

## Photochemistry of Benzenediazonium Anthracenesulfonates: Photolysis of Benzenediazonium Salts by Excitation of the Anion

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4-Substituted benzenediazonium 1,8-dimethoxyanthracene-3-sulfonates photodecompose under visible light, which is absorbed only by the anionic part, *via* intra-ion pair electron transfer from the excited anionic part to the benzene diazonium.

Spectral sensitization of the decomposition of benzenediazonium salts is of considerable interest in imaging technology.<sup>1-5</sup> Macrae and Wright reported a xanthene dye sensitized photodecomposition of a diazonium salt in a  $1 \times 10^{-2}$  mol dm<sup>-3</sup> solution which is thought to involve the formation of an ion-pair between the ground-state diazonium and dye ions.<sup>6</sup> However, they did not isolate the ion-pair to verify the proposed mechanism. We report here the synthesis of benzenediazonium anthracenesulfonates and a photodecomposition of the diazonium salts in highly diluted solutions by excitation of the anion.

4-Substituted benzenediazonium 1,8-dimethoxyanthracene-3-sulfonates **1a-c** were newly prepared by ion exchange between the corresponding 4-substituted benzenediazonium chlorides and sodium 1,8-dimethoxyanthracene-3-sulfonate.<sup>†</sup> Irradiation of the obtained diazonium salts in acetonitrile or chloroform with visible light, which is absorbed only by the 1,8-dimethoxyanthracene-3-sulfonate anion (**2**), leads to decomposition of the diazonium salts and formation of some acids. The photoreaction was followed by absorption spectrometry using a 1 cm pathlength cell. The formation of the

acids was confirmed by a non-aqueous photometric titration using a leuco dye as an acid indicator which is colourless in neutral or basic media and red in acidic medium.

Table 1 shows quantum yields of the photodecomposition at 405 nm of **1a** ( $2.5 \times 10^{-5}$  mol dm<sup>-3</sup>) and the mixture of 4-*n*-butoxybenzenediazonium tetrafluoroborate **3** and ethyl 1,8-dimethoxyanthracene-3-sulfonate **4** ( $2.5 \times 10^{-5}$  mol dm<sup>-3</sup> each) in chloroform or acetonitrile. **1a** photodecomposes over six times faster in chloroform than in acetonitrile or than the inter-molecularly sensitized system. The lifetime of fluorescence from the anthracene part of **1a** monitored at 483 nm was 14.7 ns in acetonitrile, while no fluorescence was detected for **1a** in chloroform. Conductivity analysis showed that the equivalent conductivity of **1a** was above  $100 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in the concentration range  $10^{-5}$ – $10^{-3}$  mol dm<sup>-3</sup> and that 97% of **1a** is electrolytically dissociated in acetonitrile at  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup>. In contrast, the conductivity of chloroform solutions of **1a** ( $1.0 \times 10^{-4}$ – $1.6 \times 10^{-3}$  mol dm<sup>-3</sup>) was below the lower limit of sensitivity of the measurement ( $1 \mu\Omega^{-1} \text{cm}^2$ ).

Both the singlet and triplet states of **2** are below the corresponding states of the diazonium cations ( $E_s$  ca. 82 kcal mol<sup>-1</sup>,  $E_t$  ca. 70 kcal mol<sup>-1</sup> for benzenediazonium fluoroborate;<sup>7</sup>  $E_s$  ca. 66 kcal mol<sup>-1</sup> for **4**). Despite this, the diazonium cation quenches the fluorescence of **2** with high efficiency (compare lifetimes of fluorescence of **1** with **4**, Table 2). It is thus suggested that the sensitization is due to electron transfer from the singlet excited state of **2** to the ground state of the diazonium cations. This interpretation is supported by the negative value of  $\Delta G$  of  $-19.0$  kcal mol<sup>-1</sup> calculated with the oxidation potential of **4** (1.38 eV vs. SCE) and the reduction potential of **3** ( $-0.66$  eV vs. SCE).<sup>8</sup> In acetonitrile, the anion and the cation are almost completely dissociated in the range of  $10^{-5}$ – $10^{-3}$  mol dm<sup>-3</sup>, while **1** exists predominantly as ion pairs in chloroform at any concentration. The difference of the quantum yields for photodecomposition of **1** in the two solvents is caused by the difference in separation between the ions.

Irradiation of **1** in Novolac resin at 405 nm also induces decomposition and formation of acids. This suggests that **1** can be applied as an element of chemically amplified resists, where photoacid generators are essential.<sup>9</sup>

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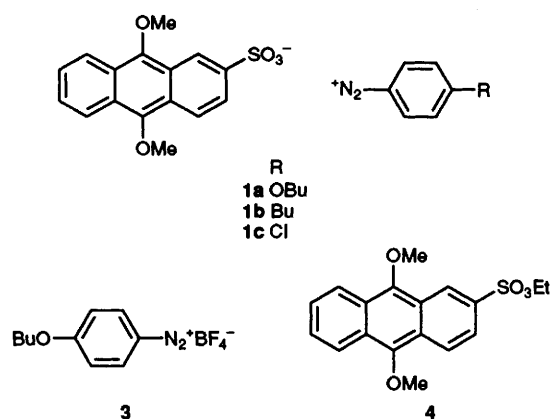


Table 1 Quantum yields for photodissociation of **1a** and the mixture of **3** and **4**

Compound(s)	In MeCN	In CHCl <sub>3</sub>
<b>1a</b>	0.07 ± 0.02	0.42 ± 0.03
<b>3</b> and <b>4</b>	0.05 ± 0.02	0.05 ± 0.01

Table 2 Lifetime of fluorescence

Compound	In MeCN	In CHCl <sub>3</sub>
<b>1a</b>	14.7	0
<b>1b</b>	15.0	0
<b>1c</b>	14.9	<sup>a</sup>
<b>3</b>	23.4	19.9

<sup>a</sup> The solubility of **1c** in chloroform was quite low.

### Footnote

<sup>†</sup> Satisfactory elemental analyses were obtained for **1a-c**. **1a**: mp 165.5–166.0 °C (decomp.), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz) δ 0.93 (t, *J* 7.3 Hz, 3H), 1.38–1.47 (m, 2H), 1.71–1.77 (m, 2H), 4.05 (s, 3H), 4.06 (s, 3H), 4.26 (t, *J* 6.5 Hz, 2H), 7.46 (d, *J* 9.5 Hz, 2H), 7.57–7.61 (m, 2H), 7.72–7.76 (m, 1H), 8.16–8.23 (m, 3H), 8.47 (s, 1H), 8.60 (d, *J* 9.2 Hz, 2H); <sup>13</sup>C NMR [(CD<sub>3</sub>)<sub>2</sub>SO, 270 MHz] δ 168.2, 148.6, 147.7, 145.1, 136.1, 125.8, 125.7, 124.6, 124.5, 124.1, 123.7, 123.3, 122.2, 122.1, 118.1, 117.4, 102.9, 69.7, 63.2, 63.0, 30.0, 18.4, 13.4; UV (MeCN) λ<sub>max</sub>/nm (log ε) 261 (5.22), 311 (4.46), 3.57 (3.72), 375 (3.86), 396 (3.77).

**1b**: mp 114.5–115.5 °C (decomp.); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz) δ 0.88 (t, *J* 7.2 Hz, 3H), 1.24–1.36 (m, 2H), 1.53–1.64 (m, 2H), 2.81 (t, *J*

7.4 Hz, 2H), 4.05 (s, 3H), 4.06 (s, 3H), 7.57–7.62 (m, 2H), 7.72–7.76 (m, 1H), 7.81 (d, *J* 8.9 Hz, 2H), 8.19–8.28 (m, 3H), 8.48 (s, 1H), 8.58 (d, *J* 8.4 Hz, 2H); <sup>13</sup>C NMR [(CD<sub>3</sub>)<sub>2</sub>SO 270 MHz] δ 158.0, 148.6, 147.7, 145.1, 132.7, 131.0, 128.9, 125.8, 125.7, 124.6, 124.5, 124.1, 123.7, 123.3, 122.2, 122.1, 118.1, 114.9, 63.2, 63.0, 35.4, 32.0, 21.5, 13.5; UV (MeCN) λ<sub>max</sub>/nm (log ε) 265 (5.25), 283 (4.28), 360 (3.73), 378 (3.87), 398 (3.78).

**1c**: mp 137.5–139.0 °C (decomp.); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz) δ 4.05 (s, 3H), 4.06 (s, 3H), 7.58–7.61 (m, 2H), 7.72–7.76 (m, 1H), 8.11 (d, *J* 8.9 Hz, 2H), 8.19–8.28 (m, 3H), 8.48 (s, 1H), 8.71 (d, *J* 8.9 Hz, 2H); <sup>13</sup>C NMR [(CD<sub>3</sub>)<sub>2</sub>SO, 270 MHz] δ 148.6, 147.7, 146.4, 145.0, 134.3, 131.5, 129.2, 125.8, 125.8, 124.6, 124.5, 124.0, 123.7, 123.3, 122.2, 122.1, 118.1, 114.7, 63.2, 63.1.

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