

Tetsuya Ishida, Makoto Sakakibara and Yoshio Ueno*

Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan

Kan-ichi Hasegawa

Nagoya University of Arts,
Shikatsu-cho, Nishikasugai-gun, 481, Japan

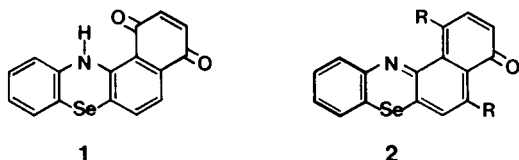
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The condensation of 2-bromo- or 2,6-dibromo-4,8-bis(alkylamino)-1,5-naphthoquinones with zinc 2-aminobenzeneselenolates gave 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenoselenazin-4-one and the 3- and/or 10-substituted compounds. These phenoselenazine derivatives absorb nearly infrared light and can be used as optical recording media for a laser beam.

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There have been extensive studies of the phenoxazine and phenothiazine ring systems in connection with the development of drugs, dyestuffs, and indicators [1-4]. In a previous paper we reported the synthesis of 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones [5]. The present work extends the synthesis of 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenoselenazin-4-one **6** and the 3- and/or 10-substituted compounds by the condensation of zinc 2-aminobenzeneselenolates **3** [6,7] and the corresponding 2-bromo- or 2,6-dibromo-4,8-bis(alkylamino)-1,5-naphthoquinones **4** [8].

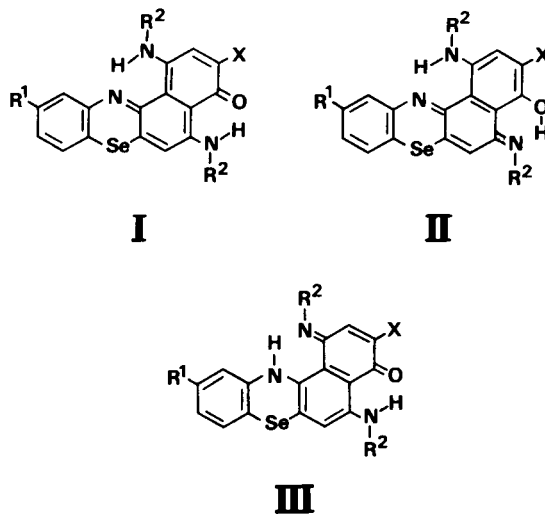
The phenoselenazinequinone derivatives **1** have been studied and such compounds have been used as optical recording dyes [9,10]. There have been few studies of 1,5-disubstituted-4*H*-benzo[*a*]phenoselenazin-4-ones shown by the general formula **2**.



The condensation of **3**, including a 4-substituent such as chloro and methoxyl groups, with **4** in ethanol in the presence of hydrochloric acid [3] at room temperature under argon atmosphere gave **6** along with some by-products. A stable intermediate **5** was also isolated from the reaction mixture, which was cyclized in ethanol in the presence of hydrochloric acid to give **6**.

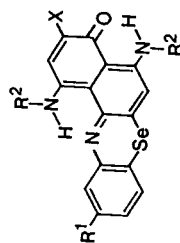
The reaction of **3** with **4** in *N,N*-dimethylformamide gave **5** as the main product in high yield without formation of **6**. Then, **5** was cyclized to **6** by the method described above. It should be noted that the two-step reaction of this condensation gave **6** in higher yield (49-78%) in comparison with the one-step reaction in acidic ethanol (18-34%). Compounds **6** absorbed near infrared light and could be used as IR dyes for a laser beam [11].

In the ¹H nmr spectra of **6a-c** in deuteriochloroform, the signals for both methyl protons were split into a doublet by the neighboring NH protons. In the cases of **6d-j**, the observed multiplicities of the methyne or methylene protons adjacent to nitrogen atoms in the 1- and 5-substituents suggest the existence of NH protons, indicating that the preponderant tautomers in chloroform are quinone monoimine forms bearing 1- and 5-bis(alkylamino) groups. The chemical shifts for quinonoid H-6 protons of **6a**, **6d** and **6f** moved to lower field than those (δ 6.41-6.65) for the corresponding 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones by 0.24-0.36 ppm. These results were consistent with the lower C _{β} shielding [12] for phenyl vinyl selenide than that for phenyl vinyl sulfide and therefore may be ascribed to the lower polarizability of the Se atom compared with the S atom. Similar arguments can be applied to the slightly higher carbonyl stretching frequencies in **6a**, **6d** and **6f** than those (1612-1624 cm⁻¹) in the corresponding sulfur derivatives.



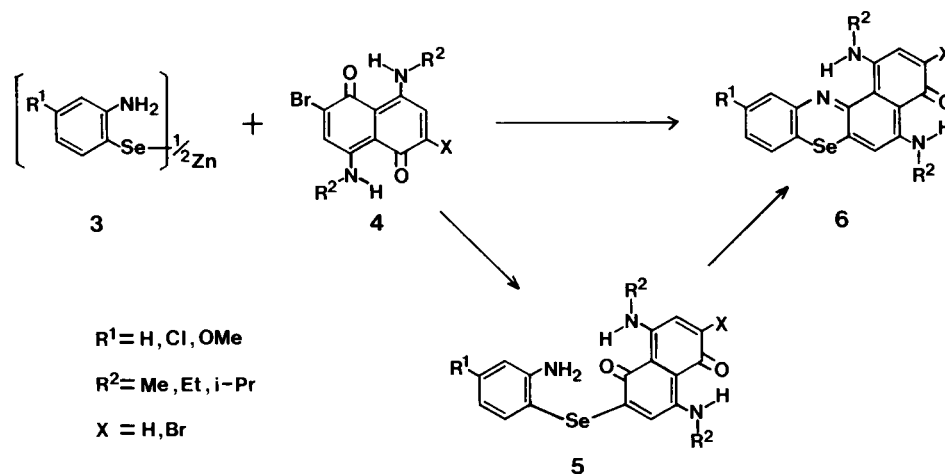
In the visible absorption spectra of **6** in chloroform, there were observed three slowly interconverting tautomers (**I**, **II** and **III** forms) to such an extent that the NH proton

Table 1
Yield, λ max and Elemental Analysis of Compounds **6**

**6**

Compound	R ¹	R ²	X	Method (Yield, %)	λ max/nm ($\epsilon \times 10^{-4}$)					Elemental Analysis (%)		
					λ_1	λ_2	λ_3	λ_4	λ_5	Found	Calcd.	C
6a	H	Me	H	A (20), B (68)	757 (1.17)	710 (0.90)	550 (0.21)	505 (0.25)	406 (0.41)	58.86 (58.70)	4.07 (4.11)	11.27 (11.41)
6b	Cl	Me	H	B (64)	752 (2.55)	692 (1.69)	559 (0.44)	514 (0.43)	410 (0.78)	53.60 (53.68)	3.45 (3.50)	10.32 (10.43)
6c	OMe	Me	H	B (71)	760 (1.97)	714 (1.47)	572 (0.41)	526 (0.40)	406 (0.61)	57.67 (57.29)	4.38 (4.30)	10.34 (10.55)
6d	H	Et	H	A (27), B (54)	757 (1.06)	707 (0.80)	550 (0.20)	506 (0.23)	406 (0.38)	60.69 (60.61)	4.76 (4.83)	10.33 (10.60)
6e	Cl	Et	H	B (72)	751 (1.78)	690 (1.18)	558 (0.32)	514 (0.32)	410 (0.56)	55.96 (55.76)	4.20 (4.21)	9.48 (9.75)
6f	H	<i>i</i> -Pr	H	B (72)	752 (1.55)	703 (1.16)	547 (0.28)	504 (0.33)	404 (0.57)	62.45 (62.26)	5.54 (5.46)	9.78 (9.90)
6g	H	<i>i</i> -Pr	Br	A (34), B (58)	775 (2.76)	718 (2.12)	548 (0.55)	508 (0.70)	413 (1.12)	52.43 (52.50)	4.31 (4.41)	8.18 (8.35)
6h	Cl	<i>i</i> -Pr	H	B (78)	748 (1.89)	684 (1.25)	556 (0.33)	510 (0.32)	408 (0.61)	57.69 (57.59)	4.85 (4.83)	9.20 (9.16)
6i	Cl	<i>i</i> -Pr	Br	A (18), B (49)	768 (1.50)	715 (1.02)	558 (0.27)	516 (0.32)	414 (0.52)	49.45 (49.14)	4.18 (3.94)	7.74 (7.81)
6j	OMe	<i>i</i> -Pr	H	B (63)	756 (1.98)	704 (1.42)	568 (0.41)	522 (0.41)	402 (0.61)	60.89 (60.79)	5.36 (5.55)	9.06 (9.25)

[a] See Experimental.



was coupled to the protons on the adjacent carbon atom on the nmr time scale. Table 1 lists their absorption characteristics, together with some physical data. As **6** showed visible absorption spectra similar to those of 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones, the two absorption bands at λ_1 and λ_2 in 680-780 nm region were assigned to form **I** i.e., **6** and those at λ_3 and λ_4 in the 500-580 nm region to form **II**; similarly the absorption band at λ_5 near 410 nm may originate from form **III**. In the cases of **6a**, **6b** and **6f** compared with the corresponding 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones, the longer absorption maxima λ_1 slightly shifted hypsochromically by 2-4 nm whereas the λ_3 and λ_4 shifted bathochromically by 8-10 and 2-3 nm, respectively; the hypsochromic shift of 11-17 nm was observed for the λ_5 of form **III**. The values (0.18-0.20) of the ratio of apparent absorbances (ϵ_3/ϵ_1) at λ_3 and λ_1 for **6a**, **6d** and **6f** were lower than those (0.23-0.24) for 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones.

The visible absorption spectra of **6** were little affected by the change of *N*-alkylation on going from *N*-methyl to *N*-isopropyl substituents. Substitution of a chloro group at the 10-position of **6a**, **6d** and **6f** resulted in the hypsochromic shifts for the λ_1 and λ_2 by 4-5 and 18-19 nm, respectively, and the bathochromic shift for the λ_3 and λ_4 by 6-9 nm. Introduction of a methoxyl group on the 10-position of **6a** and **6f** brought about a larger red shift for form **II** than for form **I**, whereas 3-bromo substitution of the parent compounds **6f** and **6h** resulted in a larger red shift for form **I** than for form **II**. The bathochromic shift (4-9 nm) for the λ_5 arising from form **III** was observed by introduction of the 3-bromo or the 10-chloro group.

EXPERIMENTAL

Melting points were determined with a Yanaco micromelting point apparatus and are uncorrected. The ir spectra were recorded on a JASCO A-102 spectrometer using potassium bromide pellets. The ultraviolet and visible spectra were obtained with a

Hitachi 150-20 UV spectrometer using 1 cm quartz cells. The absorption maxima are reported in nanometers. The ¹H nmr spectra were obtained in chloroform-*d* using a JOEL JNM-PMX 60SI NMR spectrometer. Chemical shifts are reported in ppm from TMS used as internal standard and are given in δ . The following abbreviations were used to designate the multiplicity of individual signals: s = singlet, d = doublet, q = quartet, m = multiplet and br = broad. The exact mass spectra were recorded on a Hitachi M-2000 spectrometer. For column chromatography, silica gel (Kieselgel 60, Merck, 70-230 mesh) was used.

Zinc 2-amino-4-substituted benzeneselenenolates **1**, (R¹ = H, Cl, OMe) were prepared from the corresponding 2-nitroanilines according to the method of Bauer [6] and Nishi [7] except for the case of the 4-methoxyl analogue prepared in degassed solvent under an argon atmosphere in order to prevent the oxidative formation of the diselenide.

Preparation of 1,5-Bis(alkylamino)-4*H*-benzo[*a*]phenoselenazin-4-ones.

Method A.

To a deaerated suspension of **3** (1.5 mmoles) and **4** (1 mmole) in ethanol (10 ml) was added 6*N* hydrochloric acid (2.5 ml) under an argon atmosphere. The mixture was stirred for 72 hours at room temperature. The solution was neutralized with diluted aqueous sodium carbonate solution and extracted with chloroform. The chloroform layer was dried (magnesium sulfate) and evaporated *in vacuo*. Then the residue was chromatographed on silica gel eluting with chloroform-ethyl acetate (4:1) giving **6** in 17-34% yield.

Method B.

To a deaerated suspension of **4** (1 mmole) in *N,N*-dimethylformamide (10 ml) were added **3** (1.5 mmole) under an argon atmosphere. The mixture was stirred for 24 hours at room temperature. The solution was poured into water (100 ml) and the resulting precipitate was filtered. The precipitate was dissolved in ethanol (20 ml) and 6*N* hydrochloric acid (5 ml). The solution was stirred for 24 hours at room temperature, neutralized with aqueous sodium carbonate solution and extracted with chloroform. The chloroform layer was dried (magnesium sulfate) and evaporated *in vacuo*. The residue was chromatographed on silica gel eluting with chloroform-ethyl acetate (4:1), giving **6** in 44-78% yield.

Compound 6a.

This compound had mp 191.2-193.5°; ir: 1620 (C=O), 1598 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 3.00 (d, 3H, J = 5 Hz, CH_3), 3.32 (d, 3H, J = 2 Hz, CH_3), 6.77 (s, 1H, H-6), 6.85 (d, 1H, J = 10 Hz, H-3), 7.19 (d, 1H, J = 10 Hz, H-2), 6.85-7.30 (m, 4H), 12.33 (br, 1H, N-H), 14.18 (br, 1H, N-H); ms: Calcd. for $\text{C}_{18}\text{H}_{13}\text{N}_3\text{OSe}$ = 369.0380. Found: m/e = 369.0360 (M^+).

Compound 6b.

This compound had mp 235.1-243.3° dec; ir: 1625 (C=O), 1595 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 3.08 (d, 3H, J = 5 Hz, CH_3), 3.48 (d, 3H, J = 2 Hz, CH_3), 6.75 (d, 1H, J = 10 Hz, H-3), 6.95 (s, 1H, H-6), 7.08 (d, 1H, J = 10 Hz, H-2), 6.81-7.76 (m, 3H), 12.05 (br, 1H, N-H), 14.37 (br, 1H, N-H); ms: Calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{OClSe}$ = 402.9991. Found: m/e = 402.9967 (M^+).

Compound 6c.

This compound had mp 186.2-190.5° dec; ir: 1620 (C=O), 1590 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 3.02 (d, 3H, J = 5 Hz, CH_3), 3.37 (d, 3H, J = 2 Hz, CH_3), 3.76 (s, 3H, OCH_3), 6.55 (s, 1H, H-6), 6.80 (d, 1H, J = 10 Hz, H-3), 7.18 (d, 1H, J = 10 Hz, H-2), 6.29-7.33 (m, 3H), 12.15 (br, 1H, N-H), 14.23 (br, 1H, N-H); ms: Calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2\text{Se}$ = 399.0486. Found: m/e = 399.0485 (M^+).

Compound 6d.

This compound had mp 164.5-165.2°; ir: 1625 (C=O), 1600 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 1.35 (t, 3H, J = 7 Hz, CH_3), 1.52 (t, 3H, J = 7 Hz, CH_3), 3.37 (qd, 2H, J = 7, 5 Hz, CH_2), 3.65 (qd, 2H, J = 7, 2 Hz, CH_2), 6.80 (s, 1H, H-6), 6.82 (d, 1H, J = 10 Hz, H-3), 7.16 (d, 1H, J = 10 Hz, H-2), 6.77-7.20 (m, 4H), 12.47 (br, 1H, N-H), 14.47 (br, 1H, N-H); ms: Calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{OSe}$ = 397.0693. Found: m/e = 397.0764 (M^+).

Compound 6e.

This compound had mp 145.5-147.8°; ir: 1620 (C=O), 1596 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 1.33 (t, 3H, J = 7 Hz, CH_3), 1.46 (t, 3H, J = 7 Hz, CH_3), 3.29 (qd, 2H, J = 7, 5 Hz, CH_2), 3.57 (qd, 2H, J = 7, 2 Hz, CH_2), 6.75 (d, 1H, J = 10 Hz, H-3), 6.80 (s, 1H, H-6), 7.11 (d, 1H, J = 10 Hz, H-2), 6.73-7.26 (m, 3H), 12.05 (br, 1H, N-H), 14.42 (br, 1H, N-H); ms: Calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{OClSe}$ = 431.0304. Found: m/e = 431.0306 (M^+).

Compound 6f.

This compound had mp 163.4-164.2°; ir: 1627 (C=O), 1581 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 1.34 (d, 6H, J = 6 Hz, CH_3), 1.44 (d, 6H, J = 6 Hz, CH_3), 3.70-4.43 (m, 2H, CH), 6.93 (s, 1H, H-6), 6.83 (d, 1H, J = 10 Hz, H-3), 6.70-7.40 (m, 4H), 7.31 (d, 1H, J = 10 Hz, H-2), 12.40 (br, 1H, N-H), 14.63 (br, 1H, N-H); ms: Calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{OSe}$ = 425.1006. Found: m/e = 425.0926 (M^+).

Compound 6g.

This compound had 95.0-102.2° dec; ir: 1600 (C=O), 1590

(C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 1.35 (d, 6H, J = 6 Hz, CH_3), 1.44 (d, 6H, J = 6 Hz, CH_3), 3.60-4.40 (m, 2H, CH), 6.97 (s, 1H, H-6), 6.57-7.30 (m, 4H), 7.68 (s, 1H, H-2), 13.63 (br, 1H, N-H), 14.11 (br, 1H, N-H); ms: Calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_3\text{OBrSe}$ = 503.0112. Found: m/e = 503.0107 (M^+).

Compound 6h.

This compound had mp 182.0-185.5°; ir: 1630 (C=O), 1591 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 1.32 (d, 6H, J = 6 Hz, CH_3), 1.44 (d, 6H, J = 6 Hz, CH_3), 3.60-4.37 (m, 2H, CH), 6.78 (d, 1H, J = 10 Hz, H-3), 6.86 (s, 1H, H-6), 6.73-7.20 (m, 3H), 7.25 (d, 1H, J = 10 Hz, H-2), 12.03 (br, 1H, N-H), 14.73 (br, 1H, N-H); ms: Calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_3\text{OClSe}$ = 459.0617. Found: m/e = 459.0677 (M^+).

Compound 6i.

This compound had mp 162.5-166.8° dec; ir: 1607 (C=O), 1590 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 1.37 (d, 6H, J = 6 Hz, CH_3), 1.47 (d, 6H, J = 6 Hz, CH_3), 3.40-4.34 (m, 2H, CH), 6.95 (s, 1H, H-6), 6.68-7.26 (m, 3H), 7.73 (s, 1H, H-2), 13.20 (br, 1H, N-H), 14.23 (br, 1H, N-H); ms: Calcd. for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{OBrClSe}$ = 536.9709. Found: m/e = 536.9689 (M^+).

Compound 6j.

This compound had mp 174.8-178.2° dec; ir: 1626 (C=O), 1594 (C=N) cm^{-1} ; ^1H nmr: (deuteriochloroform): δ 1.33 (d, 6H, J = 6 Hz, CH_3), 1.43 (d, 6H, J = 6 Hz, CH_3), 3.76 (s, 3H, OCH_3), 3.57-4.30 (m, 2H, CH), 6.58 (s, 1H, H-6), 6.82 (d, 1H, J = 10 Hz, H-3), 7.23 (d, 1H, J = 10 Hz, H-2), 6.37-7.33 (m, 3H), 12.66 (br, 1H, N-H), 14.67 (br, 1H, N-H); ms: Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_2\text{Se}$ = 455.1112. Found: m/e = 455.1063 (M^+).

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