

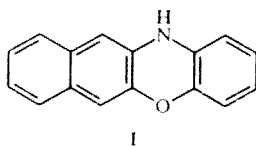
SYNTHESIS AND SPECTRAL PROPERTIES OF BENZO[b]PHENOXYAZINE DERIVATIVES

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Nitro and amino derivatives of benzo[b]phenoxazine have been synthesized. The spectroluminescence properties of the synthesized compounds are investigated.

We have shown previously that 2,7-dinitrophenoxazine, in contrast to most other nitro compounds, exhibits luminescence and lasting in alcoholic alkali solution [1, 2], while 12,14-dinitrodibenzo[b]phenoxazine, obtained by nitrating a linearly annelated naphthalene analog of phenoxazine, namely, dibenzo[b,i]phenoxazine, does not exhibit luminescence [3]. It was of interest therefore to study other condensed analogs of phenoxazine, primarily, benzo[b]phenoxazine, a compound containing benzene and naphthalene rings.

This paper describes the synthesis and spectral properties of nitro and amino derivatives of benzo[b]phenoxazine (I).



The literature has reported only the nitration of the N-acetyl derivative of compound I with fuming nitric acid in glacial acetic acid [4], which form a mixture of mono- and tetranitro derivatives, but their yields are not indicated, and the compounds were insufficiently characterized. As indicated by the authors, in the mono derivative, the nitro group is in the para position to the heterocycle nitrogen atom. However, when we reproduced this method, we isolated mainly the tetranitro derivative (according to data of ultimate analysis), but were unable to establish the location of the nitro groups, and the mononitro derivative could not be obtained at all in this manner.

It was found in the present study that, depending on the nitrogen conditions, different nitro derivatives are obtained. Thus, nitration of compound I in dimethylformamide with sodium nitrite in acetic acid gave 9-nitrobenzo[b]phenoxazine (II).

In the absence of dimethylformamide, nitration of compound I results in a mixture of compounds: 1,9-dinitrobenzo[b]phenoxazine (III) and 9-nitro-1,12-bis(benzo[b]phenoxazine) (IV). This mixture if separated by treatment with a 0.1 N solution of alcoholic alkali. The dinitro derivative III is obtained by precipitation with hydrochloric acid from the alcoholic alkali solution. Compound IV is obtained by recrystallizing from toluene the residue remaining undissolved in the alcoholic alkali. The structure of the compounds obtained was confirmed by ultimate analysis data and ESR spectra.

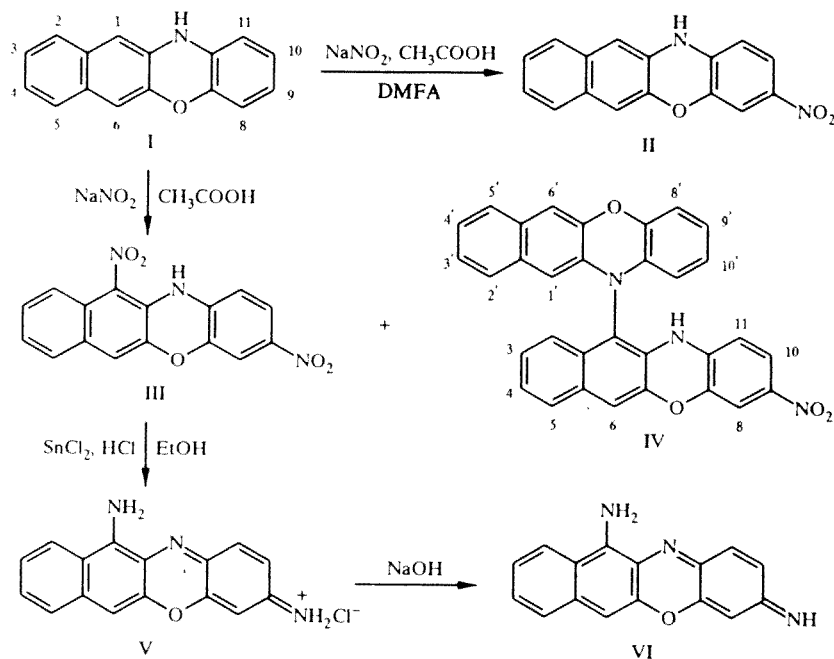
The ESR spectra of compounds I-IV are shown in Table 1. The absence of a proton at the C₍₉₎ atom in compound II and of protons at C₍₁₎ and C₍₉₎ in compounds III and IV confirms their structure.

The spectroluminescence characteristics of the synthesized compounds are presented in Table 2. As is evident from the latter, the presence of the nitro group in compounds II-IV causes a bathochromatic shift of the long-wavelength absorption bands in comparison to the unsubstituted compound I. In alcoholic alkali, their further bathochromic shift takes place as a result of the formation of the corresponding anionic forms, but in contrast to the anionic form of 2,7-dinitrophenoxazine [2], none of them exhibits luminescence properties.

TABLE 1. ESR Spectra of Compounds I-IV in DMSO-D₆ (360 MHz)

Com- pound	Empirical formula	Chemical shifts, δ , ppm												
		aromatic protons, $J_{HH'}$, Hz												
		H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₈	H ₉	H ₁₀	H ₁₁	NH		
I	C ₁₆ H ₁₁ NO	6.65 s	6.62 d	6.5 m	H ₃ +H ₄	6.67 pseudo-t	6.05 s	7.4 pseudo-t H ₁₁ +H ₈	7.07 pseudo-t	7.02 pseudo-t	7.4 pseudo-t	8.6 s		
II	C ₁₆ H ₁₀ N ₂ O ₃	6.15 s	5.98 d (8.0)	6.62 d. d (7.47; 7.82)	6.8 t (1.45; 7.47; 7.82)	6.95 d (1.42; 8.0)	7.78 d H ₆ +H ₁₀ (2.2; 8.45)	8.58 d (2.6)	—	7.78 d H ₁₀ +H ₆ (2.2; 8.45)	7.69 d (8.5.)	10.0 s		
III	C ₁₆ H ₉ N ₃ O ₅	—	7.72 d (8.0)	7.45 pseudo-t (8.0; 8.0)	7.35 pseudo-t (8.0; 8.0)	7.77 d. d (8.0; 3.0)	7.55 d (3.0)	7.41 s	—	7.65 d (9.0)	7.15 d (9.0)	9.84 s		
IV	C ₃₂ H ₁₉ N ₃ O ₄	—	7.25... 7.35 d H ₂ +H ₅	7.10 d.d	7.15 d.d	7.25... 7.35 d H ₅ +H ₂	7.42 s	7.55 s		7.57 d weakly polar component under H ₃	7.45 d weakly polar component under H ₄	9.66 s		
		H ₁ '	H ₂ '	H ₃ '	H ₄ '	H ₅ '	H ₆ '	H ₈ '	H ₉ '	H ₁₀ '	H ₁₁ '			
		6.15 s	5.95 d	6.65 d.d	6.75 d.d	6.95 d	7.22 s	7.8 d	7.7 d.d	7.2 d.d	6.85 d			

Reduction of compound III with the dichloride in alcoholic hydrochloric acid results in the formation of 1,9-diaminobenzo[b]phenoxazonium chloride (V) with an appreciable bathochromic shift of the long-wavelength absorption and to 725 nm. When it is acted on by alkali, the base (VI) is formed as in the case of Nile blue, and this results in a hypsochromic shift of the long-wavelength absorption band to 570 nm. Compounds V and VI also have practically no luminescence properties.



EXPERIMENTAL

The absorption spectra of solutions of the compounds studied were measured with a Hitachi-356 spectrophotometer, and the luminescence spectra were measured with an SDL-1 apparatus using a DKSh-1000 xenon lamp as the excitation source and with a Shimadzu RF-540 spectrofluorimeter; the quantum yields of luminescence (φ_{fl}) were measured with a quantum counter using a 1-oxazine dye [5] against standards consisting of ethanol solutions of 3-aminophthalimide ($\varphi_{\text{fl}} = 0.60$), rhodamine 6G ($\varphi_{\text{fl}} = 0.94$), and cresyl violet ($\varphi_{\text{fl}} = 0.56$) [6]. The ESR spectra were obtained with a Bruker WH-360 (360 MHz) instrument with TMS as the internal standard. The molecular masses were obtained with an MX-1320 mass spectrometer with an ionizing voltage of 50 eV.

Silica gel with a particle size of 40/100 μm was used for chromatographic purification and separation. The purity of the compounds was controlled by TLC on Silufol 254 plates.

The ultimate analysis data for C, H, and N correspond to the calculated data.

Nitration of Benzo[b]phenoxazine (I). A. To a suspension of 1 g (4.2 mmoles) of compound I in 20 ml of dimethylformamide is added 6 g (75 mmoles) of sodium nitrite, and 10 ml of acetic acid is added dropwise with stirring; the solution obtained is stirred for 15 min at 20°C, then heated on a water bath for 10 min, cooled, diluted with water, and the precipitate is filtered off, dried, and chromatographed on silica gel with benzene. There is obtained 0.4 g (33.5%) of 9-nitrobenzo[b]phenoxazine (II), mp 345°C. Found: M^+ 278. Calculated: M 278.

B. To a suspension of 2.16 g (9.2 mmoles) of compound I in 80 ml of glacial acetic acid is gradually added with stirring 1.84 g (26 mmoles) of sodium nitrite, and the mixture is allowed to stand for 3 h at room temperature. The red precipitate formed is filtered off, washed with water, and dried. The yield of the mixture of nitro products is 2.43 g. From the mixture, the dinitro derivative is extracted with 0.1 N alcoholic alkali solution until the extract turns pale blue; when 3 ml of concentrated hydrochloric acid is added, a red precipitate appears which is then washed with water, dried, and recrystallized from toluene. There is obtained 1.9 g (30%) of 1,9-nitrobenzo[b]phenoxazine (III), mp 266 °C. Found: M^+ 323. Calculated: M 323.

TABLE 2. Spectroluminescence Characteristics of Compounds I-VI

Compound	Solvent	Absorption, λ_{\max} , nm (log ϵ)	Luminescence, λ_{\max} (log ϕ)
I	Ethanol	235 (4.68), 265 (4.53), 318 (4.10), 365 (4.10)	430 (0.24)
II	Toluene	283 (4.20), 314 (4.08), 361 (4.20)	420 (0.28)
	Ethanol	235 (4.67), 265 (4.38), 436 (4.22)	Absent
	0.1 N KOH solution in ethanol	235 (4.64), 265 (4.49), 538 (4.35)	Absent
III	Toluene	284 (4.37), 355 sh (3.83), 438 (4.15)	500, 530 (around 0.05)
	Ethanol	245 (4.59), 443 (4.30)	Absent
	0.1 N KOH solution in ethanol	245 (4.28), 605 (4.55)	Absent
IV	Toluene	284 (4.58), 350 (4.26), 470 (4.52)	500, 610 (around 0.05)
	Ethanol	235 (4.65), 272 (4.60), 368 (4.20), 456 (4.44)	Absent
	0.1 N KOH solution in ethanol	235 (4.74), 272 (4.62), 365 sh (4.11), 618 (4.45)	Absent
V	Toluene	285 (4.70), 325 sh (4.10), 373 (4.30), 412 (4.30)	515 (0.30)
	Ethanol	250 (4.40), 320 (4.35), 495 (4.37), 520 sh (4.17), 725 (4.11)	760, 790 (around 0.05)
	Ethanol	246 (4.59), 303 (4.00), 470 (4.20), 570 (4.10)	760, 790 (around 0.05)

The precipitate remaining after treatment with alcoholic alkali is washed with water, dried, and recrystallized from o-dichlorobenzene. There is obtained 0.4 g (9%) of 9-nitro-1,12-bis(benzo[b]phenoxazine) (IV). mp > 40°C. Found: M^+ 509. Calculated: M 509.

1,9-Diaminobenzo[b]phenoxazonium Chloride (V, $C_{16}H_{12}ClN_3O$). A mixture of 1.1 g (4 mmoles) of compound III, 11 ml of concentrated hydrochloric acid and 10 g of tin dichloride is boiled for 5 h in 110 ml of ethanol. After cooling, the white precipitate of tin salt is filtered off and treated on a filter with 100 ml of a 0.1 N sodium hydroxide solution in ethanol; a ferric chloride solution is added, then the precipitate is filtered off, washed with water, and dried. There is obtained 0.4 g (51%) of compound V. Found: M^+ 261. Calculated: M 261.

1,9-Diaminobenzo[b]phenoxazine base (VI, $C_{16}H_{11}N_3O$). Compound V in the amount of 0.6 g is dissolved in 100 ml of a 0.15 N KOH solution in ethanol, the solution is filtered off, water is added to the filtrate, and the precipitate is filtered off and dried. There is obtained 0.5 g of compound VI. Found: M^+ 261. Calculated: M 261.

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