	3244(5)	5097(2)	75(1)					

Table 6. Bond lengths (d) in the structure of **5b**

Bond	$d/\text{Å}$	Bond	$d/\text{Å}$	Bond	$d/\text{Å}$	Bond	$d/\text{Å}$
O(1)—C(6)	1.422(3)	O(3′)—C(4′)	1.375(3)	C(7′)—C(8)	1.435(3)	C(13)—C(14)	1.382(4)
O(1)—C(2)	1.424(3)	C(4)—C(5)	1.328(3)	C(9)—C(10)	1.376(4)	C(13′)—C(14′)	1.380(5)
O(1′)—C(6′)	1.370(3)	C(4)—C(7)	1.445(3)	C(9)—C(14)	1.386(4)	C(15)—C(16)	1.517(4)
O(1′)—C(2′)	1.433(3)	C(4′)—C(7′)	1.346(3)	C(9′)—C(10′)	1.379(4)	C(15′)—C(16′)	1.530(4)
C(2)—O(3)	1.433(3)	C(4′)—C(5′)	1.439(3)	C(9′)—C(14′)	1.389(4)	C(16)—C(17)	1.514(6)
C(2)—C(15)	1.502(4)	C(5)—C(6)	1.490(3)	C(10′)—C(11′)	1.386(5)	C(16′)—C(17′)	1.514(5)
C(2)—C(19)	1.524(4)	C(5′)—C(6′)	1.332(3)	C(10)—C(11)	1.380(4)	C(17)—C(18)	1.513(5)
C(2′)—O(3′)	1.428(3)	C(6)—O(20)	1.427(3)	C(11′)—C(12′)	1.354(5)	C(17′)—C(18′)	1.503(5)
C(2′)—C(19′)	1.507(4)	C(6)—C(9)	1.522(3)	C(11)—C(12)	1.361(4)	C(18)—C(19)	1.529(4)
C(2′)—C(15′)	1.512(4)	C(6′)—C(9′)	1.471(3)	C(12′)—C(13)	1.364(4)	C(18′)—C(19′)	1.514(4)
O(3)—C(4)	1.372(3)	C(7)—C(8)	1.336(3)	C(12′)—C(13′)	1.354(5)	O(20)—C(21)	1.431(3)

4 with morpholine affords predominantly isomer **9** (Scheme 2). Finally, only one dioxenium ring of cyanine **4** undergoes aqueous-alkaline hydrolysis to form

1,3-ketoenol **11**. Apparently, the perchlorate anion is displaced from the reaction mixture by an excess of the nucleophile to form alkali perchlorate and the second

Table 7. Bond angles (ω) in the structure of **5b**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(6)—O(1)—C(2)	116.8(2)	O(3')—C(4')—C(5')	115.1(2)	C(9')—C(10')—C(11')	120.4(4)
C(6')—O(1')—C(2')	115.2(2)	C(4)—C(5)—C(6)	122.9(2)	C(9)—C(10)—C(11)	120.6(3)
O(1)—C(2)—O(3)	109.4(2)	C(6')—C(5')—C(4')	120.8(2)	C(12')—C(11')—C(10')	120.5(4)
O(1)—C(2)—C(15)	106.1(2)	O(1)—C(6)—O(20)	110.7(2)	C(12)—C(11)—C(10)	120.6(3)
O(3)—C(2)—C(15)	106.3(2)	O(1)—C(6)—C(5)	110.4(2)	C(11)—C(12)—C(13)	120.0(3)
O(1)—C(2)—C(19)	114.2(2)	O(20)—C(6)—C(5)	106.9(2)	C(13')—C(12')—C(11')	119.8(4)
O(3)—C(2)—C(19)	109.4(2)	O(1)—C(6)—C(9)	107.3(2)	C(12)—C(13)—C(14)	119.6(3)
C(15)—C(2)—C(19)	111.2(2)	O(20)—C(6)—C(9)	110.8(2)	C(12')—C(13')—C(14')	121.2(4)
O(3')—C(2')—O(1')	109.8(2)	C(5)—C(6)—C(9)	110.8(2)	C(13)—C(14)—C(9)	121.3(3)
O(3')—C(2')—C(19')	105.5(2)	C(5')—C(6')—O(1')	121.0(2)	C(13')—C(14')—C(9')	119.8(4)
O(1')—C(2')—C(19')	107.2(2)	C(5')—C(6')—C(9')	126.3(2)	C(2)—C(15)—C(16)	112.3(3)
O(3')—C(2')—C(15')	111.3(2)	O(1')—C(6')—C(9')	112.7(2)	C(2')—C(15')—C(16')	110.8(3)
O(1')—C(2')—C(15')	110.0(2)	C(8)—C(7)—C(4)	123.6(2)	C(17)—C(16)—C(15)	111.3(3)
C(19')—C(2')—C(15')	112.8(2)	C(4')—C(7')—C(8)	123.6(2)	C(17')—C(16')—C(15')	110.9(3)
C(4)—O(3)—C(2)	115.0(2)	C(7)—C(8)—C(7')	126.6(2)	C(18)—C(17)—C(16)	111.5(3)
C(4')—O(3')—C(2')	115.8(2)	C(10)—C(9)—C(14)	117.9(3)	C(18')—C(17')—C(16')	110.9(3)
C(5)—C(4)—O(3)	120.6(2)	C(10)—C(9)—C(6)	122.6(2)	C(17)—C(18)—C(19)	111.9(3)
C(5)—C(4)—C(7)	126.5(2)	C(14)—C(9)—C(6)	119.3(2)	C(17')—C(18')—C(19')	111.1(3)
O(3)—C(4)—C(7)	112.9(2)	C(10')—C(9')—C(14')	118.4(3)	C(2)—C(19)—C(18)	111.1(3)
C(7')—C(4')—O(3')	117.9(2)	C(10')—C(9')—C(6')	120.9(3)	C(2')—C(19')—C(18')	111.2(3)
C(7')—C(4')—C(5')	126.9(2)	C(14')—C(9')—C(6')	120.6(3)	C(6)—O(20)—C(21)	114.2(2)

dioxenium ring is deactivated in the course of the initial stages.

To summarize, X-ray diffraction analysis in combination with quantum-chemical calculations and monitoring of synthetic procedures by ^{1}H NMR spectroscopy established the preferred directions of the reactions of trimethinecyanines of the 1,3-dioxenium series with nucleophiles and revealed that the key stage, namely, the particular direction of the attack of the nucleophile, is apparently governed not only by static characteristic features of delocalization of the positive charge in the initial π-conjugation chain but also by the dynamic effects of the Z,E conversion of the cyanine carbocations and their polarization at the stages of formation of "tight" ionic and ionic-molecular complexes. 1,3-Dioxenylidenepropenylic derivatives of enaminoketones (of type 7) or 1,3-ketoenols (of type 11) that formed upon aminolysis and hydrolysis of trimethinecyanines may be of interest as exotic metal-chelating ligands.

Experimental

The IR spectra of the resulting compounds were recorded on a Specord IR-71 spectrometer as Nujol mulls. The ^{1}H NMR spectra were obtained on Varian VXR-300 (300 MHz) and Bruker DPX-250 (250 MHz) spectrometers in deuterated solvents. Elemental analysis was performed at the Laboratory of Microanalysis of the Scientific Research Institute of Physical and Organic Chemistry of the Rostov State University.

The quantum-chemical calculations were carried out by the PM3 method with the use of the HyperChem™ computer program (Release 4 for Windows, Molecular Modeling System, Copyright © 1994 Hypercube, Inc.).

X-ray diffraction study of compounds 3 and 5b. Crystals of **3**, $C_{31}H_{31}O_4{}^+ClO_4{}^- \cdot CHCl_3$, are monoclinic, at 153(2) K

$a = 9.404(2)$ Å, $b = 24.897(6)$ Å, $c = 14.102(4)$ Å, $\beta = 102.26(2)°$, $V = 3226(1)$ Å^3, crystal dimensions $0.5 \times 0.3 \times 0.3$ mm, space group $P2_1/n$, $Z = 4$, $d_{calc} = 1.413$ g cm^{-3}, $F(000) = 1424$, $\mu = 0.417$ mm^{-1}.

Intensities of 6070 reflections (5702 independent reflections, $R_{int} = 0.033$) were measured on an automated four-circle Siemens P3/PC diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scanning technique, $2\theta_{max} = 50°$).

Crystals of **5b**, $C_{34}H_{38}O_5$, are monoclinic, at 293(2) K $a = 17.054(5)$ Å, $b = 8.339(2)$ Å, $c = 20.810(6)$ Å, $\beta = 90.09(3)°$, $V = 2960(2)$ Å^3, crystal dimensions $0.5 \times 0.4 \times 0.2$ mm, space group $P2_1/c$, $Z = 4$, $d_{calc} = 1.182$ g cm^{-3}, $F(000) = 1128$, $\mu = 0.078$ mm^{-1}.

Intensities of 5392 reflections (5206 independent reflections, $R_{int} = 0.044$) were measured on an automated four-circle Enraf-Nonius CAD 4 diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scanning technique, $2\theta_{max} = 50°$).

The structures of **3** and **5b** were solved by direct methods with the use of the SHELXTL PLUS program package.[11] The positions of the hydrogen atoms were located from difference electron density syntheses. The full-matrix least-squares refinement based on F^2 using the 5275 and 5120 reflections with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms (525 and 504 parameters, respectively) converged to $R_1 = 0.056$ and 0.050 (using 4678 and 2972 reflections with $F > 4\sigma(F)$, respectively), $wR_2 = 0.155, 0.128$, $S = 1.04, 1.02$ for the structures of 3 and 5b, respectively. The coordinates of nonhydrogen atoms are given in Tables 1 and 5. The bond lengths and bond angles in the structure of **3** are listed in Tables 2 and 3, respectively. The bond lengths and bond angles in the structure of **5b** are given in Tables 6 and 7, respectively.

2,2-Dimethyl-6-[3-(2,2-dimethyl-6-phenyl-4*H*-1,3-dioxen-4-ylidene)prop-1-enyl]-4-methoxy-4-phenyl-4*H*-1,3-dioxene (5a). A 15% aqueous solution of benzyltrimethylammonium hydroxide (5 mL) was added to a suspension of 2,2-dimethyl-4-[3-(2,2-dimethyl-6-phenyl-4*H*-1,3-dioxen-4-ylidene)prop-

1-enyl]-6-phenyl-1,3-dioxenium perchlorate (**4a**) (2.1 g, 0.004 mol) in MeOH (20 mL). The reaction mixture was stirred at ~20 °C for 1 h. The precipitate that formed was filtered off and washed with MeOH. Compound **5a** was obtained as a yellow crystalline compound in a yield of 1.4 g (80%), m.p. 127—129 °C (from MeOH). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): 1.66 (m, 12 H); 3.02 (s, 3 H); 5.13 (s, 1 H); 5.45 (d, 1 H, $J = 7$ Hz); 5.85 (d, 1 H); 6.28 (s, 1 H); 7.00 (m, 1 H); 7.24—7.47 (m, 6 H); 7.51 (d, 2 H, $J = 7$ Hz); 7.68 (d, 2 H). Found (%): C, 75.26; H, 6.73. $C_{28}H_{30}O_5$. Calculated (%): C, 75.31; H, 6.77.

4-Methoxy-4-phenyl-2-[3-(4-phenyl-1,5-dioxaspiro[5.5]-undec-3-en-2-ylidene)prop-1-enyl]-1,5-dioxaspiro[5.5]undec-2-ene (5b) was prepared analogously to **5a** from a solution of compound **4b** (2.4 g, 0.004 mol) in MeOH (30 mL). Compound **5b** was obtained as brown-yellow crystals in a yield of 1.8 g (85%), m.p. 150—151 °C (from CH_3CN). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): 1.60—2.22 (m, 20 H); 3.05 (s, 3 H); 5.14 (s, 1 H); 5.54 (d, 1 H, $J = 7$); 5.90 (d, 1 H, $J = 7$ Hz); 6.29 (s, 1 H); 7.23—7.47 (m, 7 H); 7.52 (d, 2 H, $J = 7$ Hz); 7.70 (d, 2 H, $J = 7$ Hz). Found (%): C, 77.50; H, 7.24. $C_{34}H_{38}O_5$. Calculated (%): C, 77.54; H, 7.27.

1-Amino-6-(2,2-dimethyl-6-phenyl-4H-1,3-dioxen-4-yli-dene)-1-phenylhexa-1,4-dien-3-one (7) (or 3-amino-6-(2,2-di-methyl-6-phenyl-4H-1,3-dioxen-4-ylidene)-1-phenylhexa-2,4-dien-1-one (**8**)). A 25% aqueous solution of NH_3 (5 mL) was added to a suspension of compound **4a** (2.1 g, 0.004 mol) in MeOH (20 mL). The reaction mixture was stirred for 1 h. Then the mixture was kept at ~20 °C for 3 days, after which the reaction was completed and the product crystallized. The product was purified by recrystallization from MeOH with a small amount of an aqueous solution of NH_3. Orange crystals were obtained in a yield of 0.9 g (63%), m.p. 174—175 °C. ^{1}H NMR (250 MHz, $(CD_3)_2CO$): 1.73 (s, 6 H); 5.60 (s, 1 H); 5.65 (d, 1 H, $J = 7$ Hz); 6.25 (d, 1 H, $J = 7$ Hz); 6.39 (s, 1 H); 6.80 (s, 1 H); 7.41—7.54 (m, 6 H); 7.68—7.77 (m, 4 H); 10.50 (s, 1 H). Found (%): C, 77.16; H, 6.14; N, 3.77. $C_{24}H_{23}NO_3$. Calculated (%): C, 77.19; H, 6.21; N, 3.75.

6-(2,2-Dimethyl-6-phenyl-4H-1,3-dioxen-4-ylidene)-1-morpholino-1-phenylhexa-1,4-dien-3-one (9) (or 6-(2,2-di-methyl-6-phenyl-4H-1,3-dioxen-4-ylidene)-3-morpholino-1-phenylhexa-2,4-dien-1-one (**10**)). Morpholine (1.6 mL) was added to a suspension of compound **4a** (2.1 g, 0.004 mol) in MeOH (20 mL). The reaction mixture was stirred for 1 h and then distilled water (10 mL) was added with stirring. After 10 min, the product was filtered off. Orange crystals were obtained in a yield of 0.9 g (51%), m.p. 155—156 °C (from Bu^{t}OH upon cooling with ice). ^{1}H NMR (300 MHz, CDCl$_3$): 1.65 (s, 6 H); 3.39 (m, 4 H); 3.82 (m, 4 H); 5.60 (d, 1 H, $J = 7$ Hz); 5.92 (s, 1 H); 6.06 (s, 1 H); 6.85 (m, 1 H); 7.13 (m, 1 H); 7.32—7.50 (m, 6 H); 7.61 (m, 2 H); 7.88 (d, 2 H, $J = 7$ Hz). IR, ν/cm^{-1}: 1620, 1566, 1520, 1200. Found (%): C, 75.80; H, 6.54; N, 3.17. $C_{28}H_{29}NO_4$. Calculated (%): C, 75.82; H, 6.59; N, 3.16.

6-(2,2-Dimethyl-6-phenyl-4H-1,4-dioxen-4-ylidene)-1-hy-droxy-1-phenylhexa-1,4-dien-3-one (11). A 15% aqueous solution of methyltriethylammonium hydroxide (5 mL) was added

to a suspension of compound **4a** (0.5 g, 0.001 mol) in a mixture of Bu^{t}OH (50 mL) and acetone (5 mL). The reaction mixture was stirred for 1 h and kept for 3 days after which the reaction was completed. Then distilled water (10 mL) was added with stirring. The precipitate that formed was washed with MeCN. An orange compound was obtained in a yield of 0.05 g (13%), m.p. 228—230 °C (without recrystallization). ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 1.58 (s, 6 H); 5.63 (d, 1 H, $J = 7$ Hz); 5.97 (s, 1 H); 6.15 (d, 1 H, $J = 7$ Hz); 6.50 (s, 1 H); 7.32—7.55 (m, 6 H); 7.65 (d, 2 H, $J = 7$ Hz); 7.83 (d, 2 H, $J = 7$ Hz). Found (%): C, 76.98; H, 5.89. $C_{24}H_{22}O_4$. Calculated (%): C, 76.99; H, 5.92.

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