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Synthesis and Properties of some 7*H*,9*H*-Quinazolino-[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one Derivatives

K. Celnik and Z. Jankowski

Institute of Dyes, Technical University,
Żwirki 36, 90-924 Łódź, Poland

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SUMMARY

A number of 7H,9H-*quinazolino*[3,2-b]*benz*[d,e]*isoquinolin-7-one derivatives containing chlorine atoms, methoxy, nitro or amino groups at the 11 or 12 position of the molecule skeleton have been synthesised.*

The structure of the dyes obtained has been confirmed by elemental analysis, as well as by i.r. and n.m.r. spectroscopy. Electronic spectra in the visible range have also been recorded and the effect of the character of the substituents on the colour has been analysed.

1. INTRODUCTION

During our investigations of new heterocyclic dyes we have found 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one to be suitable for dyeing synthetic fibres, especially polyester fibres. The investigations have shown that it gives a deeper shade and displays better dyeing properties, with slightly higher fastness in use, compared with 7*H*-benzimidazo[2,1-*a*]-benz[*d*,*e*]isoquinolin-7-one.[1]

To study the effect of substituents in the structure of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one on the properties of the dye molecule, a number of derivatives have been synthesised using chlorine atoms, methoxy, nitro or amino groups substituted in positions 11 and 12. Some properties of the compounds, e.g. bright colour, good

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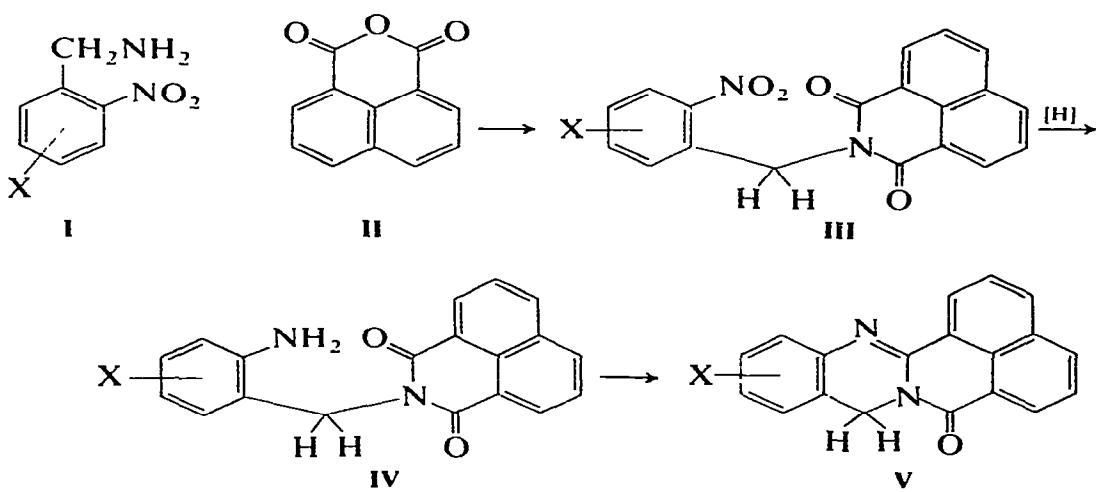
solubility in organic solvents, fluorescence and quite high-order parameters in liquid crystals, indicate the potential technical value of these dyes in various fields of technology.

2. RESULTS AND DISCUSSION

The majority of the dyes were prepared in the way presented in Scheme 1, which is similar to the method of synthesis of unsubstituted 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one.[1,2]

This method made it possible to obtain products with a high degree of purity. Acylation of the corresponding benzylamines with naphthalic anhydride took place easily, with almost quantitative yields. Some difficulties were experienced in acylation of 2,4-dinitrobenzylamine which, under the usual conditions, was prone to side reactions rather than to naphthalic anhydride acylation. However, by changing the reaction conditions and the medium, it was possible to obtain the desired product.

It was observed that when the system $SnCl_2$(HCl)MeOH was used for the reduction reaction, relatively large amounts of final products (**V**) were



Scheme 1

[a] The amino group is formed by reduction of the $X = NO_2$ group in the corresponding compounds **III**.

formed in addition to the amines (**IV**). During reduction of *N*-(dinitrobenzyl)naphthalimides, only the cyclic product (**V**, X = NH_2) was formed under the conditions of the reduction reaction and therefore in these cases the cyclisation step was not necessary.

By acylation of the amino derivatives of 7*H*,9*H*-quinazolino[3,2-*b*]-benz[*d*,*e*]isoquinolin-7-one (**V**, X = NH_2) with acetic anhydride, the corresponding acetylamino derivatives (**V**, X = NHAc) were also obtained.

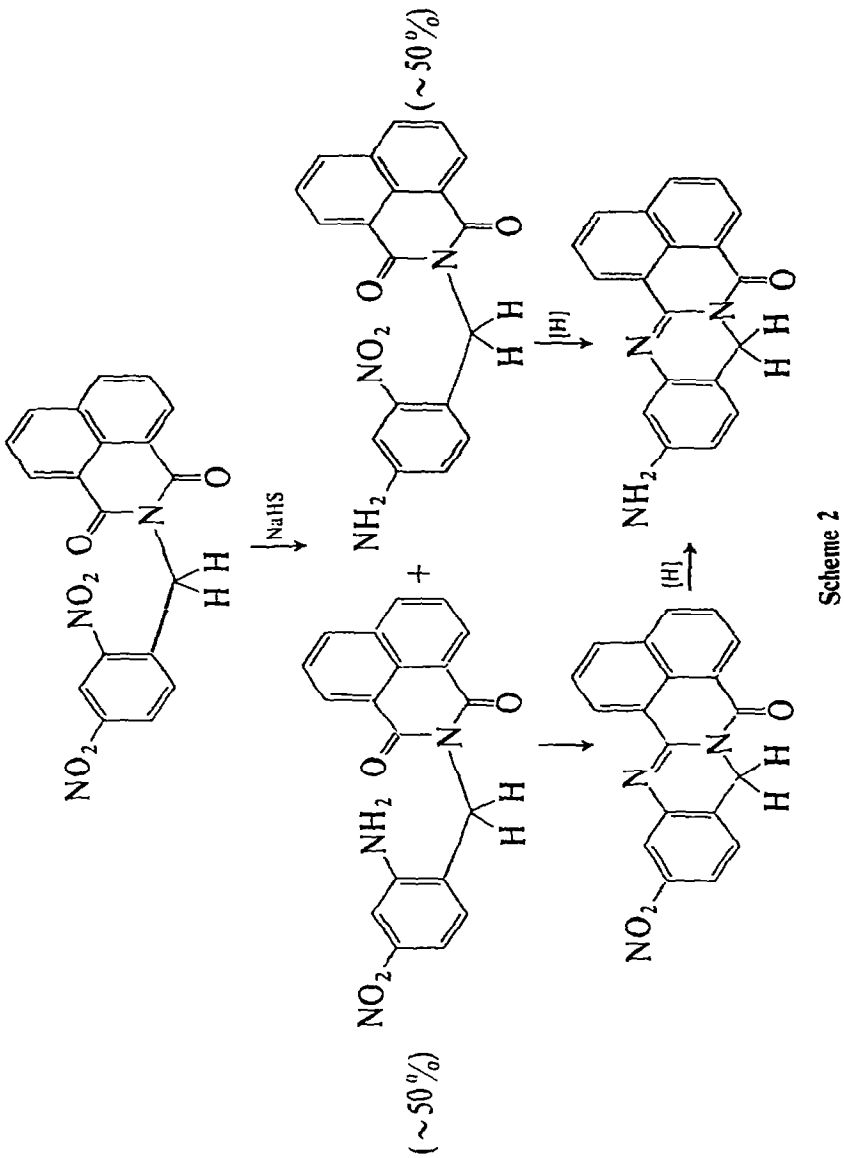
In investigating the 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one nitration process it has been found that in concentrated sulphuric acid the 11-nitro derivative is formed which, after reduction, gives an amine which is identical with the product (**V**, X = 11-NH_2) obtained from the corresponding benzylamine according to the method presented in Scheme 1. The observed direction of nitration is in agreement with that of 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one described in the literature.[3] By using that method it was possible to obtain 11-nitro-7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one and to avoid the troublesome preparation of 2,5-dinitrobenzylamine which is necessary for the synthesis of 11-amino-7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one according to the general method presented in Scheme 1.

It has been found that during treatment with sodium hydrosulphide in dioxane, only one of the nitro groups in *N*-(2,4-dinitrobenzyl)-naphthalimide is reduced (Scheme 2) so that it was possible to obtain 12-nitro-7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one.

2.1. Structural investigations

The chemical structure of the compounds obtained was confirmed by the elemental analysis and by i.r. and NMR spectrometry. The characteristics of the 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one derivatives obtained are presented in Table 1.

In the i.r. spectra of all compounds **V**, in addition to the bands which are characteristic of the substituents, there exist carbonyl group stretching bands in the range 1680–1658 cm^{-1} and C=N group stretching bands in the range 1570–1555 cm^{-1}. A comparison of the spectra of compounds **V** with those of the corresponding substrates points to the disappearance of one of the stretching bands of the carbonyl groups which are present in the spectra of compounds **III** and **IV** and to the appearance of the C=N group stretching band. The carbonyl group



Scheme 2

TABLE 1

Yield and Some Properties of 7*H*,9*H*-Quinazoline[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one Derivatives (V)

No.	Substituent and position	Yield (%)	Elemental analysis (% N)	M.p. (°C)	Main i.r. absorption bands (cm^{-1})	N.m.r. chemical shift in CF_3COOH, TMS (ppm) (integration)[a]
1	11-Cl	73	8·8	277–9	3050, 1673 (C=O), 1600, 1560 (C=N), 1362, 1280, 775	M 7·3–7·1 (2H), M 7·05–6·85 (2H), T 6·6–6·4 (2H), M 6·05 (3H), S 4·51 (2H)
2	12-Cl	79	8·8	263–4	3060, 1680 (C=O), 1600, 1565 (C=N), 1390, 1280, 777	M 7·33–7·15 (2H), M 7·07–6·91 (2H), T 6·6–6·43 (2H), M 6·2–6·1 (1H), M 6·1–6·0 (2H), S 4·55 (2H)
3	11-OCH_3	71	8·8	201–2	3050, 2940, 1670 (C=O), 1600, 1568 (C=N), 355, 777	M 7·3–7·1 (2H), M 7·05–6·85 (2H), T 6·6–6·35 (2H), M 6·2–6·03 (1H), M 9·85–5·7 (2H), S 4·53 (2H), S 5·32 (3H)
4	12-OCH_3	72	8·9	207–8	3050, 2940, 1667 (C=O), 1568 (C=N), 390, 1355, 780	M 7·33–7·15 (1H), M 7·07–6·75 (3H), M 6·56–6·3 (2H), M 5·95–5·55 (3H), S 4·33 (2H), S 3·07 (3H)
5	11-NO_2	96	12·8	>360	3070, 1680 (C=O), 1603, 1555 (C=N), 1520, 1340, 1270, 780	M 7·4–7·18 (2H), M 7·12–6·9 (2H), M 6·9–6·65 (2H), T 6·62–6·42 (2H), D 6·38–6·27 (1H), S 4·65 (2H)
6	12-NO_2	45	12·7	301–2	3100, 1680 (C=O), 1600, 1573 (C=N), 1520, 1350, 1280, 750	M 7·5–6·45 (3H), D 6·4–6·25 (1H), S 4·51 (2H)
7	11-NH_2	89	14·0	264–5	3400, 3240, 3060, 1658 (C=O), 1630, 1600, 1565 (C=N), 1380, 1270, 780	M 7·35–7·16 (2H), M 7·1–6·91 (2H), T 6·6–6·43 (2H), M 6·35–6·2 (3H), S 4·6 (2H)
8	12-NH_2	90	14·0	253–5	3420, 3360, 1665 (C=O), 1600, 1563 (C=N), 1520, 1370, 1280, 780	M 7·42–7·16 (3H), T 7·13–6·92 (2H), M 6·65–6·45 (3H), M 6·21 (2H), S 4·62 (2H)
9	11-NHAc	96	12·3	295–6	3280, 3080, 1675 (C=O), 1600, 1568 (C=N), 1385, 1280, 780	M 7·4–7·1 (2H), M 7·05–6·82 (2H), M 6·55–6·3 (3H), M 6·1 (2H), S 4·52 (2H), S 1·95 (3H)
10	12-NHAc	98	12·2	308–9	3300, 3080, 2880, 1672 (C=O), 1600, 1570 (C=N), 1390, 1360, 1280, 780	M 7·4–7·1 (2H), M 7·0–6·8 (2H), M 6·53–6·3 (3H), M 6·1 (2H), S 4·52 (2H), S 1·97 (3H)

S, singlet; D, doublet; T, triplet; M, multiplet.

bands in compounds **IV** are generally shifted toward lower wavenumbers by *ca* 20 cm^{-1} compared with those of the corresponding nitro-compounds **III**.

In the NMR spectra of the compounds **V**, in addition to the signals characteristic of the substituents, there exist three groups of signals characteristic of the structure of 7*H*,9*H*-quinazolino[3,2-*b*]-benz[*d*,*e*]isoquinolin-7-one, i.e. a signal from the CH_2 group protons within 4·0–4·6 ppm, signals from the phenylene protons within 5·8–6·2 ppm, and signals from the naphthalene protons within 6·3–7·5 ppm. In all cases the integration of the signals corresponded to the theoretical proportion of protons in the molecule.

2.2. Colour investigations

In order to determine the effect of the substituents in the derivatives obtained from 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one (**V**) on the shade, absorption spectra in the visible range were recorded. The characteristic quantities related with the long-wavelength absorption bands are given in Table 2.

Introduction of the substituents into the 7*H*,9*H*-quinazolino[3,2-*b*]-benz[*d*,*e*]isoquinolin-7-one system in position 11 or 12 generally causes

TABLE 2
Visible Absorption Maxima of 7*H*,9*H*-Quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one Derivatives (**V**)

Substituent X and position	*Absorption maximum, λ (nm)*	*Molar absorptivity, ε ($3м^{-1}$ cm^{-1})*
11-Cl	411·5	13800
12-Cl	407·4	14040
11-OCH_3	425·1	10256
12-OCH_3	416·6	11204
11-NO_2	424·4	20221
12-NO_2	402·9	11637
11-NH_2	454·5	14355
12-NH_2	376·2, 433·2	8725, 7881
11-NHAc[a]	427·7	14559
12-NHAc	414·9	11669
H	408·1	13194

[a] Ac, acetyl.

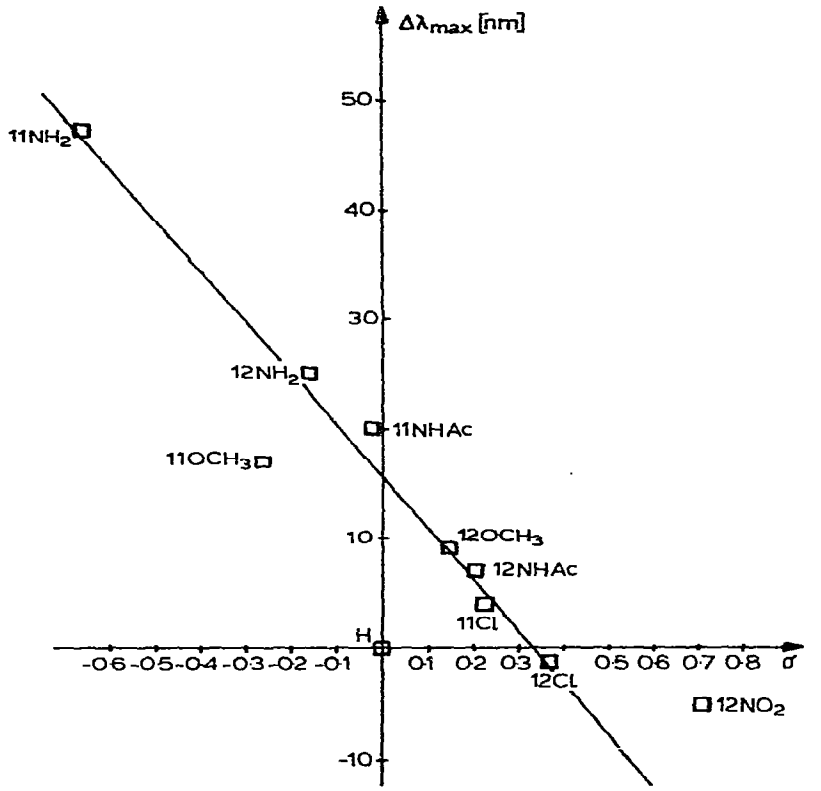


Fig. 1. Correlation of UV–Vis absorption maxima shifts due to substitution of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one with Hammett constants.

a bathochromic shift of the absorption band. However, compounds containing electron-withdrawing substituents in the position *meta* in relation to the C=N bond (i.e. V, X = 12-NO_2, X = 12-Cl) are the exceptions.

The magnitude of the observed effects is generally consistent with the electron-donating character of the substituent, as can be seen in Fig. 1, which shows the correlation between the corresponding Hammett constants[4] and the long-wavelength absorption band shift.

An interesting effect on the spectral properties is shown by the nitro group in the position *para* to the C=N bond (V, X = 11-NO_2). Here, in addition to the remarkable bathochromic shift (46 nm), a considerable increase of the molar absorptivity was observed.

In the spectrum of 12-amino-7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]-isoquinolin-7-one (V, X = 12-NH_2) there exist two separate absorption

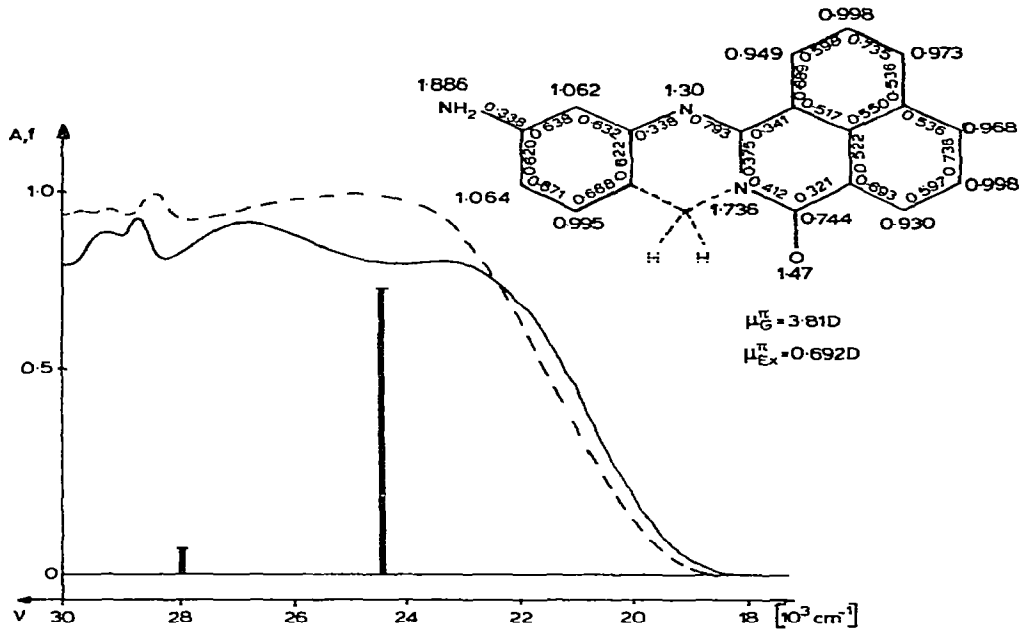


Fig. 2. A comparison of calculated data with electronic absorption spectra of 12-amino-7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one recorded in: ———, 1,4-dioxane, 0·2 cm cell, concentration $4{\cdot}68 \times 10^{-3}$M; – – – –, water–dioxane (4:1), 5·0 cm cell, concentration $1{\cdot}89 \times 10^{-4}$M.

bands with about half the molar absorptivity compared with all remaining compounds **V**. The phenomenon is probably associated with the formation of a stable dimer which requires a proton-donating solvent to be decomposed (Fig. 2).

Quantum calculations of the spectrum performed for the 12-amino derivative by the PPP method (parameters as in ref. 5) support this argument. The results of the calculations (Fig. 2) indicate that for an isolated molecule of 12-amino-7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one there is probably only one $\pi \rightarrow \pi^*$ band in the relevant part of the spectrum.

3. EXPERIMENTAL

Melting points were measured with a Boetius PHMK 05 apparatus and the values were uncorrected. The course of all reactions was controlled

chromatographically by TLC on silica gel 60 (Riedel de Haen) with cyclohexane–1,4-dioxane in a 2:1 ratio used as the eluent. The absorption spectra in the visible range were recorded for the dye solutions in 1,4-dioxane at $2{\cdot}0 \times 10^{-5}$ M concentrations, using a Jena SPECORD UV-Vis apparatus.

The method of synthesis of 2-nitrobenzylamine derivatives has been described earlier.[6]

3.1. General method of preparation of *N*-(2-nitrobenzyl)naphthalimides (III)

The hydrochloride of the appropriate 2-nitrobenzylamine (I) (0·055 mol), naphthalic anhydride (9·9 g, 0·05 mol), 50% aq. EtOH (200 cm^3) and 30% aq. NaOH (5·0 cm^3) were gradually heated to 60 °C for 1·5 h. After adding 30% aq. NaOH (0·5 cm^3) the mixture was heated to the b.p. for 30 min and refluxed for 3 h. After hot filtration and drying, products **III** (X = 11,12-Cl, 11,12-OCH_3 and 11-NO_2) were obtained with *ca* 95% yields.

3.2. Synthesis of *N*-(2,4-dinitrobenzyl) naphthalimide

Finely powdered 2,4-dinitrobenzylamine hydrochloride (17·5 g, 0·075 mol) was added at 90 °C to the solution of naphthalic anhydride (9·9 g, 0·05 mol) in 1,4-dioxane (250 cm) and then, while maintaining this temperature, anhydrous sodium acetate (6·15 g, 0·075 mol) was added in portions over 0·5 h. The mixture was refluxed for 3 h, then EtOH (300 cm^3) was added and left overnight. The precipitate was filtered off, washed with water (100 cm^3). A yield of 15·5 g (82%) of 254–5 °C m.p. product (chlorobenzene) was obtained.

3.3. General method of reduction with stannous chloride

The appropriate nitro compound (0·04 mol), methanol (300 cm^3), stannous chloride (40 g for each nitro group) and 36% aq. HCl (50 cm^3 per nitro group) were refluxed for 3 h. After filtering off, the double salt of the amine and $SnCl_6^{-2}$ was decomposed with 15% aq. NaOH (200 cm^3). Using this method compounds **IV** and compound **V** (X = 11-NH_2) were obtained with 82–90% yield.

3.4. General method of synthesis of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]-isoquinolin-7-one derivatives

Compounds **IV** (5·0 g) and AcOH (50 cm^3) were refluxed for 3 h. After filtering off, corresponding derivatives of 7*H*,9*H*-quinazolino[3,2-*b*]-benz[*d*,*e*]isoquinolin-7-one (**V**) were obtained with *ca.* 71–80% yield (Table 1).

3.5. Synthesis of 11-nitro-7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one

7*H*,9*H*-Quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one (14·2 g, 0·05 mol) was dissolved at 0 °C in concentrated H_2SO_4 (50 cm^3) and then, while maintaining the temperature within 0–5 °C, the mixture of 65% HNO_3 (3·6 cm^3, 0·05 mol) and conc. H_2SO_4 (10 cm^3) was dropped in over 1 h. Then the temperature was raised over 1 h to the ambient temperature and the reaction was continued for another hour. The product was separated by pouring on to ice (300 g) and adding 30% aq. NaOH (100 cm^3). Thereby compound **V** (X = 11-NO_2) (16·0 g, 96%) with m.p. > 360 °C (chlorobenzene) was obtained.

3.6. Synthesis of 12-nitro-7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one

30% aq. NaHS (12·0 cm^3) was added dropwise over 0·5 h to the solution of *N*-(2,4-dinitrobenzyl)naphthalimide (5·0 g, 0·013 mol) in 1,4-dioxane (120 cm^3) at 80 °C, and the reaction mixture was kept at 70–80 °C for 2 h. After pouring into water (200 cm^3) the precipitate (3·5 g) was filtered off and refluxed with AcOH (50 cm^3) for 3 h. The product was filtered off (1·8 g); the m.p. of the product was 301–2 °C (chlorobenzene).

3.7. Acetylamino derivatives of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one

These compounds were prepared by acetylation of the corresponding amino derivatives of **V** (X = NH_2) with the equimolar quantity of acetic anhydride in pyridine.

4. CONCLUSIONS

The synthesis of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one derivatives is simple and presents no difficulties. The final products are obtained with good yields (70–98 %) and a high degree of purity.

Introduction of substituents in position 11 or 12 of the 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one skeleton causes a batho- or hypso-chromic shift associated mainly with the electron-donor character of the substituent. Absorption maxima changes are observed within a narrow range of about 30 nm.

Studies are in progress on the synthesis of further 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one derivatives with substituents in some other positions of the molecule skeleton.

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