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Synthesis and Characterization of Bromoquinazolinone Substituted Spiro[isobenzofuran-1,9´-xanthene]-3-ones

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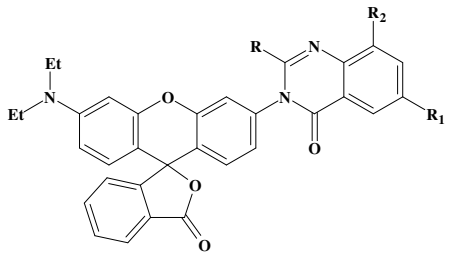
Some new bromoquinazolinone substituted fluoran compounds were synthesized by the reaction of the keto acid, 2-(4-diethylamino-2-hydroxybenzoyl)benzoic acid with different 3-(3/4-hydroxyphenyl)-2-methyl/phenylbromo-4(3H) quinazolinones in the presence of a dehydration condensing agent like sulfuric acid. Various quinazolinones were prepared by reacting different monobromo/dibromobenzoxazine-4-ones with 3-aminophenol or 4-aminophenol in the presence of pyridine as a solvent. All the synthesized fluoran compounds were identified by conventional methods such as melting point, IR, ^{1}H NMR, ^{13}C NMR, elemental analysis and UV-visible spectroscopy in organic solvents and 95% acetic acid. All these colorless fluorans develop a color in contact with electron accepting compounds.

Keywords: Fluoran, Keto Acid, Leuco Dyes, Quinazolinone, Synthesis

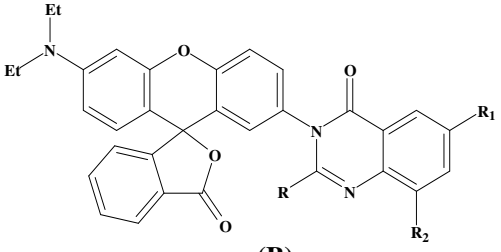
INTRODUCTION

Fluoran (spiro[isobenzofuran-1,9'-xanthene]-3-one) [1] is a class of leuco dyes which are generally substantially colorless or nearly colorless. However, when they are brought into intimate contact with electron accepting substances such as organic acids, acids clays, activated clays, phenol formaldehyde resins, metal salts of aromatic carboxylic acids, bisphenols etc., they produce coloration. Many heterocycles such as acridone [2], pyrrole [3], pyridine [4], pyrrolidine [5], morpholine [6], pyrazole [7], triazole [8], piperazine [9] were used in the preparation of fluoran compounds.

There are many applications of fluoran compounds including medical applications [10], thermal printing materials [11], organophotoreceptors [12], pressure sensitive adhesive tape [13], paint and toys [14], cosmetics [15], heat indicators [16], etc. Nowadays, fluoran compounds are widely used in



(A)



(B)

R = CH_3 or C_6H_5, R_1 = Br, R_2 = H or Br

Fig. 1. General structural formula of fluoran compounds.

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carbonless copying paper [17] and thermal sensitive recording papers. In the present study, we wish to report fluoran compounds containing various bromo-quinazolinone moieties, the general structural formula of which is shown in Fig. 1.

EXPERIMENTAL

All raw materials used were of commercial grade and were further purified by recrystallization and redistillation before use. All melting points (m.p.) are uncorrected and were determined by the open capillary method. The IR spectra of all the compounds were recorded on a Nicolet Impact-400D FT-IR spectrophotometer using KBr pellets. The ^{1}H NMR spectra were recorded on a Hitachi R-1500 spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given in ppm. ^{13}C NMR were recorded on a DPX 200 Brucker FT-NMR spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard. The absorption spectra (λ_{max}) of the compounds in chloroform and 95% acetic acid were recorded on a Shimadzu UV-240 spectrophotometer.

General procedure for the synthesis of keto acids (I). The keto acid, 2-(4-diethylamino-2-hydroxybenzoyl)benzoic acid (**I**), was prepared from N,N-diethyl-*m*-aminophenol (1 mol) with phethalic anhydride (1.1 mol) by refluxing in toluene (400 ml) for 5-6 h as previously described (m.p.: 207-8 ^{o}C) [18].

General procedure for the synthesis of quinazolin-ones (II). The various substituted benzoxazine-4-ones, were synthesized as previously reported [19-20]. The benzoxazine-4-ones used were 6-bromo-2-methyl-4H-3,1-benzoxazin-4-one (R = CH_3, R_1 = Br, R_2 = H), 6-bromo-2-phenyl-4H-3,1-benzoxazin-4-one (R = C_6H_5, R_1 = Br, R_2 = H), 6,8-dibromo-2-methyl-4H-3,1-benzoxazin-4-one (R = CH_3, R_1 = R_2 = Br), 6,8-dibromo-2-phenyl-4H-3,1-benzoxazin-4-one (R = C_6H_5, R_1 = R_2 = Br).

An equimolar mixture of various benzoxazine-4-ones and 3-amino phenols or 4-amino phenols in dry pyridine were refluxed for 10-12 h under anhydrous conditions. The reaction was monitored by TLC (solvent system: toluene:ethyl acetate, 7:3). After completion of the reaction, the reaction mixture was poured into ice cold hydrochloric acid to get quinazolin-ones **(II)**. The solid precipitates were filtered and washed with water until neutral.

Preparation of fluoran compounds (A_{1-4}, B_{1-4}). 2-(4-Diethylamino-2-hydroxybenzoyl)benzoic acid **(I)** (0.01 mol) and quinazolinone **(II)** (0.01 mol) were dissolved in conc. H_2SO_4 (10 ml) and stirred at 80-85 ^{o}C for 48 h. After the completion of the reaction, the reaction mixture was poured into ice-cold water. The precipitates were filtered and washed with water. This acid free compound was put into water and the pH was adjusted to approximately 9-10 using aqueous NaOH resulting in a light-colored fluoran compound. The product was filtered and washed with water until it reached a neutral pH. A red-colored single spot was seen in the solvent system of the TLC.

RESULTS AND DISCUSSION

The quinazolinones **(II_{a-h})** and fluorans (A_{1-4} and B_{1-4}) were prepared based on the methods described in the experimental section (Fig. 2) and characterized by elemental analysis and IR, ^{1}H NMR, ^{13}C NMR spectroscopy, as follows:

6-Bromo-3-(3-hydroxyphenyl)-2-methyl-4(3H)-quinazolinone(II_a). IRν_{max}/cm^{-1} 3401, 2923, 1695, 1589, 1321, 790, 698, 594; ^{1}H NMR (DMSO, 60 MHz) δ 9.6 (s, 1H, OH), 6.77-8.18 (m, 7H, Ar-H), 2.2 (s, 3H, Ar-CH_3).

6-Bromo-3-(3-hydroxyphenyl)-2-phenyl-4(3H)-quinazolinone(II_b). IRν_{max}/cm^{-1} 3403, 1690, 1584, 791, 699, 596; ^{1}H NMR (DMSO, 60 MHz) δ 9.45 (s, 1H, OH), 6.68-8.30 (m, 12H, Ar-H).

6,8-Dibromo-3-(3-hydroxyphenyl)-2-methyl-4(3H)-quinazolinone(II_c). IRν_{max}/cm^{-1} 3305, 2924, 1669, 1586, 1310, 791, 703, 554; ^{1}H NMR (DMSO, 60 MHz) δ 9.61 (s, 1H, OH), 6.76-8.22 (m, 6H, Ar-H), 2.29 (s, 3H, Ar-CH_3).

6,8-Dibromo-3-(3-hydroxyphenyl)-2-phenyl-4(3H)-quinazolinone(II_d). IRν_{max}/cm^{-1} 3404, 1672, 1596, 795, 699, 559; ^{1}H NMR (DMSO, 60 MHz) δ 9.25 (s, 1H, OH), 6.53-8.35 (m, 11H, Ar-H).

6-Bromo-3-(4-hydroxyphenyl)-2-methyl-4(3H)-quinazolinone(II_e). IRν_{max}/cm^{-1} 3294, 2931, 1661, 1599, 1312, 848, 577; ^{1}H NMR (DMSO, 60 MHz) δ 9.62 (s, 1H, OH), 6.29-8.18 (m, 7H, Ar-H), 2.18 (s, 3H, Ar-CH_3).

6-Bromo-3-(4-hydroxyphenyl)-2-phenyl-4(3H)-quinazolinone(II_f). IRν_{max}/cm^{-1} 3245, 1643, 1602, 842, 578; ^{1}H NMR (DMSO, 60 MHz) δ 10.14 (s, 1H, OH), 6.75-8.89 (m, 12H, Ar-H).

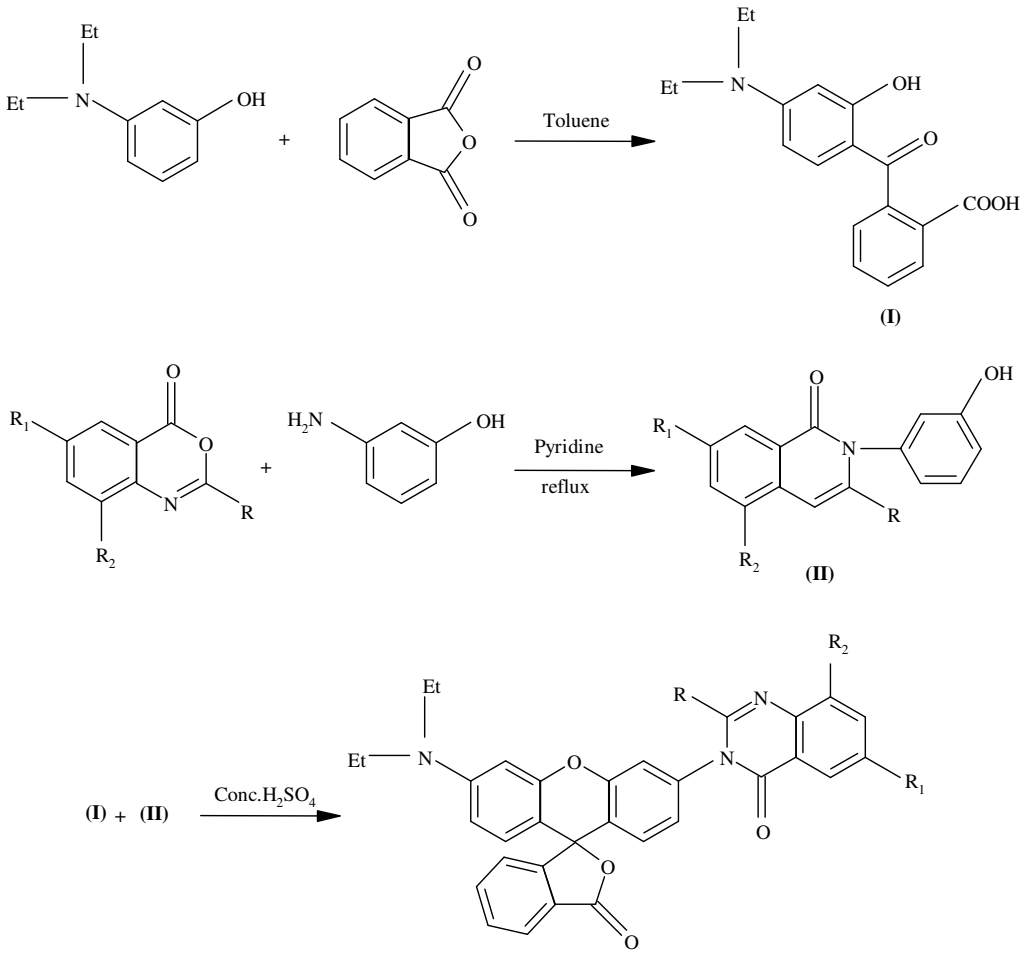

Fig. 2. General synthetic pathway for the preparation of quinazolinones and fluorans.

6,8-Dibromo-3-(4-hydroxyphenyl)-2-methyl-4(3H)-quinazolinone(II_g). IRν_{max}/cm^{-1} 3343, 2972, 1667, 1601, 1310, 834, 596; ^{1}H NMR (DMSO, 60 MHz) δ 8.15 (s, 1H, OH), 7.00-7.21 (m, 6H, Ar-H), 2.22 (s, 3H, Ar-CH_3).

6,8-Dibromo-3-(4-hydroxyphenyl)-2-phenyl-4(3H)-quinazolinone(II_h). IRν_{max}/cm^{-1} 3402, 1686, 1599, 836, 558; ^{1}H NMR (DMSO, 60 MHz) δ 9.38 (s, 1H, OH), 6.63-8.30 (m, 11H, Ar-H).

6-Diethylamino-3-(6'-bromo-2'-methyl-4'-oxo-(3'-hydroquinazolin-3'-yl)) fluoran (A_1). Found: C, 65.19; H, 4.42; N, 6.45. Calcd. for $C_{33}H_{26}BrN_3O_4$: C, 65.13; H, 4.30; N, 6.90; IRν_{max}/cm^{-1} 3072, 2972, 2938, 2858, 1776, 1680, 1595, 1441, 1326, 769, 709; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.4-7.9 (m, 13H, Ar-H), 3.2-3.5 (q, 4H, N($\underline{CH_2}$-CH_3)$_2$), 2.2-2.5 (s, 3H, Ar-CH_3), 1.2 (t, 6H, N(CH_2-$\underline{CH_3}$)$_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 168.9, 160.7, 160.3, 155.9, 155.4, 148.0, 142.3, 139.8, 138.5, 136.0, 134.8, 133.0, 132.7, 132.3, 131.9, 131.6, 130.1, 129.7, 126.4, 125.9, 125.3, 122.6, 121.9, 115.9, 108.1, 104.6, 97.4, 83.6, 44.2, 24.1, 12.3.

6-Diethylamino-3-(6'-bromo-2'-phenyl-4'-oxo-(3'-hydroquinazolin-3'-yl)) fluoran (A_2). Found: C, 68.65; H, 4.52; N, 6.03. Calcd. for $C_{38}H_{28}BrN_3O_4$: C, 68.06; H, 4.20; N, 6.26; IRν_{max}/cm^{-1} 2985, 2925, 2860, 1770, 1689, 1592, 1434, 1333, 770, 709; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.4-8.08 (m, 18H, Ar-H), 3.2-3.4 (q, 4H, N($\underline{CH_2}$-CH_3)$_2$), 1.0-1.4 (t, 6H, N(CH_2-$\underline{CH_3}$)$_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 168.6, 161.1, 160.7, 154.7, 154.6, 150.0, 143.9, 140.8, 138.2, 137.3, 134.7, 133.0, 132.2, 130.7, 130.4, 130.1, 129.5, 128.7, 128.6, 128.0,

127.2, 126.9, 125.8, 124.7, 124.5, 124.1, 123.2, 122.3, 121.8, 117.0, 109.2, 104.9, 97.5, 83.4, 44.1, 12.7.

6-Diethylamino-3-(6',8'-dibromo-2'-methyl-4'-oxo-(3'-hydroquinazolin-3'-yl)) fluoran (A_3). Found: C, 57.45; H, 3.72; N, 6.45. Calcd. for $C_{33}H_{25}Br_2N_3O_4$: C, 57.66; H, 3.66; N, 6.11; IRν_{max}/cm^{-1} 3070, 2985, 2930, 2870, 1776, 1689, 1602, 1427, 1326, 769, 702; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.4-8.2 (m, 12H, Ar-H), 3.2-3.4 (q, 4H, N($\underline{CH_2}$-CH_3)$_2$), 2.3 (s, 3H, Ar-CH_3), 1.0-1.2 (t, 6H, N(CH_2-$\underline{CH_3}$)$_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 169.3, 160.3, 160.1, 155.3, 155.2, 152.7, 149.8, 144.1, 140.5, 138.5, 135.0, 129.9, 129.8, 128.9, 128.8, 126.9, 124.9, 124.3, 123.8, 122.8, 122.4, 121.2, 119.6, 116.8, 108.8, 104.4, 9705, 83.2, 44.4, 24.6, 12.4.

6-Diethylamino-3-(6',8'-dibromo-2'-phenyl-4'-oxo-(3'-hydroquinazolin-3'-yl)) fluoran (A_4). Found: C, 60.62; H, 3.52; N, 5.89. Calcd. for $C_{38}H_{27}Br_2N_3O_4$: C, 60.90; H, 3.63; N, 5.60; IRν_{max}/cm^{-1} 2985, 2945, 2825, 1763, 1689, 1598, 1441, 1320, 780, 704; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.4-8.4 (m, 17H, Ar-H), 3.3-3.4 (q, 4H, N($\underline{CH_2}$-CH_3)$_2$), 1.0-1.2 (t, 6H, N(CH_2-$\underline{CH_3}$)$_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 169.8, 161.7, 161.2, 159.0, 158.6, 153.9, 145.3, 142.3, 137.8, 136.2, 135.0, 134.6, 132.9, 132.7, 132.4, 132.0, 131.8, 131.6, 130.9, 130.7, 130.6, 130.1, 128.0, 126.9, 126.5, 126.2, 124.1, 122.3, 120.0, 115.7, 108.2, 105.1, 97.2, 83.7, 44.3, 12.7.

6-Diethylamino-2-(6'-bromo-2'-methyl-4'-oxo-(3'-hydroquinazolin-3'-yl)) fluoran (B_1). Found: C, 65.26; H, 4.58; N, 6.84. Calcd. for $C_{33}H_{26}BrN_3O_4$: C, 65.13; H, 4.30; N, 6.90; IRν_{max}/cm^{-1} 3068, 2969, 2928, 2870, 1764, 1687, 1594, 1466, 1307, 831; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.5-8.2 (m, 13H, Ar-H), 3.3-3.4 (q, 4H, N($\underline{CH_2}$-CH_3)$_2$), 2.17(s, 3H, Ar-CH_3), 1.19-1.27 (t, 6H, N(CH_2-$\underline{CH_3}$)$_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 168.8, 160.4, 160.0, 156.1, 150.2, 148.1, 142.0, 139.2, 138.4, 135.0, 134.8, 133.7, 133.2, 132.5, 132.1, 131.8, 131.7, 129.4, 126.0, 125.5, 122.1, 121.6, 119.6, 117.2, 115.0, 104.2, 97.1, 8308, 44.2, 24.3, 12.1.

6-Diethylamino-2-(6'-bromo-2'-phenyl-4'-oxo-(3'-hydroquinazolin-3'-yl)) fluoran (B_2). Found: C, 68.37; H, 4.68; N, 6.31. Calcd. for $C_{38}H_{28}BrN_3O_4$: C, 68.06; H, 4.20; N, 6.26; IRν_{max}/cm^{-1} 2972, 2932, 2871, 1770, 1696, 1602, 1450, 1347, 838; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.4-7.6 (m, 18H, Ar-H), 3.2-3.4 (q, 4H, N($\underline{CH_2}$-CH_3)$_2$), 1.1 (t, 6H, N(CH_2-$\underline{CH_3}$)$_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 168.8, 161.4, 160.2, 154.5, 154.3, 150.3, 143.9, 140.6, 138.8, 134.2, 133.3, 133.1, 132.8, 132.5, 131.2, 130.9, 130.6, 129.6, 128.9, 128.4, 127.2, 126.7, 124.6, 124.5, 124.3, 123.0, 122.4, 121.9, 118.9, 116.7, 115.2, 104.7, 97.2, 83.6, 44.3, 12.5.

6-Diethylamino-2-(6',8'-dibromo-2'-methyl-4'-oxo-(3'-hydroquinazolin-3'-yl)) fluoran (B_3). Found: C, 57.31; H, 3.84; N, 6.04. Calcd. for $C_{33}H_{25}Br_2N_3O_4$: C, 57.66; H, 3.66; N, 6.11; IRν_{max}/cm^{-1} 3069, 2969, 2928, 2870, 1765, 1688, 1590, 1445, 1356, 820; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.5-8.2 (m, 12H, Ar-H), 3.2-3.4 (q, 4H, N($\underline{CH_2}$-CH_3)$_2$), 2.2 (s, 3H, Ar-CH_3), 1.0-1.2 (t, 6H, N(CH_2-$\underline{CH_3}$)$_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 169.1, 160.5, 160.1, 155.6, 152.5, 152.3, 149.8, 144.1, 140.4, 135.3, 131.8, 129.8, 129.7, 129.1, 128.9, 128.7, 127.6, 126.7, 125.2, 124.9, 123.3, 122.7, 119.6, 119.5, 108.8, 104.3, 97.6, 83.3, 44.4, 24.6, 12.4.

6-Diethylamino-2-(6',8'-dibromo-2'-phenyl-4'-oxo-(3'-hydroquinazolin-3'-yl)) fluoran (B_4). Found: C, 60.29; H, 3.92; N, 5.69. Calcd. for $C_{38}H_{27}Br_2N_3O_4$: C, 60.90; H, 3.63; N, 5.60; IRν_{max}/cm^{-1} 2985, 2938, 2868, 1770, 1680, 1600, 1434, 1333, 848; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.4-8.3 (m, 17H, Ar-H), 3.2-3.3 (q, 4H, N($\underline{CH_2}$-CH_3)$_2$), 1.1 (t, 6H, N(CH_2-$\underline{CH_3}$)$_2$). ^{13}C NMR ($CDCl_3$, 200 MHz) δ 169.3, 161.2, 160.9, 159.3, 153.4, 152.3, 145.1, 142.8, 138.1, 135.7, 134.2, 133.9, 133.4, 133.0, 132.9, 132.7, 132.2, 131.5, 131.2, 130.9, 130.7, 130.4, 126.8, 126.7, 126.4, 124.0, 122.8, 121.6, 120.3, 116.2, 109.5, 105.4, 97.8, 83.5, 44.7, 12.6.

The physical data of the quinazolinones (**II_{a-h}**) and fluorans (**A_{1-4}** and **B_{1-4}**) prepared are collected in Tables 1 and 2, respectively.

The IR spectra of all fluoran compounds showed the disappearance of the characteristic absorption band of the OH group of quinazolinone and the appearance of the bands at 1745-1790 cm^{-1} for the C=O group of the lactone ring and at 1640-1700 cm^{-1} for the C=O group of quinazolinone as well as other characteristic absorption bands for the rest of the molecules.

The chromogenic compounds prepared in the present work are soluble in organic solvents and are nearly colorless; however, they spontaneously show a color forming property (red) in aqueous acid solution and acidic color activating substance. Absorption spectra (λ_{max}) of the compounds in chloroform and 95% acetic acid show a single peak in chloroform due to the lactone ring but show three peaks in 95% acetic acid due to the quinone, zwitterion and lactone

Table 1. Physical Data of Quinazolinones (II_{a-h})

No.	Compound II			Mol. Wt.	Yield (%)	M.P. (°C)
	R	R_1	R_2			
II_a	CH_3	Br	H	331	69	220
II_b	C_6H_5	Br	H	393	76	260
II_c	CH_3	Br	Br	410	74	255
II_d	C_6H_5	Br	Br	472	85	215
II_e	CH_3	Br	H	331	79	284
II_f	C_6H_5	Br	H	393	73	225
II_g	CH_3	Br	Br	410	78	285
II_h	C_6H_5	Br	Br	472	81	238

Table 2. Physical Data of Fluorans (A_{1-4} and B_{1-4})

No.	Compound A_{1-4}, B_{1-4}			Yield (%)	M.P. (°C)	λ_{max} in 95% AcOH	λ_{max} in $CHCl_3$	Color on silica gel
	R	R_1	R_2					
A_1	CH_3	Br	H	63	255	495,371,274	288	Red
A_2	C_6H_5	Br	H	67	335*	498,373,282	280	Red
A_3	CH_3	Br	Br	58	265	497,370,274	280	Red
A_4	C_6H_5	Br	Br	66	311	498,372,291	297	Red
B_1	CH_3	Br	H	59	295	493,370,278	280	Red
B_2	C_6H_5	Br	H	65	231	495,372,280	280	Red
B_3	CH_3	Br	Br	61	302	494,370,282	288	Red
B_4	C_6H_5	Br	Br	64	386*	496,373,290	288	Red

*decomposition point.

forms [21-22] (Table 2).

CONCLUSIONS

The chromogenic compounds of the present investigation are soluble in organic solvent and are nearly colorless, but spontaneously exhibit a color forming property in aqueous acid solution and acidic color activating substance.

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REFERENCES

[1] M. Ramaiah, Chemistry and Applications of Leuco Dyes, Plenum Press, New York, 1997, p.159.

[2] Sumitomo Chemical Co., Ltd., Jpn. Kokai Tokkyo Koho JP 57, 191, 086 (CA 100:112305t).

[3] S. Spatz, US 3, 989, 716 (CA 86:44769n).

[4] A. Takashi, K. Kohichi, K. Makoto, M. Makoto, I. Hiroshi (Sumitomo Chemical Co., Ltd.) Jpn. 73 00, 168 (CA 80:28468j).

[5] G. Robert, P. Jean (Ciba-Geigy A.-G.) U.S. 4, 007, 195 (CA 86:173071c).
[6] Dioxan, Leonard Fox (Holiday Dyes & Chemical Ltd.) GB 2, 097, 013 (CA 98:73839p).
[7] S. Yoji (Yamada Chemical Co., Ltd., Japan) GB 2, 295, 391 (CA 125:198512j).
[8] Alsop, J. Derek (Moore Business Forms Inc.) Ger. Offen. 2, 550, 368 (CA 85:144713n).
[9] Yamamoto Synthetic Chemical Co., Ltd., Brit. 1, 336, 955 (CA 80:122413j).
[10] M. Lim, M. Marinangleli, U.S. 5, 645, 824 1997 (CA 127:152971w).
[11] T. Yano, T. Madono, H. Kawai, Jpn. Kokai Tokkyo Koho JP 2003, 170, 666 (CA 139:28667k).
[12] N. Jubran, Z. Tokarski, K.W. Law, U.S. Pat. Appl. Publ. U.S. 2004 43, 314. (CA 140:243541r).
[13] N. Sakai, Jpn. Kokai Tokyo Koho JP 2004 91, 769. (CA 140:272003x).
[14] M. Ito, Jpn. Kokai Tokyo Koho JP 2004 136, 477. (CA 140:397413n).
[15] K. Takada, Y. Yoshikawa, Jpn. Kokai Tokkyo Koho JP 2004 2, 356. (CA 140:64720b).
[16] T. Kito, M. Iido, Japan. Kokai 77,111,787 1977 (CA 88:154427y).
[17] V.G. Atkinson (Carrs Paper Ltd.) U.S. 6071852 (2000).
[18] M. Kondo, M. Tanaka, N. Sakamoto, H. Ooyoshi, Eur. Pat. EP 511, 019 1993.
[19] D.R. Desai, V.S. Patel, S.R. Patel, J. Indian Chem. Soc. 43 (1966) 353.
[20] V.K. Pandey, J. Indian Chem. Soc. 54 (1977) 1084.
[21] A.V. Despande, E.B. Namdas, J. Photochem. Photobiol. A:Chem. 110 (1997) 117.
[22] S. Kimura, T. Kodayashi, S. Ishige, Japan 71 12, 312 1968 (CA 75:50411d).