SYNTHESIS AND PROPERTIES OF ANHYDRIDE OF BENZO[k,]SELENOXANTHENE-3,4-DICARBOXYLIC ACID

A. V. Guttsait, K. A. Balodis, and I. A. Meirovits

By the reaction of the anhydride of 4-nitronaphthalene-1,8-dicarboxylic acid with 2-aminobenzoselenol zincate, followed by the action of isoamyl nitrite on the reaction mixture, the anhydride of benzo[k.l]selenoxanthene-3,4-dicarboxylic acid has been synthesized. Through the reaction of this anhydride with primary amines, a number of corresponding imides have been synthesized.

Imides of benzo[k, l]xanthene-3,4-dicarboxylic acid and benzo[k, l]thioxanthene-3,4-dicarboxylic acid are known primarily as effective luminescent dyes, distinguished by high photostability, for synthetic fibers, plastics, and nonpolar media [1-4]. A number of high-contrast liquid crystal compositions have been developed on the basis of these compounds [5, 6]. A group of Japanese investigators developed photopolymerizing compositions, highly sensitive to the visible part of the spectrum, containing as the photoinitiator of the polymerization reaction certain derivatives of benzo[k, l]xanthene-3,4dicarboxylic acid and benzo[k, l]thioxanthene-3,4-dicarboxylic acid, in mixtures with N-phenylglycine (PG) [7, 8]. It was suggested in [7] that the interaction of a benzothioxanthene dye (BTXD) in the excited triplet state with PG forms a charge transfer complex that dissociates into an anion radical BTXD⁻⁺ and a cation radical PG⁺⁺. The latter is decarboxylated to form a neutral phenylaminomethylene radical that initiates polymerization of the reaction mixture. Obviously, one of the important factors determining the effectiveness of the polymerization photoinitiator is the rate of the intercombination conversion BTXD* \rightarrow ³BTXD*. The conversion is increased by the introduction of heavy atoms into the dye-sensitizer [9]; therefore, replacement of the sulfur atom by selenium in the BTXD ring may increase the effectiveness of the photosensitizer.

The work reported here was aimed at synthesizing the previously unknown anhydride of benzo[k, l] selenoxanthene-3,4-dicarboxylic acid III and a series of imides IV, for a study of their spectral-luminescence and donor-acceptor properties.

The anhydride of benzo[k, l]thioxanthene-3,4-dicarboxylic acid is usually obtained by condensation of 4-nitro- or 4-halonaphthalic anhydride with 2-aminobenzothiol [2, 9, 10]. The anhydride of 4-(2-aminophenylthio)naphthalene-1,8-dicarboxylic acid that is formed is cyclized (Pschorr reaction) without separating it from the reaction mixture [2, 9].

The use of 2-aminobenzoselenol for the synthesis of the anhydride III presents some difficulties because of the ease of its oxidation and its photoinstability; therefore, we used the stable zinc salt V, which is readily synthesized from 2,2,-dinitrophenyl diselenide [11].

The condensation of 4-nitronaphthalic anhydride (I) with the zincate V proceeds smoothly in DMF. The anhydride II that is formed, without being separated, is subjected to cyclization by the action of isoamyl nitrite.

By reaction of the anhydride III with aliphatic amines, performed by refluxing in 2-methoxyethanol, we obtained a series of imides IVa-d with good yields. All of the compounds are orange-colored crystalline substances, with intense luminescence in solutions in the green region of the spectrum: λ_{max}^{fl} in benzene ~512-550 nm, in DMF ~540-550 nm.

The composition and structure of the compounds that were synthesized were confirmed by elemental analyses and by IR, UV, and PMR spectra. As can be seen from Table 1, the imides IVa-d have very similar spectral characteristics. We also synthesized a thio analog for comparison, the octadecylimide VI, which had been proposed previously has a luminescent dye for nonpolar media [4]. No spectral data on VI had been reported previously in the literature.

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 $R = C_4H_9$; a, $R = C_6H_{11}$; b $R = C_{18}H_{37}$; c $R = CH_2CH_2OH$

The IR spectra of the imides IVa-d are characterized by two maxima corresponding to absorption by the imide carbonyls at 1642-1654 and 1687-1693 cm⁻¹, analogous to the maxima for the imide VI and the corresponding thio analogs [10].

The UV spectra of the anhydride III and the imides IVa-d are also generally similar to those of the thio derivatives, with the exception of the spectra taken in benzene solution. For these spectra, the two long-wave maxima for the imides IV (at 455 and 470 nm) are of equal intensity, appearing on the spectra as a horizontal plateau. For the anhydride III and the imides IVa-d, we observe a slight bathochromic shift of the long-wave absorption maxima in comparison with the thio analogs (6 nm for compounds IVc and VI in DMF), which is not as significant as when the change is made from the corresponding xanthene derivatives to thioxanthene derivatives ($\sim 27-35$ nm) [1, 10].

The PMR spectra taken for compounds IVc and VI are also consistent with the proposed structures.[†] The most significant upfield shift as a result of strengthening of the electron-donor properties of the heteroatom when the change is made from IVc to VI is observed for the signals of the proton of C_6 and C_1 (0.28 and 0.19 ppm, respectively).

Our investigation of the spectral-luminescence properties of the synthesized compounds will be the subject of our next communication.

EXPERIMENTAL

The IR spectra were recorded in Specord M-80 and Specord IR-75 instruments, on suspensions in white mineral oil or hexachlorobutadiene; the UV spectra were recorded in a Specord UV-Vis spectrophotometer; the PMR spectra were recorded in a Bruker WH-90/DS instrument (90 MHz), with HMDS internal standard. The course of the reaction and the individuality of the compounds were monitored by means of TLC on Silufol plates (eluent 6:1 benzene – acetonitrile), with development in UV light.

The elemental analyses for C, H, N, and S matched the calculated values.

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	[IR spec-	177		-	[
ъ,	mp,°C	trum,ν,	Sola Jacob Sola		PMR spectrum, 6, ppm	d,
E O		cm ,	vent	$(and \log \varepsilon)$	(and SSCC, Hz)	6%
0 8		<u> </u>		(R
***			D) (77			
ш	290292	1703, 1717	DMF	470(4,35),		60
				3/6(3,04), 3/6(3,04),		
		ĺ		333пл(3.88).		ł
				292(4,05)		
IV	185187	1687, 1647	Benzene	456469(4,35),		77
				372(3,40),		
				345(3,89),		
			_	333(3,89)		
14	244245	1093, 1034	Benzene	430409(4,34),		86
				3/5(3,42), 345(3,88)		
		1		331 (3,89)		
1	1	ł		465(4,38),		
		1		373(3,42),		
			LWF	345(3,90),		
TV	109	1000 1010		334(3,90)		
17	106	1007, 1045	Benzene	373(3 40)	3.4 (1H, d, 2-H, $J = 8,40$), 3.4 (1H d 5-H $I = 7.0$) 8.31	94
	1			344(3.85).	(1H, d, 1-H, J = 8.4), 8.25 and	
				326(3,86)	7,40 (4H, m, 8-11-H), 7,74	
			DMF	467(4,33),	(1H,t, 6-H, J = 7,9), 4,09	
		1		375(3,42),	$(2H, I, N-CH_2-),$	
		1		340(3,80),	$(CH_{a})_{a}$ (CH _a)	
īv	212 214	1688 1642	DMF	466(4 25)	(C112) 16C113)	64
1.	212214	1000, 1042	D2 11	374(3.30).		04
				345(3,83),		
	}		1	334(3,83)		
VI	112,5	1690, 1645	Benzene	471(4,27),	8,57 (1H, d., 2-H, $J = 8,1$),	61
				452(4,30),	8,39 (1H,d, 5-H, J = 7,9),	
				380(3,31), 345(3,65)	δ_{12} (1H, G, 1-H, $J = \delta_{1}$), 8 18 7 35 (AH m 8-11-H)	
	{		1	323(3.70	7.46 (1H. d. 6-H. $J = 7.9$)	
			DMF	456(4,21),	4,11 (2H, t1, N-CH ₂),	
		(380(3,50),	1,790,91 (35H,	
	Į	1		345(4,20))	(CH ₂) ₁₆ CH ₃)	

 TABLE 1. Physicochemical Characteristics of Synthesized Compounds

Anhydride of Benzo[k, I]selenoxanthene-3,4-dicarboxylic acid (III). To a suspension of 0.2 g (0.82 mmoles) of the anhydride I in 3 ml of DMF, at 40°C in an argon atmosphere, 0.2 g (0.49 mmoles) of the zinc salt II was added. After 1 h, 0.2 ml (1.39 mmoles) of isoamyl nitrite was added, and the mixture was heated at 70-80°C for 30 min, up to the start of crystallization. The reaction mixture was held for 12 h at 2-5°C in a refrigerator. The precipitate was filtered off, washed with methanol and water, dried at 100°C, and crystallized from acetic anhydride. Obtained 0.17 g (60%) of compound III.

N-Octadecylimide of Benzo[k, l]selenoxanthene-3,4-dicarboxylic acid (IVc). To a solution of 0.2 g (0.57 mmoles) of the anhydride III in 20 ml of 2-methoxyethanol, 0.19 g (0.70 mmoles) of octadecylamine was added, and the mixture was refluxed for 10 h. The reaction mixture was cooled, and the precipitate was filtered off, washed with ether and water, and dried at 110°C. Obtained 0.32 g (94%) of the imide IVc. Compounds IVa,b,d were obtained analogously (see Table 1).

N-Octadecylimide of Benzo[k,l]thioxanthene-3,4-dicarboxylic acid (VI). A suspension of 0.4 g (1.31 mmoles) of the anhydride of benzo[k,l]thioxanthene-3,4-dicarboxylic acid and 0.44 g (1.64 mmoles) of octadecylamine in 25 ml of 2-methoxyethanol was refluxed for 3.5 h. After cooling, the precipitate was filtered off and washed with 10 ml of ethanol. The product was chromatographed in a column with silica gel (40/100, Chemapol, Prague), eluent benzene. The solvent was evaporated, obtaining 0.45 g (51.5%) of compound VI. After crystallization from 2:1 hexane-ethanol, recovered acicular orange crystals of the imide VI.

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