SYNTHESIS OF SPIROPYRANS CONTAINING AN ADDITIONAL CHROMOPHORE

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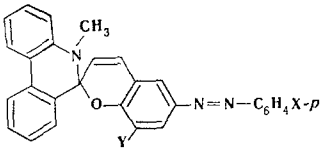
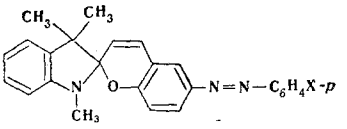
Spiropyrans of the phenanthridine and indoline series containing phenylazo or benzoyl groups as substituents in the chromene ring were synthesized. These substituents facilitate the formation of deeply colored merocyanine forms in polar solvents. The presence of a phenylazo group causes the intense color of the cyclic forms of the spiropyrans.

The spiropyrans described in the literature are colorless in the cyclic form and display photochromic properties only on irradiation with UV light. It has been shown that intramolecular transfer of energy between mutually perpendicular portions of the spiropyran molecule is possible [1]. In addition, it is known that although opening of the pyran ring occurs in the singlet excited state during direct excitation [2], photocoloration can be sensitized by triplet energy donors, for example benzophenone [3] and acetophenone, and its derivatives [4]. On the basis of these facts, an investigation of the properties of spiropyrans containing chromophore groupings as substituents seems of interest.

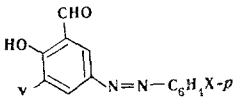
In the present paper we report the synthesis of spiropyrans of the phenanthridine and indoline series (I-VIII) containing a phenylazo group in the 6' position as an additional chromophore.



I–IV



V–VIII



IX–XII

I, III, V, VII, IX, XI X = H;
II, IV, VI, VIII, X, XII X = NO_2;
I, II, V, VI, IX, X Y = H;
III, IV, VII, VIII, XI, XII Y = OCH_3

Phenylazosalicylaldehydes IX-XII, obtained by azo coupling of salicylaldehyde and its 3-methoxy derivative with benzene- and p-nitrobenzenediazonium salts, were used as the starting compounds for the synthesis of spiropyrans containing a phenylazo group. Bands characteristic for azo compounds are present in the electronic absorption spectra of aldehydes IX-XII: an intense band of a $\pi \rightarrow \pi^*$ transition at ~335 nm, which is shifted bathochromically under the influence of NO_2 and OCH_3 groups, and a relatively low-intensity band of an $n-\pi^*$ transition at ~435 nm, which is manifested as a shoulder on the more intense band in the case of X-XII.

The phenylazosalicylaldehydes reacted readily in alcohol solution with 5,6-dimethylphenanthridinium methosulfate (in the presence of piperidine) and 1,3,3-trimethyl-2-methyleneindoline, and yellow or orange crystalline spiropyrans I-VIII were obtained in good yields. Their solutions in dioxane have the intense yellow color characteristic for aromatic azo compounds (Fig. 1). The absorption maxima of the long-

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TABLE 1. Absorption Spectra of Spiropyrans I-VIII, XIII

Compound	λ_{max}, nm (lg ε or lg ε')	
	in dioxane	in alcohol
I	245, 266, 345, 367 (4,62; 4,39; 4,31; 4,33)	240, 267*, 295*, 365, 565 (4,25; 4,04; 3,88; 4,06; 2,83)
II	237; 270*; 293*; 342*; 405 (4,57; 4,36; 4,20; 4,17; 4,40)	242, 340, 397, 530—550* (4,35; 3,95; 4,09; 3,66)
III	242, 260*, 385 (4,61; 4,47; 4,36)	245, 265*, 390, 450*, 610 (4,60; 4,53; 4,35; 4,11; 3,85)
IV	268, 420 (4,47; 4,37)	250, 265*, 320, 400, 510, 590 (4,25; 4,20; 3,84; 3,84; 4,06; 4,07)
V	247, 285, 360 (4,22; 4,38; 4,10)	245, 282, 358 (4,10; 4,28; 4,14)
VI	242, 295, 400 (4,34; 4,20; 4,29)	243, 282, 400 (4,20; 4,43; 4,26)
VII	248, 285, 380 (4,33; 4,36; 4,17)	242, 290, 380, 610 (4,31; 4,14; 4,21; 3,62)
VIII	245, 285, 412 (4,22; 4,51; 4,22)	242*, 282, 415, 625 (3,95; 4,14; 3,92; 3,09)
XIII	247, 267*, 317 (4,66; 4,56; 4,15)	245, 260*, 320, 515 (4,18; 4,12; 3,75; 2,85)

* Shoulder.

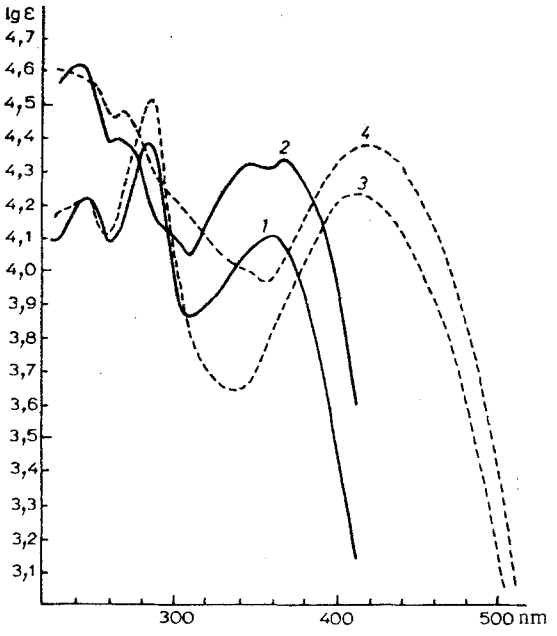


Fig. 1. Absorption spectra of spiropyrans in dioxane: 1) V; 2) I; 3) VIII; 4) IV.

wave band of I-VIII are shifted bathochromically by ~30-40 nm relative to the absorption maxima of the corresponding aldehydes.

When I-IV, VII, and VIII are dissolved in alcohol or are heated, the color deepens sharply (λ_{max} 560-620 nm); this is due to opening of the pyran ring and establishment of equilibrium between the cyclic and merocyanine forms (Fig. 2). This equilibrium is apparently established quite rapidly, since the spectra of alcohol solutions did not change on storage in the dark. The position of the equilibrium in these systems, which may simultaneously contain several stereoisomeric merocyanine forms, is quite difficult to estimate. However, taking into account the high absorption intensity near 600 nm, one can assume a considerable shift of the equilibrium to favor the open forms, especially for phenanthridine derivatives. The "apparent molar extinctions" (ε') for alcohol solutions, which were obtained by referring the experimental optical densities to the overall concentration of the compounds, are presented in Table 1.

The ease of opening of the pyran ring in the presence of a phenylazo group, which has acceptor character (σ_p 0.64), is not unexpected, particularly in alcohol solutions. It is known that acceptor substituents in the chromene ring and substituents in the 8' position stabilize the merocyanine forms [5]. The formation of the latter is also facilitated in proton-donor polar solvents. These merocyanine forms, being highly polar, usually have strong negative solvatochromism, i.e., they are more highly colored in alcohol solutions than in solvents of low polarity. A peculiarity of the phenylazospirans described here is the deep color of the alcohol solutions, a feature that is usually characteristic for solvents of low polarity. The reason for this cannot be the change in the character of the solvatochromism, since the addition of benzene or dioxane to alcohol solutions of the phenylazospirans causes a further deepening of the color. Deepening of the color is also observed when the alcohol solutions are heated. The deep color of alcohol solutions of the phenylazospirans is apparently associated with the shift of the equilibrium of the stereoisomeric merocyanine forms to favor the most deeply colored trans form. The reason for this may be the greater-than-usual difference in the energies of the stereoisomeric forms because of the considerable size of the fragments attached to the central bond.

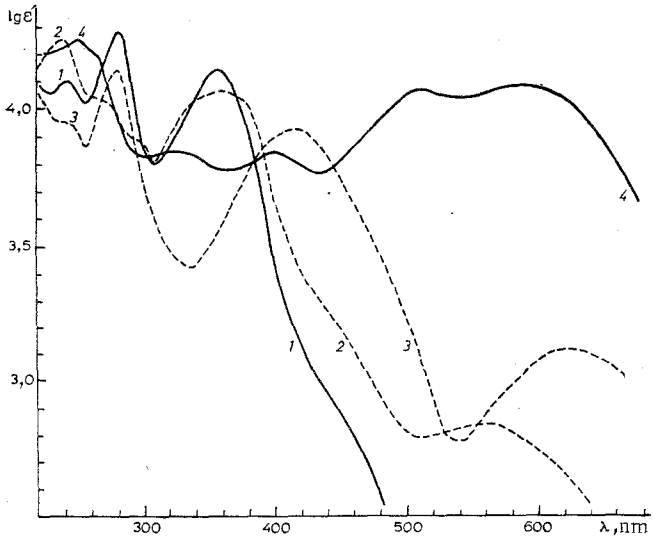
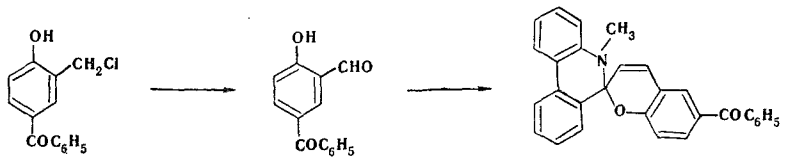


Fig. 2. Absorption spectra of spiropyrans in alcohol: 1) V; 2) I; 3) VIII; 4) IV.

In addition to the synthesis of the phenylazospirans, we also obtained XIII, which contains a benzoyl group in the 6' position.



XIV XV XIII

The 5-benzoylsalicylaldehyde (XV) necessary for this synthesis was obtained in good yield, in contrast to the patent report [6], by chloromethylation of p-hydroxybenzophenone with subsequent oxidation of XIV with urotropin. It should be noted that 3,5-di(chloromethyl)-4-hydroxybenzophenone is readily formed when the chloromethylation of p-hydroxybenzophenone is carried out under somewhat more severe conditions than those used in the preparation of XIV.

Compound XIII was isolated as colorless crystals. A solution of it in dioxane is colorless, but a solution in alcohol has an absorption maximum at 515 nm (log ε' 2.85) but is less intensely colored than solutions of the phenylazospirans. The lower intensity of the color of XIII is in agreement with the weaker acceptor effect of the benzoyl group (σ_p 0.46) as compared with the phenylazo group and, to a greater extent, the p-nitrophenylazo group.

The photochemical properties of I-XIII will be reported later.

EXPERIMENTAL

The UV spectra of solutions in dioxane, alcohol, and chloroform (c 10^{-5}-10^{-4} M, 1-10-cm cuvette) were recorded with an SF-8 spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with an IKS-22 spectrometer. Only the most characteristic strong* and moderate-intensity bands at 970-1700 cm^{-1} are indicated for the IR spectra.

5-(Phenylazo)salicylaldehyde (IX). A 100-ml portion of a solution containing 0.1 mole of benzenediazonium chloride and 0.1 mole of HCl was added to a solution of 12.2 g (0.1 mole) of salicylaldehyde in 100 ml of 4 M KOH in the course of 30 min. The brown precipitate (18 g) was removed by filtration, washed with a small amount of water, and dissolved in 100 ml of 0.1 M KOH by heating; the solution was filtered, and the filtrate was treated with charcoal and acidified to pH 5 with acetic acid. The yellow precipitate of IX was removed by filtration and crystallized twice from alcohol (1:50) to give 7.3 g (33%) of IX as light-

* The most intense bands are underlined; the broad component bands (br) are also noted.

yellow crystals with mp 127-129° [7]. UV spectrum, λ_{max}, nm (log ε), in chloroform: 264 (4.01), 335 (4.38), 435 (2.97); in 0.1 M NaOH in alcohol: 242 (3.96), 390 (4.36). IR spectrum: 1670, 1480, 1380, 1290, 1160 (br) cm^{-1}.

5-(p-Nitrophenylazo)salicylaldehyde (X). This compound was similarly obtained. Prior to separation of the precipitate, the reaction mass was acidified to pH 3-4 with acetic acid. The resulting yellow precipitate was crystallized from benzene (1:30) and toluene (1:10) to give X in 80% yield as orange crystals with mp 189-192° [8]. UV spectrum, λ_{max}, nm (log ε), in chloroform: 272 (4.07), 360 (4.45), 445 (3.18)*; in 0.1 M NaOH in alcohol: 245 (4.48), 275 (4.18),* 416 (4.34),* 470 (4.52). IR spectrum: 1665, 1525, 1480, 1345, 1290, 1175, 1100 cm^{-1}. The product was only slightly soluble in boiling alcohol (1:370).

3-Methoxy-5-(phenylazo)salicylaldehyde (XI). A total of 30 ml of a solution containing 0.05 mole of benzenediazonium chloride and 0.05 mole of HCl was added at 35-40° to a solution of 7.6 g (0.05 mole) of 3-methoxysalicylaldehyde and 72 g (1.8 mole) of NaOH in 800 ml of water, and the mixture was stirred for 1.5 h. It was then diluted with 800 ml of water, cooled, and acidified to pH 4 with acetic acid. It was then filtered to give 7.5 g of XI. Crystallization from alcohol (1:50) gave 6.8 g (53%) of XI with mp 148-150° [9]. UV spectrum, λ_{max}, nm (log ε), in chloroform: 275 (4.11), 345 (4.18), 440 (3.03)*; in 0.1 M NaOH in alcohol: 255 (3.90), 270 (3.86),* 405 (4.31). IR spectrum: 1645 (br), 1465 (br), 1395, 1320, 1285, 1270 (br), 1120, 965 cm^{-1}.

3-Methoxy-5-(p-nitrophenylazo)salicylaldehyde (XII). This compound was similarly obtained in 54% yield as orange-red crystals with mp 224° [from toluene (1:50)]. It was only slightly soluble in boiling alcohol (1:500). UV spectrum, λ_{max}, nm (log ε), in chloroform: 275 (4.36), 310 (4.21), 390 (4.51), 450* (overlaps the preceding band); in 0.1 M NaOH in alcohol: 245 (4.01),* 265 (4.08), 410 (4.06),* 495 (4.44). IR spectrum: 1650, 1515, 1460 (br), 1390, 1340, 1270 (br), 1125 cm^{-1}. Found: C 56.2; H 3.9; N 14.2%. $C_{14}H_{11}N_3O_5$. Calculated: C 55.8; H 3.6; N 14.0%.

5-Methyl-6'-(phenylazo)spiro(5,6-dihydrophenanthridine-6,2'-[2H]-chromene) (I). A 0.96-g (3 mmole) sample of 5,6-dimethylphenanthridinium methosulfate (XVI) and 0.68 g (3 mmole) of IX were dissolved in 70 ml of refluxing alcohol, and 1.8 ml (18 mmole) of piperidine was added. The solution became dark-brown, and a yellow precipitate formed in a few minutes. The mixture was refluxed for 30 min, cooled, and filtered. The solid was washed with alcohol to give 1.1 g (85%) of I. Two crystallizations from benzene (1:20) gave I as strongly electrified yellow plates with mp 220° (darkened from 217°). The product was insoluble in water, soluble in chloroform, ether, and dioxane, and slightly soluble in alcohol in the cold. The greenish-yellow color deepened to green when an alcohol solution was heated, and the initial color was restored when the solution was cooled. IR spectrum: 1650 (w), 1600, 1470, 1445, 1340, 1320, 1260, 1105, 1090, 975 cm^{-1}. Found: C 80.8; H 5.2; N 9.8%. $C_{28}H_{21}N_3O$. Calculated: C 80.9; H 5.0; N 10.1%.

5-Methyl-6'-(p-nitrophenylazo)spiro(5,6-dihydrophenanthridine-6,2'-[2H]-chromene) (II). This compound was similarly obtained using an approximately fourfold amount of alcohol because of the lower solubility of X. Compound II, with mp 232° [darkened from 227°; from toluene (1:100)], was obtained in 80% yield. The product was insoluble in petroleum ether, only slightly soluble in ether and alcohol, and less soluble in the remaining organic solvents. A yellow (in the cold) solution in benzyl alcohol became crimson-colored on heating and remained this color on cooling. IR spectrum: 1650 (w), 1610, 1595, 1520, 1470, 1440, 1430, 1405, 1345 (br), 1260, 1105, 1090, 975 cm^{-1}. Found: C 72.8; H 4.4; N 11.9%. $C_{28}H_{20}N_4O_3$. Calculated: C 73.0; H 4.3; N 12.1%.

5-Methyl-6'-phenylazo-8'-methoxyspiro(5,6-dihydrophenanthridine-6,2'-[2H]-chromene) (III). This compound was obtained in 67% yield by the method used to prepare I. It was isolated as a yellow precipitate from the green reaction mass. Recrystallization (1:330) from benzene–petroleum ether (3:7) gave a product with mp 192.5° (it turned green at 190°). The cold yellow solution in alcohol became green on heating and remained green after cooling. A solution in chloroform was light-green. IR spectrum: 1655 (w), 1605, 1575, 1465, 1440, 1385, 1280, 1250, 1120, 1100, 980 cm^{-1}. Found: C 78.5; H 5.5; N 9.6%. $C_{29}H_{23}N_3O_2$. Calculated: C 78.2; H 5.2; N 9.4%.

5-Methyl-6'-(p-nitrophenylazo)-8'-methoxyspiro(5,6-dihydrophenanthridine-6,2'-[2H]-chromene) (IV). This compound was obtained in 81% yield by the method used to prepare II (the heating time was 2.5 h). The orange product had mp 210-212°. Two crystallizations from benzene (1:500) gave a product with mp 216° (darkened from 190°). Solutions in CCl_4, $CHCl_3$, and dioxane were yellow, while a solution in acetone

*Here and elsewhere, the shoulders and points of inflection are noted.

was yellow but became crimson-colored when water was added. IR spectrum: 1640 (w), 1605, 1570, 1515, 1470, 1455, 1380, 1345, 1290, 1265, 1125, 1100, 980 cm^{-1}. Found: C 71.4; H 4.9; N 11.2%. $C_{29}H_{22}N_4O_4$. Calculated: C 71.0; H 4.5; N 11.4%.

1,3,3-Trimethyl-6'-(phenylazo)spiro(indoline-2,2'-]2H-chromene) (V). A 0.26-g (1.5 mmole) sample of freshly distilled 2-methylene-1,3,3-trimethyleneindoline (XVII) was added to a hot solution of 0.34 g (1.5 mmole) of IX in 40 ml of alcohol. The solution was green, and a yellow precipitate formed after 30 min (refluxing). The mixture was cooled and filtered to give 0.55 g (97%) of V, which had mp 180-182° after two crystallizations from benzene (1:10). The product was soluble (on heating) in CCl_4, acetone, dioxane, and petroleum ether, only slightly soluble in alcohol, and quite soluble in chloroform. All of the solutions were yellow, and only the solution in benzyl alcohol became blue-green on boiling. IR spectrum: 1660, 1610, 1575, 1480, 1415, 1320, 1250, 1110, 1080, 1015, 975 cm^{-1}. Found: C 78.5; H 5.9; N 10.4%. $C_{25}H_{23}N_3O$. Calculated: C 78.7; H 6.0; N 10.8%.

1,3,3-Trimethyl-6'-(p-nitrophenylazo)spiro(indoline-2,2'-[2H]-chromene) (VI). A 0.43-g (2.5 mmole) sample of XVI was added to a hot solution of 0.68 g (2.5 mmole) of X in 300 ml of alcohol, and the mixture was refluxed for 5 h. It was then cooled and filtered to give 1.04 g (98%) of an orange-red precipitate of VI, which was washed with alcohol. The product was soluble in benzene, chloroform, and CCl_4 and in hot alcohol, petroleum ether, and dioxane. All of the solutions were yellow, except that a boiling solution in benzyl alcohol was yellowish-green. The product had mp 201° [darkened at 198°; from alcohol (1:1000)]. IR spectrum: 1660, 1610, 1575, 1520, 1480, 1460, 1340, 1280, 1260, 1105, 1020, 970 cm^{-1}. Found: C 70.6; H 5.6; N 13.0%. $C_{25}H_{22}N_4O_3$. Calculated: C 70.4; H 5.2; N 13.1%.

1,3,3-Trimethyl-6'-phenylazo-8'-methoxyspiro(indoline-2,2'-[2H]-chromene) (VII). This compound was obtained by the method used to prepare V and was crystallized from alcohol (1:50) to give VII with mp 209-210° (turned green at 190°) in 70% yield. Yellow solutions in chlorobenzene, chloroform, and alcohol turned green on refluxing. IR spectrum: 1660 (w), 1610, 1580, 1480, 1460, 1385, 1360, 1275 (br), 1120, 1015, 970 cm^{-1}. Found: C 76.2; H 6.5; N 9.9%. $C_{26}H_{25}N_3O_2$. Calculated: C 75.9; H 6.1; N 10.2%.

1,3,3-Trimethyl-6'-(p-nitrophenylazo)-8'-methoxyspiro(indoline-2,2'-[2H]-chromene) (VIII). This compound was obtained by the method used to prepare VI (the heating time was 2.5 h) and was crystallized from benzene (1:50) to give VIII with mp 198° (turned green at ~192°) in 65% yield. IR spectrum: 1660 (w), 1610, 1520, 1490, 1470 (br), 1340, 1280, 1120, 1020, 970 (w) cm^{-1}. Found: C 68.1; H 5.5; N 12.0%. $C_{26}H_{24}N_4O_4$. Calculated: C 68.4; H 5.3; N 12.3%.

3-Chloromethyl-4-hydroxybenzophenone (XIV). A 4.56-g (0.06 mole) sample of dimethoxymethane was added to 3.96 g (0.02 mole) of p-hydroxybenzophenone in 100 ml of concentrated HCl and 4 ml of concentrated H_2SO_4, and the mixture was heated at 70° for 30 min. It was then cooled, and the precipitate was removed by filtration and washed with water until it was neutral to give 4.4 g (90%) of XIV with mp 146-150°. Two crystallizations from benzene (1:20) gave 3.36 g of XIV with mp 157°. The product was soluble in CCl_4 and alcohol. PMR spectrum: δ (CH_2) 4.29 ppm (in dioxane). IR spectrum: 3100 (br), 1640, 1600, 1570 (br), 1320, 1280 (br), 1100 cm^{-1}. Found: Cl 14.0%. $C_{14}H_{11}ClO_2$. Calculated: Cl 14.4%.

4-Hydroxy-3,5-di(chloromethyl)benzophenone. A mixture of 2 g (0.01 mole) of p-hydroxybenzophenone, 3.8 g (0.05 mole) of dimethoxymethane, 50 ml of concentrated HCl, and 2 ml of concentrated H_2SO_4 was heated at 70° while gaseous HCl was passed through it for 4.5 h. The precipitate was removed by filtration and washed with water until it gave a neutral reaction. This procedure yielded 2.2 g (76%) of colorless crystals. Crystallization from petroleum ether (1:50) gave a product with mp 122-124°. PMR spectrum: δ CH_2 4.12 ppm (singlet, 4H, in dioxane). IR spectrum: 3250 (br), 1635, 1600, 1325, 1270 (br), 1230, 1230, 1180, 1140, 1120 cm^{-1}. Found: Cl 23.8%. $C_{15}H_{22}Cl_2O_2$. Calculated: Cl 24.3%.

5-Benzoylsalicylaldehyde (XV). A mixture of 4.3 g (17 mmole) of XIV and 6.0 g (42 mmole) of hexamethylenetetramine in 43 ml of glacial acetic acid was refluxed for 4 h, after which 65 ml of 7% hydrochloric acid was added and the mixture was refluxed for another 1.5 h. The hot solution was filtered and cooled to give 1.45 g (37%) of XV with mp 86-90°. Recrystallization from hexane (1:35) gave 0.8 g of XV with mp 89-92° [6]. UV spectrum (in chloroform), λ_{max}, nm (log ε): 282 (4.14), 330 (3.49). IR spectrum: 3400, 1645 (br), 1600 (br), 1480, 1445, 1320, 1280, 1220, 1180, 1120 cm^{-1}.

5-Methyl-6'-benzoylspiro(5,6-dihydrophenanthridine-6,2'-[2H]-chromene) (XIII). A 0.5-ml (5 mmole) sample of piperidine was added to a hot solution of 0.57 g (2.5 mmole) of XV and 0.8 g (2.5 mmole) of XVI in 25 ml of alcohol. The solution became red, and a light-colored precipitate formed. After 15 min, the

precipitate was removed by filtration and washed with alcohol to give 0.92 g (89%) of XIII. Recrystallization from benzene (1:40) gave colorless crystals with mp 228-229°. Solutions in aprotic organic solvents were colorless, a solution in benzyl alcohol at room temperature was yellow, while a solution in ethanol became crimson on heating and remained crimson after cooling. IR spectrum: 1648, 1603, 1482, 1470, 1445, 1375, 1320, 1290, 1265 (br), 1220, 1180, 1120, 1095, 980 cm^{-1}. Found: C 84.4; H 5.4; N 3.3%. $C_{29}H_{21}NO_2$. Calculated: C 84.1; H 5.1; N 3.4%.

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