

Supporting Information

Decomposition of Alkene Adducts of Thianthrene Cation Radical in Nitrile Solvents.

Formation of Alkyl-2-Oxazolines and a New Class of Four-Component Products: 5-

[(1-Alkoxyalkylidene)ammonio]alkylthianthrene Diperchlorates

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General experimental procedure

The procedure for drying solvent MeCN has been described earlier. Solvents EtCN and PrCN were used as purchased. All alkenes, alcohols, 2-amino-2-methylpropanol, and 2, 4, 4-trimethyl-2-oxazoline (**6**) were from commercial sources. A 300 MHz NMR instrument was used for following changes in ^1H NMR spectra over a period of time. A 500 MHz NMR instrument was used for obtaining all chemical shifts and coupling data for compounds **5a-u** and for characterizing **6**, **6-HClO₄**, **7-HClO₄**, and **12**. These data are listed as δ (J) in ppm and Herz. Values of J have been averaged. CD_3CN was used in all cases unless otherwise stated.

NMR Data

5b, 5-[2-[(1-ethoxyethylidene)ammonio]-2-methylpropyl]thianthrenium

diperchlorate, mp 148-9^oC/dec. ^1H : 9.21, br s, 1H; 8.21 (8.0, 1.5), dd, 2H; 8.02 (8.0, 1.0), dd, 2H; 7.86 (7.8, 1.5), td, 2H; 7.76 (7.8, 1.0), td, 2H; 4.39 (7.2), q, 2H; 4.16, s, 2H; 2.16, s, 3H; 1.57, s, 6H; 1.35 (7.0), t, 3H. ^{13}C : 180.7, 137.4, 136.2, 135.0, 131.7, 131.4, 118.1, 74.8, 58.8, 48.2, 26.4, 19.1, 14.3.

5c, 5-[2-[(1-propoxyethylidene)ammonio]-2-methylpropyl]thianthrenium

diperchlorate, mp 164-5^oC/dec. ^1H : 9.26, br s, 1H; 8.23 (8.3, 1.0), dd, 2H; 8.02 (8.0, 1.3), dd, 2H; 7.86 (7.8, 1.4), td, 2H; 7.76 (7.8, 1.5), td, 2H; 4.30 (6.8), t, 2H; 4.15, s, 2H; 2.19, s, 3H; 1.75 (6.9), sext, 2H; 1.58, s, 6H; 0.90 (7.5), t, 3H. ^{13}C : 180.9, 137.4, 136.2, 135.0, 131.7, 131.4, 118.2, 79.7, 58.8, 48.5, 26.5, 22.4, 19.3, 10.3.

5d, 5-[2-[(1-isopropoxyethylidene)ammonio]-2-methylpropyl]thianthrenium

diperchlorate, mp 152-3^oC/dec. ^1H : 9.15, br s, 1H; 8.22-8.19, m, 2H; 8.01 (8.0, 1.3), dd,

2H; 7.86 (7.7, 1.3), td, 2H; 7.76 (7.8, 1.4), td, 2H; 5.06 (6.0), hept, 1H; 4.12-4.11, m, 2H;
2.25, s, 3H; 1.56 (1.5), d, 6H; 1.34 (6.5) d, 6H. ¹³C: 179.8, 137.8, 136.2, 135.0, 131.8,
131.3, 85.8, 58.7, 49.3, 26.5, 22.1, 19.1.

5e, 5-[2-[(1-butoxyethylidene)ammonio]-2-methylpropyl]thianthrenium

diperchlorate, mp 169-170°C/dec. ¹H: 9.26, br s, 1H; 8.218 (7.8, 1.3), dd, 1H; 8.216 (8.3,
0.8), dd, 1H; 8.02 (8.3, 1.3), dd, 2H; 7.86 (7.6, 1.2), td, 2H; 7.76 (7.8, 1.5), td, 2H; 4.33
(6.8), t, 2H; 4.14, s, 2H; 2.19 (0.5), d, 3H; 1.69, m, 2H; 1.57, s, 6H; 1.30 (7.3), sext, 2H;
0.914 (7.3), t, 3H; ¹³C: 180.9, 137.3, 136.2, 135.0, 131.7, 131.4, 78.1, 58.8, 49.9, 48.6,
30.8, 26.4, 19.5, 19.3, 13.7.

5f, 5-[2-[(1-cyclohexyloxyethylidene)ammonio]-2-methylpropyl]thianthrenium

diperchlorate, mp 130-1°C/dec. ¹H: 9.18, br s, 1H; 8.22 (7.8, 1.3), dd, 2H; 8.01 (8.3, 1.3),
dd, 2H; 7.86 (7.8, 1.5), td, 2H; 7.76 (7.8, 1.5), td, 2H; 4.83 (9.3, 4.4), tt, 1H; 4.12, s, 2H;
2.27, s, 3H; 1.88-1.81, m, 2H; 1.68-1.61, m, 2H; 1.58, s, 6H; 1.56-1.49, m, 3H; 1.41-1.33,
m, 2H; 1.27-1.18, m, 1H. ¹³C: 179.8, 137.4, 136.2, 135.0, 131.8, 131.3, 118.5, 89.4, 58.7,
49.6, 32.0, 26.4, 25.0, 24.0, 19.2.

5h, 5-[2-[(1-methoxybuylidene)ammonio]-2-methylpropyl]thianthrenium

diperchlorate, mp 147-9°C/dec. ¹H: 9.16, br s, 1H; 8.20 (8.0, 1.5), dd, 2H; 8.02 (8.0,
1.5), dd, 2H; 7.86 (7.8, 1.5), td, 2H; 7.75 (7.8, 1.0), td, 2H; 4.19, s, 2H; 4.15, s, 2H; 2.46
(8.0), t, 2H; 1.60 (7.7), sext, 2H; 1.55, s, 6H; 1.00 (7.0), t, 3H. ¹³C: 183.7, 137.5, 136.1,
135.0, 131.8, 131.3, 63.1, 59.3, 48.5, 33.0, 26.5, 20.1, 13.6.

5i, 5-[2-[(1-methoxyethylidene)ammonio]-2-methylbutyl]thianthrenium

diperchlorate, mp 118-120°C/dec. ¹H: 9.16, br s, 1H; 8.21 (7.8, 1.3), dd, 2H; 8.03 (6.8,
1.3), dd, 1H overlapping 8.01 (6.8, 1.3), dd, 1H; 7.86 (7.8, 1.0), td, 1H overlapping 7.85

(7.8, 1.2), td, 1H; 7.76 (7.8, 1.5), td, 1H overlapping 7.75 (7.8, 1.5), td, 1H; 4.29 (14.5), d, 1H; 4.08, s, 3H; 4.07 (15.5), d, 1H; 2.25, s, 3H; 1.96 (14.4, 7.5), dq, 1H; 1.76 (14.8, 7.3), dq, 1H; 1.53, s, 3H; 0.853 (7.3), t, 3H. ^{13}C : 181.8, 137.6, 137.5, 136.2, 136.1, 135.0, 134.9, 131.77, 131.76, 131.4, 131.3, 63.3, 62.4, 47.7, 31.8, 22.8, 18.9, 7.8.

5j, 5-[2-[(1-ethoxyethylidene)ammonio]-2-methylbutyl]thianthrenium

diperchlorate, mp 158-9 $^{\circ}\text{C}$ /dec. ^1H : 9.08, br s, 1H; 8.22 (8.0, 1.5), dd, 1H overlapping 8.21 (8.0, 1.5), dd, 1H; 8.02 (7.4, 1.5), td, 2H; 7.863 (7.8, 1.5), td, 1H overlapping 7.856 (7.8, 1.5), td, 1H; 7.77 (7.6, 1.2), td, 1H overlapping 7.76 (7.6, 1.2), td, 1H; 4.44 (9.5, 7.0), dq, 1H; 4.37 (10.0, 7.1), dq, 1H; 4.26 (14.0), d, 1H; 4.05 (14.5), d, 1H; 2.20, s, 3H; 1.99 (14.5, 7.3), dq, 1H; 1.77 (14.5, 7.4), dq, 1H; 1.56, s, 3H; 1.34(7.0), t, 3H; 0.872 (7.3), t, 3H. ^{13}C : 180.9, 137.5, 137.4, 136.3, 136.1, 135.04, 134.97, 131.79, 131.77, 131.43, 131.34, 74.9, 61.2, 47.8, 31.8, 22.9, 19.1, 14.3, 7.8.

5k, 5-[2-[(1-propoxyethylidene)ammonio]-2-methylbutyl]thianthrenium

diperchlorate, mp 130-1 $^{\circ}\text{C}$ /dec. ^1H : 9.12, br s, 1H; 8.23 (8.3, 1.8), dd, 1H overlapping 8.22 (8.3, 1.8), dd, 1H; 8.03 (7.5, 1.0), dd, 1H overlapping 8.02 (7.5, 1.0), dd, 1H; 7.862 (7.6, 1.2), td, 1H overlapping 7.855 (7.8, 1.5), td, 1H; 7.77 (7.6, 1.2), td, 1H overlapping 7.76 (7.6, 1.2), td, 1H; 4.34 (9.5, 6.8), dt, 1H; 4.28 (9.5, 6.5), dt, 1H; 4.24 (14.5), d, 1H; 4.07 (14.0), d, 1H; 2.23, s, 3H; 1.98, m, 1H; 1.82-1.70, m, 3H; 1.57, s, 3H; 0.89 (7.5), t, 3H; 0.88 (7.3), t, 3H. ^{13}C : 181.1, 137.5, 137.3, 136.2, 136.1, 135.03, 134.97, 131.80, 131.77, 131.4, 131.3, 79.8, 62.2, 48.2, 31.9, 22.9, 22.4, 19.3, 10.3, 7.8.

5l, 5-[2-[(1-isopropoxyethylidene)ammonio]-2-methylbutyl]thianthrenium

diperchlorate, mp 124-5 $^{\circ}\text{C}$ /dec. ^1H : 9.03, br s, 1H; 8.22 (8.0, 1.5), dd, 2H; 8.02 (8.0, 1.0), dd, 1H overlapping 8.01 (8.0, 1.0), dd, 1H; 7.86 (7.8, 1.5), td, 1H overlapping 7.85 (7.8,

1.5), td, 1H; 7.76 (7.9, 1.2), td, 1H overlapping 7.55 (7.8, 1.3), td, 1H; 5.08 (6.1), hept, 1H; 4.17 (14.5), d, 1H; 4.07 (14.0), d, 1H; 2.03 (14.5, 7.3), dq, 1H; 1.76 (14.8, 7.3), dq, 1H; 1.54, s, 3H; 1.33 (6.5), d, 6H; 0.861 (7.3), t, 3H. ¹³C: 180.0, 137.5, 137.4, 136.2, 136.1, 135.0, 134.9, 131.9, 131.8, 131.4, 131.3, 118.6, 118.5, 83.6, 62.0, 49.0, 31.8, 22.9, 22.1, 22.0, 19.0, 7.7.

5m, 5-[2-[(1-butoxyethylidene)ammonio]-2-methylbutyl]thianthrenium

diperchlorate, mp 157-8^oC/dec. ¹H: 9.12, br s, 1H; 8.226 (8.5, 1.8), dd, 1H overlapping 8.223 (8.0, 1.5), dd, 1H; 8.03 (8.0, 1.0), dd, 1H overlapping 8.02 (7.0, 1.0), dd 1H; 7.863 (7.6, 1.2), td, 1H overlapping 7.856 (7.8, 1.3), td, 1H; 7.765 (7.6, 1.2), td, 1H overlapping 7.756 (7.8, 1.1), td, 1H; 4.38 (10.0, 6.8), dt, 1H; 4.31 (10.0, 6.5) dt, 1H; 4.23 (14.5), d, 1H; 4.04 (14.0), d, 1H; 2.24, s, 3H; 1.98 (14.8, 7.4), dq, 1H; 1.77 (14.8, 7.2), dq, 1H; 1.68, m, 2H; 1.56, s, 3H; 1.29 (7.5), sext, 2H; 0.91 (7.5), t, 3H; 0.87 (7.3), t, 3H. ¹³C: 181.1, 137.5, 137.3, 136.3, 136.1, 135.03, 134.97, 131.79, 131.77, 131.4, 131.3, 118.5, 78.3, 62.2, 48.3, 31.9, 30.8, 22.9, 19.4, 19.3, 13.7, 7.8.

5n, 5-[2-[(1-methoxypropylidene)ammonio]-2-methylbutyl]thianthrenium

diperchlorate, mp 146-7^oC/dec. ¹H: 8.92, br s, 1H; 8.197 (8.0, 0.5), dd, 1H overlapping 8.196(8.0, 0.5), dd, 1H; 8.02 (8.0, 1.0), dd, 1H overlapping 8.01 (8.0, 1.3), dd, 1H; 7.86 (7.6, 1.2), td, 1H overlapping 7.85 (7.8, 1.3), td, 1H; 7.76 (7.8, 1.5), td, 1H overlapping 7.75 (7.8, 1.0), td, 1H; 4.34 (14.0), d, 1H; 4.14, s, 3H; 4.02 (14.5), d, 1H; 2.55, m, 2H; 1.97, m, 1H; 1.71 (14.3, 7.3), dq, 1H; 1.55, s, 3H; 1.20 (7.5), t, 3H; 0.83 (7.5), t, 3H. ¹³C: 185.1, 137.7, 137.5, 136.2, 136.1, 135.0, 134.9, 131.8, 131.34, 131.25, 118.6, 63.1, 62.6, 48.2, 31.7, 25.6, 23.0, 10.2, 7.8.

5o, 5-[3-[(1-methoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium

diperchlorate, mp 148-150°C/dec. ¹H: 9.28, br s, 1H; 8.22 (7.8, 1.3), dd, 1H; 8.14 (8.0, 1.0), dd, 1H; 8.07 (8.0, 1.0), dd, 1H; 8.01 (8.0, 1.0), dd, 1H; 7.864 (7.8, 1.5), td, 1H overlapping 7.857 (7.8, 1.2), td, 1H; 7.79 (7.8, 1.3), td, 1H; 7.75 (7.8, 1.0), td, 1H; 5.18 (7.0), q, 1H; 4.01, s, 3H; 2.12, s, 3H; 1.71, s, 3H; 1.54, s, 3H; 1.10 (7.0), d, 3H. ¹³C: 182.0, 138.5, 138.1, 136.5, 136.2, 136.1, 135.5, 132.4, 131.9, 131.8, 131.1, 120.0, 118.1, 63.2, 63.1, 58.5, 25.8, 23.7, 19.1, 14.7.

5p, 5-[3-[(1-ethoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium

diperchlorate, mp 148-149°C/dec. ¹H: 9.26, br s, 1H; 8.26 (8.0, 1.0), dd, 1H; 8.16 (7.8, 1.3), dd, 1H; 8.07 (7.8, 1.3), dd, 1H; 8.01 (7.8, 1.3), dd, 1H; 7.860 (7.8, 1.5), td, 1H overlapping 7.857 (7.8, 1.0), td, 1H; 7.79 (7.8, 1.0), td, 1H; 7.75 (7.6, 1.2), td, 1H; 5.13 (7.2), q, 1H; 4.44 (10.0, 7.2), dq, 1H; 4.23 (9.5, 7.0), dq, 1H; 2.14, s, 3H; 1.71, s, 3H; 1.57, s, 3H; 1.29 (7.0), t, 3H; 1.09 (7.0), d, 3H. ¹³C: 181.0, 138.5, 138.1, 136.6, 136.3, 136.1, 135.6, 132.4, 131.9, 131.7, 131.1, 120.3, 118.1, 74.8, 62.9, 58.5, 25.6, 24.0, 19.4, 15.0, 14.3.

5q, 5-[3-[(1-propoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium

diperchlorate, mp 143-144°C/dec. ¹H: 9.29, br, s, 1H; 8.25 (8.0, 1.5), dd, 1H; 8.17 (8.0, 1.5), dd, 1H; 8.07 (8.0, 1.5), dd, 1H; 8.01 (7.8, 1.3), dd, 1H; 7.863 (7.8, 1.5), td, 1H overlapping 7.858 (7.8, 1.5), td, 1H; 7.79 (7.8, 1.5), td, 1H; 7.75 (7.8, 1.2), td, 1H; 5.05 (7.2), q, 1H; 4.35 (9.5, 6.8), dt, 1H; 4.12 (9.5, 6.6), dt, 1H; 2.17, s, 3H; 1.71, s, 2H; 1.67, m, 3H; 1.59, s, 3H; 1.09 (7.0), d, 3H; 0.85 (7.5), t, 3H. ¹³C: 181.2, 138.5, 138.1, 136.6, 136.3, 136.1, 135.6, 132.4, 131.9, 131.7, 131.1, 120.4, 118.1, 79.8, 62.9, 59.0, 25.5, 24.2, 22.4, 19.6, 15.0, 10.4.

5r, 5-[3-[(1-isopropoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium
diperchlorate, mp 108-109^oC/dec. ¹H: 9.23, br s, 1H; 8.25 (8.0, 1.5), dd, 1H; 8.16 (8.0,
1.0), dd, 1H; 8.06 (8.0, 1.0), dd, 1H; 8.01 (7.8, 1.3), dd, 1H; 7.86 (7.8, 1.3), td, 2H; 7.80
(7.8, 1.3), td, 1H; 7.75 (7.8, 1.3), td, 1H; 5.00 (7.2), q, 1H overlapping 4.98 (6.1), hept,
1H; 2.22, s, 3H; 1.71, s, 3H; 1.59, s, 3H; 1.32 (6.5), d, 3H; 1.22 (6.5), d, 3H; 1.09 (7.0), d,
3H. ¹³C: 180.0, 138.4, 138.2, 136.6, 136.2, 136.1, 135.6, 132.6, 131.9, 131.7, 131.1,
120.6, 118.1, 85.8, 62.8, 58.8, 25.7, 24.3, 22.1, 21.2, 19.4, 15.1.

5s, 5-[3-[(1-butoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium
diperchlorate, mp 114-115^oC/dec. ¹H: 9.29, br s, 1H; 8.26 (8.0, 1.0), dd, 1H; 8.17 (8.0,
1.0), dd, 1H; 8.07 (8.0, 1.5), dd, 1H; 8.01 (8.0, 1.0), dd, 1H; 7.87 (7.8, 1.5), td, 1H
overlapping 7.86 (7.8, 1.2), td, 1H; 7.79 (7.8, 1.5), td, 1H; 7.75 (7.8, 1.2), td, 1H; 5.04
(7.0), q, 1H; 4.38 (10.0, 6.8), dt, 1H; 4.16 (9.5, 6.5), dt, 1H; 2.19, s, 3H; 1.71, s, 3H; 1.63,
m, 2H; 1.59, s, 3H; 1.25, sext, 2H; 1.09 (7.0), d, 3H; 0.91 (7.0), t, 3H. ¹³C: 181.2, 138.4,
138.1, 136.6, 136.3, 136.1, 135.6, 132.2, 131.9, 131.7, 131.1, 120.4, 118.2, 78.2, 62.8,
59.1, 30.7, 25.5, 24.3, 19.7, 15.0, 13.8.

5t, 5-[3-[(1-methoxypropylidene)ammonio]-3-methyl-2-butyl]thianthrenium
diperchlorate, mp 143-144^oC/dec. ¹H: 9.04, br s, 1H; 8.23 (8.0, 1.0), dd, 1H; 8.15 (8.0,
1.5), dd, 1H; 8.06 (8.0, 1.0), dd, 1H; 8.01 (8.0, 1.5), dd, 1H; 7.858 (8.0, 1.5), td, 1H
overlapping 7.855 (7.8, 1.2), td, 1H; 7.77 (7.8, 1.5), td, 1H; 7.45 (7.6, 1.2), td, 1H; 5.18
(7.2), q, 1H; 4.07, s, 3H; 2.47 (15.5, 7.6), dq, 1H; 2.36 (15.8, 7.7), dq, 1H; 1.71, s, 3H;
1.57, s, 3H; 1.16 (7.8), t, 3H; 1.09 (7.0), d, 3H. ¹³C: 185.0, 138.6, 138.2, 136.5, 136.2,
136.1, 135.5, 132.4, 131.8, 131.6, 131.1, 120.0, 118.1, 63.4, 63.0, 58.6, 25.72, 25.68,
24.1, 14.9, 9.7.

5u, 5-[2-[(1-methoxyethylidene)ammonio]-2-methylpentyl]thianthrenium

diperchlorate, mp 172-173^oC/dec. ¹H: 9.2, br s, 1H; 8.22 (8.5, 1.3), dd, 1H; 8.02 (7.8, 1.3), dd, 1H overlapping 8.01 (7.8, 1.8), dd, 1H; 7.86 (7.5, 1.5), td, 1H overlapping 7.85 (7.8, 1.5), td, 1H; 7.76 (7.8, 1.0), td, 1H; 7.75 (7.6, 1.3), td, 1H; 4.27 (14.0), d, 1H; 4.08 (15.5), d, 1H; 4.09, s, 3H; 2.26, s, 3H; 1.86 (13.9, 12.2, 4.4), ddd, 1H; 1.67 (14.0, 12.3, 4.5), ddd, 1H; 1.54, s, 3H; 1.25, m, 2H; 0.86, s, 3H. ¹³C: 181.8, 137.6, 137.5, 136.2, 136.1, 135.03, 134.97, 131.8, 131.7, 131.4, 131.3, 118.4, 118.3, 63.2, 62.0, 47.8, 40.8, 23.4, 18.9, 17.1, 13.9.

12, ¹H: 13.16, br s, 1H; 8.85 (2.5), d, 1H; 8.44 (8.3, 2.3), dd, 1H; 7.54 (8.5), d, 1H; 4.23 (10.8, 7.2), dq, 1H; 4.05 (10.8, 7.1), dq, 1H; 1.93, s, 3H; 1.13 (7.3), t, 3H. ¹³C: 174.3, 170.0, 149.6, 147.1, 136.6, 135.3, 126.7, 120.1, 99.8, 61.5, 20.0, 13.8.

X-Ray Crystallography and Ortep Diagrams

Each single crystal was glued to a glass fiber and mounted on a Bruker Smart 1000 diffractometer equipped with a CCD area detector. Graphite monochromated MoK α radiation ($\lambda = 0.71073\text{\AA}$) in the ω -2 θ scanning mode was used. The data were collected at room temperature and corrected for Lorentz and polarization effects. An absorption correction was applied using the program SADABS. No decay of the crystals was detected during data collection. Heavy atoms in the compounds were located using Patterson methods. The structures were solved using direct methods using the SHELXTL software package and refined by full matrix least-square techniques on F^2 . Hydrogen atoms were included in calculated positions and refined using riding model. All thermal ellipsoids are drawn at the 50% probability level.

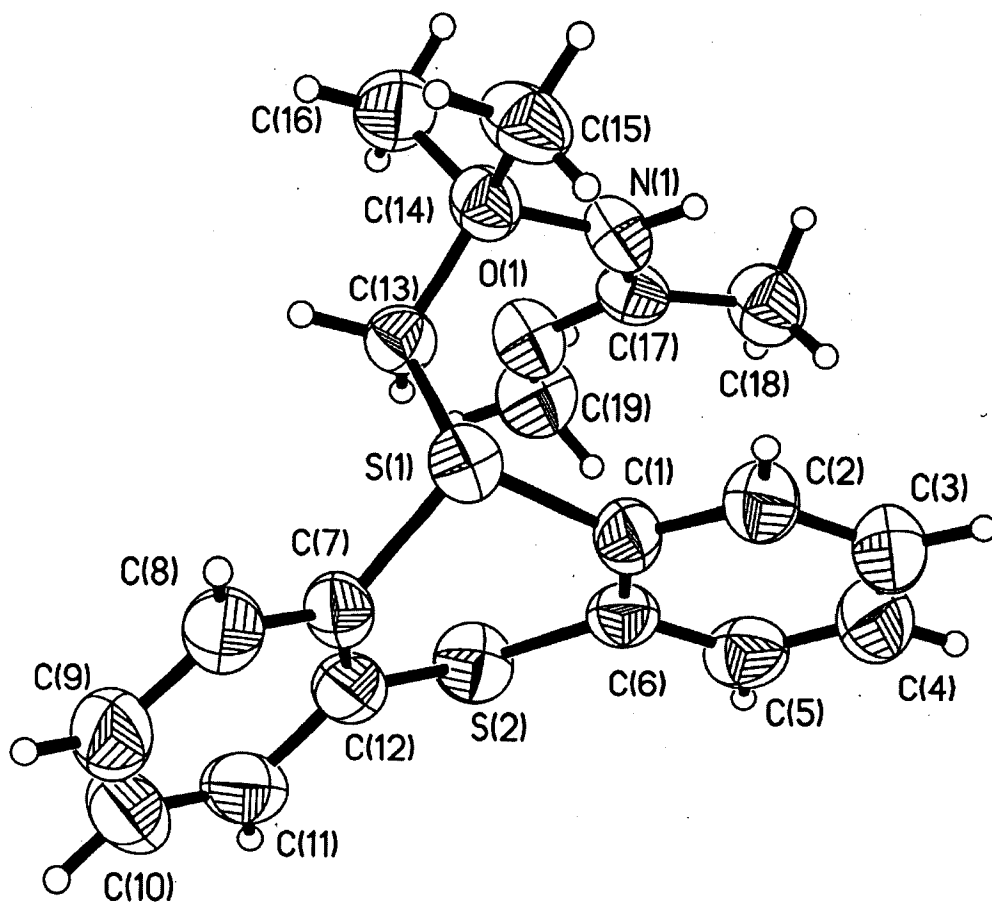


Fig. S1 Ortep diagram of 5-[2-[(1-methoxyethylidene)ammonio]-2-methylpropyl]thianthrenium diperchlorate, $C_{19}H_{23}Cl_2NO_9S_2$ (**5a**). The perchlorate ions are omitted.

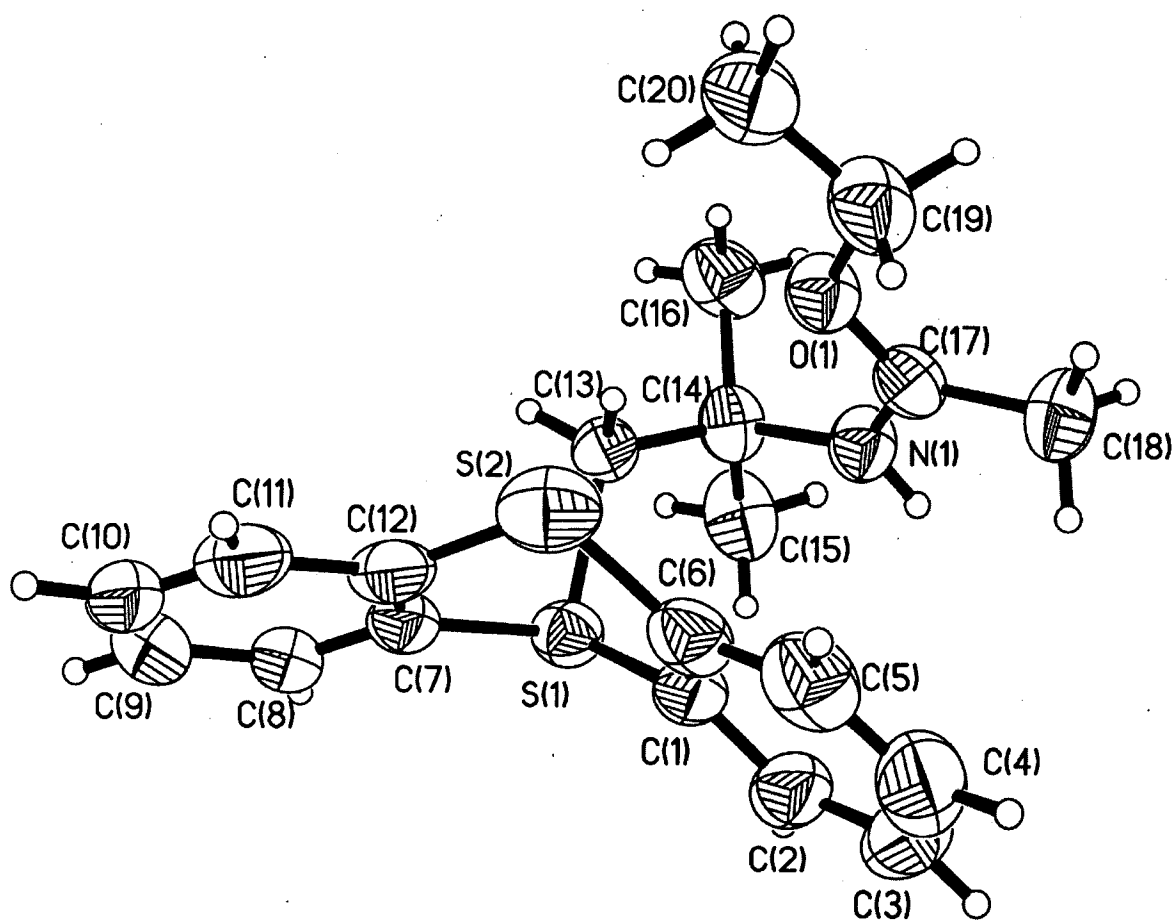


Fig. S2 Ortep diagram of 5-[2-[(1-ethoxyethylidene)ammonio]-2-methylpropyl]thianthrenium diperchlorate, $C_{20}H_{25}Cl_2NO_9S_2$ (**5b**). The perchlorate ions are omitted.

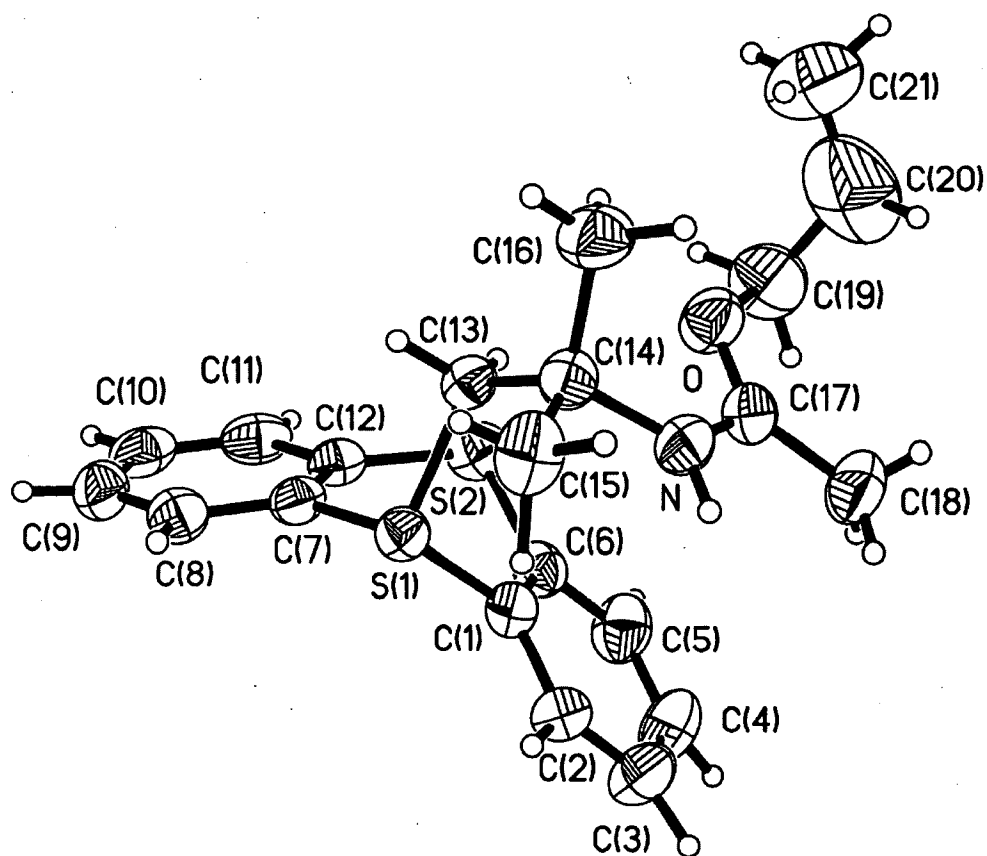


Fig. S3 Ortep diagram of 5-[2-[(1-propoxyethylidene)ammonio]-2-methylpropyl]thianthrenium diperchlorate, $C_{21}H_{27}Cl_2NO_9S_2$ (**5c**). The perchlorate ions are omitted.

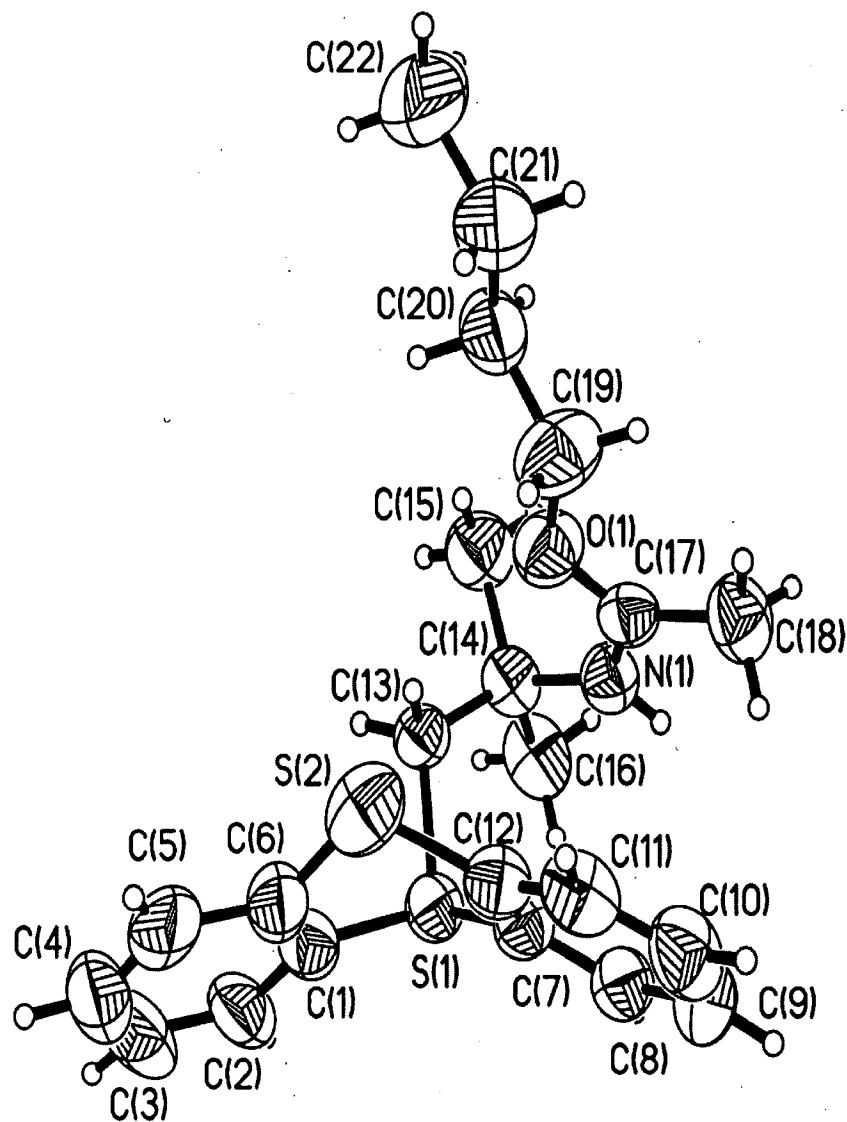


Fig. S4 Ortep diagram of 5-[2-[(1-butoxyethylidene)ammonio]-2-methylpropyl]thianthrenium diperchlorate, $C_{22}H_{29}Cl_2NO_9S_2$ (**5e**). The perchlorate ions are omitted.

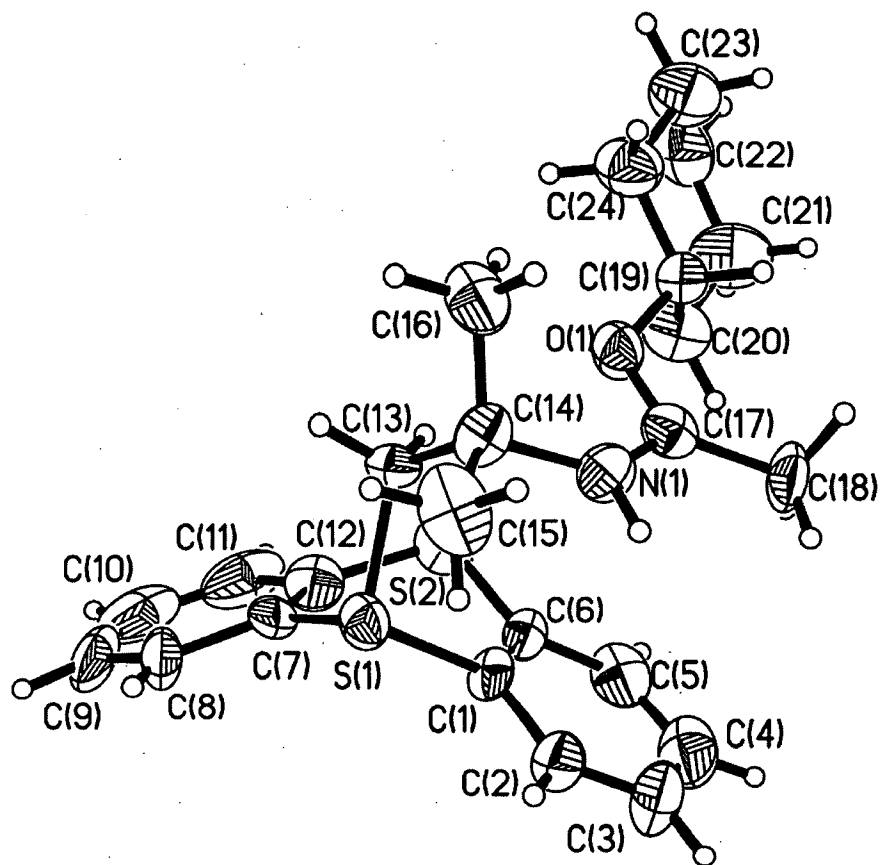


Fig. S5 Ortep diagram of 5-[2-[(1-cyclohexyloxyethylidene)ammonio]-2-methylpropyl]thianthrenium diperchlorate, $C_{24}H_{31}Cl_2NO_9S_2$ (**5f**). The perchlorate ions are omitted.

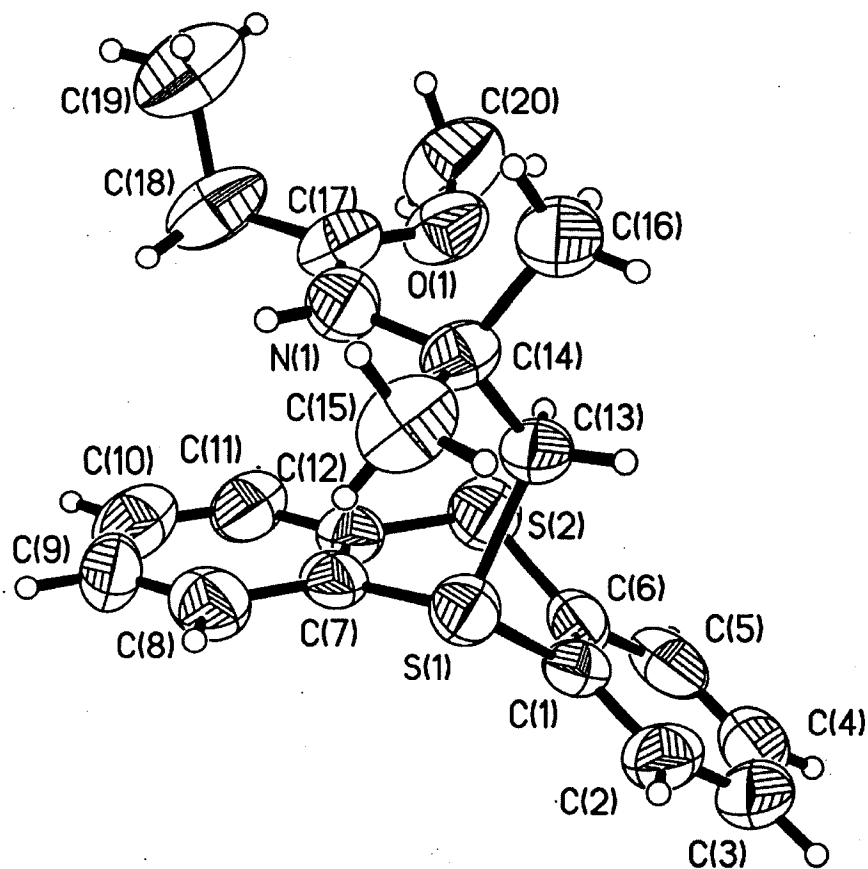


Fig. S6 Ortep diagram of 5-[2-[(1-methoxypropylidene)ammonio]-2-methylpropyl]thianthrenium diperchlorate, $C_{20}H_{25}Cl_2NO_9S_2$ (**5g**). The perchlorate ions are omitted.

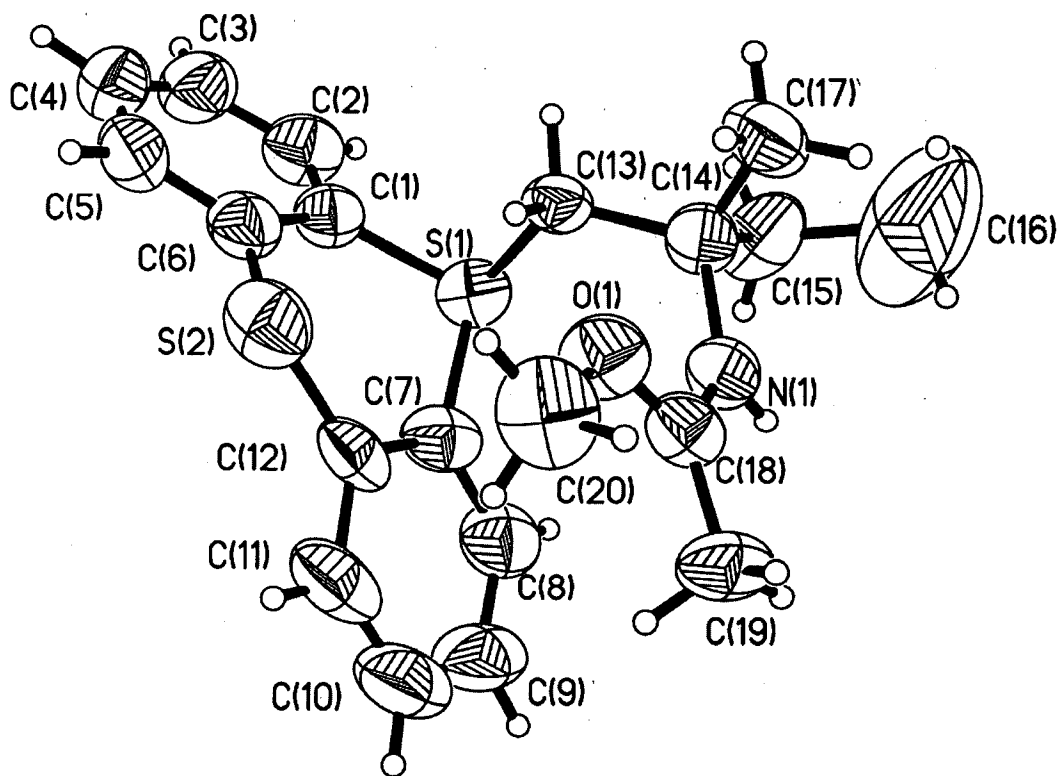


Fig. S7 Ortep diagram of 5-[2-[(1-methoxyethylidene)ammonio]-2-methylbutyl]thianthrenium diperchlorate, $C_{20}H_{25}Cl_2NO_9S_2$ (**5i**). The perchlorate ions are omitted.

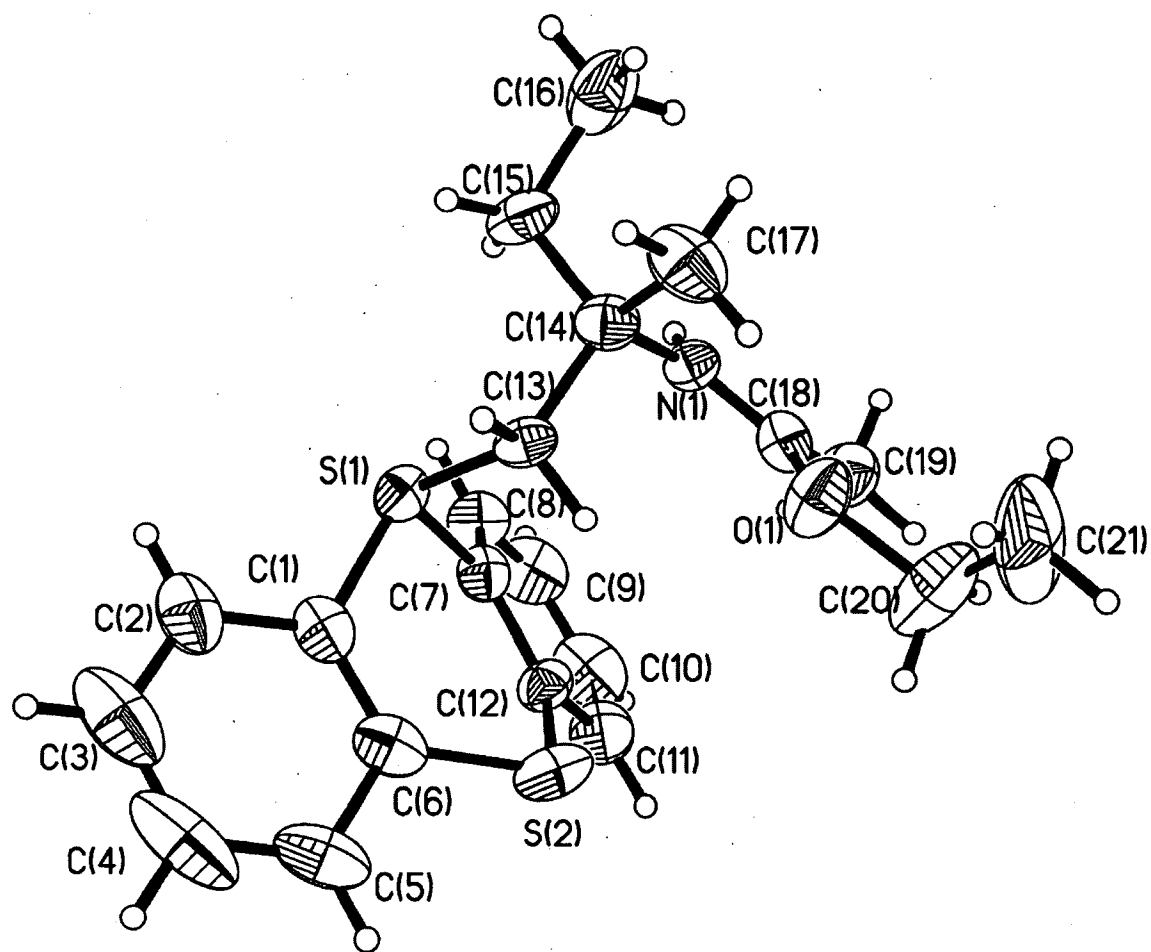


Fig. S8 Ortep diagram of 5-[2-[(1-ethoxyethylidene)ammonio]-2-methylbutyl]thianthrenium diperchlorate, $C_{21}H_{27}Cl_2NO_9S_2$ (**5j**). The perchlorate ions are omitted.

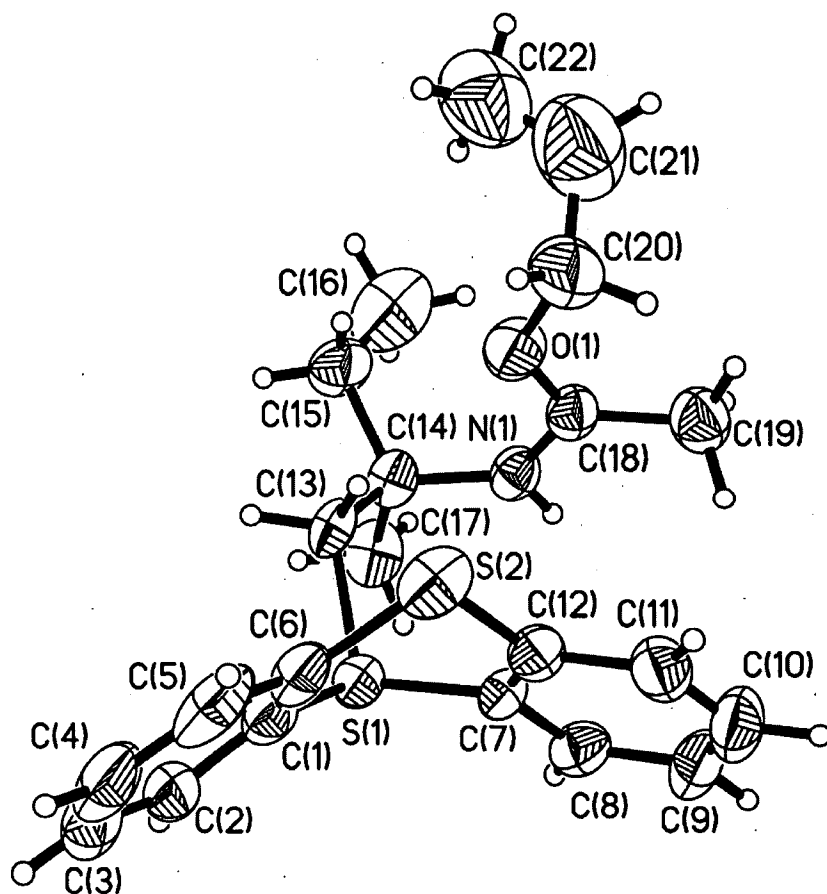


Fig. S9 Ortep diagram of 5-[2-[(1-propoxyethylidene)ammonio]-2-methylbutyl]thianthrenium diperchlorate, $C_{22}H_{29}Cl_2NO_9S_2$ (**5k**). The perchlorate ions are omitted.

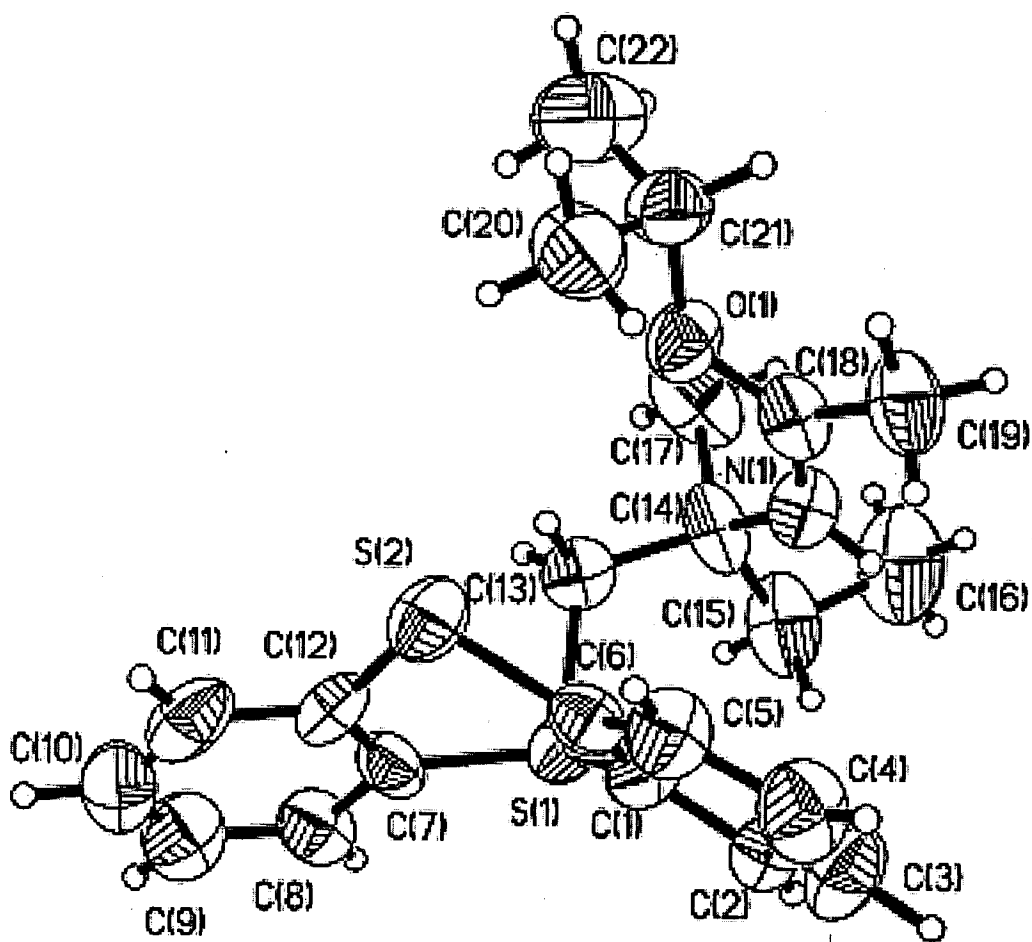


Fig. S10 Ortep diagram of 5-[2-[(1-isopropoxyethylidene)ammonio]-2-methylbutyl]thianthrenium diperchlorate, $C_{22}H_{29}Cl_2NO_9S_2$ (**5I**). The perchlorate ions are omitted.

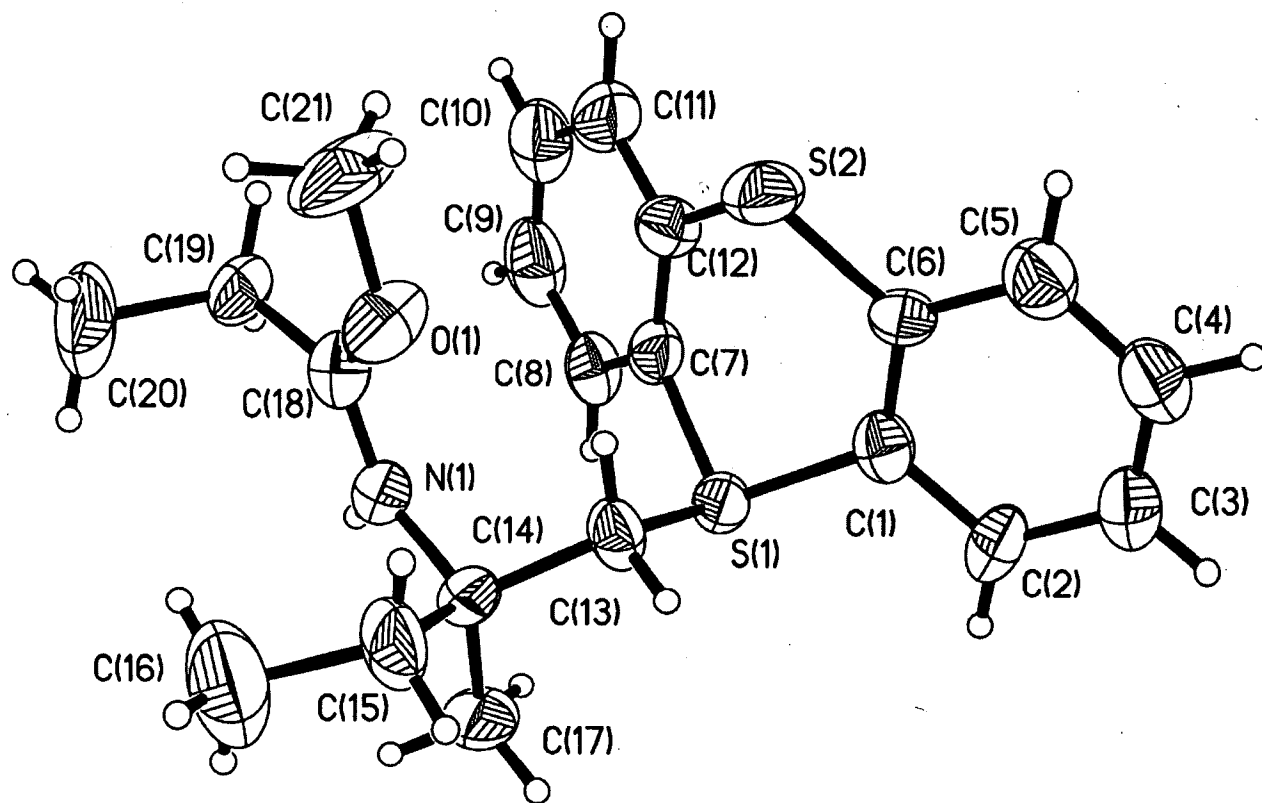


Fig. S11 Ortep diagram of 5-[2-[(1-methoxypropylidene)ammonio]-2-methylbutyl]thianthrenium diperchlorate, $C_{21}H_{27}Cl_2NO_9S_2$ (**5n**). The perchlorate ions are omitted.

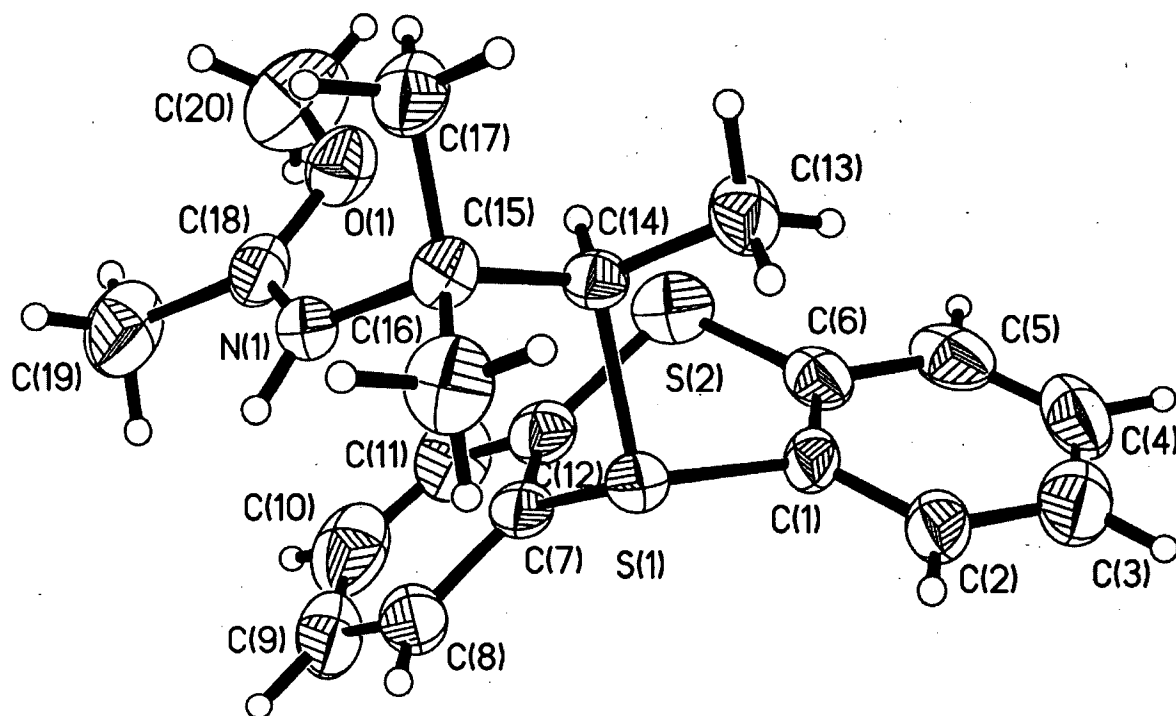


Fig. S12 Ortep diagram of 5-[3-[(1-methoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium diperchlorate, $C_{20}H_{25}Cl_2NO_9S_2$ (**5o**). The perchlorate ions are omitted.

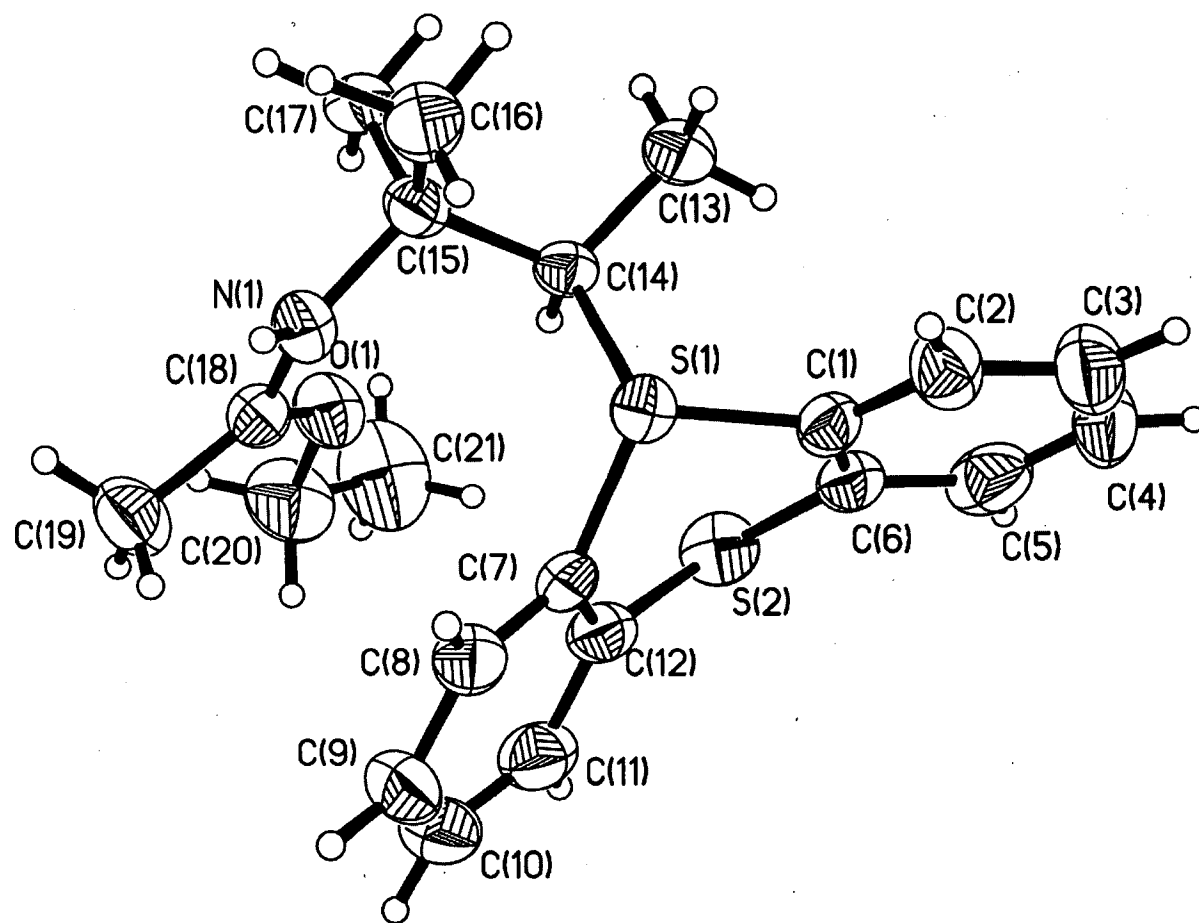


Fig. S13 Ortep diagram of 5-[3-[(1-ethoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium diperchlorate, $C_{21}H_{27}Cl_2NO_9S_2$ (**5p**). The perchlorate ions are omitted.

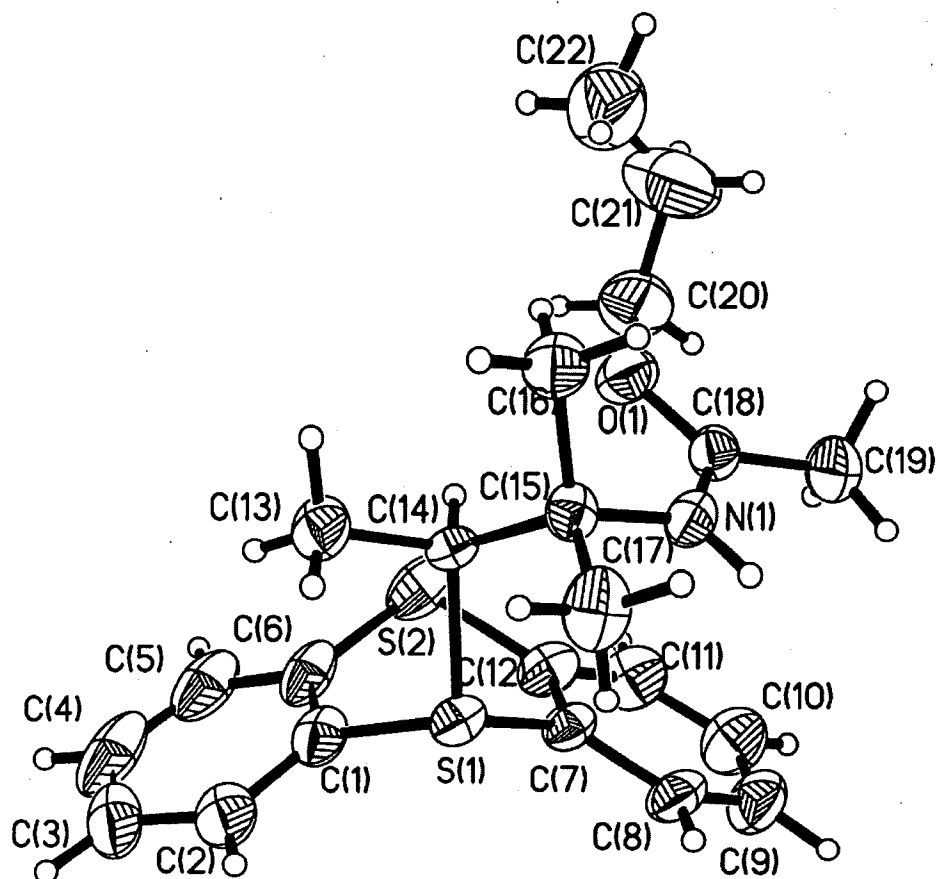


Fig. S14 Ortep diagram of 5-[3-[(1-propoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium diperchlorate, $C_{22}H_{29}Cl_2NO_9S_2$ (**5q**). The perchlorate ions are omitted.

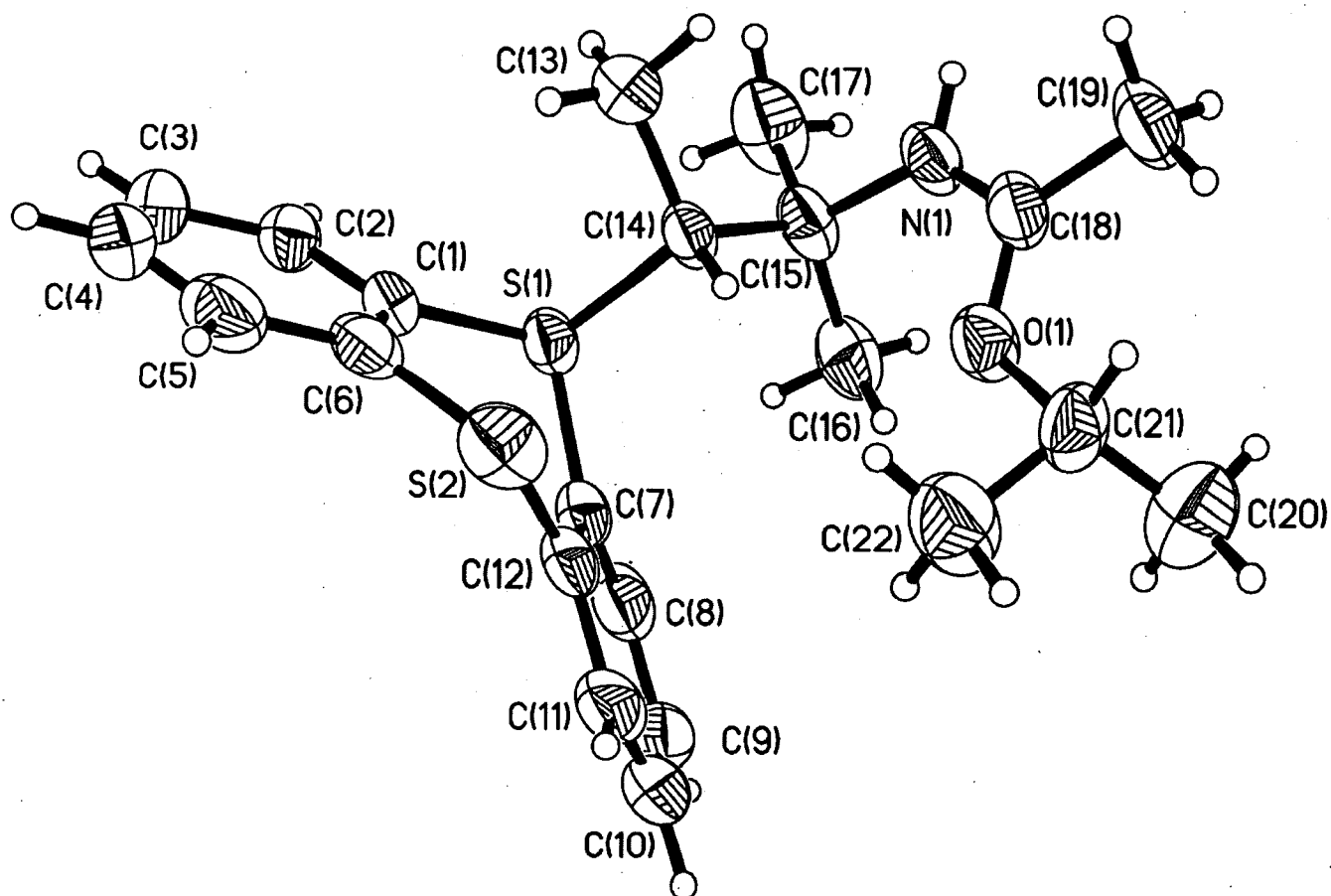


Fig. S15 Ortep diagram of 5-[3-[(1-isopropoxyethylidene)ammonio]-3-methyl-2-butyl]thianthrenium diperchlorate, $C_{22}H_{29}Cl_2NO_9S_2 \cdot CH_3CN(5r)$. The perchlorate ions and solvent of crystallization are omitted.