

1,3-DIOXENIUM CATIONS: SYNTHESIS, STRUCTURE AND TOPOMERIZATION

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Previously unknown 1,3-dioxenium perchlorates were obtained by coupling 1,3-diketones with aliphatic ketones in an acetic acid solution of perchloric acid. The dioxenium ring of 4,6-bis(*p*-methoxystyryl)-2,2-pentamethylenespiro-1,3-dioxenium perchlorate in the crystal possesses the envelope conformation, the geometry of the carbon triad being close to that of the allyl cations. Variable-temperature ^1H NMR spectra of unsymmetrical 1,3-dioxenium cations revealed the occurrence of a sufficiently fast enantiotopomerization process governed by the C—O bond dissociation–recombination mechanism.

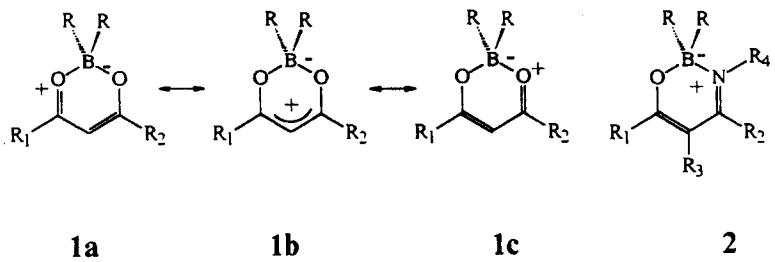
INTRODUCTION

1,3,2-Dioxaborinines (**1**) and their nitrogen-containing derivatives 1,3,2-oxazaborinines (**2**) have been known for a long time since the preparation of the first compound of this series, **1** ($\text{R}_1 = \text{Ph}$, $\text{R}_2 = \text{Me}$, $\text{R} = \text{F}$) by reaction of boron trifluoride with benzoylacetone.¹ Owing to their significant synthetic potential,^{2–5} useful spectral characteristics⁶ and peculiar stereodynamic behaviour,⁷ compounds **1** and **2** and their gallium and indium analogues⁶ have been thoroughly investigated.

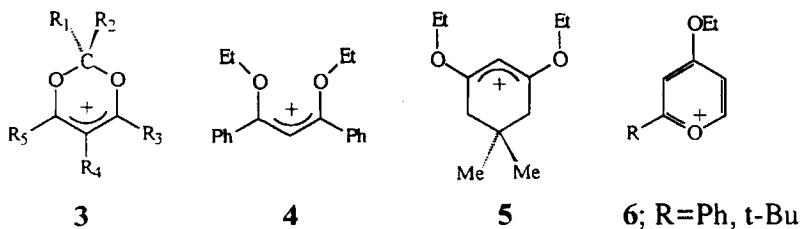
In contrast, purely organic congeners of **1** and **2** in which tetracoordinated boron is replaced by the isolobal carbon-centred group were unknown until recently.⁸ To be isoelectronic with **1** and **2**, these

compounds must bear a positive charge and, thus, be represented by cationic species, e.g. 1,3-dioxenium cation of the general type **3**. The latter could not be obtained by the procedure employed in the preparation of **1** and **2**.

Our approach to 1,3-dioxenium cations **3** is based on the use of perchloric acid as an efficient catalyst and acetic anhydride as a dehydrating agent in coupling enolizable 1,3-diketones with ketones. The formation of 1,3-diethoxypropenium cations **4** and **5** by reaction of dibenzoylmethane or dimedone, respectively, with triethyl orthoformate in the presence of HClO_4 was recently described.⁹ When benzoylacetone or pivaloylacetone is used in this reaction, the formation of cationic species similar to **4** and **5** is also a key step



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that is followed by their subsequent intramolecular cyclization to 2-phenyl- and 2-*tert*-butyl-4-ethoxypyrylium cations (6), respectively.¹⁰ Here we report the synthesis, structure and topomerization of 1,3-dioxenium perchlorates 3.

RESULTS AND DISCUSSION

Synthesis

Typically, for the preparation of perchlorates of cations 3, 0.01 mol of HClO_4 (16% solution in acetic acid prepared by addition of 57% aqueous perchloric acid to acetic anhydride) was added to equimolar amounts of 1,3-diketone (acetylacetone, benzoylacetone, etc.), ketone (acetone, cyclohexanone, etc.), and acetic anhydride. The solution was allowed to stand with stirring at 0°C for 30 min. The highly hygroscopic crystals of the perchlorates 3 thus formed were collected and purified by precipitation from nitromethane solution on adding diethyl ether.

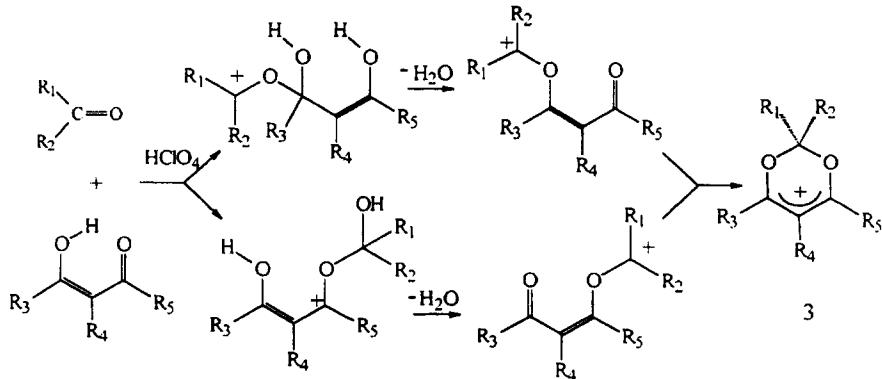
The reaction mechanism is expected to be similar to that governing the formation of 1,3-dioxanes in the acid-catalysed reaction of 1,3-diols with carbonyl compounds;¹¹ it is given in Scheme 1 which implies nucleophilic addition of the carbonyl oxygen of a ketone or enolized diketone to the carbonium centre of species formed by protonation of the initial carbonyl compounds.

1,3-Dioxenium cations 3 with methyl groups in the 4(6)-position of the ring readily react with aromatic aldehydes affording mono- or bis-styryl derivatives of type 7 and 8, respectively.⁸ Perchlorates of cations 7 and 8 are deeply coloured compounds displaying intense red fluorescence in solution at room temperature. Compared with their precursors 3, cations 7 and 8 are sufficiently stable owing to delocalization of a positive charge over the extended conjugate chain. They can be stored at air for hours without noticeable decomposition.

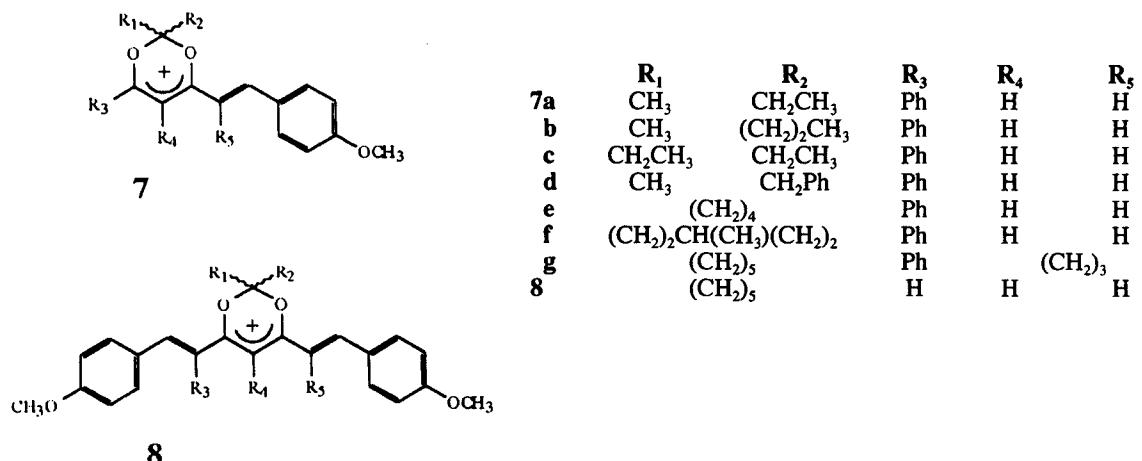
The type 3 1,3-dioxenium perchlorates which contain one or two alkyl groups in position 4 or 6 are highly hygroscopic and difficult to isolate in the pure state. Therefore, an immediate conversion into the type 7 and 8 derivatives through condensation with aromatic aldehydes was employed for their characterization. Table 1 contains data on yields, melting points, and ^1H NMR spectra of perchlorates of the cations 7a–g and 8 prepared in this way.

Molecular and crystal structure

An x-ray study of the stable crystalline 4,6-bis(*p*-methoxystyryl)-2,2-pentamethylenespiro-1,3-dioxenium perchlorate (8) ($\text{C}_{27}\text{H}_{29}\text{O}_4\cdot\text{ClO}_4\cdot\frac{1}{2}\text{H}_2\text{O}$) has been carried out. The molecular structure of this salt is shown in Figure 1. The dioxenium ring was found to possess an envelope conformation (the angle of folding along the O_1-O_2 line is 40.3°), whereas the 2,2-spiroannelated



Scheme 1



cyclohexane ring prefers a chair conformation. The bond lengths C₁C₂ = 1.377(5) and C₂C₃ = 1.391(7) Å are virtually identical within the experimental accuracy limits, as also are C₁O₁ = 1.348(5) and C₃O₂ = 1.343(5) Å. The C₁C₂ and C₂C₃ bond lengths are close to those calculated^{12,13} for the CC bonds in the allyl cation: 1.385 Å (STO-3G)¹² and 1.372 Å [6-311++G(D₁)];¹³ 1.387 Å [6-31G(D)]¹³ in tetramethylallyl cation.

This comparison clearly indicates the mode of the electron distribution in the 1,3-dioxenium ring of the cation 8 and presumably in cations 3 in general, and confirms their close relation to the allyl cation family.

Stereodynamics

The ¹H NMR spectrum of the 1,3-dioxenium cation 8 and those of other symmetrical 2,2-pent-

Table 1. 1,3-Dioxenium perchlorates 7a-g and 8^a

Compound	M.p. (°C)	Yield (%)	¹ H NMR (CDCl ₃), δ (ppm)
7a	188-190	49	1.17(3H, t); 1.94(3H, s); 2.33(2H, m); 3.90(3H, s); 6.99(2H, d); 7.44(1H, d); 7.60(2H, t); 7.76(1H, t); 7.80(1H, s); 7.97(2H, d); 8.20(2H, d); 8.38(1H, d)
7b	162-164	47	1.03(3H, t); 1.62(2H, m); 2.23(2H, m); 3.90(3H, s); 6.99(2H, d); 7.44(1H, d); 7.61(2H, t); 7.75(1H, t); 7.82(1H, s); 7.98(2H, d); 8.20(2H, d); 8.38(1H, d)
7c	177-178	44	1.10(6H, t); 2.32(4H, q); 3.87(3H, s); 6.98(2H, d); 7.45(1H, d); 7.60(2H, t); 7.75(1H, t); 7.81(1H, s); 7.96(2H, d); 8.20(2H, d); 8.38(1H, d)
7d	223-224	62	1.89(3H, s); 3.51(2H, s); 3.89(3H, s); 7.01(2H, d); 7.21(2H, m); 7.34(3H, m); 7.48(1H, d); 7.60(2H, t); 7.74(1H, t); 7.88(1H, s); 7.97(2H, d); 8.15(2H, d); 8.30(1H, d)
7e	180-183	60	2.01(4H, m); 2.40(4H, m); 3.86(3H, s); 6.85(2H, d); 7.43(1H, s); 7.60(2H, t); 7.74(1H, t); 7.76(1H, s); 7.96(2H, d); 8.18(2H, d); 8.40(1H, s)
7f	196-197	55	1.06(3H, d); 1.38-2.09(7H, m); 2.60(2H, m); 3.88(3H, s); 6.99(2H, d); 7.42(1H, d); 7.60(2H, t); 7.72(1H, t); 7.81(1H, s); 7.97(2H, d); 8.20(2H, d); 8.34(1H, d)
7g	116-118	58	1.68(2H, m); 1.86(8H, m); 2.37(4H, m); 2.92(2H, m); 3.04(2H, m); 3.91(3H, s); 7.06(2H, d); 7.59(2H, d); 7.70(1H, t); 7.86(4H, m); 8.38(1H, s)
8	200-202	70	1.60(2H, m); 1.75(4H, m); 2.18(4H, m); 3.84(6H, s); 6.91(4H, d); 6.95(2H, d); 7.21(1H, s); 7.75(4H, d); 8.06(2H, d)

^a All the compounds listed gave satisfactory elemental analyses; IR spectra of all the compounds show absorption bands at 1100 cm⁻¹ (ClO₄⁻), 1180-1300 cm⁻¹ (C—O—C) and 1520-1610 cm⁻¹ (C=C, C=C_{arom}).

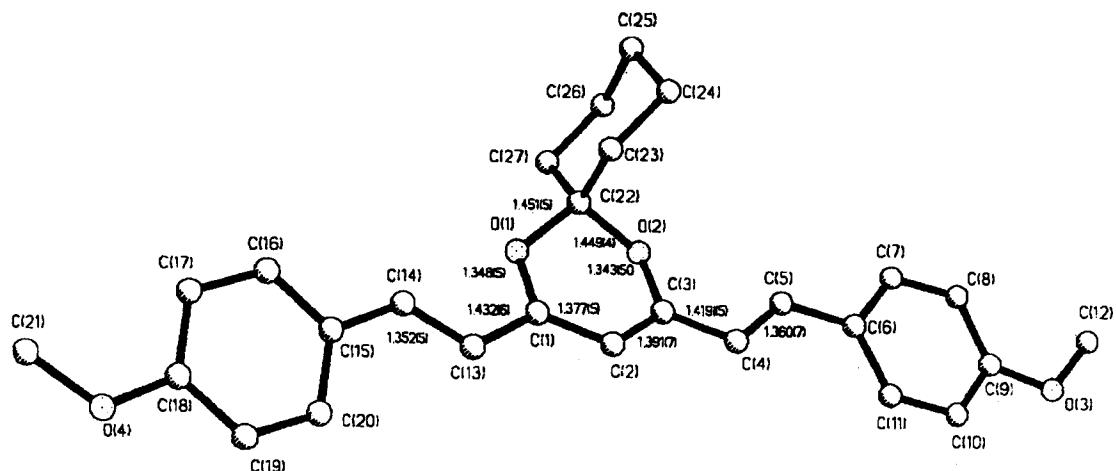


Figure 1. Structure of 4,6-bis(*p*-methoxystyryl)-2,2-pentamethylenespiro-1,3-dioxenium cation 8, as a fragment of its perchlorate $C_{27}H_{29}O_4 \cdot ClO_4 \cdot \frac{1}{2} H_2O$

amethylenespiroannelated 1,3-dioxenium cations **3** ($R_3 = R_5$) consists of three distinct multiplet signals of α -, β - and γ -methylene protons with an intensity ratio 4:4:2.⁸ In contrast, the spectra of unsymmetrical cations **3** ($R_3 \neq R_5$, e.g. $R_3 = Ph$, $R_5 = Me$ or $CH = CH_2C_6H_4OCH_3-p$) at ambient temperature display more complex patterns owing to the pairwise chemical inequivalence of protons within each of the methylene groups. Figure 2 shows the temperature dependence of the AB-type quartet signal of the α -methylene protons of 2,2-pentamethylenespiro-4-phenyl-6-(*p*-methoxystyryl)-1,3-dioxenium perchlorate,⁸ component peaks of the quartet being additionally split owing to coupling with protons of the vicinal β -methylene group. The variable-temperature 1H NMR spectrum of the α -methylene protons in this cation clearly indicates the trend to simplification to a common triplet signal, even though total averaging could not be achieved in the

solvents used without decomposition at high temperature. Such a spectral behaviour illustrates the process of inversion of tetrahedral configuration at the prochiral spirocarbon centre. The energy barriers of the enantiotopomerization in nitrobenzene-*d*₅ solution have been calculated by computational lineshape simulations; these are given in Table 2.

The magnitude of the energy barriers obtained is significantly larger than that expected for the ring inversion of 1,1-disubstituted cyclohexanes (9–12 kcal mol⁻¹).¹⁴ It should be, most probably, associated with the dissociation–recombination mechanism of the inversion featured in Scheme 2.

This kind of intramolecular dissociative mechanism that involves cleavage of the B–N bonds followed by rotation about the B–O bonds and recyclization was found to govern inversion of configuration at the stereogenic boron centres in the 1,3,2-oxazaborines **2**.⁷

Table 2. Activation parameters of enantiotopomerization at the spiro carbon center in perchlorates of 2- R_1 -2- R_2 -4-phenyl-6- R_3 -1,3-dioxenium **3**^a

R_1	R_2	R_3	k_{23} (s ⁻¹)	ΔG_{25}^* (kcal mol ⁻¹)	ΔH^* (kcal mol ⁻¹) ^b	ΔS^* (e.u.)
$(CH_2)_5^c$		CH ₃	$<6 \times 10^{-2}$	$>19.1^d$	—	—
$(CH_2)_5^c$		$(CH)_2C_6H_4OCH_3-p$	1.3×10^{-3}	21.4	17.4 ± 0.1	-13.4 ± 0.2
$(CH_2)_2CH(CH_3)(CH_2)_2$		$(CH)_2C_6H_4OCH_3-p$	1.0×10^{-4}	22.9	16.7 ± 0.1	-16.6 ± 0.4
$(CH_2)_4$		$(CH)_2C_6H_4OCH_3-p$	0.9×10^{-2}	20.2	17.1 ± 0.1	-13.8 ± 0.3

^a Activation parameters were calculated from rate constants estimated in the range 40–160 °C, the thermostating step being 10 °C.

^b 1 kcal = 4.184 kJ.

^c For preparation and characteristics, see Ref. 8.

^d Decomposes above 70 °C.

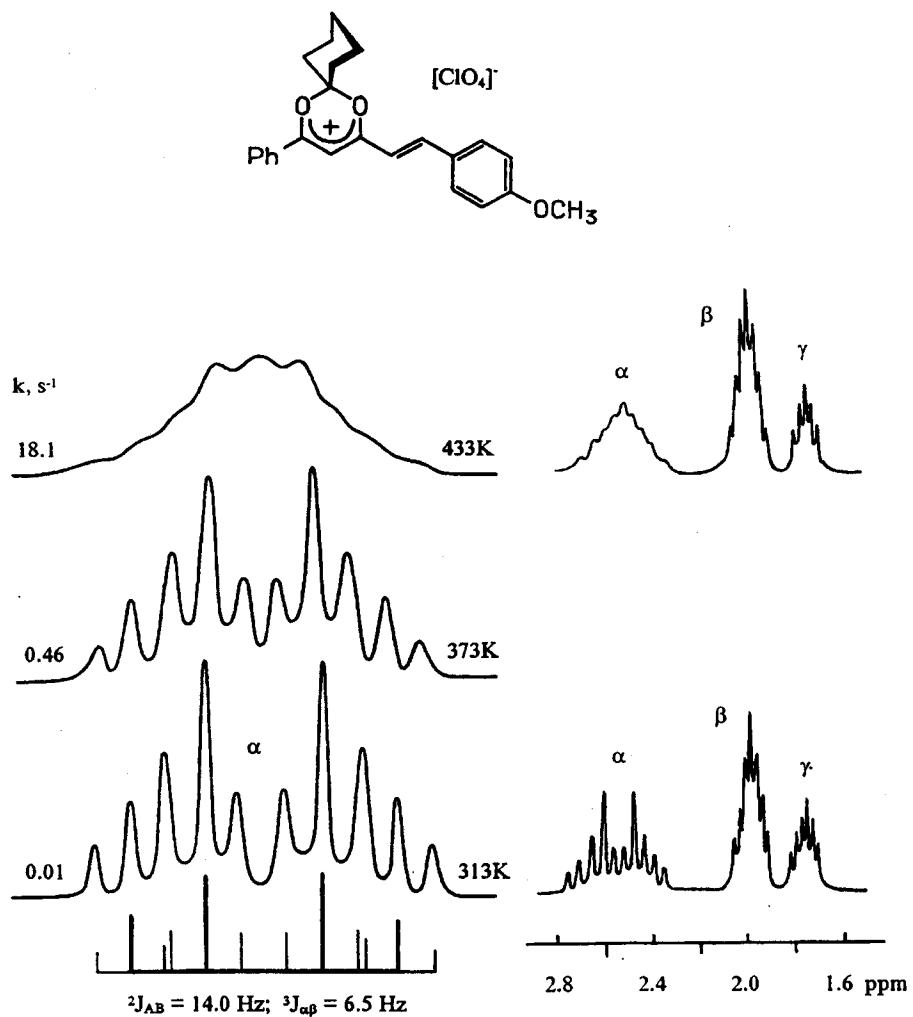
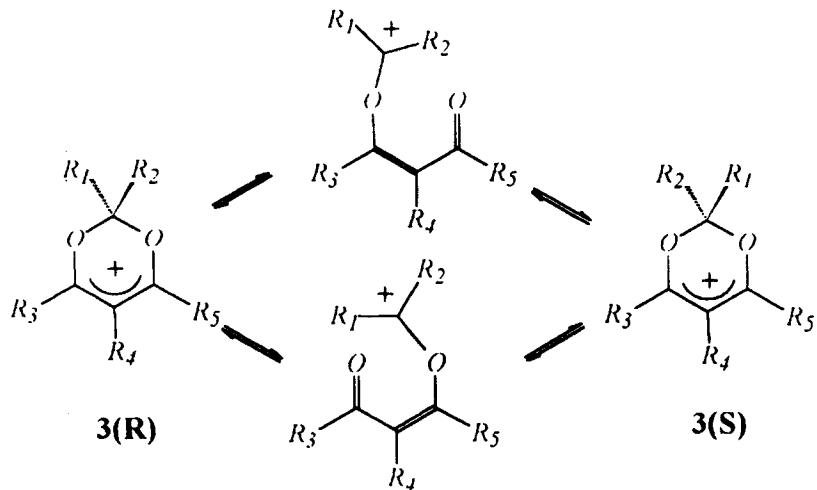


Figure 2. Part of the ^1H NMR spectrum of 4-phenyl-6-(*p*-methoxystyryl)-2,2-pentamethylenespiro-1,3-dioxenium perchlorate* featuring resonance signals of the α - γ methylene protons and temperature dependence of the α -methylene proton signals



Scheme 2

A similar ionization mechanism due to the rupture of C—O bonds followed by internal return of ion pairs has been also established for topomerization of dioxolane carboxylates.¹⁵ The latter process, and also that of the 3(R) = 3(S) topomerization, as portrayed in Scheme 2, is a tendency known to be common to many organic reactions in which a covalent compound dissociates to form ion pairs.¹⁵

EXPERIMENTAL

Crystal data for perchlorate of the cation 8: $C_{27}H_{29}O_4^{+}ClO_4^{-}\frac{1}{2}H_2O$, $M = 525.96$, triclinic, space group $P\bar{1}$, at $-100^{\circ}C$, $a = 9.939(5)$, $b = 10.270(5)$, $c = 13.921(7)$ Å, $\alpha = 79.72(2)$, $\beta = 74.70(2)$, $\gamma = 68.73(2)$ °, $V = 1271(2)$ Å³, $D_{\text{calc}} = 1.347$ g cm⁻³,

$Z = 2$. Data were measured on a Siemens P3/PC diffractometer with Mo K α radiation ($\lambda = 0.7107$ Å, graphite monochromator) using the $\theta/2\theta$ scan technique ($2\theta \leq 54^{\circ}$). The structure was solved by the direct method and refined anisotropically by a full-matrix least-squares procedure on the basis of 2906 reflections with $I > 4\sigma(I)$. The oxygen atom of the solvating water and oxygen atoms of the disordered ClO_4^- anion were refined isotropically after refinement of the occupied position. All hydrogen atoms were located geometrically and refined in the rigid model with fixed $U_{\text{iso}} = 0.08$ Å². The final discrepancy factors are $R = 0.0634$ and $R_w = 0.0639$ for 2906 independently observed reflections ($I \geq 4\sigma$). Atomic coordinates, bond lengths, bond angles and thermal atomic parameters have been deposited at the Cambridge Crystallographic

Table 3. Bond lengths in the perchlorate of 4,6-bis(*p*-methoxystyryl)-2,2-pentamethylenespiro-1,3-dioxenium cation (8)

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
O_1-C_1	1.348(5)	C_4-C_5	1.360(7)	$C_{15}-C_{20}$	1.402(6)
O_1-C_{22}	1.451(5)	C_5-C_6	1.445(5)	$C_{16}-C_{17}$	1.392(7)
O_2-C_3	1.343(5)	C_6-C_7	1.403(7)	$C_{17}-C_{18}$	1.394(7)
O_2-C_{22}	1.449(4)	C_6-C_{11}	1.411(5)	$C_{18}-C_{19}$	1.392(5)
O_3-C_9	1.359(5)	C_7-C_8	1.392(6)	$C_{19}-C_{20}$	1.379(7)
O_3-C_{12}	1.437(7)	C_8-C_9	1.395(6)	$C_{22}-C_{23}$	1.511(5)
O_4-C_{18}	1.370(6)	C_9-C_{10}	1.399(7)	$C_{22}-C_{27}$	1.501(6)
O_4-C_{21}	1.434(5)	$C_{10}-C_{11}$	1.369(5)	$C_{23}-C_{24}$	1.537(6)
C_1-C_2	1.377(5)	$C_{13}-C_{14}$	1.352(5)	$C_{24}-C_{25}$	1.529(6)
C_1-C_{13}	1.432(6)	$C_{14}-C_{15}$	1.457(6)	$C_{25}-C_{26}$	1.522(5)
C_2-C_3	1.391(7)	$C_{15}-C_{16}$	1.402(5)	$C_{26}-C_{27}$	1.534(6)
C_3-C_4	1.419(5)				

Table 4. Bond angles ω in 4,6-bis(*p*-methoxystyryl)-2,2-pentamethylenespiro-1,3-dioxenium cation (8)

Angle	ω (°)	Angle	ω (°)
C ₁ —O ₁ —C ₂₂	116.9(3)	C ₁ —C ₁₃ —C ₁₄	121.5(4)
C ₃ —O ₂ —C ₂₂	117.0(3)	C ₁₃ —C ₁₄ —C ₁₅	127.5(4)
C ₅ —O ₃ —C ₁₂	117.9(3)	C ₁₄ —C ₁₅ —C ₁₆	119.0(4)
C ₁₈ —O ₄ —C ₂₁	117.5(4)	C ₁₄ —C ₁₅ —C ₂₀	122.8(3)
O ₁ —C ₁ —C ₂	120.0(4)	C ₁₆ —C ₁₅ —C ₂₀	118.1(4)
O ₁ —C ₁ —C ₁₃	114.9(3)	C ₁₅ —C ₁₆ —C ₁₇	122.2(4)
C ₂ —C ₁ —C ₁₃	125.0(4)	C ₁₆ —C ₁₇ —C ₁₈	118.0(3)
C ₁ —C ₂ —C ₃	119.5(4)	O ₄ —C ₁₈ —C ₁₇	123.9(3)
O ₂ —C ₃ —C ₂	119.2(3)	O ₄ —C ₁₈ —C ₁₉	115.3(4)
O ₂ —C ₃ —C ₄	115.8(4)	C ₁₇ —C ₁₈ —C ₁₉	120.8(4)
C ₂ —C ₃ —C ₄	125.0(4)	C ₁₈ —C ₁₉ —C ₂₀	120.5(4)
C ₃ —C ₄ —C ₅	121.6(4)	C ₁₅ —C ₂₀ —C ₁₉	120.3(3)
C ₄ —C ₅ —C ₆	127.3(4)	O ₁ —C ₂₂ —O ₂	109.3(3)
C ₅ —C ₆ —C ₇	118.6(3)	O ₁ —C ₂₂ —C ₂₃	109.5(4)
C ₅ —C ₆ —C ₁₁	123.1(4)	O ₂ —C ₂₂ —C ₂₃	110.1(3)
C ₇ —C ₆ —C ₁₁	118.3(3)	O ₁ —C ₂₂ —C ₂₇	106.9(3)
C ₆ —C ₇ —C ₈	121.6(4)	O ₂ —C ₂₂ —C ₂₇	106.6(3)
C ₇ —C ₈ —C ₉	118.8(4)	C ₂₃ —C ₂₂ —C ₂₇	114.3(3)
O ₃ —C ₉ —C ₈	124.7(4)	C ₂₂ —C ₂₃ —C ₂₄	110.6(4)
O ₃ —C ₉ —C ₁₀	115.1(4)	C ₂₃ —C ₂₄ —C ₂₅	110.3(3)
C ₈ —C ₉ —C ₁₀	120.2(4)	C ₂₄ —C ₂₅ —C ₂₆	111.0(3)
C ₉ —C ₁₀ —C ₁₁	120.8(4)	C ₂₅ —C ₂₆ —C ₂₇	111.5(4)
C ₆ —C ₁₁ —C ₁₀	120.3(4)	C ₂₂ —C ₂₇ —C ₂₆	111.5(3)

Table 5. Atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) in 4,6-bis(*p*-methoxystyryl)-2,2-pentamethylenespiro-1,3-dioxenium perchlorate (8)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>	OCP
O ₁	-3325(3)	7097(3)	4497(2)	31(1) ^a	C ₂₀	-4949(4)	5213(4)	1983(3)	32(2) ^a	—
O ₂	-1896(3)	6437(3)	5729(2)	31(1) ^a	C ₂₁	-8415(4)	7392(5)	-134(3)	60(2) ^a	—
O ₃	3355(3)	1283(3)	9596(2)	50(1) ^a	C ₂₂	-3185(4)	7468(4)	5415(3)	29(2) ^a	—
O ₄	-7441(3)	6158(3)	302(2)	51(1) ^a	C ₂₃	-4559(4)	7509(4)	6216(3)	32(2) ^a	—
C ₁	-3134(4)	5739(4)	4454(3)	30(2) ^a	C ₂₄	-4523(5)	8066(4)	7160(3)	38(2) ^a	—
C ₂	-2374(4)	4713(4)	5087(3)	30(2) ^a	C ₂₅	-4315(5)	9501(4)	6900(3)	42(2) ^a	—
C ₃	-1728(4)	5080(4)	5723(3)	28(2) ^a	C ₂₆	-2904(4)	9423(4)	6112(3)	38(2) ^a	—
C ₄	-829(4)	4117(4)	6355(3)	29(2) ^a	C ₂₇	-2883(4)	8834(4)	5168(3)	33(2) ^a	—
C ₅	-339(4)	4560(4)	7020(3)	31(2) ^a	Cl	728(2)	8611(2)	7144(1)	72(1) ^a	—
C ₆	587(4)	3699(4)	7698(3)	29(2) ^a	O ₁ ^b	1985(6)	8615(6)	7443(4)	67(2)	0.63
C ₇	891(4)	4357(4)	8377(3)	34(2) ^a	O ₂ ^b	89(6)	10000(6)	6697(5)	66(2)	0.67
C ₈	1793(4)	3594(4)	9039(3)	37(2) ^a	O ₃ ^b	-391(24)	8995(26)	8144(16)	82(6)	0.21
C ₉	2425(4)	2144(4)	9011(3)	36(2) ^a	O ₄ ^b	388(20)	7497(15)	7206(15)	61(4)	0.26
C ₁₀	2126(4)	1474(4)	8340(3)	36(2) ^a	O ₅ ^b	2092(10)	7765(10)	7386(7)	64(2)	0.39
C ₁₁	1219(4)	2227(4)	7700(3)	32(2) ^a	O ₆ ^b	-137(14)	9925(14)	7194(11)	66(4)	0.30
C ₁₂	3663(4)	1898(4)	10328(3)	61(2) ^a	O ₇ ^b	-233(14)	7797(13)	7615(10)	67(3)	0.42
C ₁₃	-3720(4)	5486(4)	3697(3)	31(2) ^a	O ₈ ^b	1117(14)	8281(13)	6027(9)	58(3)	0.31
C ₁₄	-4695(4)	6535(4)	3240(3)	32(2) ^a	O ₉ ^b	809(17)	7606(18)	6510(16)	58(4)	0.22
C ₁₅	-5394(4)	6429(4)	2473(3)	30(2) ^a	O ₁₀ ^b	135(31)	9351(28)	8388(21)	86(8)	0.15
C ₁₆	-6559(4)	7588(4)	2206(3)	37(2) ^a	O ₁₁ ^b	-503(19)	8351(24)	7962(15)	67(5)	0.24
C ₁₇	-7277(4)	7563(4)	1479(3)	38(2) ^a	O ₁₂ ^b	1791(20)	8282(17)	5948(12)	49(4)	0.30
C ₁₈	-6820(4)	6328(5)	1020(3)	37(2) ^a	O ₁ ^c	832(11)	8583(10)	4692(7)	80(3)	0.333
C ₁₉	-5674(4)	5160(4)	1279(3)	36(2) ^a						

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*(*ij*) tensor.^b Disordered ClO₄⁻.^c molecule of water.

Data Center. Tables 3, 4 and 5 contain data on bond lengths, bond angles and atomic coordinates of the perchlorate of cation **8** respectively.

IR spectra were recorded using a Specord IR-71 spectrometer.

^1H NMR spectra and variable-temperature ^1H NMR spectra were obtained with a Varian Instrument Unity-300 Fourier transform spectrometer (300 MHz). The rates and energy barriers of enantiotopomerisation of the prochiral carbon-2 in 1,3-dioxenium cations **3** were obtained from variable-temperature ^1H NMR spectra of α -methylene protons of the cyclohexane (cyclopentane) ring of **3** by a computational procedure.¹⁶

Chemical analyses were performed by the Rostov University Chemistry Department Microanalytical Laboratory.

Melting points are given uncorrected.

General procedure for the preparation of 4(6)-(p-methoxystyryl)-1,3-dioxenium perchlorates.^{7a-g,8} To a mixture of 0.01 mol of ketone, 0.01 mol of 1,3-diketone and 0.01 mol (1 ml) of acetic anhydride, 0.01 mol (5 ml) of a 16% solution of HClO_4 in acetic acid was added. The solution was allowed to stand at 18–20 °C for 20–30 min, then, a twofold volume of dry diethyl ether was added. The mixture was shaken and the ether layer was decanted from the deposited oil. The oil was washed twice with dry diethyl ether, and subsequently 5 ml of AcOH , 1 ml (0.01 mol) of Ac_2O and 1 ml (0.008 mol) of *p*-methoxybenzaldehyde were added. In the case of **3** (R_3 and $\text{R}_5 = \text{CH}_3$), the amounts of Ac_2O and *p*-methoxybenzaldehyde were doubled. The mixture was warmed to 50–60 °C and crystallization was initiated by cooling. Dark crystals of the product were filtered off. Recrystallization from nitromethane gave pure perchlorates of the cations **7a–g** and **8**.

ACKNOWLEDGEMENT

Support by the Russian Fund for Fundamental Research

(Grant Nos 93-03-18692 and 94-03-09256) is gratefully acknowledged.

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