

9-Phenylxanthen-9-ylum and 9-Phenylthioxanthen-9-ylum Ions: Comparison of *o*- and *p*-Substitutions in the 9-Phenyl Group by Cyclic Voltammetry and Visible Spectra

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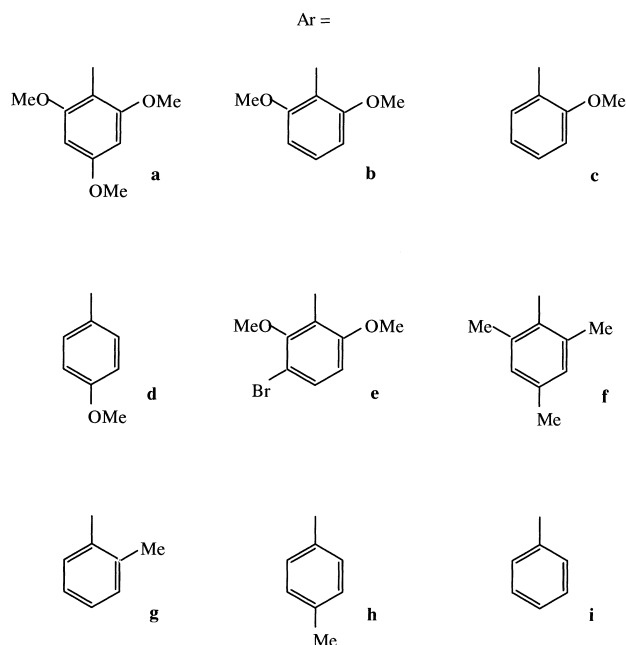
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9-Arylxanthen-9-ylum (**3a–i**) and 9-arylthioxanthen-9-ylum (**4a,b,e–i**) perchlorates [aryl = 2,4,6-(MeO)₃C₆H₂ (**a**), 2,6-(MeO)₂C₆H₃ (**b**), 2-MeOC₆H₄ (**c**), 4-MeOC₆H₄ (**d**), 3-Br-2,6-(MeO)₂C₆H₂ (**e**), 2,4,6-Me₃C₆H₂ (**f**), 2-MeC₆H₄ (**g**), 4-MeC₆H₄ (**h**), C₆H₅ (**i**)] were prepared by the reactions of 9-arylxanthen-9-ols or 9-arylthioxanthen-9-ols with perchloric acid. Their LUMO and HOMO levels were estimated from the redox potential (E_0) in cyclic voltammetry and $\lambda_{\max}$ in the UV–visible spectra measured for a 1,2-dichloroethane solution, and were compared with those of 9-aryl-1,8-dimethoxyxanthen-9-ylum ions (**8b,i**). We found that 1) both the LUMO and HOMO levels varied almost in the same order of substituent on the 9-phenyl group; 2) the MeO-group on the 9-phenyl group was more effective to raise both the HOMO and LUMO levels than the Me-group; 3) the HOMO levels of **3** and **4** were more sensitive than the LUMO levels to the change in the 9-aryl group; 4) *p*-substitution by MeO- or Me-groups was more effective to raise the HOMO and LUMO levels than *o*-substitution; 5) the presence of two *o*-MeO groups was more effective to raise the HOMO and LUMO levels than one *o*-MeO group; 6) a *m*-bromination of 9-aryl group in **3b** or **4b** greatly lowered both LUMO and HOMO levels, as observed for **3e** or **4e**; 7) both the HOMO and LUMO levels of **8b** and **8i** were higher than those of **3b** and **3i**, respectively; 8) the LUMO level of **3b** was higher than that of **8i**, the isomer.

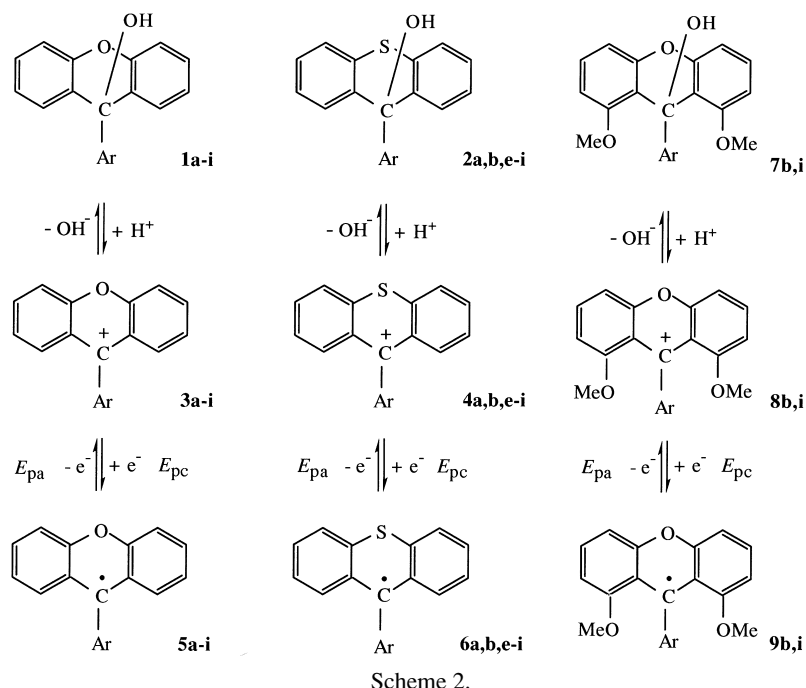
Triphenylcarbenium ions bearing at least four *ortho*-methoxy groups are stable even in dilute aqueous hydrochloric acid,^{1–5} and show a reversible redox behavior.⁶ The stability of 9-phenylxanthen-9-ylum ions also varies drastically depending on the position of the methoxy substituent, namely on the 9-phenyl group or on the xanthen ring.⁷ It is expected that *o*-substitution on the 9-phenyl group may cause a considerable steric influence against the xanthen skeleton to reduce the coplanarity. For further understanding the positional effect of a substituent, we report here on the electrochemical property (cyclic voltammetry) as well as the UV–visible spectra of 9-arylxanthen-9-ylum and -thioxanthen-9-ylum ions (Schemes 1 and 2). The results also merit a future study of 9-arylxanthen-9-yl and 9-arylthioxanthen-9-yl radicals as well as 9-arylxanthen-9-ylum and 9-arylthioxanthen-9-ylum ions, which have recently received intense attention with implications for ferromagnetic materials,⁸ fluorescent dyes,⁹ materials for molecular memory or molecular switches,¹⁰ and sensitizing dyes for solar cells.¹¹

Results and Discussion

Preparations. 9-Arylxanthen-9-ols (**1**) and 9-arylthioxanthen-9-ols (**2**) have generally been prepared by the reactions of xanthen or thioxanthen with the corresponding Grignard reagent.^{12–16} Since the aryllithiums can very easily be prepared using commercial 15% solution of butyllithium, we used it for preparing **1b**.⁷ Although 9-arylxanthen-9-ols such as **1d** and **1f–h** have long been known, their reported physical properties such as melting point and so on differed depending on the liter-



atures probably due to the polymorphism.^{13–15} Compounds **1e** and **2e** were prepared by the reaction of **1b** or **2b** with *N*-bromosuccinimide (NBS). Compound **2e** was obtained as a mixture of two isomers, of which the ¹H and ¹³C NMR could be understood from the difference of the relative positions of the



hydroxyl group and the bromine. These *mono*-brominated compounds were obtained even when NBS was used in a large excess. Treatments of **1a-i** or **2a,b,e-i** with perchloric acid in acetone or in diethyl ether resulted to give the 9-arylthioxanthen-9-yliums (**3a-i**) or 9-arylthioxanthen-9-ylum perchlorates. Although **3i** and **4i** were quite sensitive to moisture, the salts such as **3a,b** and **4a,b** could be handled without any special care for the moisture. It is worth noting here that the formation of a salt is not necessarily reversible. A preliminary experiment showed that the treatment of **4a**, for an example, with aqueous potassium hydroxide resulted to give a complex mixture of a variety of products including **2a** and possibly 9-arylthioxanthen-3-ol, as observed more than ten MeO proton resonances in the ^1H NMR spectrum.

The ^1H and ^{13}C NMR spectral data of **1-4** are summarized in Tables 1 and 2, respectively. The ^1H spectra of 9-arylthioxanthen-9-ols generally showed the resonances at δ 7.33 $\pm$ 0.04 (double doublets, 1,8- or 4,5-H), δ 7.23 $\pm$ 0.05 (triple doublets, 2,7- or 3,6-H), δ 7.12 $\pm$ 0.06 (double doublets, 4,5- or 1,8-H), and δ 6.99 $\pm$ 0.05 (triple doublets, 3,6- or 2,7-H) with $J_{\text{H}} = 7-8$ Hz and 1-2 Hz, respectively. The resonances of 9-arylthioxanthen-9-ols were more sensitive to the 9-aryl group, and were observed in the regions δ 8.0-7.3, δ 7.4-7.2, δ 7.4-7.1, and δ 7.3-7.0, respectively. Those of 9-arylthioxanthen-9-yliums and 9-arylthioxanthen-9-yl radicals were observed at lower magnetic field such as δ 8.95-7.56, reflecting the cationic character, and were also sensitive to the 9-aryl group. Similarly, the ^{13}C spectra of 9-arylthioxanthen-9-yliums and 9-arylthioxanthen-9-yl radicals were observed at a lower field than those of 9-arylthioxanthen-9-ols and 9-arylthioxanthen-9-yl radicals, respectively.

Cyclic Voltammetry and UV-Visible Spectra. Voltammograms of 9-arylthioxanthen-9-ylum ions, measured for a 1,2-dichloroethane solution, showed either reversible or irreversible redox waves with one-electron transfer, depending on the compound (Table 3), as typically shown in Fig. 1. Most of **3**

showed both cathodic and anodic waves with the peak separation ($\Delta E_{\text{p}} = E_{\text{pa}} - E_{\text{pc}}$) near 60 mV and with the peak current ratio ($i_{\text{pa}} / i_{\text{pc}}$) close to one, thus indicating the reversibility of the redox behavior to form the 9-phenylthioxanthen-9-yl radicals. Although 9-*o*-tolylthioxanthen-9-ylum ion **3g** also showed both cathodic and anodic waves, the $i_{\text{pa}} / i_{\text{pc}}$ value was ca. 2/3. 9-Phenylthioxanthen-9-ylum ion **3i** showed only the cathodic wave (E_{pc}). Thus, it is expected that either *o*- or *p*-substitution of the methoxy group on the 9-phenyl group makes the 9-phenylthioxanthen-9-yl radical (**5**) more inert than methyl substitution. In contrast and very interestingly, all of the 9-arylthioxanthen-9-ylum ions **4a,b,e-i** showed reversible redox waves under the same conditions. The inertness of the 9-phenylthioxanthen-9-yl radical (**6i**) can be understood by delocalization of the spin density on the sulfur atom as well as on the central carbon.⁸ In contrast, the voltammograms of 9-aryl-1,8-dimethoxyxanthen-9-ylum ions (**8b,i**) showed irreversible redox waves, suggesting the lability of the corresponding radicals (**9b,i**). It has been reported that **5i** dimerizes between the 9-carbons.¹⁷ Such a dimerization must be difficult for **5g** and **9i** due to a steric reason. It has also been known that the triphenylmethyl radical dimerizes to give 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene.¹⁸⁻²⁰ Thus, it can most probably be expected that the radicals **5g** and **9i** dimerize at the 9-carbon of one molecule and the *p*-carbon of another molecule. If so, the inertness of **5a-f,h** can be understood by steric protection at the 9-carbon or at the *p*-carbon. Although the reason for the lability of **9b,i** is unknown at present, it seems to be related to the much higher reactivity of **8i** than **3b**, the positional isomers.⁷

The E_{pc} (mV vs aq Ag/AgCl) potentials of **3** shifted to higher potential in the following order: **3a** (-25) > **3b** (+20) ~ **3d** (+20) > **3h** (+55) > **3c** (+70) ~ **3f** (+70) > **3g** (+90) > **3e** (+120) > **3i** (+225), and those of **4** in an analogous order: **4a** (-10) > **4b** (+15) > **4f** (+50) > **4h** (+55) > **4i** (+70) > **4g** (+80) > **4e** (+120), as visualized in Fig. 2.

Table 1. ^1H NMR Spectral Data^{a)} for 9-Arylxanthene and -thioxanthene Derivatives

Compound	Xanthene protons ^{b)}	Others ^{c)}
1a	7.36, 7.21 7.10, 6.98.	7.52s (OH), 6.12s (3',5'-H), 3.76s (4'-MeO), 3.56s (2',6'-MeO).
1b^{e)}	7.36, 7.22 7.12, 6.98.	7.65s (OH), 7.20t[8] (4'-H), 6.58d[8] (3',5'-H), 3.56s (MeO).
1c	7.3–6.9m. ^{d)}	7.95dd[10] (6'-H), 7.3–6.9m. ^{d)} 7.27s (OH), ^{d)} 6.70d[10], 3.73s (MeO).
1d	7.37, 7.28, 7.17, 7.05.	7.31s (OH), 7.29d[10] and 6.80d[10] (Ar-H), 3.73s (Meo).
1e	7.26, 7.24, 7.14, 6.99.	6.93s (OH), 7.45d (4'-H), 6.52d (5'-H), 3.78s and 3.40s (6'- and 2'-MeO).
1f	7.29, 7.17, 7.14, 7.00.	6.80s (3',5'-H), 2.26s (4'-Me), 2.12brs (2',6'-Me), 2.06s (OH).
1g	7.30, 7.19, 7.06, 6.99.	8.34dd[8] (6'-H), 7.39td[7] (5'-H), 7.25td[7] (4'-H), 7.00dd[7] (3'-H), 2.43s (OH), 1.43s (2'-Me).
1h	7.35, 7.27, 7.08, 7.04.	7.39dd[8] and 7.17dd[7] (2',3',5',6'-H), 2.63s (OH), 2.29s (4'-Me).
1i	7.33, 7.27, 7.19, 7.06.	7.42–7.37m, 7.29d[8], 7.17s (OH).
2a	7.35, 7.25, 7.12, 7.05.	7.06s (OH), 6.16s (3',5'-H), 3.79s (4'-MeO), 3.58s (2',6'-MeO).
2b	7.32, 7.24, ^{d)} 7.13, 7.04.	7.24 (OH), ^{d)} 7.24 (4'-H), ^{d)} 6.61d[8] (3',5'-H), 3.60s (MeO).
2e	8.14dd, 7.51dt, 7.31dt, 6.98dd.	5.93s (OH), 7.72d (4'-H), 6.70d (5'-H), 3.84s and 3.18s (6'- and 2'-MeO).
2nd isomer	8.30dd, 7.24dd, 7.17dt, 7.06dt.	6.22s (OH), 7.51d (4'-H), 6.57d (5'-H), 3.79s and 3.39s (6'- and 2'-MeO).
2f	7.34, 7.21, 7.08, 7.06.	6.85s (3',5'-H), 2.30brs (2',6'-Me), 2.17s (OH), 2.09s (4'-Me).
2g	8.16, 7.38, 7.36, 7.31.	7.23m and 7.07m (Ar), 2.52s (OH), 1.55s (2'-Me).
2h	8.03, 7.40, 7.37, 7.28.	6.96d[8] and 6.84d[8] (Ar), 2.57s (OH), 2.24s (4'-Me).
2i	8.02, 7.41, 7.37, 7.28.	7.18–7.16m (3H), 6.99–6.96m (2H), 2.81s (OH).
3a	8.50, 8.40, 8.14, 7.93.	6.43s (3',5'-H), 4.04s (MeO), 3.68s (MeO).
3b^{e)}	8.55, 8.54, 8.05, 7.95.	7.72t[8] (4'-H), 6.89d[8] (3',5'-H), 3.67s (MeO).
3c	8.52, 8.44, 8.07, 7.77.	7.77t[8], 7.57d[8], 7.34t[8], 7.26d[8], 3.73s (2'-MeO).
3d	8.41, 8.34–8.27, 7.89.	7.76d[9], 7.30d[9], 4.02s (4'-MeO).
3e	8.60m (4H), 8.00m (4H). ^{d)}	7.93d[9] (4'-H), ^{d)} 6.96d[9] (5'-H), 3.68s (MeO), 3.45s (MeO).
3f	8.62, 8.56, 7.97, 7.91.	7.18s (3',5'-H), 2.48s (4'-Me), 1.84s (2',6'-Me).
3g	8.57–8.48m, 7.97–7.87m,	7.67–7.64m, ^{d)} 7.56–7.48m. ^{d)}
		7.67–7.64m, ^{d)} 7.56–7.48m, ^{d)} 2.06s (2'-Me).
3h	8.48, 8.38, 8.21, 7.91.	7.66d[8] and 7.58d[8] (2',3',5',6'-H), 2.60s (4'-Me).
3i	8.55–8.4, 8.16, 7.91.	7.78m.
4a	8.81, 8.35, 8.33, 8.00.	6.34s (3',5'-H), 4.02s (MeO), 3.61s (MeO).
4b	8.89, 8.36, 8.25, 8.00.	7.72t[8] (4'-H), 6.69d[8] (3',5'-H), 3.60s (MeO).
4e	8.94, 8.40, 8.25, 8.07.	7.93d[8], 6.99d[8], 3.63s and 3.35s (6'- and 2'-MeO).
4f	8.95, 8.41, 8.14, 8.03.	7.19s (3',5'-H), 2.50s (4'-Me), 1.73s (2',6'-Me).
4g	8.36, 8.13, 8.00, 7.56.	8.90d[9] (6'-H), 7.67t[9] (5'-H), 7.55t[8] (4'-H), 7.34d[8] (3'-H), 1.93s (2'-Me).
4h	8.80, 8.33, 8.30, 7.99.	7.55d[8] and 7.45d[8] (2',3',5',6'-H), 2.60s (4'-Me).
4i	8.80, 8.34, 8.24, 8.00.	7.78–7.72m (3H), 7.58–7.54m (2H).
7b	7.20, 6.78, 6.55, 3.55 (1,8-MeO)	7.42 (OH), 7.11t, 6.69d, 6.38d, 4.09s (MeO), 3.05s (MeO).
7i^{e)}	7.22, 6.82, 6.53, 3.54 (1,8-MeO)	7.33d, 7.16t, 7.06t, 4.79 (OH).
8b	7.70, 7.38, 7.18, 3.64 (1,8-MeO)	7.70d, 7.46t, 3.69s (MeO).
8i	8.33, 7.72, 7.06, 3.56 (1,8-MeO)	7.53–7.47m, 7.31–7.25m.

a) In CDCl_3 (δ/ppm ; s = singlet, brs = broad singlet, d = doublet, t = triplet, dd = double doublets, td = triple doublets, m = multiplet). b) Xanthene ring protons; 1,8- or 4,5-H (doublet or double doublets with $J_{\text{H}} = 7\text{--}8$ Hz and 1–2 Hz), 2,7- or 3,6-H (triplet or triple doublets with $J_{\text{H}} = 7\text{--}8$ Hz and 1–2 Hz, or multiplet), 4,5- or 1,8-H (doublet or double doublets with $J_{\text{H}} = 7\text{--}8$ Hz and 1–2 Hz), 3,6- or 2,7-H (triplet or triple doublets with $J_{\text{H}} = 7\text{--}8$ Hz and 1–2 Hz). c) The coupling constants J_{H} greater than 2 Hz are given in square brackets in Hz, while those less than 2 Hz are omitted for clarity. d) Overlapped. e) Data from Ref. 1.

The E_0 (mV vs aq Ag/AgCl) potentials of **3** and **4** shifted to higher potentials almost in the same orders as the E_{pc} poten-

tials: **3a** (+18) > **3b** (+65) ~ **3d** (+65) > **3h** (+90) > **3c** (+110) > **3f** (+115) > **3g** (+125) > **3e** (+165), and **4a**

Table 2. ^{13}C NMR Spectral Data^{a)} for 9-Arylxanthen-9-yl and -thioxanthen-9-yl Derivatives.

Com- pounds	δ
1a	162.2, 158.1, 149.6, 128.7, 127.9, 122.4, 116.8, 115.6, 93.1, 71.5 (C–OH), 56.4 (2',6'-MeO), 55.2 (4'-MeO).
1b^{b)}	157.3, 149.5, 128.9, 128.4, 128.3, 128.0, 127.8, 123.9, 122.4, 115.5, 106.7, 71.75 (C–OH), 56.5 (2',6'-MeO).
1c	155.9, 150.0, 136.0, 128.8, 128.6, 128.1, 127.0, 125.9, 122.8, 120.4, 115.8, 112.7, 68.8 (C–OH), 55.6 (2'-MeO).
1d	158.0, 151.2, 142.0, 129.4, 128.9, 128.7, 127.5, 124.1, 123.3, 116.4, 116.1, 113.1, 75.0 (C–OH), 58.8 (4'-MeO).
1e	158.8, 154.6, 149.5, 133.3, 129.8, 128.4, 127.8, 127.5, 122.6, 115.9, 110.7, 109.7, 72.2, 62.3 (2'-MeO), 56.5 (6'-MeO).
1f	149.2, 138.2, 137.2, 136.4, 131.6, 128.9, 128.2, 127.8, 123.4, 116.2, 74.2, 24.2 (4'-Me), 20.6 (2',6'-Me).
1g	150.0, 143.7, 135.7, 131.9, 129.3, 128.7, 127.8, 125.8, 123.5, 125.7, 125.3, 116.3, 69.8, 20.6 (2'-Me).
1h	145.1, 136.3, 129.0, 128.9, 128.6, 127.3, 126.1, 123.5, 116.4, 70.3, 21.0 (4'-Me).
1i	149.6, 147.9, 129.0, 129.0, 127.9, 127.1, 126.7, 126.2, 123.5, 116.4, 70.4.
2a	160.5, 158.4, 139.0, 129.3, 128.5, 126.4, 125.2, 124.5, 116.2, 92.9, 77.0, 56.5 (2',6'-MeO), 55.2 (4'-MeO).
2b	157.6, 138.6, 129.1, 129.0, 128.6, 126.5, 125.2, 124.3, 123.6, 106.5, 77.0, 56.5 (2',6'-MeO).
2e	157.3, 157.0, 141.2, 138.7, 134.3, 129.4, 128.0, 125.5, 125.1, 122.2, 110.4, 109.7, 78.6, 63.0 (2'-MeO), 55.5 (6'-MeO).
2nd isomer	157.0, 155.3, 138.0, 133.3, 129.6, 129.5, 128.2, 127.0, 125.4, 125.0, 110.5, 109.9, 77.3, 62.3 (2'-MeO), 56.6 (6'-MeO).
2f	138.2, 138.2, 137.4, 136.3, 131.5, 128.8, 128.8, 127.5, 126.1, 125.2, 80.0, 24.3 (2',6'-Me), 20.7 (4'-Me).
2g	147.8, 135.7, 133.4, 132.2, 131.7, 130.9, 127.3, 127.0, 125.4, 124.8, 123.8, 78.0, 23.7 (2'-Me).
2h	140.2, 140.0, 137.4, 131.4, 128.6, 127.1, 126.8, 126.5, 126.3, 125.9, 76.9, 21.1 (4'-Me).
2i	143.1, 139.7, 131.4, 127.9, 127.6, 127.1, 126.8, 126.5, 126.3, 126.0, 76.9.
3a	174.3, 167.1, 160.0, 158.9, 144.9, 132.7, 129.7, 125.8, 120.5, 102.2, 92.7, 56.9 (2',6'-MeO), 56.8 (4'-MeO).
3b	174.9, 159.1, 158.4, 145.5, 135.7, 132.2, 130.1, 125.6, 120.7, 108.9, 105.8, 56.9 (2',6'-MeO).
3c	175.4, 159.3, 157.5, 145.4, 135.0, 132.5, 132.2, 130.1, 125.2, 122.0, 120.2, 118.2, 113.5, 56.7 (2'-MeO).
3d	175.7, 164.8, 159.1, 144.5, 135.0, 133.1, 124.6, 124.6, 124.2, 120.5, 115.9, 56.7 (4'-MeO).
3e	171.9, 159.5, 157.9, 155.5, 145.9, 138.5, 131.9, 130.5, 125.4, 120.8, 116.3, 110.9, 108.8, 62.6 (6'-MeO), 57.3 (2'-MeO).
3f	178.8, 159.6, 145.9, 142.3, 136.6, 131.3, 130.8, 129.7, 128.6, 125.3, 121.1, 21.2 (4'-Me), 20.1 (2',6'-Me).
3g	177.1, 159.6, 145.7, 137.1, 132.4, 132.1, 131.9, 131.7, 130.5, 130.0, 126.9, 125.3, 120.7, 20.0 (2'-Me).
3h	176.4, 159.3, 145.0, 144.6, 132.8, 132.0, 130.6, 130.1, 129.0, 124.8, 120.5, 21.6 (4'-Me).
3i	176.2, 159.5, 145.4, 133.2, 132.8, 131.8, 131.4, 130.3, 130.0, 124.9, 120.6.
4a	170.7, ^{c)} 165.8, 159.3, 148.5, 138.5, 136.0, 132.1, 132.0, 128.6, 105.0, ^{c)} 92.5, 56.8 (2',6'-MeO), 56.7 (4'-MeO).
4b	170.5, 158.3, 148.7, 138.8, 135.6, 134.5, 132.3, 131.5, 128.7, 112.1, 105.7, 56.8 (2',6'-MeO).
4e	167.1, 157.7, 155.3, 149.0, 138.7, 137.5, 135.2, 132.5, 131.0, 128.8, 119.7, 110.6, 108.8, 62.0 (2'-MeO), 57.2 (6'-MeO).
4f	174.0, 149.3, 141.7, 138.9, 136.6, 134.8, 132.8, 132.0, 130.9, 129.7, 129.0, 21.2 (4'-Me), 19.9 (2',6'-Me).
4g	172.8, 149.5, 138.7, 137.0, 135.8, 135.3, 132.4, 131.7, 131.6, 131.1, 129.8, 128.7, 127.0, 19.8 (2'-Me).
4h	173.2, ^{c)} 149.2, 142.3, 138.4, 136.6, 132.7, 131.9, 131.5, 130.6, 130.2, 128.5, 21.5 (4'-Me).
4i	172.6, 149.4, 138.5, 136.5, 135.6, 132.0, 131.6, 131.4, 130.3, 129.7, 128.5.
7b	158.0, 150.0, 127.8, 127.1, 127.1, 125.4, 117.5, 108.5, 108.0, 106.3, 105.5, 69.4, 57.1 (2',6'-MeO), 56.4, 56.0 (1,8-MeO).
7i^{b)}	158.0, 149.2, 149.2, 129.1, 126.4, 126.2, 125.4, 115.7, 109.4, 106.7, 70.6, 55.9 (1,8-MeO).
8b	173.0, 162.8, 157.8, 156.2, 146.4, 132.1, 117.8, 111.0, 109.2, 109.2, 104.9, 58.3 (1,8-MeO), 56.7 (2',6'-MeO).
8i	175.7, 162.8, 157.9, 146.8, 140.3, 129.0, 128.3, 125.0, 117.8, 110.7, 109.6, 57.9 (1,8-MeO).

a) In CDCl_3 (δ/ppm). b) Data from Ref. 1. c) Uncertain because the signal was very weak.

(+35) > **4b** (+50) > **4h** (+100) > **4f** (+105) > **4i** (+120) > **4g** (+125) > **4e** (+165).

The E_0 or E_{pc} potentials must be parallel to the lowest unoccupied molecular orbital (LUMO) energy of these ions **3**, and **4**, as shown in Fig. 2. The E_{pc} potentials of **8b,i** are also included in Fig. 2. We have been interested in the effects of 1,8-dimethoxy substitutions,⁷ since the presence of such groups would increase the stability of 9-arylxanthen-9-ylum by a π -electron-donation, but would interfere the π -conjugation of the 9-aryl group with the 9-arylxanthen-9-ylum π -system by a steric interaction between the 1,8-dimethoxy groups and the 9-aryl group.

Both series of salts **3** and **4** are deeply colored, and the UV-visible spectra measured for 1,2-dichloroethane solution (Table 2) showed one or two bands in the visible region with $\log \epsilon = 3.3 - 4.0$. The UV-visible spectra of some 9-(*p*-substitutedphenyl)xanthen-9-ylum and thioxanthen-9-ylum ions have been reported, as measured in the presence of an acid,^{14,21–26} as well as the xanthen-9-ylum and thioxanthen-9-ylum ions themselves.²³ The formation of radicals, such as **5i** and **6i**, by intermolecular charge transfer to **3i** and **4i** has been inferred.²⁴ In our previous paper, we reported on the UV-visible spectra of **3b**, **3i**, **8b**, and **8i**, as measured in aqueous hydrochloric acid.⁷ These visible band energies at the longest ab-

Table 3. Redox Potentials^{a)} and UV-visible Spectral Data^{b)} of 9-Arylxanthen-9-ylum and -thioxanthen-9-ylum Ions

Compound	$E_o^c)$ /mV	$E_{pc}^d)$ /mV	$E_{pa}^e)$ /mV	$\Delta E_p^f)$ /mV	$i_{pa}/i_{pc}^g)$	$\lambda(1)_{max}$ /nm (log ϵ)	$\lambda(2)_{max}$ /nm (log ϵ)	$\lambda(3)_{max}$ /nm (log ϵ)
3a	18	-25	60	85	0.96	377 (4.27)	456 (3.50)	560 (3.83)
3b	65	20	110	90	1.00	377 (4.27)	469 (3.69)	
3c	100	60	140	80	0.89	380 (4.28)	454 (3.70)	
3d	65	20	110	90	0.90	376 (4.25)	511 (4.26)	
3e	165	120	210	90	0.96	378 (4.20)	451 (3.83)	
3f	115	70	160	90	0.98	377 (4.27)	452 (3.58)	
3g	125	90	160	70	0.62	377 (4.27)	449 (3.68)	
3h	90	55	125	70	0.94	376 (4.26)	461 (3.94)	480 (3.92)
3i	—	225	—	—	~0	381 (4.27)	453 (3.85)	
4a	35	-10	80	90	0.98	383 (4.28)	526 (3.67)	573 (3.62)
4b	60	15	105	90	0.96	384 (4.28)	499 (3.73)	529 (3.70)
4e	165	120	210	90	1.00	386 (4.23)	499 (3.65)	529 (3.59)
4f	105	50	160	90	0.95	383 (4.28)	498 (3.73)	528 (3.68)
4g	125	80	170	90	0.83	383 (4.21)	497 (3.72)	529 (3.64)
4h	100	55	145	90	0.93	384 (4.20)	503 (3.84)	531 (3.74)
4i	120	70	170	100	0.94	386 (4.22)	500 (3.80)	531 (3.74)
8b	15	-40	70	110	0.54	348 (4.09)	454 (3.98)	
8i	—	155	—	—	~0	347 (4.23)	469 (4.14)	

a) Measured for $ClCH_2CH_2Cl$ solution; in mV vs $Ag/AgCl$. b) Measured for $ClCH_2CH_2Cl$ solution. c) Redox potential. d) Cathodic peak potential. e) Anodic peak potential. f) Peak separation. g) Peak current ratio.

sorption maxima must be related to the LUMO–HOMO energy differences, from which the HOMO levels in Fig. 2 were directly calculated. We shall show in our next report that such HOMO and LUMO levels of aryl-bis(2,6-dimethoxyphenyl)methyl salts calculated in an analogous way correlate very well with the Hamett σ^+ value of the *p*-substituent in the aryl group.

The findings derived from the results given in Table 3, as well as Fig. 2, may be summarized as follows: 1) both the LUMO (or E_{pc} , E_o potentials) and HOMO (or λ_{max}) levels varied in almost the same order of substituent on the 9-phenyl group; 2) the MeO-group on the 9-phenyl group was more effective to raise both the HOMO and LUMO levels than the Me-group, as expected from the electron-donating property; 3) the HOMO levels of **3** and **4** were more sensitive than the LUMO levels to the change of the 9-aryl group; 4) *p*-substitution by the MeO- or Me-groups was more effective to raise the HOMO and LUMO levels than *o*-substitution, as observed between **3c** and **3d**, **3g** and **3h**, or **4g** and **4h**, of which the cause may be understood by a steric effect of the *o*-substituent to interfere the coplanarity of the phenyl group with the xanthen plane and to interfere the π -conjugation of the 9-aryl group with the xanthen-9-ylum π -system; 5) the presence of two *o*-MeO groups was more effective to raise the HOMO and LUMO levels than one *o*-MeO group, as observed between **3b** and **3c**; 6) *m*-bromination of the 9-aryl group in **3b** or **4b** greatly lowered both the LUMO and HOMO levels, as observed for **3e** or **4e**, which may also be understood by an increase of the steric effect as the origin; namely, the presence of the *m*-bromine atom in **3e** or **4e** would force the adjacent 2'-methoxy

methyl group away toward the central cationic carbon or above the xanthen plane to interfere the coplanarity of the aryl group with the xanthen plane, and the two π -electron systems must separate each other to lower the HOMO level and, interestingly, the LUMO level, too; 7) both the HOMO and LUMO levels of **8b** and **8i** were higher than those of **3b** and **3i**, respectively, as expected from the electron-donating property of the MeO-groups at the 1,8-positions; 8) the LUMO level of **3b** was higher than that of **8i**, the isomer, indicating that the LUMO level is more affected by methoxy substitution on the 9-phenyl group, rather than at the 1,8-positions of the xanthenylum skeleton.

Based on these findings, the isolation, a measurement of the ESR spectra, and crystal structural analyses of some of these radicals **5** and **6** are in progress.

Comparison of the Stability (pK_{R^+}) with the Reduction Potential. The stability (pK_{R^+}) of **3b** (4.80) measured in hydrochloric acid showed that it is far more stable than **8b** (1.14), **3i** (0.75), and **8i** (−0.81).⁷ Since the pK_{R^+} value is a parameter associated with the energy for an electrophilic reaction of the carbenium ion with the hydroxide anion, it is worth comparing with the reduction potential or the LUMO energy level. As mentioned above (Table 3), the LUMO energy decreased in the order **8b** (−75) > **3b** (+20) > **8i** (+150) > **3i** (+225), and was not in parallel with pK_{R^+} . The stability of the carbenium ions or the basicity of the parent alcohol is often affected not only by the electronic effect but also by the steric effect between the carbenium ion and the hydroxide ion.^{12,27} The highest stability of **3b**, thus, must be attributed to the steric effect as well as to the electronic effect of two *o*-MeO groups in the parent alcohol **1b**. An explanation of the stability orders (**3b** > **8b**

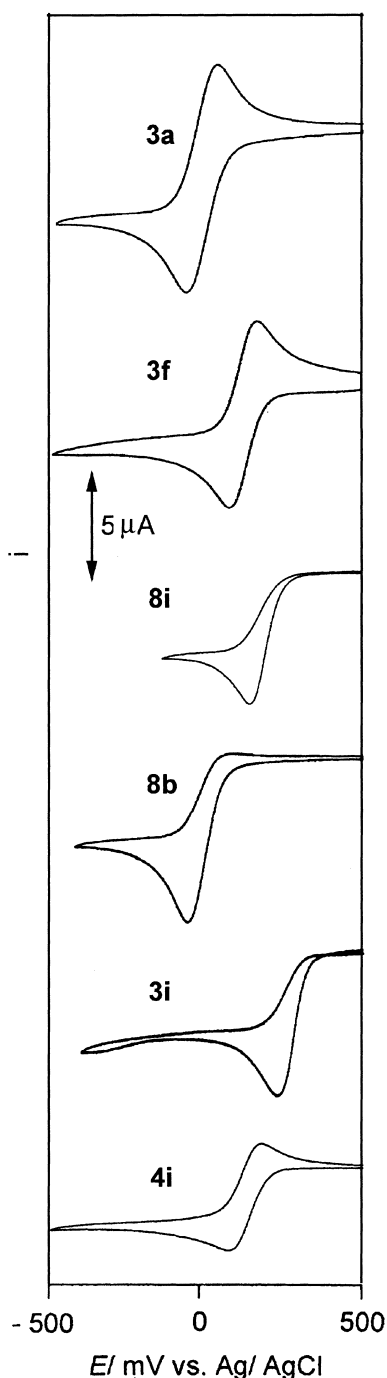


Fig. 1. Typical cyclic voltammograms of 9-Arylxanthen-9-ylum and -thioxanthen-9-ylum Ions.

A cyclic voltammetric measurement was done at 25 °C. Concentration of the ions was 1 mmol dm⁻³ in 1,2-dichloroethane containing 0.1 mol dm⁻³ tetrabutylammonium perchlorate. Potential sweep rate was 20 mV s⁻¹.

and **3i** > **8i**), however, is still difficult, because the parent alcohols (**1b** and **1i**) must be less crowded than **7b** and **7i**, respectively. Ethoxy-group substitution at the 1,8-positions of xanthenol has been reported to increase the basicity of 1,8-diethoxyxanthen-9-ol (+1.38),²⁸ as compared with that of xanthen-9-ol (-0.17;²⁸ -0.21²). The basicity of 1,3,6,8-tet-

ramethoxyxanthen-9-ol has also been reported to be very high (+6.0).²⁷ These reported results are in accord with both the electronic and steric effects. On the other hand, the stability of 9-methyl-1,3,6,8-tetramethoxyxanthen-9-ylum ion (p*K*_R⁺, 4.03) is very comparable with that of 3,6-dimethoxy-9-methylxanthen-9-ylum ion (p*K*_R⁺, 4.30).²⁷ We are also interested in the LUMO level order of the isomers, **3b** > **8i**, since it is the same order with the carbenium stability, **3b** > **8i**. The higher stability and kinetic inertness of **3b** are in parallel with the higher LUMO energy level.

Experimental

General. The ¹H and ¹³C NMR spectra were recorded for solutions in CDCl₃ using JEOL Model JNM-GX-270 and JEOL Model ECP-GX-500 spectrometers, respectively. The IR spectra were recorded for Nujol® mulls using a Shimadzu FTIR-8300 spectrophotometer. Cyclic voltammetric measurements were made at 25 °C, as described previously.⁶ The UV-visible spectral data were recorded using a Shimadzu UV-160 spectrophotometer.

Preparations of 9-arylxanthen-9-ols (**1b**, **1i**, **7b**, and **7i**) and the 9-arylxanthen-9-ylum salts (**3b**, **3i**, **8b**, and **8i**) were reported previously.⁷

Preparations of 9-Arylxanthen-9-ols (1a,c,d, f-h) and 9-Arylthioxanthen-9-ols (2a,b, f-i). **Method A.** The organolithium reagents were prepared by the reaction of a 15% hexane solution of butyllithium and a slight excess of 1,3,5-trimethoxybenzene, 2-bromoanisole, or 4-bromoanisole under argon. The mixture was stirred for 2 h at room temperature to give a white suspension. It was diluted by adding toluene, xanthone was added at 0 °C, and the mixture was stirred for 24 h at room temperature to give light-yellow solution. It was well washed with water. To the organic layer was added hexane, and the mixture was cooled to -30 °C to give white crystals of **1a**, **1c**, or **1d**.

Method B. The Grignard reagent was prepared by the reaction of magnesium (an excess) and 2-bromomesitylene, 2-bromotoluene, 4-bromotoluene, or bromobenzene in THF containing a small amount of 1,2-dibromoethane as the initiator at 80 °C under argon. A THF solution of xanthone or thioxanthone was added at 0 °C, and the mixture was stirred for 24 h at room temperature to give a suspension. It was concentrated under reduced pressure, and the residue was dissolved in toluene and 0.1 M hydrochloric acid. The aqueous layer was washed twice with toluene. The combined toluene layer was dried with magnesium sulfate, concentrated, diluted with hexane, and cooled to -30 °C to give white crystals of **1f-h** and **2f-i**.

9-(2,4,6-Trimethoxyphenyl)xanthen-9-ol (1a). In 80% yield; mp 180–181 °C; IR 3450 cm⁻¹ (OH). Found: C, 72.39; H 5.56%. Calcd for C₂₂H₂₀O₅: C, 72.51; H, 5.53%.

9-(2-Methoxyphenyl)xanthen-9-ol (1c). In 79% yield; mp 168–170 °C [reported, 164–164.5 °C];¹⁴ IR 3500 cm⁻¹ (OH). Found: C, 78.64; H 5.36%. Calcd for C₂₀H₁₆O₃: C, 78.93; H, 5.30%.

9-(4-Methoxyphenyl)xanthen-9-ol (1d). In 81% yield; mp 110–113 °C (after recrystallization from 2-propanol) [reported, 128–129 °C,¹⁴ 120–121 °C,¹⁵ 146–147 °C¹⁶]; IR 3504 and 3433 cm⁻¹ (OH).

9-(Mesityl)xanthen-9-ol (1f). In 63% yield; mp 181–183 °C [reported, 192.5–193.5 °C¹³]; IR 3510 cm⁻¹ (OH). Found: C, 83.39; H 6.44%. Calcd for C₂₂H₂₀O₂: C, 83.52; H, 6.32%.

9-(2-Tolyl)xanthen-9-ol (1g). In 67% yield; mp 178–180 °C [reported, 165–166 °C²⁹]; IR 3514 cm⁻¹ (OH). Found: C, 83.03;

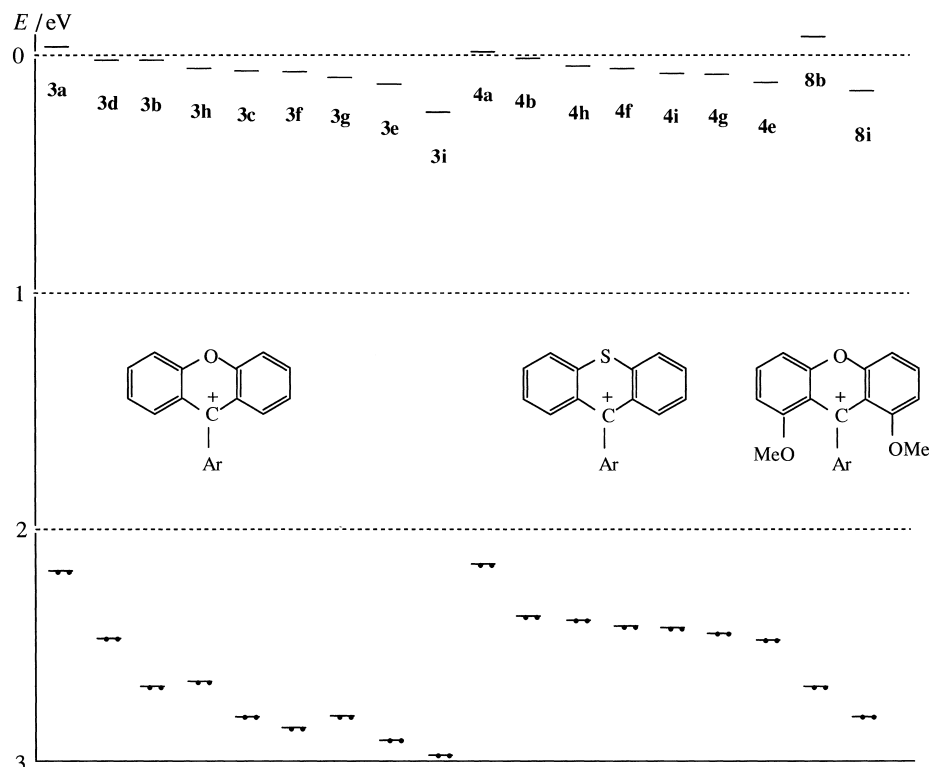


Fig. 2. Estimated LUMO and HOMO levels of 9-Arylxanthen-9-yl and -thioxanthen-9-yl Ions.

A LUMO level of the ions was estimated from the corresponding E_0 values against the Ag/AgCl, without any corrections regarding the solvation energy, liquid junction potential, and so on.

H 5.73%. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%.

9-(4-Tolyl)xanthen-9-ol (1h). In 74% yield; mp 138–139 °C [reported, 146.5–147 °C,¹⁴ 141–142 °C,³⁰ 150 °C³¹]; IR 3510 cm^{-1} (OH). Found: C, 82.90; H 5.82%. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%.

9-(2,4,6-Trimethoxyphenyl)thioxanthen-9-ol (2a). In 42% yield; mp 165–166 °C; IR 3435 cm^{-1} (OH).

9-(2,6-Dimethoxyphenyl)thioxanthen-9-ol (2b). In 59% yield; mp 191–192 °C; IR 3450 cm^{-1} (OH). Found: C, 71.79; H, 5.27%. Calcd for $C_{21}H_{18}O_3S$: C, 71.98; H, 5.18%.

9-(Mesityl)thioxanthen-9-ol (2f). In 30–57% yield; mp 148–153 °C; IR 3450 cm^{-1} (OH). Found: C, 79.37; H, 6.19%. Calcd for $C_{22}H_{20}OS$: C, 79.48; H, 6.06%.

9-(2-Tolyl)thioxanthen-9-ol (2g). In 56% yield; mp 78–80 °C; IR 3350 cm^{-1} (OH).

9-(4-Tolyl)thioxanthen-9-ol (2h). In 62% yield; mp 155–157 °C [reported, 164–165 °C¹⁴]; IR 3320 cm^{-1} (OH).

9-(Phenyl)thioxanthen-9-ol (2i). In 78% yield; mp 103–105 °C [reported, 104–105 °C¹⁴]; IR 3350 cm^{-1} (OH).

These compounds are very soluble in chloroform, acetone, toluene, and diethyl ether, soluble in acetonitrile, methanol and ethanol, poorly soluble in 2-propanol, and insoluble in hexane.

Preparation of 9-(3-Bromo-2,6-dimethoxyphenyl)xanthen-9-ol (1e). To a suspension of **2d** (1.672 g, 5 mmol) in acetone (20 mL) was added an acetone (30 mL) solution of *N*-bromosuccinimide (1.335 g, 7.5 mmol). The mixture was stirred for 24 h at room temperature to give a yellow solution. After it was concentrated to ca. a third volume, water (100 mL) was added, and the resultant light-green solid was recrystallized from acetone to give white crystals of **1e** in 59% yield; mp 177–178 °C; IR 3439 cm^{-1}

(OH). Found: C, 60.91; H, 4.19%. Calcd for $C_{21}H_{17}BrO_4$: C, 61.03; H, 4.15%. The compound is soluble in acetone, ethyl methyl ketone, and toluene, poorly soluble in methanol, ethanol, 2-propanol, and insoluble in hexane. It is insoluble in 6 M hydrochloric acid, although the crystals took a red color.

Preparation of 9-(3-Bromo-2,6-dimethoxyphenyl)thioxanthen-9-ol (2e). To a suspension of **2b** (3.50 g, 10 mmol) in *N,N*-dimethylformamide (DMF) (40 mL) was added a DMF (60 mL) solution of NBS (2.68 g, 15 mmol). The mixture was stirred for 24 h at room temperature to give a red solution. It was poured into water (300 mL) at 0 °C, and the resultant pink precipitates were recrystallized from DMF (20 mL) to give pink or white crystals of **2e** in 31% yield; mp 110–120 °C; IR 3382 cm^{-1} (OH). The ¹H NMR spectrum showed that it is a mixture of two isomers, **2e-1** and **2e-2**, in almost the same ratio. The mixture (1.0 g) was recrystallized from acetone (17 mL), and one of the isomers **2e-1** (0.40 g) crystallized in pure form of white crystals; mp 213–214 °C; IR 3354 cm^{-1} (OH). The compound was soluble in toluene and acetone. It was insoluble in 6 M hydrochloric acid, although the crystals took red color.

Preparations of 9-Arylxanthen-9-yl Perchlorates (3a,c-i) and 9-Arylthioxanthen-9-yl Perchlorates (4a,b,e-i).

Method A. To a suspension of **1** or **2** (1 mmol) in acetone (10 mL) was added 60% aqueous perchloric acid (0.10–0.19 mL, an excess) to give a deeply colored solution or suspension. It was stirred at room temperature for 0.5–1.0 h to give deeply colored crystals of **3** or **4** in 60–85% yields.

Method B. To a solution of **1** or **2** (1 mmol) in diethyl ether (10 mL) was added 60% aqueous perchloric acid (0.12 mL, 1.3 mmol) to give a deeply colored suspension. The suspension was

stirred at room temperature for 1 h to give deeply colored crystals of **3** or **4** in 80–95% yields.

Most of the salts were characterized by ^1H NMR and ^{13}C NMR spectra (Tables 1 and 2) and some representatives were characterized also by elemental analyses.

9-(2,4,6-Trimethoxyphenyl)xanthen-9-ylum Perchlorate (3a). Dark-purple crystals; mp not observed below 230 °C; IR 1100 cm^{-1} (ClO_4). Found: C, 59.15; H, 4.43%. Calcd for $\text{C}_{22}\text{H}_{19}\text{Cl}_{11}\text{O}_8$: C, 59.14; H, 4.29%.

9-(3-Bromo-2,6-dimethoxyphenyl)xanthen-9-ylum Perchlorate (3e). Dark-red crystals; mp not observed below 230 °C; IR 1097 cm^{-1} (ClO_4). Found: C, 50.88; H, 3.27%. Calcd for $\text{C}_{21}\text{H}_{16}\text{BrCl}_{11}\text{O}_7$: C, 50.88; H, 3.25%.

9-(2,6-Dimethoxyphenyl)thioxanthen-9-ylum Perchlorate (4b). Dark-red crystals in 71% yield; mp not observed below 230 °C; IR 1087 cm^{-1} (ClO_4). Found: C, 58.14; H, 3.93%. Calcd for $\text{C}_{21}\text{H}_{17}\text{Cl}_{11}\text{O}_6\text{S}$: C, 58.27; H, 3.96%.

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