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Synthesis and characterisation of coloured monomers based on 2-methylresorcinol

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Abstract

Some new coloured monomers having electron-withdrawing groups were synthesized from 2-methylresorcinol, and their structures were confirmed by ^{1}H-NMR, IR, and combustion analyses. The effects of substituents in the diazo components on colour and NMR properties were examined. The effects of solvent polarity on the chemical shifts in NMR spectra were also determined. Explanations for the observed effects are presented.

Keywords: 2-Methyl resorcinol derivatives; Bifunctionalized colourant monomer; Synthesis; Structure elucidation; Substituent effects

1. Introduction

The design and synthesis of bifunctional colourants has received considerable attention in recent years, because such colorants can be utilized as monomers for functional polymers via polyaddition and polycondensation reactions [1–3]. In related studies, it has been reported that resorcinol undergoes coupling reactions under different pH conditions, to give monoazo and disazo dyes for textile fibers and leather [4]. However, there has been no report concerning the use of 2-methylresorcinol as a precursor in the synthesis of coloured monomers having electron-withdrawing groups.

In this paper, we report the synthesis and characterisation of the novel bifunctional colourants shown in Figs. 1 and 2. Characterisation includes a determination of the effects of solvents on the chemical shifts of the protons associated with the hydroxyl groups of the resorcinol moiety.

2. Results and discussion

2.1. Synthesis

Diazotisation of the weakly basic amines using $NaNO_2$ and H_2SO_4 followed by coupling with 2-methylresorcinol under acidic conditions produced the target monoazo dyes. The dyes were purified by recrystallisation from acetone and subjected to NMR analysis to determine which of the possible pairs of position isomers (A or B) had formed. Results of the NMR studies are summarized in the next section.

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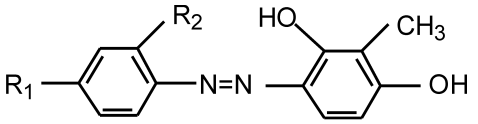


BCM-1 (R_1=NO_2, R_2= NO_2)
BCM-2 (R_1=NO_2, R_2= CN)
BCM-3 (R_1=CF_3, R_2= NO_2)
BCM-4 (R_1=NO_2, R_2= CF_3)

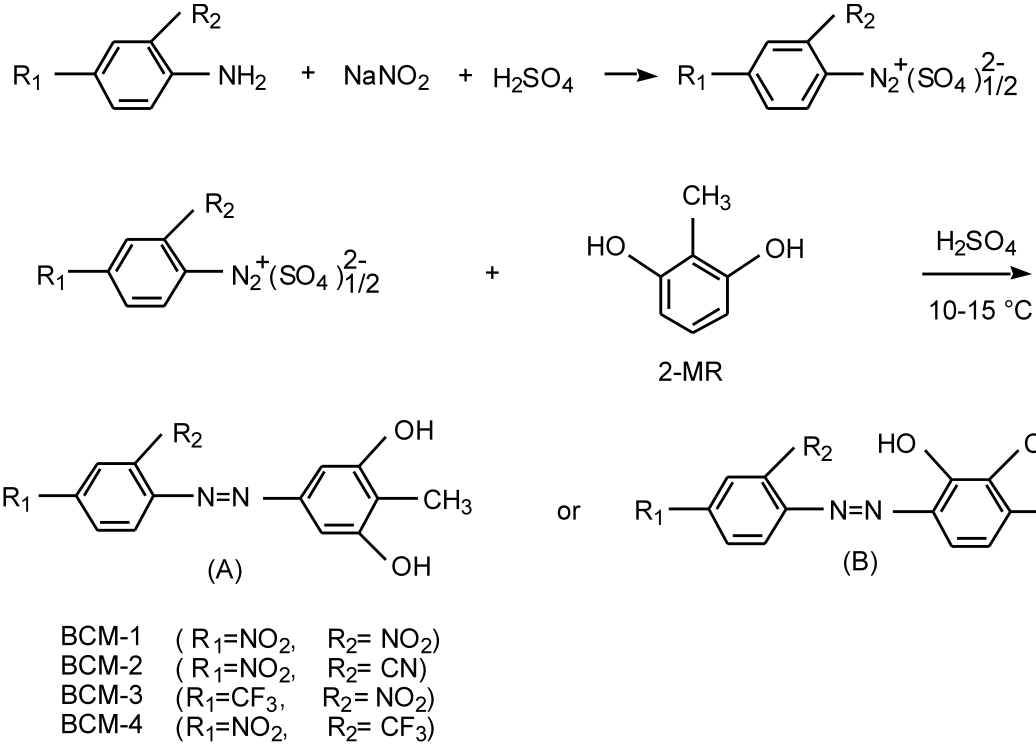
Fig. 1. 2-Methylresorcinol-based colourants prepared in this study.

2.2. Structure characterisation by ^{1}H-NMR [5]

Figs. 3 and 4 contain ^{1}H-NMR spectra of **BCM-1**. In the former, the signals at the lower field (14.66 and 11.39 ppm) are assignable to phenolic hydroxyl protons (f and g). In the latter figure, which shows an expanded aromatic region, the doublets at 7.332 (Hd) and 6.698 ppm (He) could be used to establish the structure of the isomer produced. If structure (A) were correct for **BCM-1**, He would appear as a singlet rather than a doublet. Spectra for the other 3 dyes (**BCM-1–BCM-3**) also showed a pair of doublets in the 6.5–7.5 region. Consequently, it could be concluded that compound (B) was the product of the reaction.

In the expanded region of the ^{1}H-NMR spectra of compounds **BCM-1–BCM-4**, protons Ha, Hb, and Hc in **BCM-1** and **BCM-2** were observed at virtually the same positions, with proton Ha giving the signal furthest downfield in each case (Fig. 4). The latter observation is expected, since Ha has two adjacent electron-withdrawing groups. The signals for protons H-3a and H-4a were observed further upfield (8.6 ppm) than those for H-1a and H-2a (8.9 ppm) of **BCM-1** and **BCM-2**. This is consistent with the stronger electron-withdrawing character of the NO_2 group than CF_3. For the same reason, H-4b was further downfield (8.5 ppm) than H-3b (8.2 ppm).

On comparing H-1d and H-2d or H-3d and H-4d, there was a marked difference in chemical shifts. Signals for H-2d and H-4d were observed at



BCM-1 (R_1=NO_2, R_2= NO_2)
BCM-2 (R_1=NO_2, R_2= CN)
BCM-3 (R_1=CF_3, R_2= NO_2)
BCM-4 (R_1=NO_2, R_2= CF_3)

Fig. 2. Synthesis of some 2-methylresorcinol-based dye monomers.

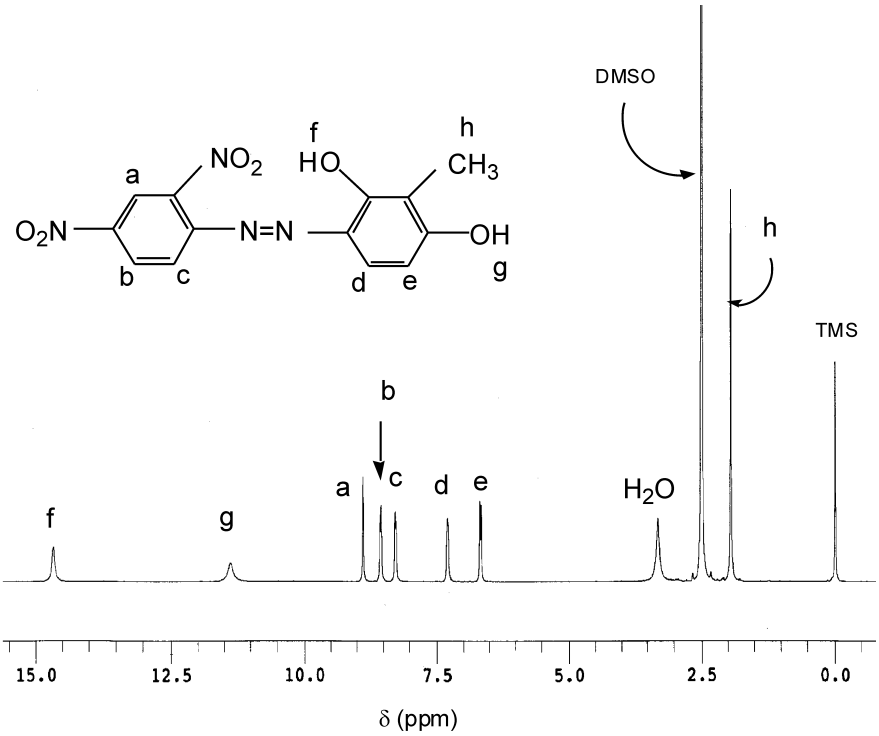


Fig. 3. ^{1}H-NMR (400 MHz) spectrum of **BCM-1** in DMSO-d_6.

lower field than for H-1d and H-3d. This would suggest the existence of interactions between two substituted phenyl rings, including intramolecular hydrogen bonding between –NO_2 and –OH (Fig. 6). The shape of the UV–visible absorption spectrum and the location of the phenolic hydroxyl groups in the ^{1}H-NMR spectra are consistent with this idea.

2.3. Substituent and solvent effect on the ^{1}H-NMR chemical shifts of phenolic hydroxyl protons

Solvents, reagent concentrations and temperature affected the ^{1}H-NMR chemical shifts of the OH protons in the dye employed in this study. Fig. 5a shows signals for the phenolic protons of **BCM-1**, and Table 1 summarizes the ^{1}H-NMR data for the phenolic protons all four dyes.

The chemical shift of proton Hf was affected by ring substituents and the solvents employed. When DMSO-d_6 was used as the solvent, protons Hg appeared near 11.3 ppm. When acetone-d_6 was used, it appeared near 10.1 ppm. The proton shielding

Table 1
^{1}H-NMR chemical shifts (ppm) of phenolic protons in DMSO-d_6 and acetone-d_6

	BCM-1		**BCM-2**		**BCM-3**		**BCM-4**	
	DMSO	Acetone	DMSO	Acetone	DMSO	Acetone	DMSO	Acetone
Hf	14.66	13.42	12.85	13.42	13.89	14.20	12.88	13.36
Hg	11.39	10.06	11.35	10.05	11.22	10.84	11.29	10.00
Δδ	3.27	***3.36***	1.50	***3.37***	2.67	***3.36***	1.59	***3.36***

differences among **BCM-1**, **BCM-2**, **BCM-3** and **BCM-4** was only 0.1 ppm for Hg in DMSO and acetone, indicating that the position of Hg was mainly affected by the two solvents (Table 1). Due to higher polarity, the Hg signal appeared at lower field (11.3 ppm) in DMSO than in acetone. The Hf signal appeared at lower field than the signal for Hg, probably due to the electron-withdrawing effect of the *para*-arylazo group. Table 1 also shows the ^{1}H-NMR chemical shift differences ($\Delta\delta$) between Hf and Hg signals. The difference in acetone was 3.36–3.37 in all cases, while it was in the range of 1.50–

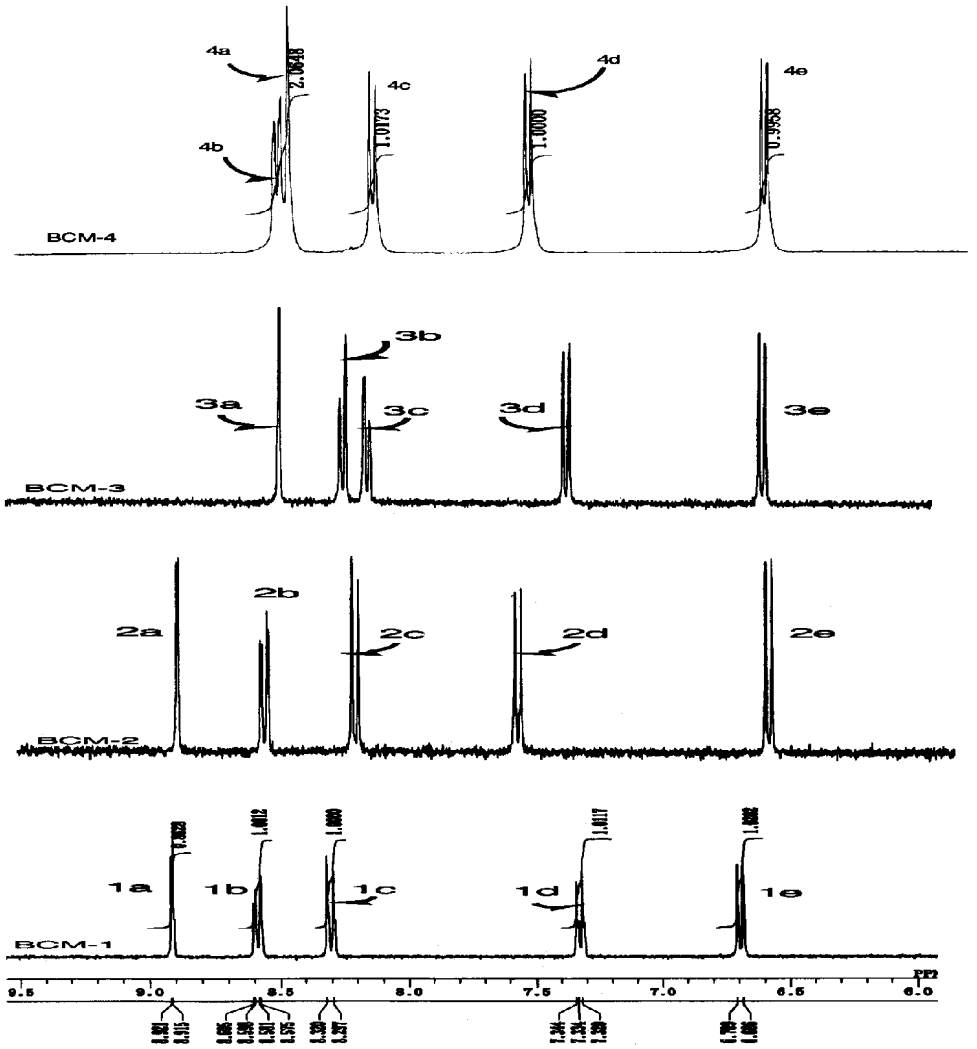


Fig. 4. ^{1}H-NMR (400 MHz) spectra of **BCM-1–BCM-4** in DMSO-d_6.

3.27 in DMSO. The change was greater in DMSO when an *ortho*-NO_2 group was present.

In the case of **BCM-1** and **BCM-3**, signals due to Hg disappeared when D_2O was added (see Fig. 5b), but Hf signals remained. In the case of Hf, intramolecular H-bonding inhibits the exchange.

2.4. IR spectral data

The azo compounds were also characterized by IR spectroscopy. All showed absorptions at 1450–1400 and 1500–1300 cm^{-1} (stretching vibration) that were assigned to a diazo group and a nitro group, respectively. The spectrum of **BCM-2** contained a peak at 2245 cm^{-1}, which is characteristic of a cyano group (Fig. 7). The spectra of **BCM-3** and **BCM-4** contained a peak at 1132 cm^{-1}, which was assigned to the CF_3 group [6,7].

2.5. UV–visible absorption spectra

The visible absorption spectra of all compounds were recorded in $CHCl_3$ and acetone, and molar extinction coefficients were calculated (Table 2). In

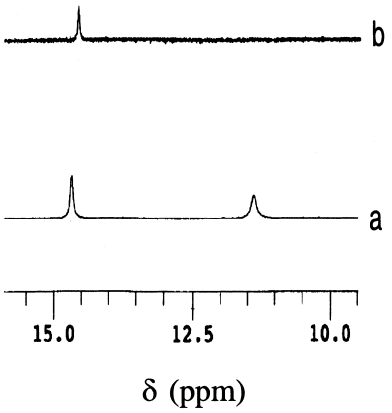


Fig. 5. Expanded ^{1}H-NMR (400 MHz) spectra of **BCM-1** in DMSO-d_6 without (a) and with (b) D_2O.

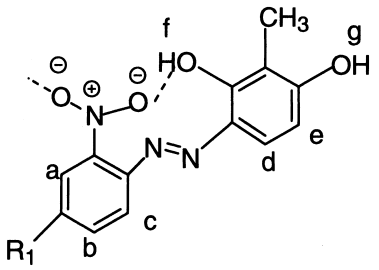


Fig. 6. Intramolecular H-bonding in **BCM-1** and **BCM-3**.

$CHCl_3$, **BCM-1** gave an absorption at a longer wavelength (418 nm) than **BCM-3** (408 nm). This was expected because the nitro group is a stronger electron-withdrawing group than trifluoromethyl group. Comparing **BCM-1** and **BCM-2**, there was a marked hypsochromic (23 nm) from 441 nm for **BCM-2** to 418 nm for **BCM-1** (in $CHCl_3$). Comparing **BCM-3** and **BCM-4**, there was also a marked hypsochromic shift (15 nm) when CF_3 is used instead of NO_2. Moreover, the absorption spectra of color monomers (**BCM-1**and **BCM-3**) with nitro group *ortho* to azo group were shifted over 13 nm, compared to **BCM-2** and **BCM-4**, both in chloroform and in acetone. The molar extinction coefficients were $2.7–3.5\times10^{-4}$ l/mol cm.

Table 2
UV–visible data for **BCM-1**–**BCM-4** in $CDCl_3$ and acetone

Compound	$CHCl_3$		Acetone	
	λ_{max} (nm)	$\varepsilon\times10^{-4}$ (l/mol cm)	λ_{max} (nm)	$\varepsilon\times10^{-4}$ (l/mol cm)
BCM-1	418	2.94	418	3.00
BCM-2	441	2.72	431	2.93
BCM-3	408	3.49	408	2.66
BCM-4	423	2.80	422	2.72

Using acetone as the solvent, the order of the absorption maxima varied in the same way as in $CDCl_3$. In DMF, the absorption maximum for **BCM-4** was shifted to 554 nm and the molar absorptivity value became 5.37×10^4 l/mol cm, which was much higher than the values in $CHCl_3$ and acetone (Fig. 8). These differences can be attributed to the higher polarity of DMF.

2.6. Summary

We have described the synthesis of four 2-methyl resorcinol-based azo monomers substituted with electron-withdrawing groups. Their structures were established by ^{1}H-NMR, IR spectroscopy, and elemental analysis. The effects of ring substituents on color and the ^{1}H-NMR chemical

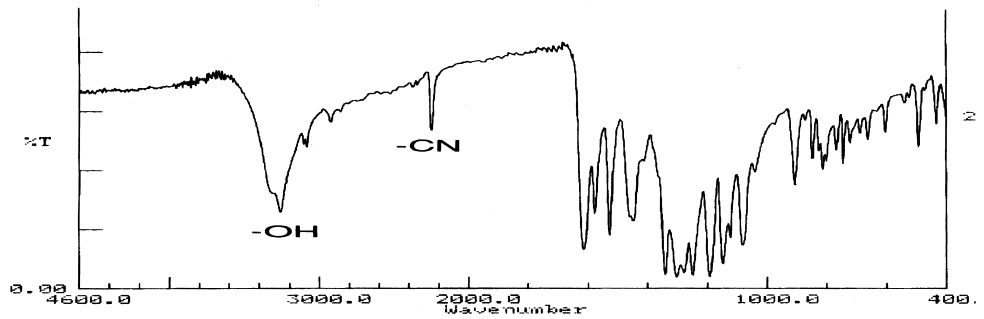


Fig. 7. IR spectrum of **BCM-2**.

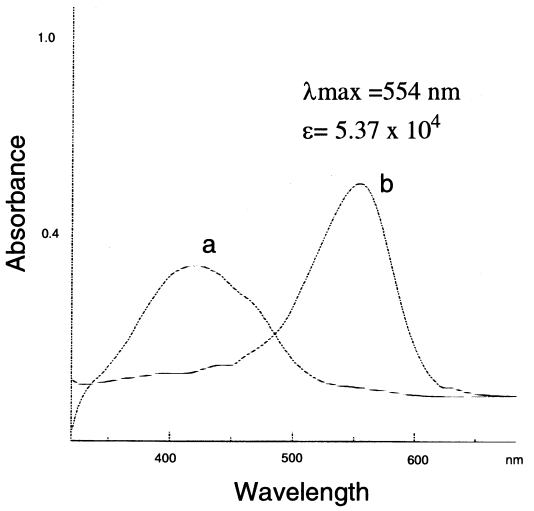


Fig. 8. UV–visible spectra of **BCM-4** in acetone (a) and DMF (b).

shifts of aromatic protons were discussed. The choice of the NMR solvent had a significant impact on the chemical shifts of proton associated with the phenolic hydroxyl groups, and it was found that the difference in the chemical shifts of the two phenolic protons was a constant value (3.36 ppm) when acetone was used as the solvent. The visible absorption spectra of the color monomers with nitro group *ortho* to azo group were remarkably shifted towards the blue by more than 13 nm in chloroform and acetone.

3. Experimental

3.1. General

Melting points were measured on a micro melting point apparatus (YANACO) and IR spectra were recorded on an FT/IR-5300 spectrometer (Japan Spectroscopic Co. Ltd.) in KBr. ^{1}H-NMR (400 MHz) spectra were recorded on a Jeol JNM-EX400 spectrometer. Chemical shifts are given in ppm with TMS as an internal standard. UV–visible spectra were recorded on a Ubest-50 spectrometer (Japan spectroscopic Co. Ltd.). Organic chemicals are purchased from Tokyo Kasei Company and used without further purification.

The synthesis of dyes **BCM-1**–**BCM-4** is illustrated below in the preparation of **BCM-1**.

3.2. 2′,4′-Dihydroxy-3′-methyl-2,4-dinitroazobenzene (**BCM-1**)

Powdered $NaNO_2$ (8.3 g, 0.12 mol) was added slowly to 95% H_2SO_4 (150 ml) at $<5^\circ$C over a 1.5 h period. After the addition was completed, the mixture was stirred until a solution was obtained. Then 2,4-dinitroaniline (18.16 g, 0.1 mol) was slowly added at 5–10°C over 60 min. The resultant mixture was heated to 70–75°C with stirring for 30 min, and then cooled to room temperature to obtain the diazo compound.

The diazonium salt solution was added dropwise with stirring to a cooled solution of 2-methyl resorcinol (6.2 g, 0.05 mol) in 95% H_2SO_4 (10 ml), 250 ml water, 10 ml ethanol, and 1–2 drops of polyethylene glycol mono-4-nonylphenyl ether at 10–15°C over 60 min. After the addition was completed, the mixture was stirred for an additional 30 min at room temperature and the volume was adjusted to 350 ml with water. The red solid precipitate was filtered, washed with water, and dried at 40°C under vacuum for 24 h to give an 87% crude yield. Recrystallization from acetone gave dark red needles, m.p. 223.5–225.0°C. ^{1}H-NMR (DMSO-d_6): δ H = 8.92 (d, J = 2.4 Hz, Ha), 8.59 (dd, J = 2.4 Hz, Hb), 8.31 (t, J = 2.4 Hz, Hc), 7.33 (d, J = 2.4 Hz, Hd), 6.70 (d, He), 2.10 (s, 3H, Hh). FT–IR (KBr): 3453 (–OH), 1489 (s) and 1336 (s) (aromatic –NO_2), 1407 (s) (stretching vibrations, –N=N–), 1416 (alkene C–H, –CH_3). Anal. calcd. for $C_{13}H_{10}N_4O_6$: C, 49.06; H, 3.17; N, 17.60. Found: C, 49.04; H, 2.83; N, 17.24.

3.3. 2′,4′-Dihydroxy-3′-methyl-2-cyano-4-nitroazobenzene (**BCM-2**)

This dye was prepared from 2-amino-5-nitrobenzonitrile as orange-red needles (82%), m.p. 243.5–245.0°C. ^{1}H-NMR (DMSO-d_6): δ H = 8.90 (d, J = 2.4 Hz, Ha), 8.59 (dd, J = 2.4 Hz, Hb), 8.25 (d, J = 2.4 Hz, Hc), 7.65 (d, Hd), 6.73 (d, He), 2.148 (s, 3H, Hh). FT–IR (KBr): 3260 (s, –OH), 2245.3 (stretching vibration, –CN), 1415 (s) (stretching vibration, –N=N–), 1526 (s) and 1343

(s, aromatic $-NO_2$), 1449 (alkene C–H, $-CH_3$). Anal. calcd. for $C_{14}H_{10}N_4O_4$: C, 56.38; H, 3.38; N, 18.78. Found: C, 56.24; H, 3.35; N, 18.85.

3.4. 2′,4′-Dihydroxy-3′-methyl-4-trifluoromethyl-2-nitroazobenzene (**BCM-3**)

This dye was prepared using 3-nitro-4-amino-benzotrifluoride. The crude product was recrystallized from ethanol to yield red needles (91%), m.p. 205.5–207°C. ^{1}H-NMR (DMSO-d_6): δ H = 8.52 (S, Ha), 8.28 (d, Hb), 8.19 (d, Hc), 7.43 (d, Hd), 6.68 (d, He), 2.07 (s, 3H, Hh). FT–IR (KBr, cm^{-1}): 3196 (s, –OH), 1428 (s) (stretching vibration –N=N–), 1572 (s) and 1319 (s, aromatic $-NO_2$), 1437 (s) (alkene C–H, $-CH_3$), 1132 (m, C–F). Anal. calcd. for $C_{14}H_{10}N_3O_4F_3$: C, 49.28; H, 2.95; N, 12.31. Found: C, 49.24; H, 3.12; N, 12.24.

3.5. 2′,4′-Dihydroxy-3′-methyl-2-trifluoromethyl-4-nitroazobenzene (**BCM-4**)

The dye was prepared using 5-nitro-2-amino-benzotrifluoride, giving 89.4% m.p. 221–222.5°C. ^{1}H-NMR (DMSO-d_6): δ H = 12.87 (s, br, Hf), 11.26 (s, br, Hg), 8.69 (d, Hb), 8.48 (s, Ha), 8.22 (d, Hc), 7.62 (d, Hd), 6.70 (d, He), 2.00 (s, 3H), FT–IR (KBr): 3196 (s, –OH), 1428 (s) (stretching vibration, –N=N–), 1572 (s) and 1319 (s, aromatic $-NO_2$), 1437 (s) (alkene C–H, $-CH_3$), 1132 (m, C–F). Anal. calcd. for $C_{14}H_{10}N_3O_4F_3$: C, 49.28; H, 2.95; N, 12.31; F, 16.59. Found: C, 49.37; H, 3.07; N, 12.09; F, 16.61.

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