Substituent Effects on the Inclusion of 1-Alkyl-6-Alkoxy-Quinolinium in 4-Sulfonatocalix[n]arenes

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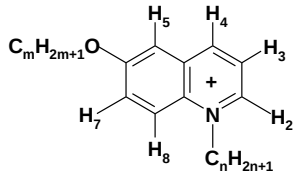

X^- with $X^- = I^-$ or Br^-

Synthesis

1-Methyl-6-methoxy-quinolinium iodide ($C_1C_1OQ^+I^-$) was synthesized as described previously[1]. ^{1}H NMR (DMSO): 4.0 (s, 3H, 0-CH_3); 4.60 (s, 3H, N-CH_3); 7.90 (m, 2H, H_5 and H_7); 8.10 (m, 1H, H_3); 8.43 (d, 1H, H_8); 9.10 (d, 1H, H_4); 9.30 (d, 1H, H_2).

1-Ethyl-6-methoxy-quinolinium bromide ($C_2C_1OQ^+Br^-$), 1-butyl-6-methoxy-quinolinium iodide ($C_4C_1OQ^+I^-$), 1-hexyl-6-methoxy-quinolinium bromide ($C_6C_1OQ^+Br^-$) and 1-octyl-6-methoxy-quinolinium bromide ($C_8C_1OQ^+Br^-$) were synthesized as follows: 6-methoxyquinoline with a 10% molar excess of 1-bromoethane, 1-iodobutane, 1-bromohexane or 1-bromooctane was heated at 90°C in toluene (or in acetonitrile) in a closed vessel for 18 hours. After cooling, water was added, and the aqueous phase was extracted several times by diethyl ether. After evaporation of the aqueous phase, oily compounds were obtained; they turned in waxy compounds after drying under vacuum (except $C_2C_1OQ^+Br^-$ that was isolated as a beige powder).

^{1}H NMR (DMSO)

$C_2C_1OQ^+Br^-$: 1.58 (t, 3H, CH_3); 4.0 (s, 3H, O-CH_3); 5.05 (q, 2H, N-CH_2); 7.90 (m, 2H, H_5 and H_7); 8.10 (m, 1H, H_3); 8.53 (d, 1H, H_8); 9.09 (d, 1H, H_4); 9.35 (d, 1H, H_2)

$C_4C_1OQ^+I^-$: 0.92 (t, 3H, CH_3); 1.38 (m, 2H, CH_3-$\underline{CH_2}$); 1.92 (m, 2H, CH_3-CH_2-$\underline{CH_2}$); 4.0 (s, 3H, O-CH_3); 5.03 (t, 2H, N-CH_2); 7.90 (m, 2H, H_5 and H_7); 8.13 (m, 1H, H_3); 8.55 (d, 1H, H_8); 9.12 (d, 1H, H_4); 9.39 (d, 1H, H_2)

$C_6C_1OQ^+Br^-$: 0.85 (t, 3H, CH_3); 1.27 (m, 4H, CH_3-($\underline{CH_2}$)$_2$); 1.37 (m, 2H, CH_3-$(CH_2)_2$-$\underline{CH_2}$); 1.93 (m, 2H, CH_3-$(CH_2)_3$-$\underline{CH_2}$); 4.0 (s, 3H, O-CH_3); 5.03 (t, 2H, N-CH_2); 7.90 (m, 2H, H_5 and H_7); 8.12 (m, 1H, H_3); 8.55 (d, 1H, H_8); 9.12 (d, 1H, H_4); 9.38 (d, 1H, H_2)

[1] C. D. Geddes, K. Apperson, and D. J. S. Birch: *Dyes Pigments* **44**, 69-74 (2000)

$C_8C_1OQ^+Br^-$: 0.83 (t, 3H, CH_3); 1.22 (m, 8H, CH_3-($\underline{CH_2}$)$_4$); 1.36 (m, 2H, CH_3-(CH_2)$_4$-$\underline{CH_2}$); 1.93 (m, 2H, CH_3-(CH_2)$_5$-$\underline{CH_2}$); 4.0 (s, 3H, O-CH_3); 5.03 (t, 2H, N-CH_2); 7.91 (m, 2H, H_5 and H_7); 8.12 (m, 1H, H_3); 8.55 (d, 1H, H_8); 9.12 (d, 1H, H_4); 9.38 (d, 1H, H_2)

1-Methyl-6-ethoxy-quinolinium iodide ($C_1C_2OQ^+I^-$), 1-methyl-6-butoxy-quinolinium iodide ($C_1C_4OQ^+I^-$), and 1-methyl-6-hexoxy-quinolinium iodide ($C_1C_6OQ^+I^-$) were synthesized as follows: in the first step, 6-hydroxyquinoline was mixed with twice a molar excess of K_2CO_3 in 3:7 water:dimethylformamide solvent. After stirring at room temperature during one hour, an equimolecular amount of 1-bromoethane (or 1-bromobutane, or 1-bromohexane) was added. The mixture was heated for 6 hours at 90°C. After cooling, the mixture was filtered and the liquid phase was extracted twice with diethylether. 6-Ethoxyquinoline (or 6-butoxyquinoline, or 6-hexoxyquinoline) was obtained after drying and evaporation of the organic phase. The quinoline derivatives were purified by column chromatography over silica gel with dichloromethane as eluent. In the second step, the quinoline derivatives were heated at 90°C with a 10% molar excess of iodomethane in toluene for 6 hours. After cooling, the iodide salts were filtered and washed with diethyl ether, and then dried under vacuum.

^{1}H NMR (DMSO)

$C_1C_2OQ^+I^-$: 1.45 (t, 3H, CH_3); 4.29 (q, 2H, O-CH_2); 4.60 (s, 3H, N-CH_3); 7.91 (m, 2H, H_5 and H_7); 8.09 (m, 1H, H_3); 8.43 (d, 1H, H_8); 9.08 (d, 1H, H_4); 9.30 (d, 1H, H_2)

$C_1C_4OQ^+I^-$: 0.97 (t, 3H, CH_3); 1.50 (m, 2H, CH_3-$\underline{CH_2}$); 1.81 (m, 2H, CH_3-CH_2-$\underline{CH_2}$); 4.22 (t, 2H, O-CH_2); 4.60 (s, 3H, N-CH_3); 7.90 (m, 2H, H_5 and H_7); 8.09 (m, 1H, H_3); 8.42 (d, 1H, H_8); 9.08 (d, 1H, H_4); 9.30 (d, 1H, H_2)

$C_1C_6OQ^+I^-$: 0.89 (t, 3H, CH_3); 1.34 (m, 4H, CH_3-($\underline{CH_2}$)$_2$); 1.47 (m, 2H, CH_3-(CH_2)$_2$-$\underline{CH_2}$); 1.82 (m, 2H, CH_3-(CH_2)$_3$-$\underline{CH_2}$); 4.21 (t, 2H, O-CH_2); 4.60 (s, 3H, N-CH_3); 7.90 (m, 2H, H_5 and H_7); 8.10 (m, 1H, H_3); 8.42 (d, 1H, H_8); 9.08 (d, 1H, H_4); 9.30 (d, 1H, H_2)

ITC experiments

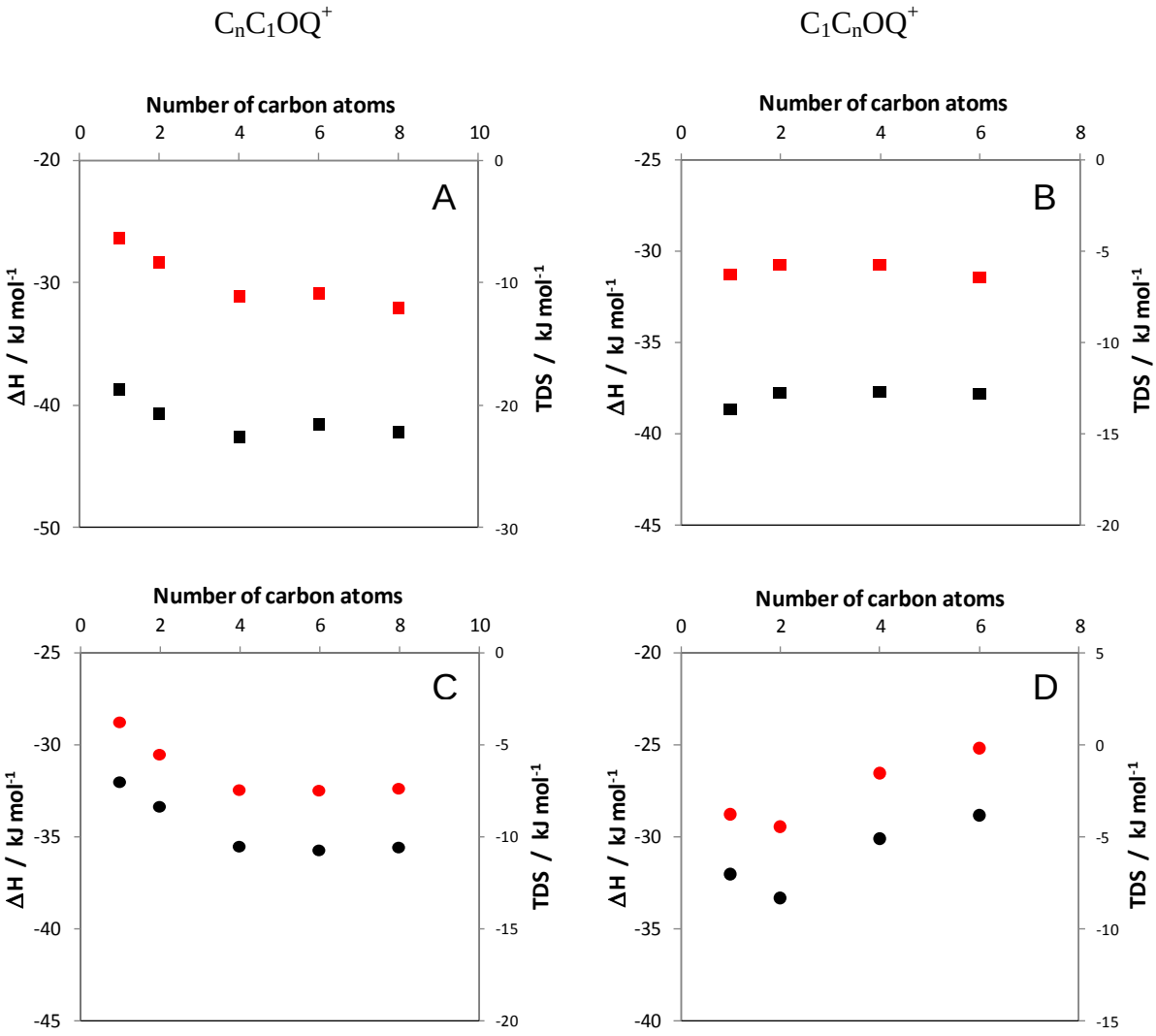

Figure S1 Enthalpic (black) and entropic (red) contributions related to the formation of $C_nC_1OQ^+$–SCX4 (A), $C_1C_nOQ^+$–SCX4 (B), $C_nC_1OQ^+$–SCX6 (C), and $C_1C_nOQ^+$–SCX6 (D) complexes as a function of the alkyl or alkoxy chain length at pH 7 and 298 K.

^{1}H NMR experiments

Table S1. Variations of the ^{1}H NMR chemical shift related to the quinolinium species $C_nC_1OQ^+$, as observed upon their complexation with SCX4. These data were determined at 2:1 SCX4:$C_nC_1OQ^+$ molar ratio and a total concentration of 10 mM.

Δδ (ppm)	H2	H3	H4	H5	H7	H8	N-CH_3	O-CH_3			
$C_1C_1OQ^+$[a]	-3.695	-3.565	-2.848	-0.553	-0.287	-0.669	-1.074	-0.085			
Δδ (ppm)	H2	H3	H4	H5	H7	H8	N-CH_2(α)	O-CH_3	CH_2(β)	CH_2(γ)	CH_3
$C_2C_1OQ^+$	-3.624	-3.634	-3.095	-0.565	-0.255	-0.524	-0.889	-0.044	--	--	-0.557
$C_4C_1OQ^+$	-3.532	-3.640	-3.209	-0.613	-0.269	-0.477	-0.757	-0.061	-0.460	-0.438	-0.244
$C_6C_1OQ^+$	-3.525	-3.762	-3.343	-0.655	-0.291	-0.473	-0.732	-0.077	-0.409	-0.113	0.001
$C_8C_1OQ^+$	-3.558	-3.797	-3.382	-0.668	-0.299	-0.492	-0.737	-0.079	-0.405	0.061	0.044

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Table S2. Variations of the ^{1}H NMR chemical shift related to the quinolinium species $C_1C_nOQ^+$, as observed upon their complexation with SCX4. These data were determined at 2:1 SCX4:$C_1C_nOQ^+$ molar ratio and a total concentration of 10 mM.

Δδ (ppm)	H2	H3	H4	H5	H7	H8	N-CH_3	O-CH_3			
$C_1C_1OQ^+$[a]	-3.695	-3.565	-2.848	-0.553	-0.287	-0.669	-1.074	-0.085			
Δδ (ppm)	H2	H3	H4	H5	H7	H8	N-CH_3	O-CH_2(α)	CH_2(β)	CH_2(γ)	CH_3
$C_1C_2OQ^+$	-3.661	-3.492	-2.740	-0.671	-0.259	-0.666	-1.060	-0.125	--	--	-0.033
$C_1C_4OQ^+$	-3.714	-3.541	-2.789	-0.514	-0.262	-0.647	-1.076	-0.035	-0.025	0.007	0.02
$C_1C_6OQ^+$	-3.731	-3.554	-2.795	-0.508	-0.262	-0.652	-1.08	-0.031	-0.016	0.003	0.034

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Table S3. Comparison of the ^{1}H chemical shift variation induced for the protons of $C_1C_1OQ^+$ upon complexation with SCX4 and SCX6. The corresponding molar ratios were SCX4:$C_1C_1OQ^+$ = 2:1 and SCX6:$C_1C_1OQ^+$ = 3:1.

Δδ (ppm)	H2	H3	H4	H5	H7	H8	N-CH_3	O-CH_3
SCX4[a]	-3.695	-3.565	-2.848	-0.553	-0.287	-0.669	-1.074	-0.085
SCX6	-1.6275	-1.367	-1.232	-1.056	-0.3785	-0.7535	-0.831	-0.583

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Table S4: Comparison of the ^{1}H chemical shift change occurring for the protons of $C_4C_1OQ^+$ and $C_1C_4OQ^+$ upon complexation with SCX6. In both cases, the molar ratio SCX6:$C_nC_mOQ^+$ (m = 1, n = 4 or m = 4, n = 1) was set to 3:1.

$C_4C_1OQ^+$	H2	H3	H4	H5	H7	H8	N-CH_2(α)	O-CH_3	CH_2(β)	CH_2(γ)	CH_3
Δδ (ppm)	[a]	-1.326	-0.98	-0.79	[a]	[a]	-0.689	-0.461	-0.522	-0.532	-0.452
$C_1C_4OQ^+$	H2	H3	H4	H5	H7	H8	N-CH_3	O-CH_2	CH_2(β)	CH_2(γ)	CH_3
Δδ (ppm)	[a]	-1.384	-1.009	-0.699	[a]	-0.63	-0.835	-0.407	-0.396	-0.37	-0.35

[a] These values were not reported, due to the overlap of this ^{1}H NMR peak with another one.