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SYNTHESIS AND THE EXTRACTABILITY OF AMINOBENZOCROWN ETHER DERIVATIVES CONNECTED BY AN AZULENEQUINONE: AZULENE-BIS(AMINOBENZO-15-CROWN-5) FRAMEWORK AS A USEFUL POTASSIUM CATION CAPTURE

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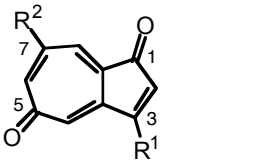
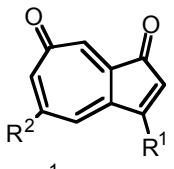
Abstract – Bis(aminobenzocrown ether)s connecting with azulenequinones (**6** – **9**) were prepared by the nucleophilic substitution reaction of the corresponding dibromo-azulenequinones (**5**) with 4'-aminobenzo-15-crown-5 or -18-crown-6 and the high extractability of 3,7(5)-bis(aminobenzo-15-crown-5)-azulene-quinones (**8**) for potassium cation was revealed and explained by a plausible 2/1 sandwich-type complex formation.

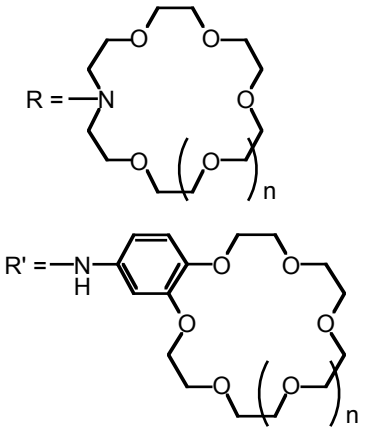
Macrocyclic receptors having both cation sensitive chromophore and redox switching property are interesting class of compounds.[1-7] Understanding the factors governing the interplay of those properties and molecular recognition is important in the context of both biochemistry and material science.[8] In the course of our research towards this direction, aimed at the preparation of new host compounds based on azulene-crown ether framework, we already reported the synthesis of azacrown ethers connecting with azulenequinones (AzQs) (**1** – **4**)[9] by the nucleophilic substitution of 1-aza-15-crown-5 or -18-crown-6 with 3,7-dibromo-1,5-AzQ (**5a**)[10] or 3,5-dibromo-1,7-AzQ (**5b**).[10] Among them 3,5-bis(aza-18-crown-6)-1,7-AzQ (**4b**) showed a singular complexation of sodium or potassium cation, *i. e.*, hopping of the former cation between the two crown ring moieties, so called *play catch*, or the *sandwiched conformation* of the latter complex.[9] Elucidation of those phenomena, however, was not enough because



1a: R^1 = R (n = 0), R^2 = Br
2a: R^1 = R (n = 1), R^2 = Br
3a: R^1 = R^2 = R (n = 0)
4a: R^1 = R^2 = R (n = 1)
5a: R^1 = R^2 = Br
6a: R^1 = R' (n = 0), R^2 = Br
7a: R^1 = R' (n = 1), R^2 = Br
8a: R^1 = R^2 = R' (n = 0)
9a: R^1 = R^2 = R' (n = 1)



1b: R^1 = R (n = 0), R^2 = Br
2b: R^1 = R (n = 1), R^2 = Br
3b: R^1 = R^2 = R (n = 0)
4b: R^1 = R^2 = R (n = 1)
5b: R^1 = R^2 = Br
6b: R^1 = R' (n = 0), R^2 = Br
7b: R^1 = R' (n = 1), R^2 = Br
8b: R^1 = R^2 = R' (n = 0)
9b: R^1 = R^2 = R' (n = 1)



of the paucity of the extractability of the related compounds (**1** – **4**) for alkali metal cations no more than their amphiphilic property.

Instead of aminobenzocrown ethers linked with AzQs, their aminobenzo-analogs were designed to overcome those problems. We report herein the synthesis of aminobenzocrown-AzQs (**6** – **9**) from dibromo-AzQs (**5**), and the unexpectedly high extractability of 3,7(5)-bis(aminobenzo-15-crown-5)-1,5(7)-azulenequinones (**8a** and **8b**) for potassium cation and mechanism.

RESULTS and DISCUSSION

Considering the properties that the five-membered ring moiety (C-3 position) of dibromo-AzQ (**5a** or **5b**) is more reactive than the seven-membered ring one (C-7 for **5a** or C-5 for **5b**),[10] 3-(aminobenzo-15-crown-5)-7(5)-bromo-AzQ (**6a,b**) or -18-crown-6)-7(5)-bromo-AzQ (**7a,b**) was synthesized by the reaction of **5a** or **5b** with 2.5 mol equivalent of 4'-aminobenzo-15-crown-5 (AB15C5) or -18-crown-6 (AB18C6) respectively in CH_2Cl_2 at room temperature for 51 – 68 h. **6** or **7** was obtained in good to moderate yield as red to orange powder or needles (Table 1).

On the other hand, bis(aminobenzocrown)-AzQ (**8a,b** or **9a,b**) was obtained in low yield by the general synthetic conditions of bis(amine)-AzQ derivatives,[10] *i. e.*, treatment of **5** with excess amount of AB15C5 or AB18C6 in ethanol under refluxed conditions. However, from the careful examination of the conditions, we found out that treatmentof **5** with 4.5 mol equivalent of AB15C5 or AB18C6 in DMF at 60 °C for 27 – 38 h afforded them in good to moderate yields. The obtained **8** or **9** was orange, red or brown powder and has a corresponding melting point as shown in Table 1.

Table 1. Yields, appearances, and melting points of aminobenzocrown ethers connecting with AzQs

Compound	Yield[a] (%)	Appearance	mp (°C)
6a	93	red needles	258-260
6b	68	red powder	206-208
7a	68	orange needles	222 (decomp)
7b	78	orange powder	197-198
8a	79	orange powder	271 (decomp)
8b	63	red powder	149-152
9a	76	orange powder	209 (decomp)
9b	57	brown powder	143-146

[a] Isolated yield

All mono(aminobenzocrown) derivatives (**6** and **7**) showed molecular ion peaks (MH^+: **6a**; *m/z* 518, **6b**; *m/z* 518, **7a**; *m/z* 562, **7b**; *m/z* 562) and their isotropic peaks (MH^++2) arising from the bromo atom in FAB-MS spectra. The □ bands for CO stretching vibration at 5-membered ring moiety (C-1 position) in

the IR spectra of **6** and **7** (ν_{CO}: 1661 – 1668 cm^{-1}) are shifted by more 40 cm^{-1} further lower wave-number region than those of **5**. These results indicate that the aminobenzocrown ether moiety was introduced at C-3 position of AzQ.[10] The ^1H NMR resonances of H-2 of **6** and **7** (δ: 5.86 – 5.89) were found at upfield by about 1.0 ppm from those of **5**, supporting these reason.[10] As for the bis(aminobenzocrown ether)s (**8** and **9**), FAB-MS spectra of them gave molecular ion peaks (MH^+: **8a**; *m/z* 721, **8b**; *m/z* 721, **9a**; *m/z* 809, **9b**; *m/z* 809). The ν frequencies for CO stretching vibration at seven-membered ring moiety (C-5 for **a** series, C-7 for **b** series) in the IR spectra of **8** and **9** (ν_{NH}: 1561 – 1568 cm^{-1}) are shown at lower wave-number region than those of **6** and **7**. By further introduction of aminobenzocrown ether at C7(5) position of AzQ, the ^1H NMR resonances of adjacent protons from nitrogen atom at seven-membered ring moiety of **8** and **9** (H-8 and 6 for **a** series, H-4 and 6 for **b** series) were found at upfield by about 0.2 (H-8 or 4) and 1.3 ppm (H-6) from those of **6** and **7** (*e.g.*, **6a** *vs.* **8a**: δ, 7.53 *vs.* 7.33 and 7.35 *vs.* 6.07). The chemical shifts at crown moiety of **6** – **9** were found at a slight low field from those of mother AB-15-C-5 and -18-C-6 because of the anisotropic effects of AzQ moiety. Those data, including analytical ones, are coincided with the structures proposed for **6a**,**b**, **7a**,**b**, **8a**,**b** and **9a**,**b** respectively.

The affinities of aminobenzocrown ethers connecting with AzQs toward alkali metal ions were examined by biphasic solvent extraction.[11] A CH_2Cl_2 solution of host (1.0 x 10^{-4} M) was used as an organic phase. In aqueous solution, metal picrate (3.0 x 10^{-3} M) and metal chloride (1.0 x 10^{-1} M) were dissolved. The biphasic mixture was stirred vigorously for 24 h and then UV-VIS spectra of the aqueous phase were measured. The extractability for each cation was estimated from the definition indicated in experimental section and the results of them are summarized in Table 2.

For lithium ion, **6** – **9a** did not show the extractability at all. The affinity of **6** or **7** toward sodium or potassium ion was slightly lower than that of corresponding non-substituted host, 15-crown-5 (15C5), 18C6, AB15C5 or AB18C6 (*e.g.*, **6a** *vs.* AB15C5 for Na^+, 3 *vs.* 9 %; **6b** *vs.* AB15C5 for Na^+, 2 *vs.* 9 %; **7a** *vs.* AB18C6 for K^+, 65 *vs.* 76 %; **7b** *vs.* AB18C6 for K^+, 49 *vs.* 76 %) except for that of **6b** toward potassium ion. The similar decrement of **8** with sodium ion was observed (*e.g.*, **8b** *vs.* AB15C5 for Na^+, 3 *vs.* 9 %). These results indicate that the AzQ moiety connecting with ABC plays a role of steric hindrance to inhibit the complexation of hosts with cations. Comparing with mono(aminobenzocrown ether)s (**6a** or **6b**), the extractability of bis(aminobenzocrown ether)s (**8a** or **8b**), an AB15C5 derivative, toward potassium cation was quite high (**8a** *vs.* **6a** for K^+, 89 *vs.* 12 %; **8b** *vs.* **6b** for K^+, 90 *vs.* 32 %), regardless of too large size of potassium cation to fit the cavity. Therefore these high extractabilities are arising from not the independent actions of each ABC ring moiety, but the interplay between two crown moieties with the cation. Considering the diluted concentration of the extraction (1.0 x 10^{-4} M for the host), this interaction must be intramolecular. That is, these phenomena could be explained by the plausible formation of a 2/1 sandwich-type complex between **8** and potassium cation. Various bis(macrocyclic polyether)s are shown much more effective complexing agents for potassium cation than are the corresponding mono(cyclic ligand)s: the proximity of ligands in a dimer favors the formation of sandwich-type speacies.[12] Such sandwiched conformations of both **8a** and **8b** with the cation are considered feasible from their CPK modeling study. Further work aimed at their dynamic equilibrium is now under investigation. As for **9** (AB18C6 derivatives), because of the feasible water

solubility of **9a**, the extractability toward potassium cation was not so high as we expected. The affinity of **9b**, which has high water solubility, could not be determined.

Table 2. Extractability of (aminobenzocrown)-AzQs (**6** - **9**) for alkali metal ions

Host	Extractability [a] / %		
	Li^+	Na^+	K^+
6a	0	3	12
6b	0	2	32
7a	0	4	65
7b	0	2	49
8a	0	8	89
8b	0	3	90
9a	0	6	34
9b	- [b]	- [b]	- [b]
15C5	2	23	21
18C6	3	14	86
AB15C5	1	9	17
AB18C6	3	10	76

[a] Organic phase (CH_2Cl_2); [host] = 1.0×10^{-4} M. Aqueous phase; [metal picrate] = 3.0×10^{-5} M and [metal chloride] = 1.0×10^{-1} M.
[b] Not determined because of the water soluble property of the host

To our disappointment, neither the expected functionality as a color sensor nor a metal ion transfer carrier using their redox property[4-7] was recognizable by the electrochemical instability of **6** – **9** (recognized from the poor reversibility of their cyclic voltammograms).[9,10] However, the high extractability of **8a**,**b** for potassium cation was observed, suggesting that azulene-bis(aminobenzo-15-crown-5) framework are useful as a potassium cation capture. AzQ-hosts containing appropriate substituents at C2-position are expected to exert the redox switching property since 2-substituted AzQs[10] have some electrochemical stability.

EXPERIMENTAL

Mps were determined with a Mitamura air-bath apparatus and are uncorrected. ^1H and ^{13}CNMR spectra were determined with Bruker AC-300, AM-400 and/or ARX-400 spectrometers. IR spectra were determined with a Perkin Elmer System 2000 FT instrument and electronic spectra (UV-VIS) with a JASCO V-560 spectrophotometer. MS spectra were determined with JEOL JMS-DX 303 spectrometer.

Unless otherwise stated the spectra were taken in the following solvents/media: IR, KBr; UV-VIS, H_2O; ^1H and ^{13}CNMR, DMSO-d_6; MS spectra were taken by fast atom bombardment (FAB) method with NBA or thioglycerol as matrix. The progress of most reactions was followed by TLC using Merck Kieselgel $60F_{254}$.

Typical experimental procedure for the synthesis of mono(aminobenzocrown)-azulenequinone (6 or 7): A solution of **5** (50 mg, 0.16 mmol) and 2.5 mol *equiv.* of aminobenzocrown ether (4'-aminobenzo-15-crown-5 or 4'-aminobenzo-18-crown-6) in dry CH_2Cl_2 (10 mL) was stirred at rt for 51 – 68 h. The reaction mixture was purified by silica gel column chromatography (eluted by CH_2Cl_2 and MeOH successively) and then recrystallized from CH_2Cl_2 / MeOH to give mono(aminobenzocrown)-azulenequinone (**6** or **7**).

Physical data of mono(aminobenzocrown)-azulenequinone (6 or 7): 3-(aminobenzo-15-crown-5)-7-bromo-1,5-azulenequinone (**6a**): yield 93 %; red needles; mp 258 – 260 °C; δ_H 3.62 (8H, m), 3.77 (4H, m), 4.07 (4H, m), 5.89 (1H, s), 6.92 (1H, dd, *J* 8.5, 2.5), 6.98 (1H, d, *J* 2.5), 7.01 (1H, d, *J* 8.5), 7.17 (1H, d, *J* 2.1), 7.35 (1H, t, *J* 2.1), 7.53 (1H, d, *J* 2.1), 9.96 (1H, br s); δ_C 68.5, 68.7 (2C), 68.8, 69.7, 69.8, 70.5 (2C), 103.6, 109.2, 114.1, 115.6, 127.9, 128.2, 128.5, 131.8, 135.4, 138.4, 140.9, 142.7, 146.7, 162.5, 183.5, 186.2; ν_{max}/cm^{-1} 1661, 1584; *m/z* 520 (MH^++2, 96 %), 518 (MH^+, 100 %); Anal. Calcd for $C_{24}H_{24}NO_7Br$: C, 55.61; H, 4.67; N, 2.70. Found: C, 55.61; H, 4.56; N, 2.65. 3-(aminobenzo-15-crown-5)-5-bromo-1,7-azulenequinone (**6b**): yield 68 %; red powder; mp 206 – 208 °C; δ_H 3.62 (8H, m), 3.78 (4H, m), 4.08 (4H, m), 5.87 (1H, s), 6.83 (1H, d, *J* 2.6), 6.92 (1H, dd, *J* 8.5, 2.5), 6.97 (1H, d, *J* 2.5), 7.02 (1H, d, *J* 8.5), 7.35 (1H, br d, *J* 2.6), 7.91 (1H, br s), 10.05 (1H, br s); ν_{max}/cm^{-1} 1668, 1584; *m/z* 520 (MH^++2, 18 %), 518 (MH^+, 19 %); Anal. Calcd for $C_{24}H_{24}NO_7Br$: C, 55.61; H, 4.67; N, 2.70. Found: C, 55.65; H, 4.60; N, 2.65. 3-(aminobenzo-18-crown-6)-7-bromo-1,5-azulenequinone (**7a**): yield 68 %; orange needles; mp 222 °C (decomp); δ_H 3.53 (4H, br s), 3.56 (4H, m), 3.61 (4H, m), 3.77 (4H, m), 4.10 (4H, m), 5.88 (1H, s), 6.91 (1H, dd, *J* 8.6, 2.4), 6.98 (1H, d, *J* 2.4), 7.02 (1H, d, *J* 8.6), 7.17 (1H, d, *J* 2.1), 7.35 (1H, t, *J* 2.1), 7.53 (1H, d, *J* 2.1), 9.97 (1H, br s); ν_{max}/cm^{-1} 1667, 1582; *m/z* 564 (MH^++2, 10 %), 562 (MH^+, 10 %) ; Anal. Calcd for $C_{24}H_{28}NO_8Br \cdot 3/2H_2O$: C, 52.98; H, 5.30; N, 2.38. Found: C, 53.14; H, 5.17; N, 2.24. 3-(aminobenzo-18-crown-6)-5-bromo-1,7-azulenequinone (**7b**): yield 78 %; orange powder; mp 197 – 198 °C; δ_H 3.53 (4H, br s), 3.56 (4H, m), 3.61 (4H, m), 3.77 (4H, m), 4.11 (4H, m), 5.86 (1H, s), 6.83 (1H, d, *J* 2.6), 6.91 (1H, dd, *J* 8.6, 2.4), 6.97 (1H, d, *J* 2.4), 7.03 (1H, d, *J* 8.6), 7.35 (1H, br d, *J* 2.6), 7.91 (1H, br s), 10.05 (1H, br s); ν_{max}/cm^{-1} 1668, 1582; *m/z* 564 (MH^++2, 8 %), 562 (MH^+, 10 %); Anal. Calcd for $C_{24}H_{28}NO_8Br \cdot 1/2CH_3OH$: C, 55.03; H, 5.23; N, 2.49. Found: C, 54.73; H, 4.96; N, 2.39.

Typical experimental procedure for the synthesis of bis(aminobenzocrown)-azulenequinone (8 or 9): A solution of **5** (50 mg, 0.16 mmol) and 4.5 mol *equiv.* of aminobenzocrown ether (4'-aminobenzo-15-crown-5 or 4'-aminobenzo-18-crown-6) in dry DMF (10 mL) was stirred at 60 °C for 27 – 38 h. The reaction mixture was filtered and the residue purified by silica gel column chromatography (eluted by CH_2Cl_2 and MeOH successively) and then recrystallized from CH_2Cl_2 / MeOH to give bis(aminobenzocrown)-azulenequinone (**8** or **9**).

Physical data of bis(aminobenzocrown)-azulenequinone (8 or 9): 3,7-bis (aminobenzo-15-crown-5)-

1,5-azulenequinone (**8a**): yield 79 %; orange powder; mp 271 °C (decomp); δ_H 3.62 (16H, br s), 3.78 (8H, m), 4.05 (4H, m), 4.08 (4H, m), 5.78 (1H, s), 6.07 (1H, br d, *J* 2.5), 6.77 (1H, dd, *J* 8.5, 2.3), 6.83 (1H, d, *J* 2.3), 6.92 (1H, dd, *J* 8.5, 2.3), 7.00 (1H, d, *J* 2.3), 7.01 (1H, d, *J* 8.5), 7.02 (1H, d, *J* 8.5), 7.16 (1H, d, *J* 2.5 Hz), 7.33 (1H, br s), 9.14 (1H, br s), 10.09 (1H, br s); δ_C 68.5, 68.6, 68.8 (4C), 68.9 (2C), 69.8 (4C), 70.5 (4C), 102.5, 109.1, 110.9 (2C), 114.1, 114.4, 115.3, 117.2, 122.4, 129.4, 132.0, 132.2, 136.9, 137.9, 146.4, 146.6, 148.9, 149.2, 152.0, 163.0, 182.8, 187.6; ν_{max}/cm^{-1} 1654, 1561; *m/z* 721 (MH^+, 31 %); Anal. Calcd for $C_{38}H_{44}N_2O_{12}$: C, 63.32; H, 6.15; N, 3.89. Found: C, 63.03; H, 6.09; N, 3.77. 3,5-bis(aminobenzo-15-crown-5)-1,7-azulenequinone (**8b**): yield 63 %; red powder; mp 149 – 152 °C; δ_H 3.61 (4H, br s), 3.56 (12H, br s), 3.77 (8H, m), 4.05 (8H, m), 5.75 (1H, s), 6.09 (1H, br d, *J* 1.8), 6.44 (1H, dd, *J* 8.5, 2.3), 6.66 (1H, d, *J* 1.8), 6.70 – 7.00 (3H, m), 6.81 (1H, d, *J* 2.3), 6.94 (1H, d, *J* 8.5), 7.37 (1H, br s), 8.75 (1H, br s), 9.90 (1H, br s); ν_{max}/cm^{-1} 1652, 1568; *m/z* 721 (MH^+, 41 %); Anal. Calcd for $C_{38}H_{44}N_2O_{12}\cdot 2CH_2Cl_2\cdot 1/2H_2O$: C, 53.40; H, 5.49; N, 3.11. Found: C, 53.46; H, 5.62; N, 3.33. 3,7-bis(aminobenzo-18-crown-6)-1,5-azulenequinone (**9a**): yield 76 %; orange powder; mp 209 °C (decomp); δ_H 3.53 (8H, br s), 3.56 (8H, m), 3.61 (8H, m), 3.77 (8H, m), 4.06 (2H, m), 4.10 (6H, m), 5.77 (1H, s), 6.06 (1H, br s), 6.76 (1H, br d, *J* 8.6), 6.81 (1H, br s), 6.91 (1H, br d, *J* 8.6), 6.99 (1H, br s), 7.00 (1H, br d, *J* 8.6), 7.02 (1H, br d, *J* 8.6), 7.13 (1H, br s), 7.30 (1H, br s), 9.06 (1H, br s), 9.91 (1H, br s); ν_{max}/cm^{-1} 1652, 1568; *m/z* 809 (MH^+, 52 %); Anal. Calcd for $C_{42}H_{52}N_2O_{14}\cdot 1/2H_2O$: C, 61.68; H, 6.53; N, 3.43. Found: C, 61.81; H, 6.45; N, 3.36. 3,5-bis(aminobenzo-18-crown-6)-1,7-azulenequinone (**9b**): yield 57 %; brown powder; mp 143 – 146 °C; δ_H 3.53 (4H, br s), 3.54 (4H, br s), 3.56 (8H, br s), 3.61 (8H, m), 3.76 (8H, m), 4.08 (8H, m), 5.63 (1H, br s), 6.07 (1H, br s), 6.61 (1H, br s), 6.70 – 6.90 (2H, m), 6.74 (1H, dd, *J* 7.9, 2.6), 6.81 (1H, d, *J* 2.6), 6.94 (1H, d, *J* 7.9), 7.00 (1H, d, *J* 7.9), 7.36 (1H, br s), 8.75 (1H, br s); ν_{max}/cm^{-1} 1651, 1568; *m/z* 809 (MH^+, 5 %); Anal. Calcd for $C_{42}H_{52}N_2O_{14}\cdot 2CH_2Cl_2\cdot 3/2H_2O$: C, 52.54; H, 5.91; N, 2.79. Found: C, 52.52; H, 5.87; N, 2.84.

Typical procedure for the extraction measurements of (6 – 9), azacrown ethers or aminobenzocrown ethers in the presence of alkaline metal ions: An aqueous solution (5.0 mL) of metal picrate (3.0 x 10^{-5} M) and metal chloride (1.0 x 10^{-1} M) and a CH_2Cl_2 solution (5.0 mL) of the host (1.0 x 10^{-4} M) were stirred vigorously in a capped vial for 24 h at rt. The amounts of picrate anion in the aqueous phase were determined by UV-VIS spectroscopy monitoring at 356 nm. The extractability was calculated according to a following equation. All experiments were carried out in three times and the respective results were averaged.

$$\text{Extractability (\%)} = ([Pic^-]_{aq,0} - [Pic^-]) / [Pic^-]_{aq,0} \times 100$$

where $[Pic^-]_{aq,0}$ is the concentration of picrate in the aqueous phase after extraction without host (blank test), and $[Pic^-]$ is the concentration of picrate in the aqueous phase after extraction with host.

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