Synthesis and properties of naphthoquinonylamino-substituted benzocrown ethers

E. G. Lubenets,* S. Z. Kusov, L. V. Ektova, V. N. Kobrina, L. M. Kornaukhova, V. S. Kobrin, I. K. Korobeinicheva, and N. I. Sagalaeva

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
9 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 235 4752

Naphthoquinonylaminobenzocrown ethers were synthesized by reactions of 4'-aminobenzocrown ethers with 1,4-naphthoquinones. A hypsochromic shift of the long-wave absorption band was found to appear in the electron spectra when the compounds synthesized reacted with alkaline or alkaline-earth metal salts.

Key words: crown ethers; 1,4-naphthoquinone; piperidine.

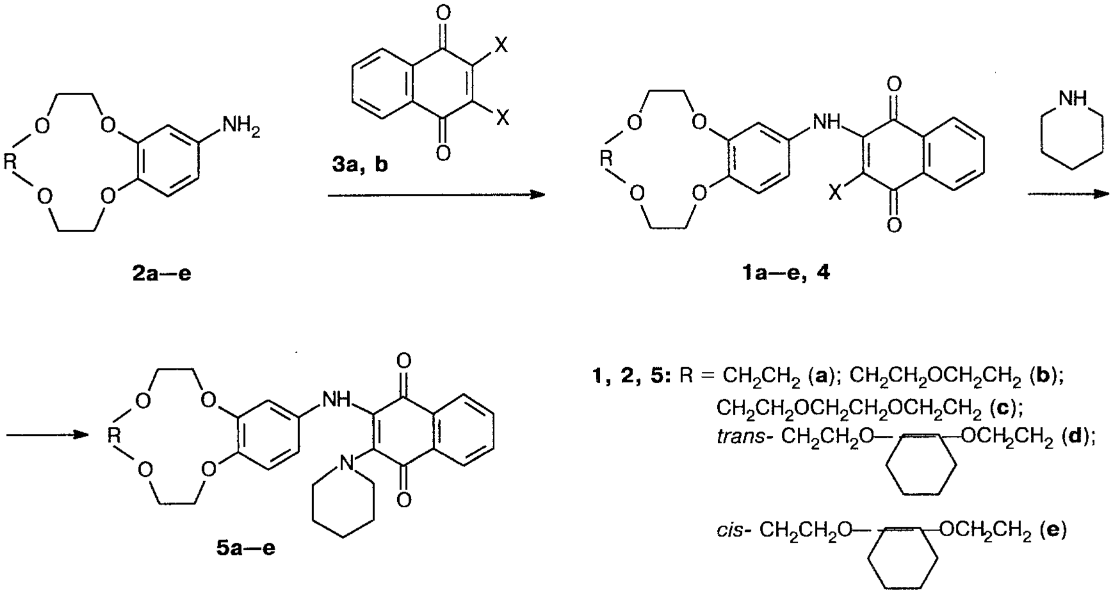
Chromogenic crown ethers are promising compounds that can be used as indicators or selective photometric agents for the determination of alkaline and alkaline-earth metal cations.[1] In particular, macrocycles of this type have been prepared by the introduction of a quinone chromophore group into a crown ether molecule.[2] We carried out a synthesis of naphthoquinole derivatives of aminobenzocrown ethers and studied the interaction of these ethers with alkaline and alkaline-earth metal salts.

N-(2-Chloro-1,4-naphthoquinon-3-yl)-4'-aminobenzocrown ethers (**1a—e**) were synthesized by the treatment of 4'-aminobenzocrown ethers (**2a—e**) with 2,3-dichloro-1,4-naphthoquinone (**3a**) in the presence of copper acetate (Scheme 1).

Compounds **1b,c** are also formed by boiling crown ethers **2b,c** with quinone **3a** in toluene in the presence of potash. *N*-(1,4-Naphthoquinon-3-yl)-4'-aminobenzo-18-crown-6 (**4**) is obtained by treating 4'-aminobenzo-18-crown-6 (**2c**) with 1,4-naphthoquinone (**3b**), similarly to the known procedure.[2] Compounds **1a—e** and **4** are stable during storage. In water—organic solvent systems they are practically completely distributed in the organic phase.

The reactions of compounds **1a—e** with piperidine

Scheme 1



1, 2, 5: R = CH_2CH_2 (**a**); $CH_2CH_2OCH_2CH_2$ (**b**); $CH_2CH_2OCH_2CH_2OCH_2CH_2$ (**c**); *trans-* CH_2CH_2O—OCH_2CH_2 (**d**); *cis-* CH_2CH_2O—OCH_2CH_2 (**e**)

1a—e: X = Cl
3: X = Cl (**a**); H (**b**)
4: R = $CH_2CH_2OCH_2CH_2OCH_2CH_2$; X = H

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Table 1. Long-wave absorption maxima of compounds **1a—d**, **4**, and **5b** and their shifts* in the presence of metal salts (λ_{max}/nm)

Salt	Compound					
	4	**1a**	**1b**	**1c**	**1d**	**5b**
$NaClO_4$	477.7 (−1.8)	485.0 (−1.8)	482.2 (−10.6)	489.9 (−4.8)	485.0 (−6.8)	— —
KSCN	474.1 (−5.4)	485.0 (−1.8)	485.5 (−7.3)	492.0 (−2.7)	488.5 (−3.3)	449.0; 585.0 (−7.4) (−5.6)
NH_4SCN	470.5 (−9.0)	485.0 (−1.8)	488.5 (−4.3)	482.2 (−12.5)	484.7 (−7.1)	446.0; 482.0 (−10.4) (−8.6)
$Ba(SCN)_2$	467.0 (−12.5)	—	480.1 (−12.7)	481.4 (−13.3)	481.8 (−10.0)	438.8; 481.8 (−17.6) (−8.8)

* In parentheses.

afford photo-sensitive *N*-(2-piperidino-1,4-naphthoquinon-3-yl)-4′-aminobenzocrown ethers (**5a—e**).[3]

The electron absorption spectra of compounds **1a—e** and **4** contain one broad band in the visible region at a position close to that observed for 2-arylamino-1,4-naphthoquinones and related to a π—π^* transition with intramolecular charge transfer from the nitrogen-containing substituent to the quinoid nucleus.[4] A comparison of the electron absorption spectra of compounds **1a—e** and **4** showed that the chlorine atom at position 2 of the quinoid nucleus causes a bathochromic shift of the long-wave band, probably due to charge stabilization on the acceptor center.[1] The spectra of compounds **5a—e** in the visible region have two absorption bands resulting from the existence of two intersecting conjugated systems, ArNH—C=C—C_4=O and C_5H_{10}N—C=C—C_1=O. It should be noted that an increase in the macrocycle size brings about a small shift in λ_{max} towards longer wavelengths.

When metal salts are added to solutions of compounds **1a—d** or **4** in acetonitrile (Table 1), the long-wave bands in the electron absorption spectra undergo a hypsochromic shift; the absolute value of $\Delta\lambda$ increases on passing from single-charged cations to a barium cation. This agrees qualitatively with the regularities found previously for derivatives of phenylazacrown ethers.[2] When metal salts are added to a solution of compound **5b**, a hypsochromic shift is observed for both bands in the spectra, with a more pronounced shift for the short-wave band.

Experimental

IR spectra were recorded on a UR-20 spectrometer for KBr pellets. Mass spectra (EI, 70 eV) were obtained on a Finnigan Mat-8200 instrument. Electron absorption spectra were recorded with a Beckman DU-8 spectrophotometer in CH_3CN. The molecular formulas of compounds **1d,e**, **4**, and **5e** were determined from accurate values of mass numbers. Benzo-12-crown-4 and benzo-15-crown-5 were prepared at the Experimental Plant of the Scientific Research Institute of Organic Chemistry, Syberian Branch of the Russian Academy of Sciences. Benzo-18-crown-6 was synthesized according to the known procedure.[6] Compounds **2a—e** were prepared by nitration of the corresponding benzocrown ethers[7] followed by reduction of the nitroso derivatives.[8] The yields and m.p. of compounds **2a—c** agree with the literature data.[7—9] The yields and physico-chemical parameters of compounds **1a—e**, **4**, and **5a—e** are given in Tables 2 and 3.

***Trans* and *cis* isomers of 4′-nitrobenzocyclohexano-18-crown-6.** The yield of the *trans* isomer was 83 %, m.p. 92—93.5 °C (from EtOH). Found (%): C, 57.83; H, 7.25; N, 3.48. MS, *m/z*: 411 $[M]^+$. The yield of the *cis* isomer was 78 %, oil purified by complexation with Ca^{2+} as reported previously.[10] Found (%): C, 58.51; H, 7.41; N, 3.44. $C_{20}H_{29}NO_2$. Calculated (%): C, 58.38; H, 7.10; N, 3.40. MS, *m/z*: 411 $[M]^+$.

***Trans* and *cis* isomers of 4′-aminobenzocyclohexano-18-crown-6 (2d and 2e).** The yield of **2d** was 55 %, m.p. 93—95 °C (from EtOH). MS, *m/z*: 381 $[M]^+$. The yield of **2e** was 52 %, oil purified by complexation with Ca^{2+} by analogy to the procedure described previously.[10] MS, *m/z*: 381 $[M]^+$.

***N*-(2-Chloro-1,4-naphthoquinon-3-yl)-4′-aminobenzocrown ethers (1a—e).** A mixture of compound **2a—e** (5 mmol), **3a** (5.3 mmol), sodium acetate (5 mmol), copper acetate (7 mmol), and EtOH (70 mL) was boiled for 3 h with stirring. The mixture was poured into water (50 mL) and kept at 22 °C for 18 h. The precipitate was filtered off, dried over P_2O_5, and chromatographed on SiO_2 (the fractions were eluted with a benzene—chloroform mixture (1 : 1) and chloroform). The orange zone was isolated.

***N*-(2-Chloro-1,4-naphthoquinon-3-yl)-4′-aminobenzocrown ethers (1b,c).** A mixture of compound **2b** or **2c** (15.7 mmol), **3a** (13.2 mmol), potash (21.7 mmol), and toluene (100 mL) was boiled for 12 h with stirring and then chromatographed similarly to the above experiment. The yields of compounds **1b** and **1c** were 57 and 78 %, respectively.

***N*-(1,4-Naphthoquinon-3-yl)-4′-aminobenzo-18-crown-6 (4).** A mixture of compound **2c** (5 mmol), **3b** (8 mmol), copper acetate (2.5 mmol), and EtOH (50 mL) was stirred for 15 h at 22 °C. Compound **4** was isolated by a procedure similar to that reported for 2-[(4,7,10,13-tetraoxa-10-azacyclopentadecyl)phenylamino]-1,4-naphthoquinone.[2]

***N*-(2-Pyperidino-1,4-naphthoquinon-3-yl)-4′-aminobenzo-18-crown-6 (5a—e).** A solution of compound **1a—e** (3.5 mmol) in piperidine (25 mL) was boiled for 4 h. The piperidine was distilled off, and the precipitate was dissolved in $CHCl_3$ (25 mL) and washed with water (2 × 25 mL). The organic layer was dried with $MgSO_4$ and concentrated, and the residue

Table 2. *N*-(1,4-Naphthoquinon-3-yl)-4′-aminobenzocrown ethers (**1a—e, 4**)

Compound	Yield (%)	M.p. /°C	λ_{max}/nm (ε)	Found/Calculated (%)				Molecular formula
				C	H	Cl	N	
1a	62	176—177	486.8 (4560)	61.48 61.46	4.65 4.69	8.73 8.26	3.15 3.26	$C_{22}H_{20}ClNO_6$
1b	62	150—152	492.8 (4200)	60.77 60.82	5.11 5.10	7.58 7.48	3.20 2.96	$C_{24}H_{24}ClNO_7$
1c	50	141—143	494.7 (4170)	60.58 60.29	5.46 5.45	7.12 6.84	2.76 2.70	$C_{26}H_{28}ClNO_8$
1d*	74	157—159	491.8 (4000)	—	—	—	—	$C_{30}H_{34}ClNO_8$
1e*	70	123—126	—	—	—	—	—	$C_{30}H_{34}ClNO_8$
4**	56	152—155	479.5 (3020)	—	—	—	—	$C_{26}H_{29}NO_8$

*Found: mol. weight 571.1966. **Found: mol. weight 483.1907.

Table 3. *N*-(2-Pyperidino-1,4-naphthoquinon-3-yl)-4′-aminobenzocrown ethers (**5a—e**)

Compound	Yield (%)	M.p. /°C	λ_{max}/nm (ε)	Found/Calculated (%)			Molecular formula
				C	H	N	
5a	66	134—136	448.5 (2360) 587.2 (2320)	67.83 67.77	6.43 6.32	5.71 5.85	$C_{27}H_{30}N_2O_6$
5b	57	121—123	456.4 (2240) 590.6 (1980)	66.60 66.65	6.77 6.56	5.25 5.36	$C_{29}H_{34}N_2O_7$
5c	62	92—95	457.9 (2890) 592.4 (2690)	65.62 65.71	6.95 6.76	4.46 4.94	$C_{31}H_{38}N_2O_8$
5d	69	113—115	455.2 (2120) 589.7 (1980)	67.57 67.72	7.51 7.14	3.99 4.51	$C_{35}H_{44}N_2O_8$
5e*	64	85—88	451.8 (1510) 588.9 (1280)	—	—	—	$C_{35}H_{44}N_2O_8$

* Found: mol. weight 620.3098.

was chromatographed on SiO_2. The admixtures were successively eluted with benzene and a benzene—chloroform mixture (1 : 1). Compounds **5a—e** were eluted with a C_6H_6—EtOH—$CHCl_3$ (2 : 1 : 1) mixture.

Reactions of naphthoquinonylaminobenzocrown ethers with metal salts. An inorganic salt (10 mmol) was added to a solution of compound **1a—d**, **4**, or **5b** (0.1 mmol). The mixture was stirred for 1 h, and the changes in the positions of the long-wave absorption maxima in the spectra were recorded to within ±0.1 nm.

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