

SYNTHESIS OF 2-R-FLUORANTHENO[2,3-d]- AND 2-R-FLUORANTHENO[3,2-d]OXAZOLES

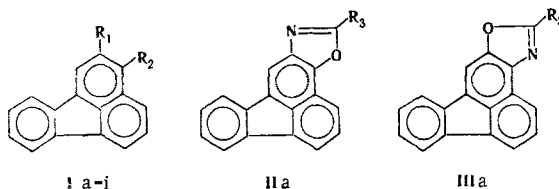
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2-R-Fluorantheno[2,3-d]- and 2-R-fluorantheno[3,2-d]oxazoles were synthesized, and their UV and IR spectra were studied. Ten new compounds are described.

We have previously described a new series of 2-R-fluorantheno[8,9-d]oxazoles with a heterocyclic system in the phenylene portion of the fluoranthene molecule [1]. The present paper is devoted to a study of the synthesis and spectral characteristics of fluoranthenooxazoles with an oxazole residue on the naphthalene portion of the molecule. Considering the available data (Table 1), the compounds obtained in this study can be considered to be probable optical bleaches.

The essential similarity between the reactivities of the o-hydroxynitro derivatives of fluoranthene and their analogs of the naphthalene series has been demonstrated, and this is an additional confirmation of the existence of an inhibiting interaction of the phenylene and naphthalene portions in the fluoranthene molecule [2]. However, one should not understand this to mean a complete analogy between the reactivities of the compounds being compared here; thus acylation of 2-nitro-3-hydroxyfluoranthene (Ib), obtained by a known method from 2-nitro-3-aminofluoranthene (Ia) [3], proceeds most completely for its sodium salt (Ic), while Ib itself is unstable under the conditions of the acylation of β -nitro- α -naphthol [4]. The acylation of 2-hydroxy-3-nitrofluoranthene (Ig) (the latter was obtained from 2-acetamido-3-nitrofluoranthene (If) [5] under conditions close to those in the synthesis of α -nitro- β -naphthol [6]) did not raise any special difficulties. The different tendencies of Ib and Ig with respect to acylation can probably be explained by steric shielding of the hydroxyl group in Ig by the adjacent peri-oriented 4-hydrogen atom and the nitro group.



Ia $R_1=NO_2$, $R_2=NH_2$; b $R_1=NO_2$, $R_2=OH$; c $R_1=NO_2$, $R_2=ONa$; d $R_1=NO_2$, $R_2=OCOCH_3$;
e $R_1=NO_2$, $R_2=OCOC_6H_5$; f $R_1=NHCOCH_3$, $R_2=NO_2$; g $R_1=OH$, $R_2=NO_2$; h $R_1=OCOCH_3$,
 $R_2=NO_2$; i $R_1=OCOC_6H_5$, $R_2=NO_2$; II a III a $R_3=CH_3$; II b, III b $R_3=C_6H_5$

2-R-Fluorantheno[2,3-d]- (IIa, b) and 2-R-fluorantheno[3,2-d]oxazoles (IIIa, b) were obtained in good yields by prolonged refluxing of the appropriate acetates and benzoates (Ib and Ig) in acetic acid with zinc according to the method in [7].

The IR spectra of IIa, b and IIIa, b contain characteristic absorption bands of the vibrations of the benzoxazole ring and the stretching vibrations of the C-O-C bond in the benzoxazole ring at 1600-1610, 1550-1570, 1235, 1050-1060, and 925-930 cm^{-1} [8, 9]. The formation of an intramolecular hydrogen bond of the chelate type between the hydroxyl group and the oxygen atom of the nitro group was noted in Ib and Ig (a very broad intense absorption band is found at 2500-3200 cm^{-1}) [10].

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TABLE 1. Data from UV Spectra

Compound	λ_{max} , nm			log ϵ		
	β' band	β band	p band	β' band	β band	p band
IIa	242	264, 274, 280, 292	304*, 314, 320, 352, 360	4,65	4,40, 4,48, 4,47, 4,63	3,63, 3,65, 3,72, 3,86, 3,90
IIb	232	254, 268, 276, 304	320, 338, 344	4,38	4,29, 4,18, 4,23, 4,64	4,05, 4,03, 4,01
IIIa	240	258, 268, 274, 284, 294	306*, 312*, 330, 356, 370	4,75	4,40, 4,41, 4,45, 4,56, 4,76	3,72, 3,82, 3,92, 3,92, 4,18
IIIb	234	270, 276, 310	326, 368, 385	4,57	4,10, 4,17, 4,62	4,42, 4,64, 4,40

*The noted λ_{max} values were assigned to the p bands according to the magnitude of log ϵ .

Three regions of absorption maxima – 230–245, 250–310, and 315–390 nm (Table 1) – which, according to the well-known classification [11] for polycyclic hydrocarbons, particularly for fluoranthene, should be assigned, respectively, to the β' , β , and p bands, can be noted in the UV spectra of IIa, b and IIIa, b. The UV spectra of IIa, b and IIIa, b retain the general form of the UV spectrum of unsubstituted fluoranthene; in addition to this, one should note the bathochromic shift of the most intense β bands in the spectra of IIb and IIIb (304–310 nm) as compared with the spectra of IIa and IIIa (292 and 294 nm), which is caused by lengthening of the conjugation chain in IIb and IIIb; a similar effect was noted for 2-R-fluorantheno[8,9-d]-oxazoles [1].

In organic solvents (chloroform, acetone, etc.) all of the fluoranthenooxazoles obtained in this study have blue fluorescence in UV beams, in contrast to the starting compounds, which have green fluorescence.

EXPERIMENTAL

The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. The UV spectra of solutions in 95% ethanol (10^{-4} – 10^{-5} mole/liter) were recorded with an SF-4 spectrophotometer.

2-Nitro-3-hydroxyfluoranthene Sodium Salt (Ic). A mixture of a solution of 0.5 g (1.9 mmole) of Ia in 50 ml of ethanol and 42 ml (116 mmole) of a 10% sodium hydroxide solution was refluxed for 1 h, after which the solution was filtered, and the filtrate was cooled to give 0.33 g (61%) of red needles with mp > 350°. Found: C 67.4; H 2.6; N 4.7%. $C_{16}H_8NaNO_3$. Calculated: C 67.3; H 2.8; N 4.9%.

2-Nitro-3-acetoxyfluoranthene (Id). A solution of 0.69 g (8.75 mmole) of acetyl chloride in 50 ml of acetone was added with stirring to a suspension of 0.5 g (1.75 mmole) of Ic in 75 ml of acetone, and the solution was stirred for 2 min. It was then diluted with water and worked up to give 0.49 g (91%) of yellow plates of Id with mp 170–171.5° (dec., from isopropyl alcohol). Found: C 71.0; H 3.5; N 4.4%. $C_{18}H_{11}NO_4$. Calculated: C 70.8; H 3.6; N 4.6%.

2-Nitro-3-benzoxoyfluoranthene (Ie). A 1.23-g (8.75 mmole) sample of benzoyl chloride was added with stirring to a suspension of 0.5 g (1.75 mmole) of Ic in 25 ml of pyridine, and the solution was heated to 55–60°. It was then cooled, diluted with water, and worked up to give 0.58 g (91%) of long yellow needles of Ie with mp 197–198° (dec., from n-butyl alcohol). Found: C 75.1; H 3.75; N 3.8%. $C_{23}H_{13}NO_4$. Calculated: C 75.2; H 3.6; N 3.8%.

2-Hydroxy-3-nitrofluoranthene (Ig). A mixture of a solution of 1.22 g (4 mmole) of If in 100 ml of ethanol and 80 ml of a 10% sodium hydroxide solution (220 mmole) was refluxed for 6 h, after which the solution was filtered, and the filtrate was neutralized with concentrated hydrochloric acid to give 0.97 g (95%) of fine yellow needles of Ig with mp 163–164° (dec., from acetic acid). Found: C 73.2; H 3.55; N 5.2%. $C_{16}H_9NO_3$. Calculated: C 73.0; H 3.45; N 5.3%.

2-Acetoxy-3-nitrofluoranthene (Ih). A 3.06-g (30 mmole) sample of acetic anhydride was added with stirring to a solution of 1.3 g (5 mmole) of Ig in 70 ml of pyridine, and the solution was heated to 55–60°. It was then cooled and diluted with water to give 1.42 g (94%) of long yellow needles of Ih with mp 173–174° (from benzene–petroleum ether). Found: C 70.9; H 3.55; N 4.45%. $C_{18}H_{11}NO_4$. Calculated: C 70.8; H 3.6; N 4.6%.

2-Benzoxy-4-nitrofluoranthene (Ii). The procedure used to synthesize Ie was used to obtain this compound in 92% yield from Ig. The long yellow needles had mp 195–196° (from aqueous acetic acid). Found: C 75.1; H 3.8; N 3.75%. $C_{23}H_{13}NO_4$. Calculated: C 75.2; H 3.6; N 3.8%.

2-Methylfluorantheno[2,3-d]oxazole (IIa). A 0.8-g (12.3 mmole) sample of zinc dust was added to a solution of 0.4 g (1.3 mmole) of Ig in 70 ml of acetic acid, and the mixture was refluxed for 10 h. It was then filtered, and the filtrate was cooled, diluted with water, and worked up to give a light-gray product, which was chromatographed in chloroform on silica gel (5 g). Elution with chloroform gave a green band, from which 0.14 g (42%) of light-green fine needles of IIa, with mp 182.5–183.5° (from aqueous ethanol), was isolated. Found: C 84.15; H 4.2; N 5.5%. $C_{18}H_{11}NO$. Calculated: C 84.1; H 4.3; N 5.45%.

2-Phenylfluorantheno[2,3-d]oxazole (IIb). The procedure used to synthesize IIa was used to obtain this compound from Ie. Elution with chloroform gave a dark band, from which IIb was isolated in 72% yield. The light-gray fine needles had mp 192.5–193.5° (from toluene–petroleum ether). Found: C 86.7; H 4.55; N 4.2%. $C_{23}H_{13}NO$. Calculated: C 86.6; H 4.1; N 4.4%.

2-Methylfluorantheno[3,2-d]oxazole (IIIa). The procedure used to synthesize IIa was used to obtain this compound from Ih in 60% yield. The light-gray fine needles had mp 189–190° (from carbon tetrachloride). Found: C 84.0; H 4.4; N 5.6%. $C_{18}H_{11}NO$. Calculated: C 84.1; H 4.3; N 5.45%.

2-Phenylfluorantheno[3,2-d]oxazole (IIIb). The procedure used to synthesize IIa was used to obtain this compound from Ii in 64% yield. The light rose-colored fine needles had mp 206–207° (from toluene–petroleum ether). Found: C 86.4; H 4.0; N 4.5%. $C_{23}H_{13}NO$. Calculated: C 86.6; H 4.1; N 4.4%.

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