SYNTHESIS AND PROPERTIES OF 4-ETHOXYFLUORANTHENOPYRYLIUM SALTS AND FLUORANTHENOPYRONES

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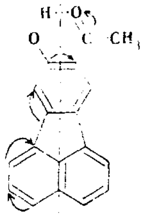
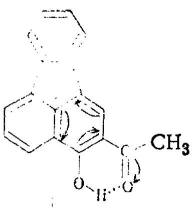
The mutual effect of the parts of the fluoranthene molecule was studied in the case of the pyrylation reactions of isomeric o-hydroxy ketones of fluoranthene [11-hydroxy-12-acetyl-(phenylene part) (I) and 4-hydroxy-3-acetyl-fluoranthene (naphthalene part) (I')]. Pyrylium salts were obtained, and the yields were higher from I than from I'; this indicates conjugation of the π-electron systems of the parts of the fluoranthene molecule. Fluorantheneopyrones and their derivatives were also obtained. It is shown that the mutual effect of the parts of the fluoranthene molecules does not have a substantial influence on the results of the reactions that take place in the pyrone ring. The structures of the compounds obtained were proved by alternative synthesis.

In order to establish the existence of the mutual effect of the phenylene and naphthalene parts of the fluoranthene molecule we selected the previously synthesized [1, 2] isomeric o-hydroxy ketones of fluoranthene — 11-hydroxy-12-acetyl- (phenylene part) (I) and 4-hydroxy-3-acetyl-fluoranthene (naphthalene part) (I') — as the subjects of investigation. The pyrylation of the indicated compounds, the foundation for which was laid by the research of Dorofeenko and co-workers [3-6], was, however, selected as the subject of the present study.

The data that we obtained during a study of the UV spectra of I and I' indicate the existence of a mutual effect of the parts of the fluoranthene molecule: we discovered considerable (15-40 nm) bathochromic shifts of the absorption bands [the β', β, and p bands (after Clar and Stephen [7])] in the case of I as compared with I', which constitutes evidence for the high degree of conjugation of the π electrons of the acetyl group with the π electrons of the aromatic system of I, the structure of which is the most preferred structure from the point of view of an increase in the degree of delocalization of the π electrons.



I



I'

The existence of a mutual effect of the parts of the fluoranthene molecule was also manifested in the pyrylation reactions of isomeric o-hydroxy ketones I and I', as a consequence of which pyrylium salt IIa is obtained in higher yield than the isomeric II'a (via a modified method [3]). These results are in agreement with the mechanism of pyrylation [3]: attack on the acetyl group by the diethoxycarbonium cation is more effective for I because of the higher density of the negative charge on its acetyl group than in the case of I'. For the same reason, pyrylium salt II'b was not obtained at all from o-hydroxycinnamoylfluoranthene (III'), whereas the isomeric IIb was obtained by the method in [4] from the corresponding o-hydroxycinnamoylfluoranthene (III) [8], which is formed in higher yield than the isomeric III'.

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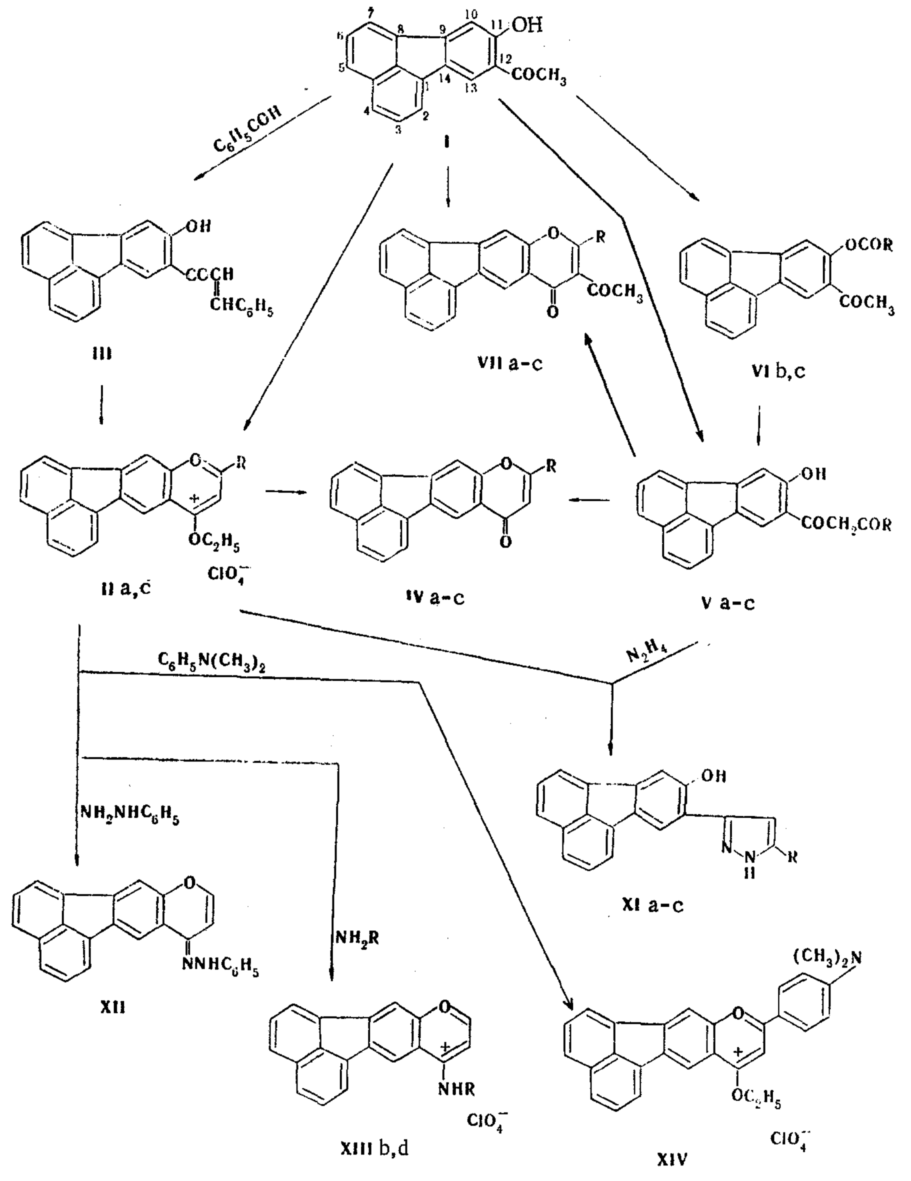


a R=H; b R=C_6H_5; c R=CH_3; d R=$C_6H_4OCH_3$

The IR spectra of 4-ethoxyfluoranthenopyrylium salts IIa,b and II'a contain intense absorption bands of a pyrylium cation (1625-1630, 1530-1545, and 1450-1495 cm^{-1}), an ethoxy group (1250-1260 cm^{-1}), and a ClO_4^- ion (1090-1095 cm^{-1}).

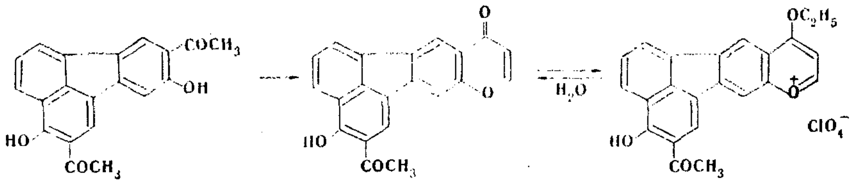
The corresponding fluoranthenopyrones (IVa,b and IV'a) were obtained in almost quantitative yields by saponification of 4-ethoxyfluoranthenopyrylium salts IIa,b and II'a. In order to prove the structures of IVa,b and IV'a we synthesized o-hydroxy β-ketaldehydes Va and V'a and o-hydroxy β-diketones Vc and V'c, respectively, by Claisen condensation via modified methods [9] from o-hydroxy ketones I and I' with ethyl formate (and simultaneously with ethyl acetate); the products were then converted to the corresponding fluoranthenopyrones IVa,c and IV'a,c. Compounds IVc and IV'c were also obtained by intramolecular Claisen rearrangement of the corresponding esters VIc and VI'c [1, 2, 10].

We were unable to obtain o-hydroxy β-diketones Vb and V'b directly by Claisen condensation of I and I' with ethyl benzoate [11]. Compounds Vb and V'b were synthesized by Baker–Venkataraman rearrangement of esters VIb and VI'b [1, 2, 12] and were converted to the corresponding fluoranthenopyrones (IVb and IV'b).

Samples of fluoranthenopyrones IVa,b and IV'a obtained by different methods were identical to one another with respect to their melting points, IR spectra, chromatographic mobilities, and the results of mixed-melting-point determinations.

Compounds Va-c and V'a-c are readily acetylated by acetic anhydride with the subsequent formation of 3-acetylfluoranthenopyrones (VIIa-c and VII'a-c). The latter are not obtained in the case of similar treatment of IVa-c and IV'a-c with acetic anhydride. Derivatives VIIc and VII'c were also obtained by the Kostanecki–Robinson reaction [13] from I and I'.

The existence of the often-mentioned effect of the parts of the fluoranthene molecule was also manifested in the pyrylation of a compound obtained in the present research, 4,12-dihydroxy-3,11-diacetylfluoranthene (VIII), from which a compound (X) that has a pyrone ring in only one of the parts of the fluoranthene molecule (evidently the phenylene part, which is the most active part for reactions of this type) was synthesized through the corresponding pyrylium salt (IX):



VIII X IX

A similar case has been described [3] for resodiacetophenone in which, in contrast to VIII, the functional groups are located in one ring. The negative result in the attempted preparation of bispyrylium salts for both cases indicates conjugation of the π-electron systems of the phenylene and naphthalene parts of the fluoranthene molecule.

The next step in our research was to study the reactions of pyrylium salts IIa and II'a with hydrazine hydrate, phenylhydrazine, and some amines. It was established that o-hydroxyfluoranthenylpyrazoles (XIa and XI'a) are obtained with hydrazine hydrate [5]. Identical products (XIa-c and XI'a-c) were obtained from IVa-c, IV'a-c, Va-c, and V'a-c with hydrazine hydrate [14]. Fluoranthenopyrone 4-phenylhydrazones (XII and XII') were obtained with phenylhydrazine, 4-arylaminofluoranthenopyrylium perchlorates (XIIIb,d and XIII'b,d) were obtained with primary amines, and 4-ethoxy-2-(4'-dimethylaminophenyl)fluoranthenopyrylium perchlorates (XIV and XIV') were obtained with tertiary amines. These results are in agreement with the data in [5, 6]; appreciable differences in the conditions under which the indicated reactions were carried out and in their outcome were not observed for isomeric products IIa and II'a. Since the reactions take place in the pyrone ring, the structure of the fluoranthene does not have a substantial effect on the results.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The individuality of the compounds was established by thin-layer chromatography (TLC) on Silufol UV-254 plates in chloroform and on the basis of the results of elementary analysis.

11-Hydroxy-12-acetylfluoranthene (I). This compound was obtained as light-yellow needles (from acetic acid) by the method described in [1].

4-Hydroxy-3-acetylfluoranthene (I'). This compound was obtained as a light-yellow substance (from benzene) by the method described in [2].

4-Ethoxyfluorantheno[11', 12':5,6]pyrylium Perchlorate (IIa). A 0.15-ml (1.5 mmole) sample of 70% perchloric acid was added to a solution of 0.2 g (0.77 mmole) of I in 1 ml (4.6 mmole) of freshly distilled ethyl orthoformate, and the mixture was refluxed for 15 min. It was then cooled, another 1 ml of ethyl orthoformate was added, and the mixture was again refluxed for 5 min. It was then cooled and diluted with ether, and the precipitate was removed by filtration to give red IIa (from glacial acetic acid).

2-Phenyl-4-ethoxyfluorantheno[11',12':5,6]pyrylium Perchlorate (IIb). This compound was obtained as a cherry-red substance from III by the method used to prepare 4-ethoxyflavylium perchlorate [4].

4-Ethoxyfluorantheno[3',4':5,6]pyrylium Perchlorate (II'a). This compound was obtained as a reddish-brown substance (from glacial acetic acid) by a method similar to that used to prepare IIa.

11-Hydroxy-1(cinnamoyl)fluoranthene (III). A 0.2-ml (2.8 mmole) sample of benzaldehyde was added to a solution of 0.4 g (1.54 mmole) of I in a mixture of 8 ml of 40% KOH solution

TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	Fluorescence in UV light	Found, %		Empirical formula	Calc., %		Yield, %
			C	H		C	H	
I	195—196	Yellow			$C_{18}H_{12}O_2$			40
I'	173—174	Yellow-green			$C_{18}H_{12}O_2$			60
IIa	259—260	—	Cl	8,9	$C_{21}H_{15}ClO_6$	Cl	8,9	83
IIb	254—255	—	Cl	7,5	$C_{27}H_{19}ClO_6$	Cl	7,5	51
IIa	248—250	—	Cl	8,9	$C_{21}H_{15}ClO_6$	Cl	8,9	47
III	131—132	Blue-green	86,0	4,7	$C_{25}H_{16}O_2$	86,1	4,6	93
III'	130—131	Brown	85,9	4,5	$C_{25}H_{16}O_2$	86,1	4,6	76
IVa	204—205	Bright-blue	84,3	3,7	$C_{19}H_{10}O_2$	84,5	3,3	99
IVb	250—251	Blue-green	86,7	4,1	$C_{25}H_{14}O_2$	86,7	4,0	96
IVc	192—193	Bright-blue	84,1	4,3	$C_{20}H_{12}O_2$	84,5	4,2	92
IV'a	252—253	Bright-blue	84,4	4,2	$C_{19}H_{10}O_2$	84,5	3,7	99
IV'b	276—277	Blue-green	86,0	4,8	$C_{25}H_{14}O_2$	86,7	4,0	94
IV'c	247—248	Bright-blue	84,0	5,2	$C_{20}H_{12}O_2$	84,5	4,2	92
Va	164—165	Blue-green	79,4	4,2	$C_{19}H_{12}O_3$	84,3	4,2	72
Vb	174—175	Dark-green	82,2	4,6	$C_{25}H_{16}O_3$	82,5	4,4	82
Vc	147—148	Pale-azure	79,3	4,8	$C_{20}H_{14}O_3$	79,5	4,6	53
V'a	194—195	Pale-blue	79,3	3,9	$C_{19}H_{12}O_3$	79,3	4,1	70
V'b	176—177	Dark-green	82,5	4,5	$C_{25}H_{16}O_3$	82,5	4,4	80
V'c	144—145	Pale-blue	79,6	5,3	$C_{20}H_{14}O_3$	79,5	4,6	50
VIb	132—133	Azure			$C_{25}H_{16}O_3$			55
VIc	169—170	Azure			$C_{20}H_{14}O_3$			33
VI'b	144—145	Light-green			$C_{25}H_{16}O_3$			52
VI'c	124—125	Light-green			$C_{20}H_{14}O_3$			32
VIIa	218—219	Blue	80,7	3,9	$C_{21}H_{12}O_3$	80,9	3,8	64
VIIb	189—190	Blue-green	81,3	6,8	$C_{27}H_{27}O_3$	81,4	6,7	59
VIIc	281—282	Blue	81,0	4,3	$C_{22}H_{14}O_3$	81	4,3	87
VII'a	250—251	Blue	80,8	3,9	$C_{21}H_{12}O_3$	80,9	3,8	62
VII'b	214—215	Blue	81,3	6,9	$C_{27}H_{27}O_3$	81,4	6,8	54
VII'c	247—248	Blue	80,9	4,4	$C_{22}H_{14}O_3$	81	4,3	86
VIII	260—261	Light-brown	75,6	4,9	$C_{20}H_{14}O_4$	75,9	4,8	17,5
IX	244—245	—	Cl	7,6	$C_{23}H_{17}ClO_8$	Cl	7,8	73,8
X	177—178	Blue	78,0	3,7	$C_{21}H_{12}O_4$	76,1	3,6	83,2
XIa	246—247	Green	N	9,8	$C_{19}H_{12}N_2O$	N	9,8	69
XIb	248—249	Green	N	7,8	$C_{25}H_{16}N_2O$	N	7,8	62
XIc	242—243	Green	N	9,4	$C_{20}H_{14}N_2O$	N	9,4	73
XI'a	217—218	Green	N	9,8	$C_{19}H_{12}N_2O$	N	9,8	65
XI'b	270—271	Green	N	7,8	$C_{25}H_{16}N_2O$	N	7,8	53
XI'c	241—242	Green	N	9,4	$C_{20}H_{14}N_2O$	N	9,4	72
XII	247—248	Green	N	7,8	$C_{25}H_{16}N_2O$	N	7,8	75
XII'	196—197	Green	N	7,8	$C_{25}H_{16}N_2O$	N	7,8	70
XIIIb	294—295	—	N	3,2	$C_{25}H_{16}ClNO_5$	N	3,1	76
XIIId	331—332	—	N	2,9	$C_{25}H_{18}ClNO_6$	N	2,9	69
XIII'b	270—271	—	N	3,1	$C_{25}H_{16}ClNO_5$	N	3,1	72
XIIId	277—278	—	N	2,9	$C_{26}H_{18}ClNO_6$	N	2,9	67
XIV	296—297	—	N	2,7	$C_{29}H_{24}ClNO_6$	N	2,7	65
XIV'	283—284	—	N	2,7	$C_{29}H_{24}ClNO_6$	N	2,7	63

and 8 ml of ethanol, and the mixture was heated at 80°C for 5 min, after which it was allowed to stand at room temperature for 12 h. The addition of dilute acetic acid produced a light-yellow precipitate. Compound III was obtained as fine needles (from isopropyl alcohol).

4-Hydroxy-3-(cinnamoyl)fluoranthene (III'). This compound was obtained as a light-orange substance (from isopropyl alcohol) by the method used to prepare III.

Fluorantheno[11',12':5,6]-4-pyrone (IVa). A) By refluxing IIa in an aqueous alcohol mixture. Compounds IVb,c and IV'a,b,c were obtained in the same way as IVa from, respectively, Vb,c and V'a,b, while IVb and IV'a were also obtained from II'a and IIb.

B) Dry HCl was bubbled through an acetone solution of Va, during which a white precipitate formed. Compound IVa was obtained as white needles (from benzene—petroleum ether).

1-(11'-Hydroxy-12'-fluoranthenyl)-1,3-propanedione (Va). Three drops of absolute ethanol and 0.2 g (8.7 mg-atom) of granulated sodium metal were added to a solution of 0.2 g (0.77 mmole) of I in a mixture of 15 ml of ethyl formate and 1 ml of toluene, and the suspension was stirred at room temperature for 4 h, after which it was allowed to stand for 12 h. The precipitated sodium salt of Va was separated and treated on the filter with dilute acetic acid. The product was obtained as light-brown needles (from benzene).

1-(11'-Hydroxy-12'-fluoranthenyl)-3-phenyl-1,3-propanedione (Vb). This compound was obtained by Baker—Venkataraman rearrangement [12] of ester VIb [1]. The product was a light-brown substance (from benzene).

1-(11'-Hydroxy-12'-fluoranthenyl)-1,3-butanedione (Vc). Three drops of absolute ethanol and 0.2 g (8.7 mg-atom) of granulated sodium metal were added to a solution of 0.2 g (0.77 mmole) of I in a mixture of 15 ml of ethyl acetate and 0.5 ml of toluene, and the suspension was stirred at room temperature for 4 h, after which it was allowed to stand for 12 h. It was then poured into cold water, and the aqueous mixture was acidified with weak acetic acid and shaken with aqueous NaOH solution. The aqueous alkaline solution was separated, and an orange-yellow substance [from petroleum ether—benzene (7:3)] was precipitated by acidification with acetic acid.

1-(4'-Hydroxy-3'-fluoranthenyl)-1,3-propanedione (V'a). A 0.1-g (4.35 mg-atom) sample of granulated sodium metal was added to a solution of 0.2 g (0.77 mmole) of I' in 10 ml of ethyl formate, and the suspension was stirred at room temperature for 4 h. It was then poured into cold water, and the aqueous mixture was then worked up as in the case of Vc to give yellow plates of V'a (from 80% ethanol).

1-(4'-Hydroxy-3'-fluoranthenyl)-3-phenyl-1,3-propanedione (V'b). This compound was obtained by a method similar to the procedure used to prepare Vb. The product was obtained in the form of light-yellow needles (from petroleum ether—benzene).

1-(4'-Hydroxy-3'-fluoranthenyl)-1,3-butanedione (V'c). A 0.1-g (4.35 mg-atom) sample of granulated sodium metal was added to a solution of 0.2 g (0.77 mmole) of I' in 10 ml of ethyl acetate, and the mixture was refluxed for 4 h in a flask equipped with a calcium chloride tube. The mixture was then worked up as in the case of Vc to give a yellow product [from petroleum ether—benzene (7:3)].

3-Acetylfluoranthenopyrones (VIIa-c and VII'a-c). These compounds were obtained by refluxing the corresponding Va,b,c and V'a,b,c in acetic anhydride.

4,12-Dihydroxy-3,11-diacetylfluoranthene (VIII). This compound was obtained as light-yellow needles (from benzene) [15] by a method similar to the procedure used to obtain I and I'.

4'-Hydroxy-3'-acetyl-4-ethoxyfluorantheno[12',11':5,6]pyrylium Perchlorate (IX). This compound was obtained as a red substance (from glacial acetic acid) by the method used to prepare IIa.

4'-Hydroxy-3'-acetylfluorantheno[12',11':5,6]-4-pyrone (X). This compound was obtained as a greenish-yellow substance (from alcohol) by method A for the preparation of IVa.

o-Hydroxyfluoranthenylpyrazoles (XIa-c and XI'a-c). A) A mixture of perchlorate IIa (II'a), a twofold excess of hydrazine hydrate, and acetic acid was refluxed for 50 min, after which it was cooled and diluted with water, and the precipitated XIa (XI'a) was removed by filtration and crystallized from isopropyl alcohol—water.

B) These compounds were also obtained by refluxing a mixture of IVa-c, IV'a-c, or Va-c and V'a-c with a small excess of hydrazine hydrate in ethanol for 1 h.

Fluoranthenopyrone 4-Phenylhydrazones (XII and XII'). These compounds were obtained from the corresponding perchlorate and phenylhydrazine by method A for the preparation of XIa.

4-Arylaminofluoranthenopyrylium Perchlorates (XIIIb,d and XIII'b,d). These compounds were obtained from the corresponding perchlorate and aniline (for XIIIb and XIII'b) or p-anisidine (for XIIId and XIII'd) by method A for the preparation of IXa.

4-Ethoxy-2-(4'-dimethylaminophenyl)fluoranthenopyrylium Perchlorates (XIV and XIV'). These compounds were obtained by heating a mixture of IIa (II'a) with a twofold excess of N,N-dimethylaniline in acetic anhydride at 95°C for 50 min. The mixture was cooled, and the reaction product was precipitated with diethyl ether.

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4-(5-ARYL-2-OXAZOLYL)PHTHALIC ANHYDRIDES

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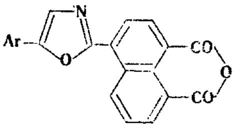
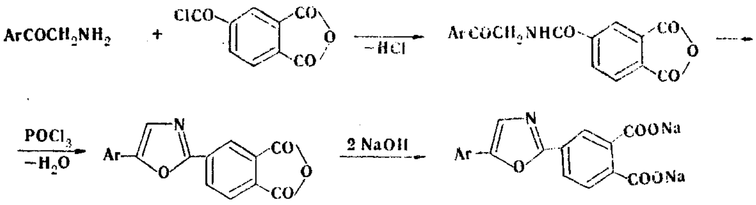
4-(5-Aryl-2-oxazolyl)-substituted phthalic anhydrides were synthesized from 4-chloroformylphthalic anhydride and various ω-aminomethyl aryl ketones. The spectral-luminescence properties of solutions of the products in toluene and 5% NaOH solution were investigated. It is shown that the introduction of substituents with different electronic natures in the 5-phenyl ring of 4-(5-phenyl-2-oxazolyl)phthalic anhydride has a significant effect on the spectral-luminescence characteristics of the synthesized compounds.

We have previously described [1-3] 4-(5-aryl-2-oxazolyl)-substituted naphthalic anhydrides (I), which are effective organic luminophores that are used in the preparation of daytime fluorescent pigments and dyes [4].



I

The present communication is devoted to the synthesis and study of the spectral-luminescence properties of analogous compounds that contain a phthalic anhydride grouping (II). The synthesis was accomplished via the following scheme, which includes the Robinson–Gabriel reaction:



II a-j

III

In view of the high reactivities of both the anhydride and chloroformyl groups of 4-chloroformylphthalic anhydride it readily reacts with two molecules of amine. To prevent reaction at the anhydride grouping we carried out the condensation in a water–benzene medium

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