Chemistry of Heterocyclic Compounds, Vol.35, No. 3, 1999

SYNTHESIS OF 1,3,4-OXADIAZOLE AND XANTHEN-2-ONE LUMINOPHORIC EPOXIDE MONOMERS

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Epoxide derivatives of 2,5-bis-oxyphenyl-1,3,4-oxadiazoles and fluorescein, which are luminescent epoxide monomers, are synthesized. Their luminescence properties are studied.

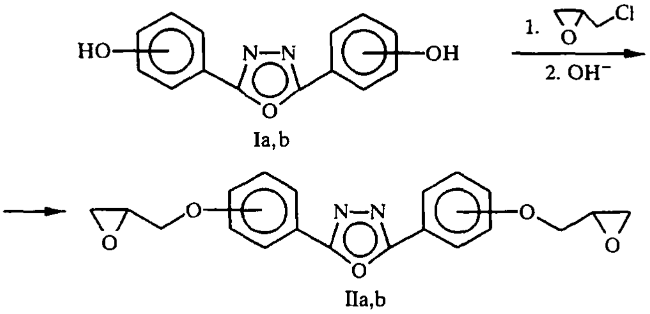
Luminescent epoxide monomers are relatively unknown in the literature [1, 2]. We proposed the epoxide monomer 1,3-diglycidyl-4,5-diphenylimidazol-2-one (DGDPI) as a luminophore and prepared luminescent epoxide polymers based on it [3]. The monomer is valuable because it can produce a high-quality (without defects) colorless polymeric casting and coatings that luminesce intensely upon UV irradiation.

Luminophores that do not contain epoxide groups such as 2,5-diphenyloxazole are used as additives to the epoxide resin and the liquid curing agents in polymeric epoxide luminophoric compositions (for example, scintillators) [4]. Nevertheless, finding effective epoxide-containing monomers is important because they can improve the luminescence characteristics of the compositions owing to the incorporation of the luminophore into the polymeric structure and the formation of a rigid luminophore system.

We synthesized new epoxide-containing systems based on classical 1,3,4-oxadiazole and xanthene luminophores. In particular, glycidyl ethers of 4,4'- and 3,3'-dihydroxy-2,5-diphenyloxadiazoles and of fluorescein were prepared.

The 2,5-bis(4- and 3-hydroxyphenyl)-1,3,4-oxadiazoles Ia,b are necessary for the synthesis. They were prepared from a mixture of the hydroxybenzoic acids and hydrazine hydrate in orthophosphoric acid by gradually increasing the temperature from 100 to 180°C. The proposed method is a modification of the known synthesis of 2,5-diaryl-1,3,4-oxadiazole derivatives [5] that consists of a reaction between hydrazine hydrate and acids in polyphosphoric acid. The IR spectra of Ia samples are identical to those reported previously [6] for compounds prepared by the literature method [7].

The bisphenols Ia,b were glycidylated in an excess of epichlorohydrin in the presence of NaOH and quaternary ammonium salts. The reaction proceeds readily if the temperature is gradually raised from 20 to 90°C.



Ia,b

IIa,b

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TABLE 1. Properties of Glycidyl Luminophore Monomers

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	R_f*	Wavelength		Luminescence quantum yield, η	Luminescence lifetime t, ns*	Yield, %
		C	H	N			absorption, λ, nm (log ε)	luminescence, λ, nm			
IIa	$C_{20}H_{18}N_2O_5$	$\frac{65{,}9}{65{,}5}$	$\frac{5{,}0}{4{,}9}$	$\frac{7{,}6}{7{,}7}$	192...195	0,80	302 (3,51)	358	0,92	1,43	67
IIb	$C_{20}H_{18}N_2O_5$	$\frac{65{,}4}{65{,}5}$	$\frac{4{,}9}{4{,}9}$	$\frac{7{,}9}{7{,}7}$	120...122	0,85	280 (4,33)	350	0,63	2,29	70
DGDPI	—	—	—	—	133...134	—	285 (3,87)	412	0,19	7,56	—
IV	$C_{26}H_{20}O_7$	$\frac{70{,}0}{70{,}3}$	$\frac{4{,}7}{4{,}5}$	—	115...120	0,88	456 (4,47)	530 552	0,82	3,71	87
V	—	—	—	—	98...100	—	254 (4,00)	376	0,11	3,02	—
VI	—	—	—	—	130...133	—	312 (3,82)	367	0,14	2,16	—

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* Spectral characteristics are obtained as before [11]; quantum yields of luminophores are given relative to quinine bisulfate (η_0 0.54) for IIa,b in DMF and the remaining compounds in ethanol.

TABLE 2. Spectral Characteristics of the Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm
IIa	3060 w (CH arom., CH_2 ep.) 1607 m (C=C arom.)	2,76 m (CH_2O ep.); 3,31 m (CHO); 3,84 d 4,06 d; 4,32 d; 4,51 d (CH_2O phen.) 7,16 m; 8,03 m (CH arom.)
IIb	3070 w (CH arom., CH_2 ep.) 1550 m (C=N); 1600 m 1490 br (C=C arom.); 975 w.; 930 m 870 s (C—O ep.)	2,93 m (CH_2O ep.); 3,48 m (CHO); 4,03 d 4,19 d; 4,55 d; 4,79 d (CH_2O phen.) 7,68 m; 8,06 m (CH arom.)
IV	3060 w (CH arom., CH_2 ep.) 1720 s (C=O carb.); 1640 s (C=O quin.) 1596 s; 1513 s; 1500 br (C=C arom.) 965 w; 908 m; 860 s (C—O ep.)	2,77 m; 2,93 m (CH_2O ep.); 3,49 m (CHO) 3,47...4,51 m (CH_2O eth.) 6,46...8,32 m (CH arom.)

Hydrolysis of the epoxide is not significant under these conditions. It does occur rather extensively if the heating is performed in the presence of more concentrated base.

The monomers IIa,b were isolated as colorless crystalline materials that fluoresce upon UV irradiation. They were purified until the absorption spectra were constant by recrystallization from the appropriate solvents. The composition and structure of IIa,b were confirmed by elemental analysis and spectral properties (Table 1) and by PMR and IR spectra (Table 2). Their purity was estimated by TLC.

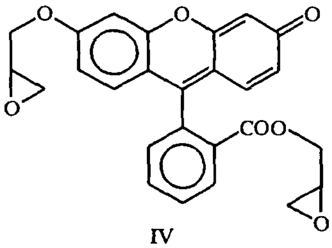
Monomers IIa,b contain 23.2 and 23.3% (calculated 23.5%) epoxide groups, respectively.

The PMR spectra of IIa,b contain signals for protons of cyclic CH_2O groups (2.76-2.93), CHO (3.31-3.46), noncyclic CH_2O groups (3.84-4.79), which are characteristic of glycidyl moieties, and signals for aromatic protons (7.16-8.06 ppm).

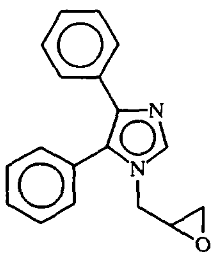
Bands for stretching vibrations of aromatic C=C bonds (~1500 and 1600-1610 cm^{-1}) and C–H (3060 cm^{-1}) are observed in the IR spectra. The latter apparently coincide with the absorption band for the CH_2 bond in the oxirane ring.

The preparation of epoxide monomers based on fluorescein is basically the same as that of epoxide resins based on phenolphthalein and its analogs. However, the reaction of phenolphthalein with epichlorohydrin with subsequent dehydrochlorination by base is known to form oligomeric diglycidyl derivatives of *p*-hydroxyphenyl-*o*-carboxyphenylmethylenquinone [8]. Therefore, we used the approach that was used to synthesize IIa,b to prepare the epoxide derivatives of fluorescein III. Glycidylation in the presence of an excess of base and quaternary ammonium salts produces a viscous substance that readily crystallizes by adding water to its acetone solution. The product is a crystalline orange compound with about the number of epoxide groups calculated for the diglycidyl derivative IV (17.3%, calculated 19.4%). Elemental analysis also is consistent with a diglycidyl derivative. The IR spectrum contains bands for the C=O bonds of quinoid (1640) and carboxyl (1720 cm^{-1}) groups. TLC confirms that the epoxide dye IV is pure (R_f 0.85). The slightly reduced content of epoxide groups compared with the calculated value is due to partial oligomerization. The data suggest that IV is 7-glycidyloxy-9-(2-glycidyloxycarbonylphenyl)-2-xanthone.

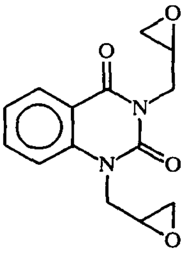
However, gradually increasing the temperature to 100°C under the conditions noted above (version A) and prolonged (10 h) boiling of the fluorescein with epichlorohydrin with subsequent dehydrochlorination by base (version B) do not produce the same products. This is evident from the color change of the solution from orange to yellow. In this instance the reaction products contain less of the monomer IV and primarily form 2,7-diglycidyloxyxanthen-9-spiro-3-phthalide. The presence of the latter was confirmed by isolating under these conditions (method B) a crystalline almost yellow dioxirane with close to the calculated number of epoxides (16.5%). The slight decrease in epoxide content compared with the calculated value is due to partial oligomerization.



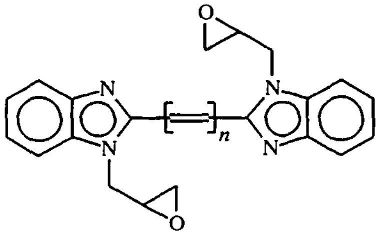
IV



V



VI



VII $n = 1$, VIII $n = 2$

Let us compare the luminescence properties for the glycidyl derivatives of the conjugated heterocyclic systems described in our work (IIa,b and IV) and those synthesized previously, (DGDPI) [3], 1-glycidyl-4,5-diphenylimidazole (V), 1,3-diglycidyl-2,4-quinazolindione (VI) [9], 1,2-bis(1-glycidylbenzimidazol-2-yl)ethylene (VII), and 1,4-bis(1-glycidylbenzimidazol-2-yl)butadiene (VIII) [10].

The monomers IIa,b, the luminescence of which is due to the linear chain of aromatic (phenyl and oxadiazole) cores, have comparatively high luminescence quantum yields and short emission lifetimes in DMF. (They are difficultly soluble in alcohol.) Therefore, the higher photoluminescence quantum yield for the *para*-substituted IIa compared with the *meta* isomer IIb is quite natural. A number of other epoxide luminophores that were studied in ethanol possessed the interesting feature ascribed to the imidazole structure in the luminescence of the ethylene compounds. Thus, compounds V, DGDPI, which can be viewed as structures with a *cis*-stilbene moiety built into the imidazole ring, luminescence with rather high Stokes shifts (127 and 122 nm, respectively) compared with other studied compounds was observed. However, the *cis*-ethylene derivatives do not luminesce [1]. It should be mentioned that 1,3-diglycidylbenzimidazol-2-one does not luminesce although 1,3-diglycidyl-2,4-quinazolinedione (VI), which also contains the carbamide moiety in the condensed ring, does luminesce with a small quantum yield. Compounds with the imidazole rings at a terminal position in the ethylene chain, e.g., benzimidazole dervitatives of alkenes such as 1,2-bis(1-glycidylbenzimidazol-2-yl)ethylene (VII) and 1,4-bis(1-glycidylbenzimidazol-2-yl)butadiene (VIII), which have a longer conjugation chain than the compounds mentioned above, fluoresce in nearly the same region as the monomer DGDPI (VII, 438; VIII, 443 nm) and do not have large Stokes shifts [VII, 67 nm, λ_{abs} 371 nm (log ε 4.47); VII, 65 nm, λ_{abs} 378 (log ε 4.60)]. The glycidyl derivative of IV, which has a long conjugated system, has a high quantum yield and a small Stokes shift.

Compounds IIa,b-VIII can be incorporated into the structure of epoxide polymers with known curing agents (amines, acid anhydrides). The polymers retain their luminescence properties. The monomers IIa,b and VI can be stably stored. They do not dye upon UV irradiation.

Thus, the new epoxide luminophores synthesized by us, IIa,b and IV, can be used to fabricate polymeric luminophores and scintillators.

EXPERIMENTAL

PMR spectra were recorded on a Gemini-200 (Varian) instrument in CDC13 (IV) and DMSO-d_6 (IIa,b) with HMDS internal standard. IR spectra were taken on a UR-20 spectrometer in nujol with slit program 4 and scan rate 160 cm^{-1}/min. Solvents for recrystallization were: DMF for IIa and VI; propan-2-ol for IIb; acetone–water for IV; and ether for V. TLC was performed on Silufol plates in $CDCl_3$–methanol 10:1 with visualization by iodine.

Bis(4- or 3-hydroxyphenyl)-1,3,4-oxadiazoles Ia and Ib. A. Mixture of *p*- or *m*-hydroxybenzoylhydrazine (15.2 g, 0.1 mol) and *p*-hydroxybenzoic acid (13.8 g, 0.1 mol) in orthophosphoric acid (85% solution, 100 ml) was heated successively at 100°C (1 h), 120°C (1 h), 140°C (1 h), 160°C (1 h), and 180°C (1 h). The water evolved was gradually removed. The reaction mixture was poured onto ice. The precipitate was filtered off, washed with water, and recrystallized from DMF. Yield of pure oxadiazoles Ia and Ib 14.0 g (55%) and 15.2 g (60%), respectively. The compounds are identical to those reported previously [6].

Bis(4- and 3-glycidyloxyphenyl)-1,3,4-oxadiazoles IIa and IIb. B. Bis(4- or 3-hydroxyphenyl)-1,3,4-oxadiazole Ia or Ib (25.4 g, 0.1 mol) and granulated NaOH (8.8 g) were mixed with epichlorohydrin (157 ml, 2 mol) and treated with tetraethylammonium chloride (0.33 g, 2 mmol). The mixture was stirred at 20°C for 30 min. The temperature was gradually raised as follows: 40°C (0.5 h), 50°C (0.5 h), 60°C (0.5 h), 70°C (1 h), 80°C (2 h), and 90°C (1 h). The precipitate was filtered off and thoroughly washed with water to remove salts. The mother liquor was evaporated and combined with the first portion. Most of the 4,4'-isomer, was found in the precipitate with the salt, but the 3,3'-isomer - in the mother liquor. Compounds IIa and IIb are colorless crystalline substances that are soluble in aprotic polar solvents. IIb is moderately soluble in ethanol and acetone.

7-Glycidyloxy-9-(2-glycidyloxycarbonylphenyl)-2-xanthone (IV). Mixture of fluorescein (16.6 g, 0.05 mol) and granulated NaOH (6.6 g, 0.165 mol) was treated with epichlorohydrin (78.4 ml, 1 mol) and tetraethylammonium chloride (0.17 g, 1 mmol). The mixture was heated with stirring to 40°C. Stirring was continued with the following heating regime: 40°C (1 h), 50°C (1 h), 60°C (1 h), 70°C (2 h), 80°C (2 h), and 90°C (0.5 h). The precipitate was filtered off. The mother liquor was passed through a thin (2 cm) layer of aluminum oxide, evaporated under vacuum, washed with hexane, and dried under vacuum at 30-40°C. The viscous orange substance crystallizes readily upon addition of water to its acetone solution. The orange crystals of the dioxirane IV contain 17.3% epoxide groups (calculated 19.4%) and 0.4% Cl; mp 115-120°C (from propan-2-ol–hexane 1:10).

Glycidylimidazole V and Bis(1-glycidylbenzimidazol-2-yl)alkenes VII and VIII were prepared by the literature method [10] by glycidylation of the corresponding imidazoles with epichlorohydrin in the presence of bases. Monomer VI was synthesized by the literature method [9] by successive condensation of 2,4-quinazolinedione with epichlorohydrin and dehydrochlorination of the condensation product by bases.

REFERENCES

1. R. N. Nurmukhametov, *Absorption and Luminescence of Aromatic Compounds* [in Russian], Khimiya, Moscow (1971), p. 216.
2. N. N. Barashkov and O. A. Gunder, *Fluorescent Polymers* [in Russian], Khimiya, Moscow (1987), p. 166.
3. N. I. Korotkikh, V. M. Artemov, L. B. Kanskaya, and O. P. Svaika, USSR Pat. No. 938550; *R. Zh. Khim.*, No. 3, 3N114P (1993).
4. F. Markley, "Plastic scintillators from cross-linked epoxy resins", in: *Organic Scintillators,* Gordon and Breach, New York (1966), p. 303.
5. Great Britain Pat. No. 896219; Off. J. (Pat.) 1962.
6. B. M. Krasovitskii, L. M. Kutsyna, L. D. Kornilovskaya, N. F. Levchenko, and N. I. Mal'tseva, *Zh. Prikl. Spektrosk.*, **9**, 485 (1968).
7. A. P. Grekov, L. M. Kulakova, and O. P. Shvaika, *Zh. Org. Khim.*, **39**, 3054 (1959).
8. J. Winstra, R. P. Kurkijy, and N. H. Reinking, *Ind. Eng. Chem.*, **52**, 127 (1960).
9. N. I. Korotkikh, G. A. Losev, V. A. Chernov, and O. P. Shvaika, USSR Pat. No. 1547277 (1989).
10. N. I. Korotkikh and O. P. Shvaika, *Zh. Org. Khim.*, **32**, 1076 (1996).
11. N. N. Baraskkov, T. V. Sakhno, N. N. Alekseev, T. M. Murav'eva, L. M. Bulgakova, and L. A. Gorbunov, *Zh. Prikl. Spektrosk.*, **53**, 386 (1990).