Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Photochemical degradation of halogenated estrogens under natural solar irradiance

Reid P. Milstead, Keeton T. Nance, Kulananalu S. Tarnas, Kira E. Egelhofer, and David R. Griffith

Electronic Supplementary Information

Summary:

12 pages

Figure S1. Tube racks in place during a sunlight exposure experiment. The front row (left side of image) contains foil-covered dark control tubes.

Figure S2. An example HPLC-UV chromatogram (280 nm) for a standard mixture of E2 and monoBrE2 ("Standard 6") and for direct photolysis solutions at t_0, t_{16d}, t_{28d} during the Feb 2015 experiment (pH 5.6).

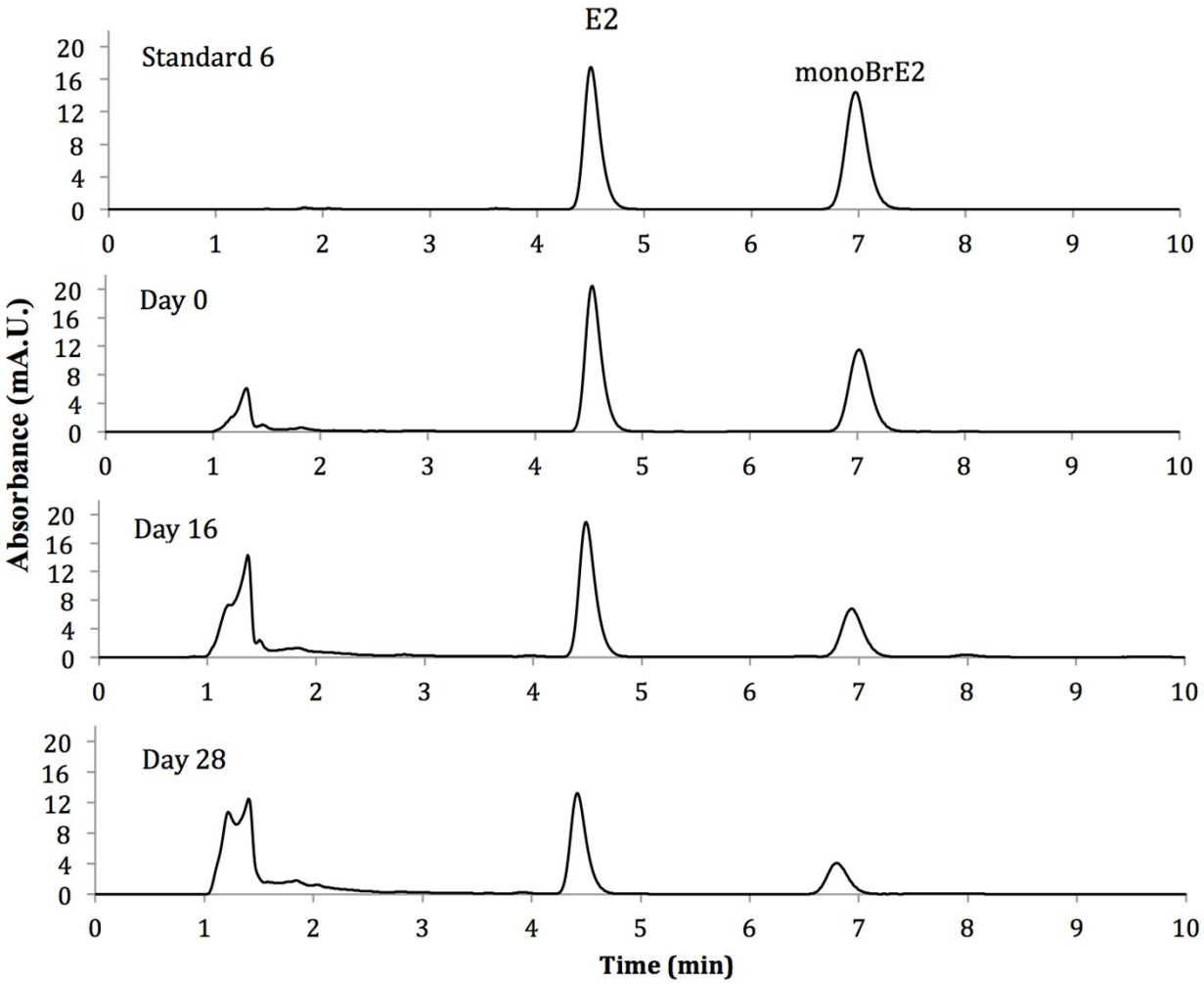

Figure S3. Typical photolysis experiment time course data (monoBrE2; Mar 2016), plotted as a) peak area and b) natural log of the t_0 normalized peak area, where the negative slope of the regression line is the observed first order rate constant (k_{obs}). Dark controls (e.g., foil covered tubes) are represented as filled circles and suggest that estrogen degradation in the dark is minimal over the course of the experiment.

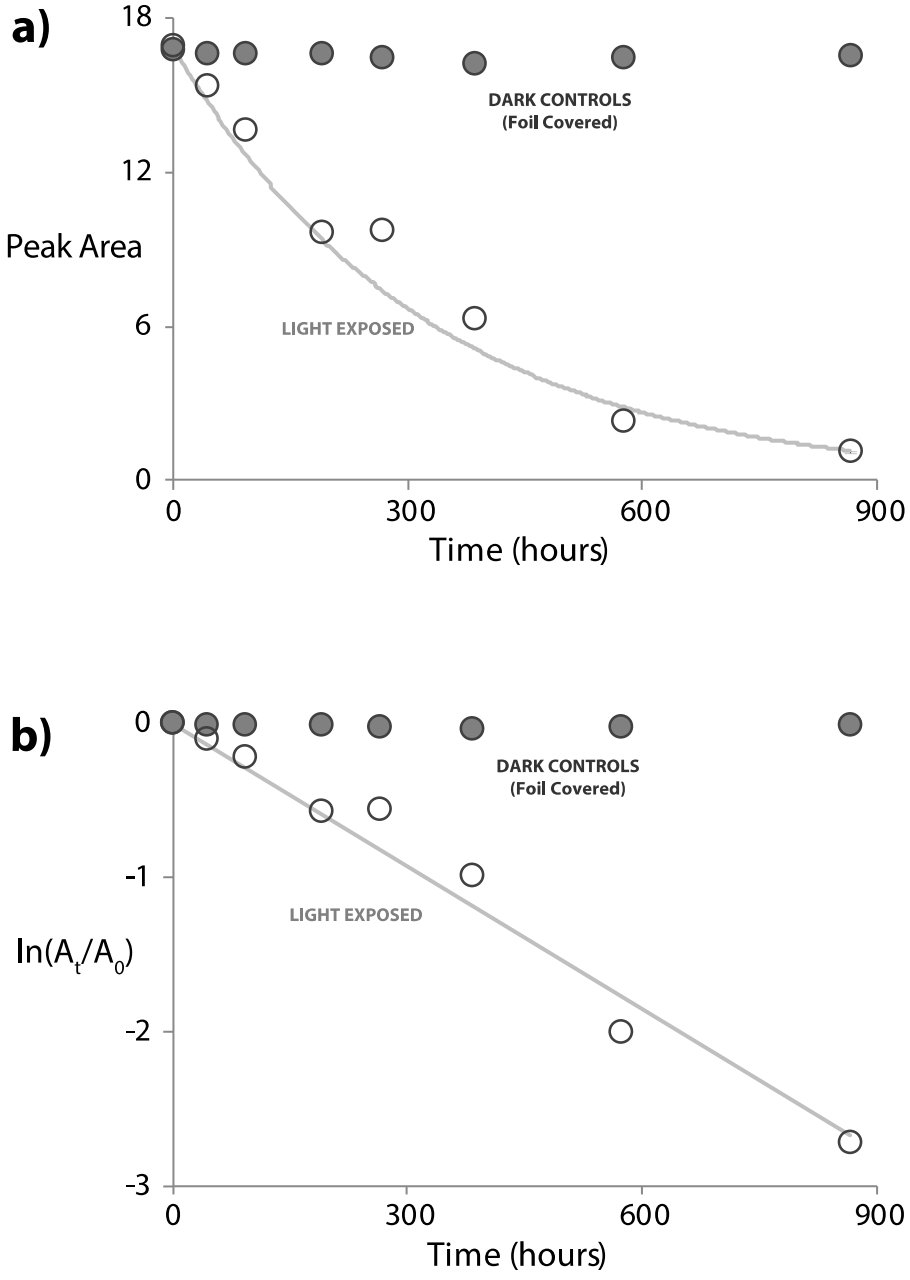

Figure S4. The molar absorptivity spectra of E2 and three of its halogenated derivatives are more intense and red-shifted for the phenolate form (pH 12 - 13; solid lines) compared to the phenol form (pH 5.6; dashed lines). Spectra were acquired in 50:50 methanol/water.

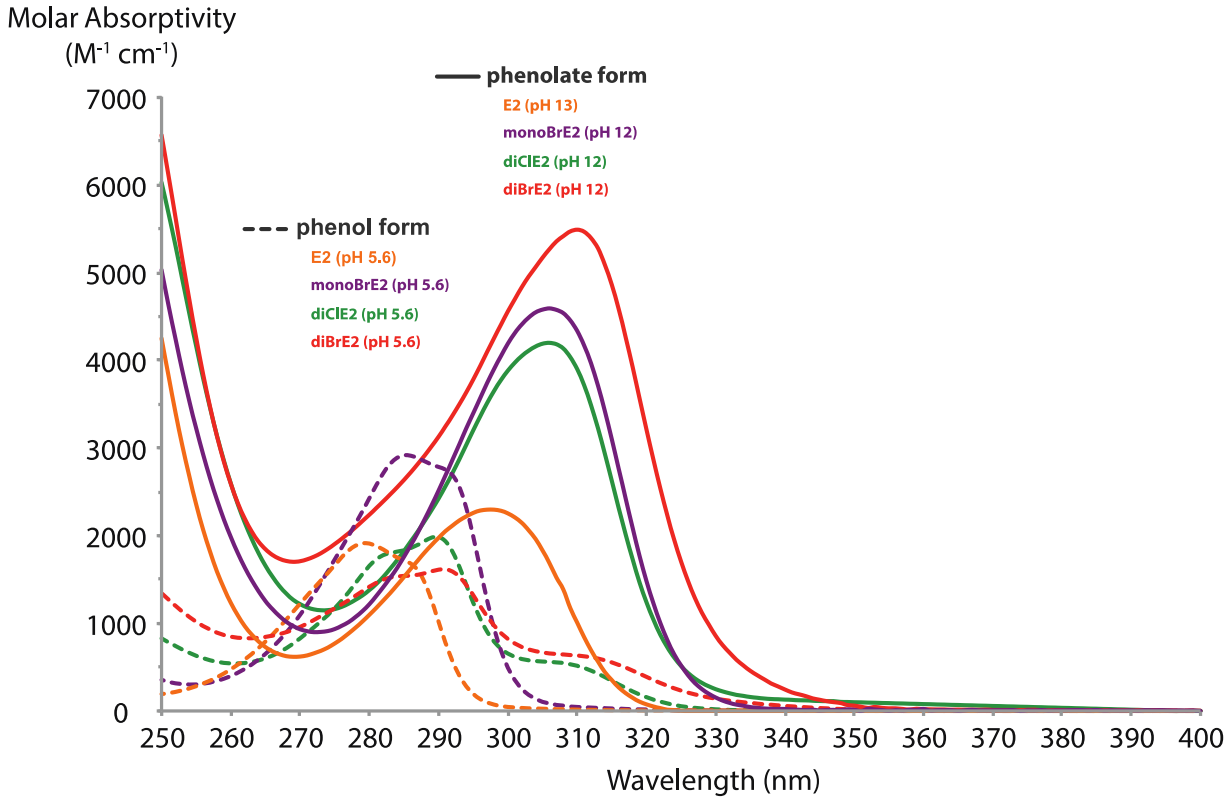

Figure S5. Direct photochemical degradation rates of E2 (pH 13) and three of its halogenated derivatives (pH 12), exposed to natural sunlight on 20 July 2018, are significantly faster than those measured at 5.6 in February 2015 and 2016 (Figure 4; Figure S6) due to significantly larger quantum yields and greater overlap between phenolate molar absorptivity spectra and the solar spectrum.

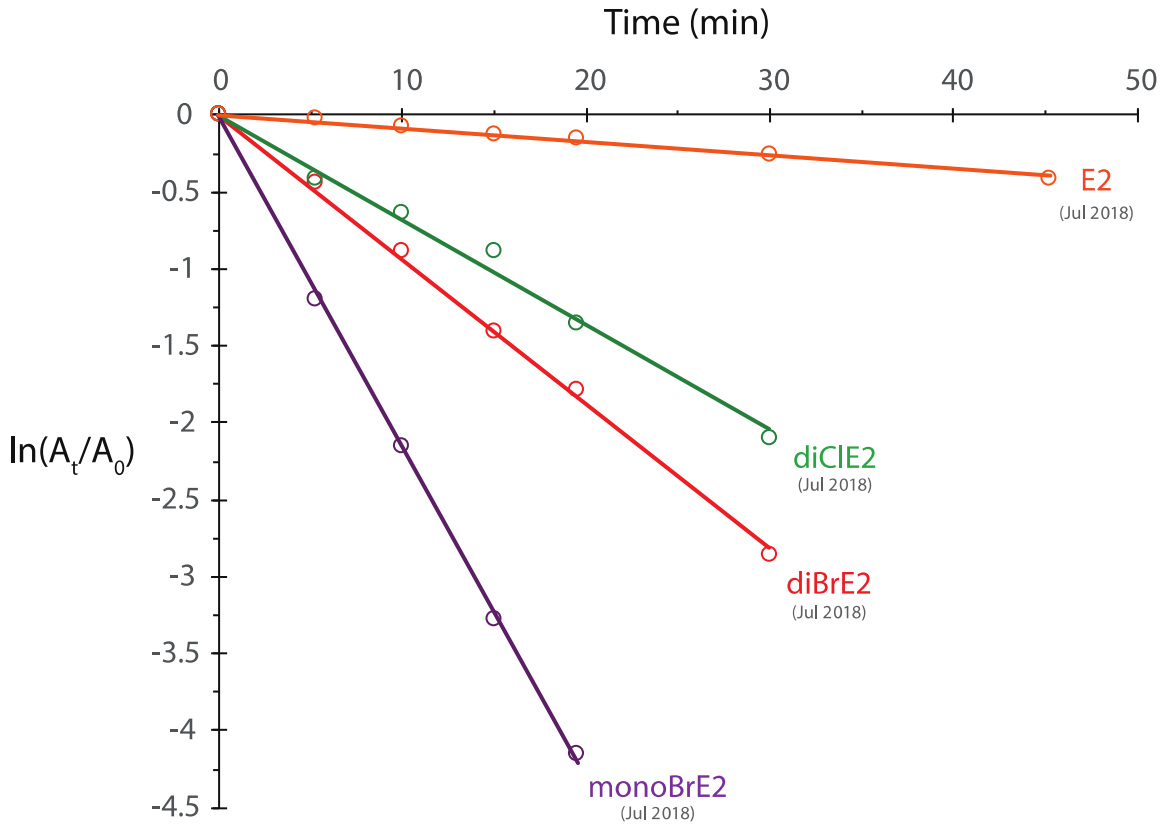

Figure S6. Direct photochemical degradation of E2 and three of its halogenated derivatives at pH 5.6 during the fall, winter, and spring seasons of 2015 and 2016 shows increasing rates as halogenation increases. Differences in photolysis rates of monoBrE2 and diBrE2 are attributed to seasonal differences in solar irradiation and small variability in solution pH.

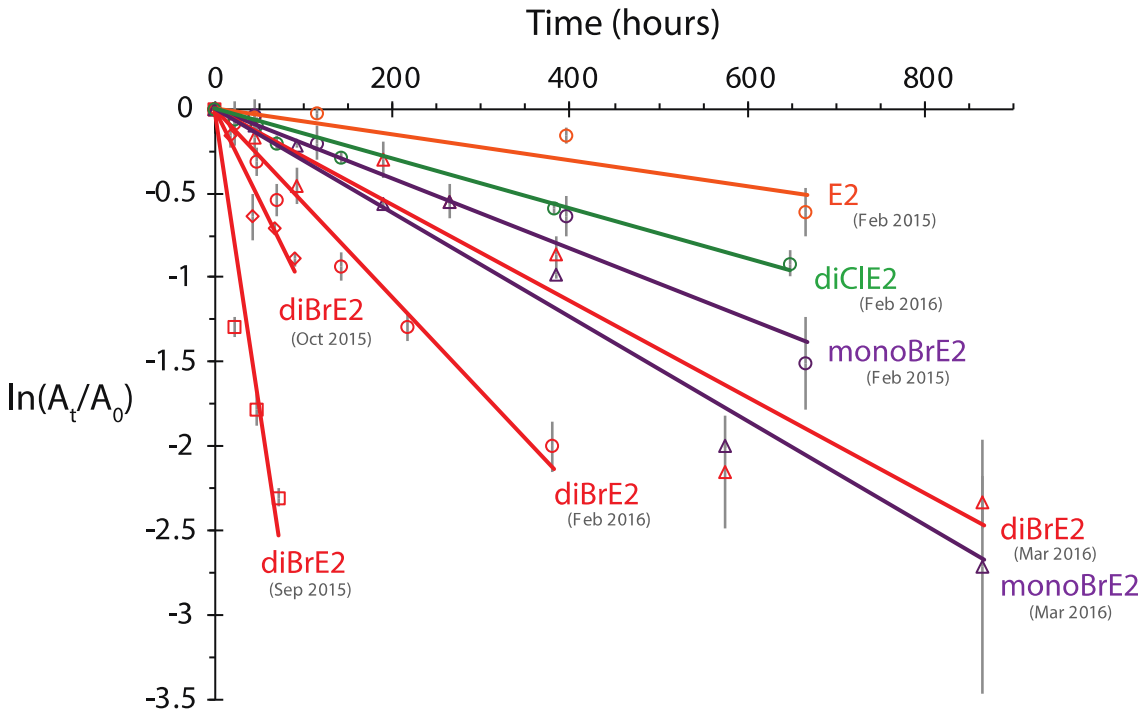

Figure S7. The direct photolysis rate of diBrE2 (10 July 2017; 25 July 2018) at pH 7 is slower in the presence of the quenchers sorbic acid and histidine. Rates are not significantly affected by the presence of isopropyl alcohol (IPA) or in solutions that were deoxygenated via sparging with N_2.

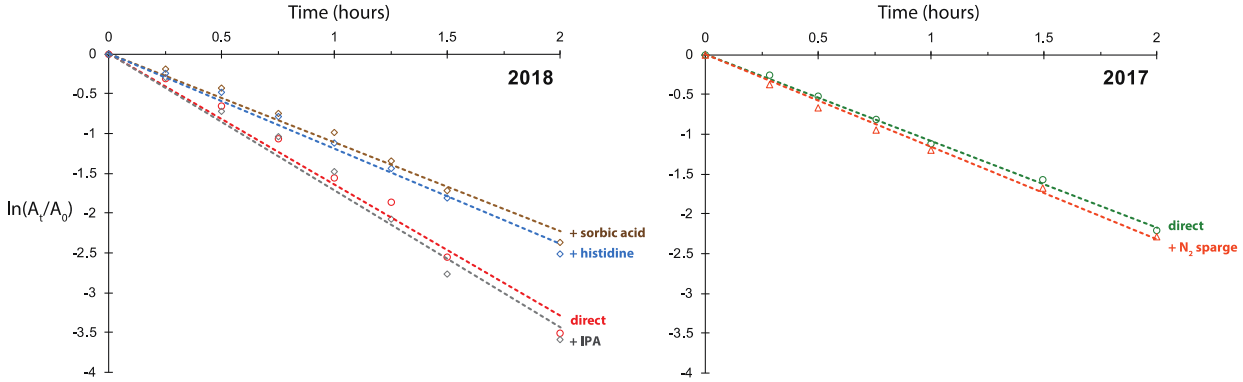

Table S1. Direct photolysis experimental conditions.

Estrogen	Date	Nominal Estrogen Concentration[a] (μM)	Actinometer[b,c,d]	Actinometer Concentration (μM)	Pyridine Concentration (mM)	pH	Methanol by Volume (%)
E2	13 Feb - 13 Mar 2015	3.77 ± 0.10	PNAP/ PYR	9.89 ± 0.14	48.8 ± 1.6	5.6[e]	0.197
monoBrE2		2.95 ± 0.08					
diBrE2	8 - 17 Sep 2015	3.08 ± 0.04	PNAP/ PYR	10.04 ± 0.07	49.5 ± 0.7	5.6[e]	0.100
diBrE2	14 - 18 Oct 2015	3.08 ± 0.07	PNAP/ PYR	10.04 ± 0.05	49.5 ± 0.3	5.6[e]	0.100
diBrE2	6 Feb - 4 Mar 2016	2.51 ± 0.19	PNAP/ PYR	10.04 ± 0.05	49.5 ± 0.3	5.6[e]	0
diClE2		3.63 ± 0.23					
monoBrE2	14 Mar - 19 Apr 2016	2.33 ± 0.11	PNAP/ PYR	10.04 ± 0.05	49.5 ± 0.3	5.6[e]	0
diBrE2		1.72 ± 0.09					
diBrE2	20 Jun - 8 Jul 2016	1.67 ± 0.19	PNAP/ PYR	10.00 ± 0.06	49.5 ± 0.3	4.0	0
diBrE2	5 Jun 2017	1.95 ± 0.19	PNA/ PYR	10.01 ± 0.12	5.00 ± 0.15	7.0	0
diBrE2	19 Jun 2017	2.25 ± 0.05	PNA/ PYR	10.01 ± 0.12	5.00 ± 0.15	7.0	0
diBrE2	10 Jul 2017	2.441 ± 0.016	PNA/ PYR	9.99 ± 0.23	5.00 ± 0.06	7.0	0
E2	20 Jul 2018	4.4 ± 0.4	PNA/PYR	10.007 ± 0.023	12.006 ± 0.027	13.0	0
monoBrE2		3.13 ± 0.29				12.0	
diBrE2		2.33 ± 0.05				12.0	
diClE2		3.81 ± 0.29				12.0	

[a] Predicted E2 aqueous solubility ~ 3.9 mg L^{-1} (14 μM);[1] predicted diBrE2 aqueous solubility ~ 0.32 mg L^{-1} (0.74 μM)[2]
[b] PNAP: *p*-nitroacetophenone
[c] PNA: *p*-nitroanisole
[d] PYR: pyridine
[e] pH of ultrapure deionized water was 5.6 ± 0.1

Table S2. Indirect photolysis experimental conditions.

Estrogen	Date	Nominal Estrogen Concentration[a] (μM)	Actinometer[b,c,d]	Actinometer Concentration (μM)	Pyridine Concentration (mM)	pH	Methanol by Volume (%)	SRHA[e] Concentration (mg L^{-1})
diBrE2	20 Jun - 8 Jul 2016	2.19 ± 0.09	PNAP/ PYR	10.00 ± 0.06	49.5 ± 0.3	4.0	0	5.16 ± 0.06
diBrE2	5 Jun 2017	1.95 ± 0.19	PNA/ PYR	10.01 ± 0.12	5.00 ± 0.15	7.0	0	4.90 ± 0.20
diBrE2	19 Jun 2017	2.25 ± 0.05	PNA/ PYR	10.01 ± 0.12	5.00 ± 0.15	7.0	0	4.88 ± 0.04
diBrE2	10 Jul 2017	2.441 ± 0.016	PNA/ PYR	9.99 ± 0.23	5.00 ± 0.06	7.0	0	4.960 ± 0.025

[a] Predicted diBrE2 aqueous solubility ~ 0.32 mg L^{-1} (0.74 μM)[2]
[b] PNAP: *p*-nitroacetophenone
[c] PNA: *p*-nitroanisole
[d] PYR: pyridine
[e] SRHA: Suwannee River Humic Acid (standard II)

Table S3. Characteristics of solutions used to determine molar absorptivity.

Estrogen	pH	Concentration (μM)	Methanol by Volume (%)	λ_{max}[b] (nm)	$\varepsilon_{\lambda max}$[c] ($M^{-1}$ cm^{-1})
E2	4.0	380.4 ± 1.3	50	280	1921 ± 19
diBrE2	4.0	307.6 ± 1.2	50	290	1370 ± 40
E2	5.6[a]	380.4 ± 1.3	50	279	1910 ± 60
monoBrE2	5.6[a]	282 ± 6	50	285	2920 ± 150
diBrE2	5.6[a]	307.6 ± 1.2	50	291	1617 ± 19
diClE2	5.6[a]	430.7 ± 1.8	50	290	1990 ± 110
diBrE2	7.0	na[b]	50	292	1822 ± 4
E2	13.0	95.5 ± 2.9	50	298	2300 ± 80
monoBrE2	12.0	74.7 ± 2.3	50	306	4590 ± 140
diBrE2	12.0	117.3 ± 2.4	50	310	5490 ± 110
diClE2	12.0	107.7 ± 2.6	50	306	4200 ± 90

[a] pH of ultrapure deionized water was 5.6 ± 0.1

[b] pH 7 spectrum calculated as a weighted average of diBrE2 spectra at pH 4 and pH 12

[b] λ_{max}: wavelength of peak absorbance (above 250nm)

[c] $\varepsilon\lambda_{\square\square\square}$: molar absorptivity at the wavelength of peak absorbance

REFERENCES

1. S. H. Yalkowsky and R. M. Dannenfelser, *The AQUASOL DATABASE of aqueous solubility, Version 5*, University of Arizona, Tucson, AZ, USA, 1992.

2. USEPA, *Estimation Programs Interface Suite for Microsoft Windows, v 4.11*, Washington, DC, USA, 2013.