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The Synthesis and Characterization of UV-Absorbing Azo-Pigments and Their Polymerizable Acryloyloxy and Methacryloyloxy Derivatives

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ABSTRACT

Mono- and diazo compounds of 5-(2-nitrophenyl-azo-)2,2',4,4'-tetrahydroxybenzophenone and 5,5'-di(2-nitrophenyl-azo-)2,2',4,4'-tetrahydroxybenzophenone have been synthesized by the azo-coupling reaction of o-nitrobenzenediazonium chloride with 2,2',4,4'-tetrahydroxybenzophenone. Esterification of the mono-azo compound with acryloyl and methacryloyl chloride gave the monomeric acryloyloxy and methacryloyloxy azo-pigments in 57 and 59% yield. Reductive cyclization of the mono-azo compound gave a yellow product containing two types of ultra-violet absorbers, i.e. benzophenone and benzotriazole units. All compounds were characterized by their IR, UV, and ^1H *NMR.*

1 INTRODUCTION

The formation of coloured coatings usually involves the incorporation of a monomeric pigment into a polymeric matrix together with other additives such as UV absorbers to stabilize the polymer from degradation. The pigment and the UV stabilizer are simply mixed with the polymeric matrix, thus remaining chemically independent in the final coating matrix, and share the disadvantages of limited compatibility, volatility, and migration from the polymer matrix to the surrounding media causing deterioration of the coloured coating with the possible problems of toxicity to the adjacent environment.

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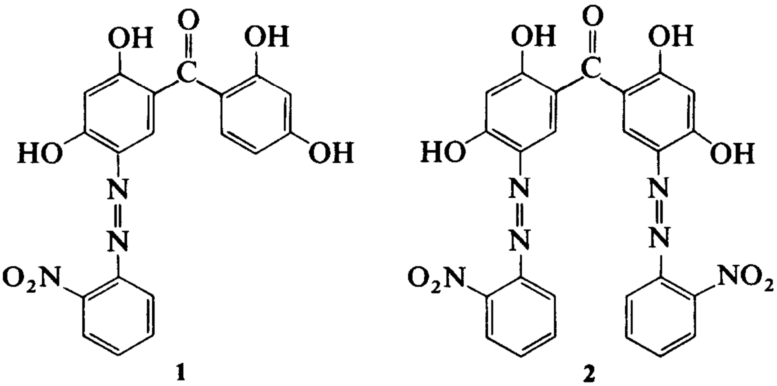
Extensive work has recently been undertaken to introduce dyes and pigments into the backbone of the polymer chain to form coloured compositions with excellent properties.[1-5] We have reported the synthesis of several phenyl-azo dihydroxynaphthalenes containing a polymerizable acryloyloxy group in the 3- or 7-position of the naphthalene ring,[6] which were homopolymerized and copolymerized with styrene.[7]

In this work, phenyl-azo compounds containing the ultra-violet absorbing moiety of 2,2′,4,4′-tetrahydroxybenzophenone and its polymerizable derivatives of acryloyloxy and methacryloyloxy monomers were synthesized and characterized. The homo- and copolymerization of the acryloyloxy and methacryloyloxy monomers with styrene and acrylates will be the subject of future work.

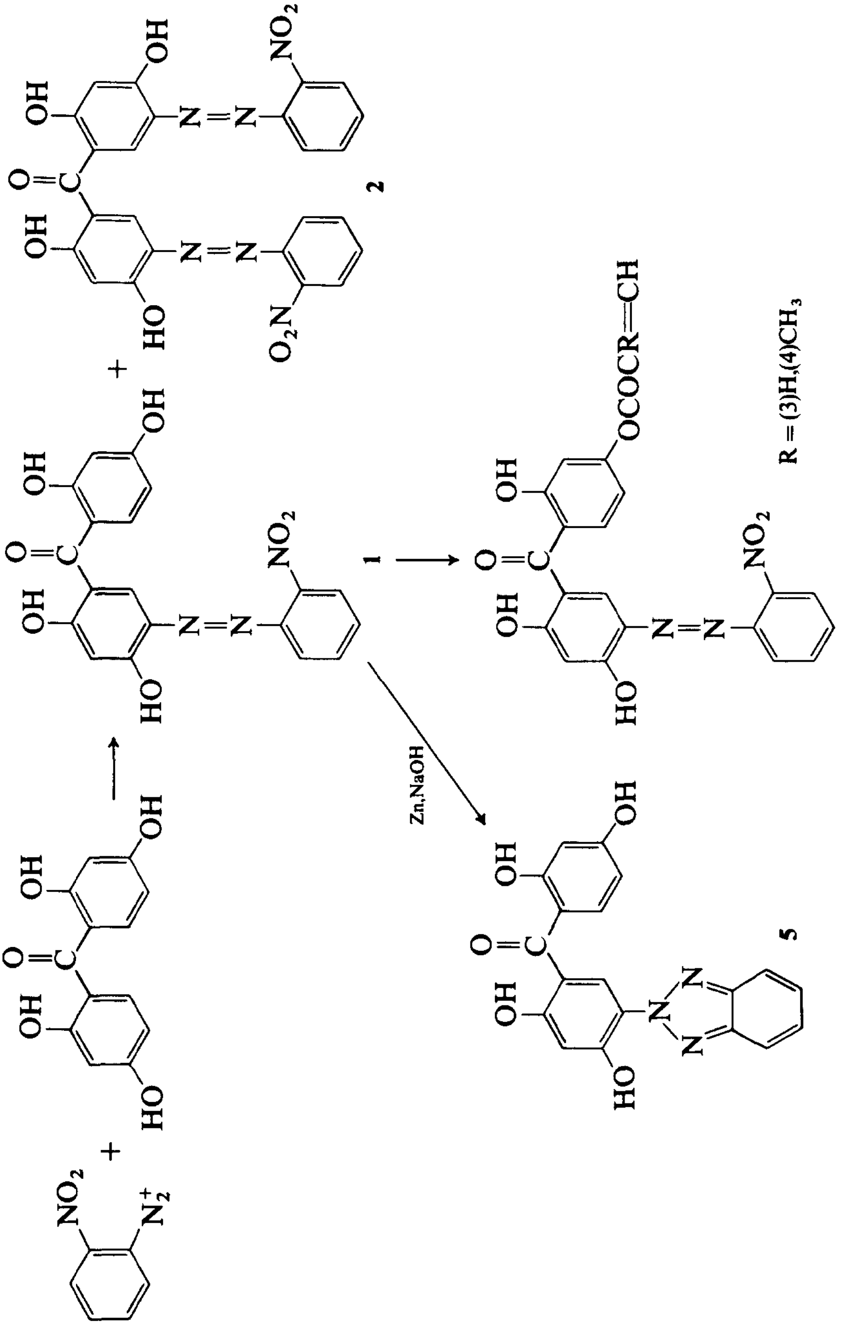
2 RESULTS AND DISCUSSION

The mono and diazo compounds of the general formulae 1 and 2 (Scheme 1) were isolated in 62% and 4% yields, respectively, from the azo-coupling reaction of 2-nitrobenzenediazonium chloride with 2,2′,4,4′-tetrahydroxybenzophenone in a solution of ethanol (Scheme 2).



Scheme 1

Alternatively, when 2-nitrobenzenediazonium chloride was added slowly at 0°C to 2,2′,4,4′-tetrahydroxybenzophenone in a mixture of water and ethanol and in the presence of sodium bicarbonate, the mono-azo compound I was the only product, being obtained in high yield (92%), as a dark red crystalline compound. The coupling reaction involves electrophilic attack by the diazonium salt, mainly at the 5-position of the 2,2′,4,4′-tetrahydroxybenzophenone. This was confirmed by ^1H NMR, which showed four signals for —OH protons at 9·2, 11·7, 12·9, and 16·3 ppm, which correspond to the presence of three types of hydroxyl groups. The lower field



R = (3)H,(4)CH$_3$

Scheme 2

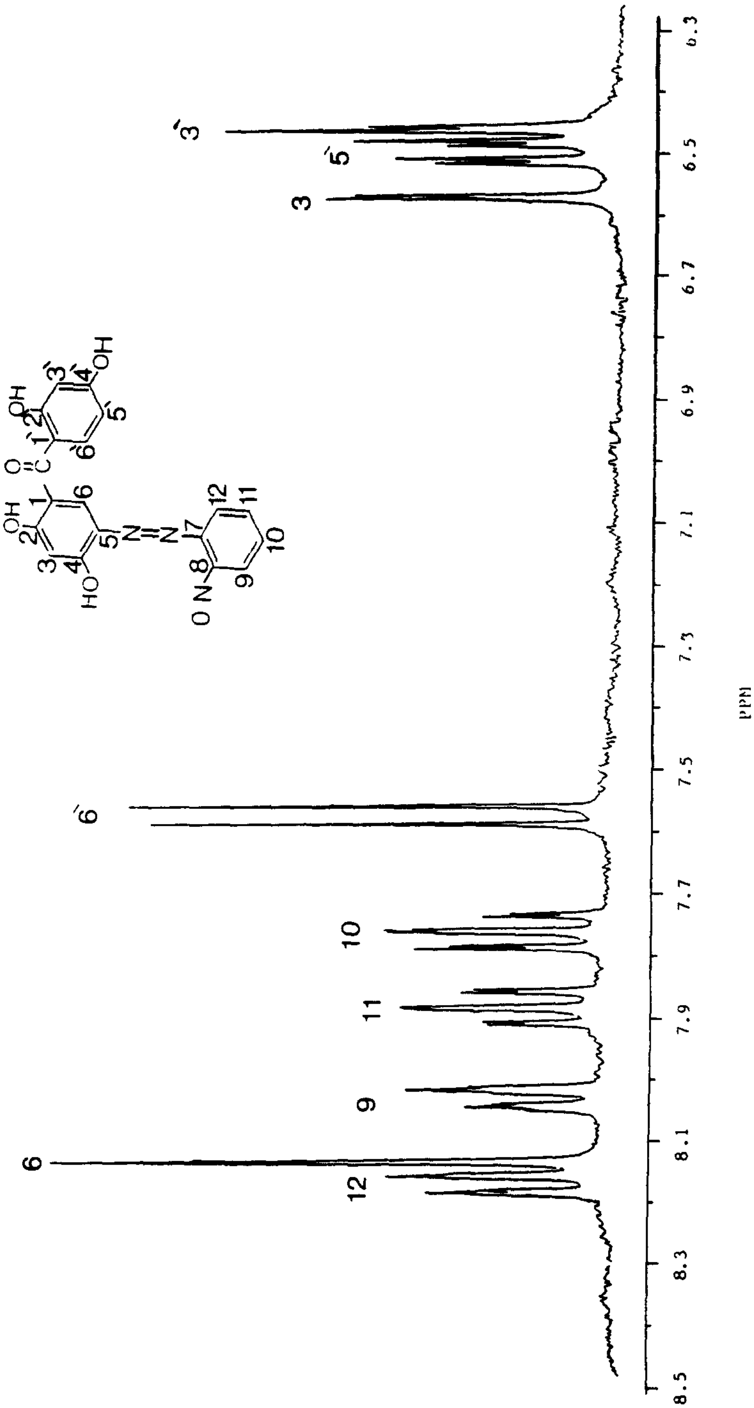


Fig. 1. ^{1}H NMR spectrum of compound **1** in deuterated acetone.

signal at 16·3 ppm is typical for protons involved in the azo-hydrazone tautomerism at the 4-position.[6] The signals at 11·7 and 12·9 ppm are attributed to the —OH protons involved in the keto-enol tautomerism at the 2 and 2′-positions.[8] The signal at 9·2 ppm is attributed to the pendant —OH group at the 4′-position.[6,9] The 300-MHz ^{1}H NMR spectra of 5-(2-nitrophenyl-azo-)2,2′,4,4′-tetrahydroxybenzophenone is shown in Fig. 1.

Esterification of 1 with acryloyl and methacryloyl chloride was carried out in a two-phase system of the Schotten–Baumann type. The acryloyloxy 3 and methacryloyloxy 4 compounds were isolated as red crystals from ethanol in 57% and 59% yields, respectively (Scheme 2).

Although four hydroxyl groups are available for esterification, only the pendant hydroxyl group at the 4′-position took part in the reaction. This was confirmed by ^{1}H NMR, which showed that the introduction of acryloyl or methacryloyl group into the azo-compound 1 results in the disappearance of the signal at 9·2 ppm, which is attributed to the pendant hydroxyl group at the 4′-position. The ^{1}H NMR spectra of the compounds 3 and 4 show the normal chemical-shift values expected for the parent azo compound 1 (Fig. 1) but show in addition the chemical shifts of the acryloyloxy and methacryloyloxy groups. The acryloyloxy group $—OCOCH{=}CH_2$ appears as three double doublets, which were coupled to each other, at δ 6·05 (^{1}H, dd, J 10·0 and 1·1 Hz), 6·40 (^{1}H, dd, J 10·0 and 17·2 Hz) and 6·65 (^{1}H, dd, J 17·2 and 1·1 Hz). The two double doublets centered at 6·05 and 6·65 ppm are attributed to the *cis*- and *trans*-methylene protons $=CH_2$. The third doublet centred at 6·40 ppm is attributed to the methine proton $—CH{=}$. The methacryloyloxy group $—OCOCMe{=}CH_2$ appears as three singlets at 2·05, 5·85, and 6·30 ppm, which corresponds to the methyl group and to the non-equivalent methylene protons $=CH_2$.

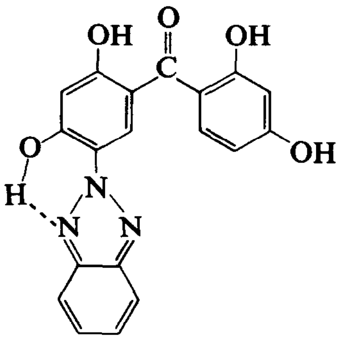
When compound 1 was treated with 2N NaOH and zinc powder for a period of 24 h, at room temperature, the azo compound 1 underwent reductive cyclization and gave the benzotriazole compound 5 in 70% yield as yellow crystals from an ethanol–water mixture (1:1 by volume) (Scheme 2). The route to the triazole compound 5 is based, as previously reported, on the synthesis of dihydroxynaphthyl-2*H*-benzotriazole.[10]

The ^{1}H NMR spectra for the benzotriazole compound 5 showed four singlets at δ 8·8, 9·9, 11·4, and 12·8 ppm, arising from the hydroxyl groups. The singlet of the hydroxyl group at 9·9 ppm is typical of protons involved in an intra-molecular hydrogen bond between the —OH group at the 4-position of the benzophenone and the nitrogen group of the benzotriazole ring[10,11] (Scheme 3).

The protons H7–H10 of the benzotriazole ring form an AA′BB′ complex spin-system. The H7 and H10 protons that form the AA′ part are centred as a multiplet at δ 8·05 ppm. The H8 and H9 that form the BB′ part are centered

TABLE 1
Properties and Analytical Data for Compounds 1–5

Compound	*Yield*	*Solvent*	*Appearance*	*M.p.*	*Required*			*Found*		
					C	*H*	*N*	*C*	*H*	*N*
1	92	DMSO	Dark red	232–234	57·72	3·29	10·63	57·7	3·3	10·5
2	4	DMSO	Orange	294–296	55·14	2·94	15·44	55·2	2·8	15·8
3	57	DMSO/H_2O	Red	132–134	58·79	3·34	9·35	58·5	3·5	9·2
4	59	DMSO/H_2O	Red	128–130	59·61	3·67	9·07	59·8	3·6	8·9
5	70	ElOH/H_2O	Yellow	226–228	62·8	3·58	11·57	62·6	3·6	11·7



Scheme 3

as a multiplet at 7·6 ppm. In agreement with the literature,[10,12] H7 and H10 protons are deshielded by the adjacent triazole ring.

The characterization data for compounds 1–5 are summarized in Table 1. The ^{1}H NMR chemical-shift data for compounds 1, 3, 4, and 5 are shown in Table 2.

The IR spectrum of compound 1 exhibits a strong band in the range of 2980–3400 cm^{-1} corresponding to the pendant hydroxyl substituent at the 4′-position. For compound 2, the absence of absorption in the range of 2980–3400 cm^{-1} is due to the involvement of the four hydroxyl groups in keto-enol tautomerism in the 2 and 2′-positions, and azo-hydrazone tautomerism in the 4 and 4′-positions. The IR spectra of compounds 3 and 4 exhibit the $>$C=O absorption band at 1740 cm^{-1} (ester carbonyl), and no absorption was observed in the 3000–3500-cm^{-1} region. Compound 5 shows a strong band in the region of 3070–3400 cm^{-1} for the pendant hydroxyl group at the 4′-position. In all cases, the presence of partial

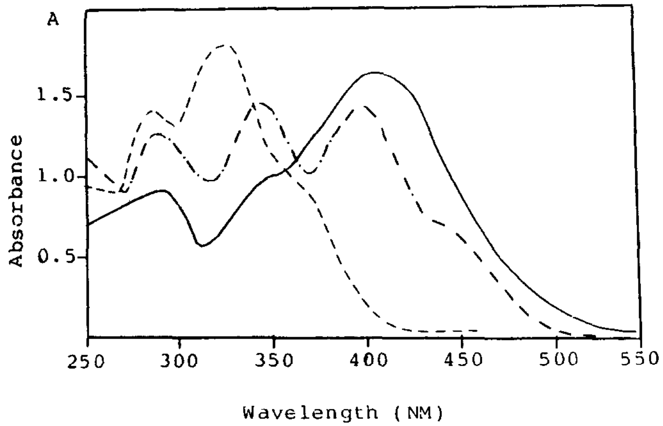
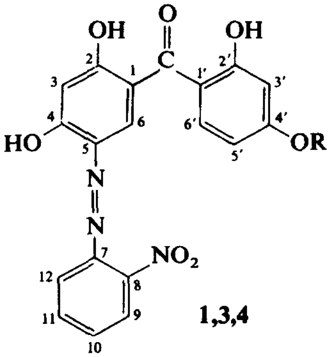


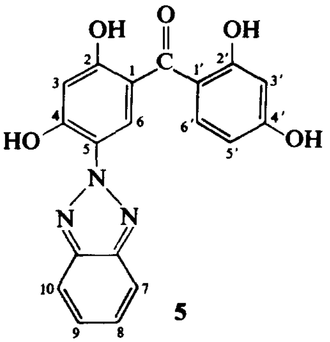
Fig. 2. UV spectra of **1**, (———); **2**, (— —); and **5**, (- - - -) in CHCl$_3$.

TABLE 2

^{1}H NMR Chemical-Shift Data for Compounds 1, 3, 4, and 5



1,3,4



5

Compound	*R*	*Chemical shift (ppm)*
1	H	6·48 (1H, d, J 2·2 Hz, H3′), 6·54 (1H, dd, J 9·0 and 2·2 Hz, H5′), 6·58 (1H, d, J 1·0 Hz, H3), 7·58 (1H, d, J 9·0 Hz, H6′), 7·75 (1H, ddd, J 8·8, 8·9 and 1·0 Hz, H10), 7·9 (1H, ddd, J 8·8, 8·9 and 1·0 Hz, H11), 8·03 (1H, d, J 8·8 Hz, H9), 8·15 (1H, d, J 1·0 Hz, H6), 8·18 (1H, d, J 8·8 Hz, H12), 9·3 (1H, S, OH-4′), 11·7 (1H, S, OH-2), 12·9 (1H, S, OH-2′), 16·3 (1H, S, OH-4)
3	$-\underset{13}{COCH}{=}\underset{14}{CH_2}$	6·05 (1H, dd, J 10·0 and 1·1 Hz, H14-cis, 6·40 (1H, dd, J 10·0 and 17·2 Hz, H13, 6·65 (1H, dd, J 17·2 and 1·1 Hz, H14-trans), 6·50 (1H, d, J 2·2 Hz, H3′), 6·54 (1H, dd, J 9·0 and 2·2 Hz, H5′), 6·58 (1H, d, J 1·0 Hz, H3), 7·58 (1H, d, J 9·0 Hz, H6′), 7·73 (1H, ddd, J 8·8, 8·9 and 1·0 Hz, H10), 7·90 (1H, ddd, J8·8, 8·9 and 1·0 Hz, H11), 8·0 (1H, d, J 8·8 Hz, H9), 8·15 (1H, d, J 1·0 Hz, H6), 8·18 (1H, d, J 8·8 Hz, H12), 11·9 (1H, S, OH-2), 13·2 (1H, S, OH-2′), 16·4 (1H, S, OH-4)
4	$-\underset{13}{COC(CH_3)}{=}\underset{14}{CH_2}$	2·05 (1H, S, CH_3), 5·85 (1H, S, H14), 6·30 (1H, S, H14), 6·46 (1H, d, J 2·2 Hz, H3′), 6·54 (1H, dd, J 9·0 and 2·2 Hz, H5′), 6·60 (1H, d, J 1·0 Hz, H3), 7·58 (1H, d, J 9·0 Hz, H6′), 7·75 (1H, ddd, J 8·8, 8·9 and 1·0 Hz, H10), 7·90 (1H, ddd, J 8·8, 8·9 and 1·0 Hz, H11), 8·0 (1H, d, J 8·8 Hz, H9), 8·15 (1H, d, J 1·0 Hz, H6), 8·2 (1H, d, J 8·8 Hz, H12), 12·0 (1H, S, OH-2), 13·3 (1H, S, OH-2′), 16·2 (1H, S, OH-4)
5		6·52 (1H, d, J 2·3 Hz, H3′), 6·58 (1H, dd, J 2·3 and 8·83 Hz, H5′), 7·55 (1H, S, H3), 7·62 (2H, m, H8 and H9), 7·75 (1H, d, J 8·8 Hz, H6′), 8·05 (3H, m, H6, H7, H10), 8·8 (1H, S, OH-4′), 9·9 (1H, S, OH-4), 11·4 (1H, S, OH-2), 12·8 (1H, S, OH-2′)

TABLE 3
UV/Visible Spectra of the AZO Compounds 1–5 in $CHCl_3$

Compound	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$ ($dm^3\,mol^{-1}\,cm^{-1}$)	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$ ($dm^3\,mol^{-1}\,cm^{-1}$)	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$ ($dm^3\,mol^{-1}\,cm^{-1}$)
1			350S	2·35	420	2·5
2	285	*	355	*	415	*
3			350S	2·40	415	2·6
4			350S	2·45	420	2·5
5	2·90	1·6	325	2·30	350S	1·2

S = Shoulder.
* = Partially soluble.

bonding between the hydroxyl groups at the 2 and 2′-positions and the carbonyl group of the benzophenone moiety is responsible for the weak carbonyl absorption at low wave number (around $1610\,cm^{-1}$).

The ultra-violet spectra for compounds 1, 3, and 4 in chloroform are similar (Table 3), with strong absorption bands in the range from 375 nm to about 550 nm, and shoulders at 350 nm, with extinction coefficients in the range of 2·5–2·7 litre/mol cm × 10^4. The UV spectrum of the azo compound 2 had three absorptions at 258, 355, and 410 nm. In the case of the benzotriazole 5, a λ_{max} value of 325 nm and an extinction coefficient of 2·3 litre/mol cm × 10^4 were found. The ultra-violet spectra for compounds 1, 2, and 5 are shown in Fig. 2.

3 EXPERIMENTAL

3.1 General

Melting points were determined on a MELT.TEMP capillary-melting-point apparatus at 2°C/min rate of temperature increase and are uncorrected. Infra-red spectra were run in KBr discs on a Beckman spectrometer, Model 4260. ^1H NMR spectra were recorded on a Bruker AM 300 in deuterated acetone, with an internal deuterium lock, and ^1H chemical shifts are referenced in tetramethyl silane as an internal standard (at δ 0·00). Ultra-violet absorptions were measured in chloroform on a Perkin–Elmer 33 spectrometer.

3.2 5-(2-Nitrophenyl-azo-)2,2′,4,4′-tetrahydroxybenzophenone

3.2.1 In ethanol solution

A solution of 2-nitroaniline (27·0 g, 0·2 mol) in hydrochloric acid ($100\,cm^3$) was cooled to 0°C and treated with sodium nitrite (14·0 g, 0·2 mol). The cold solution of the 2-nitrobenzenediazonium salt was then added, over a period of 1 h, to a solution of 2,2′,4,4′-tetrahydroxybenzophenone (74·0 g, 0·3 mol) in ethanol ($200\,cm^3$) cooled to 5°C. The azo compound separated immediately in the form of dark red crystals. After the reaction mixture had been stirred for 6 h at 0°C, the solid precipitated out was isolated and recrystallized from DMSO to give dark red needles of the mono-azo compound 5-(2-nitrophenyl-azo-)2,2′,4,4′-tetrahydroxybenzophenone (74·0 g, 62%) m.p. 232–234°C. The infra-red spectrum (KBr) showed absorptions at $2900–3500\,cm^{-1}$ (—OH stretching) and $1610\,cm^{-1}$ ($>$C=O stretching). The ^1H NMR chemical-shift data are presented in Table 2, and the ultra-violet numeric values are presented in Table 3. The second fraction precipitated out as orange needles after 20 h at 0°C and was shown to be the disazo compound 5,5′-di(2-nitrophenyl-azo-)2,2′,4,4′-tetrahydroxybenzophenone (6·6 g, 4%) m.p. 294–296°C. The infra-red spectrum (KBr) showed absorption at 1610 cm^{-1} ($>$C=O stretching). Electronic spectra data are presented in Table 3.

3.2.2 In aqueous solution

The solution of 2-nitrobenzenediazonium salt (from 2-nitroaniline, 27·0 g, 0·2 mol, and sodium nitrite, 14·0 g, 0·2 mol) was added to a mixture of 2,2′,4,4′-tetrahydroxybenzophenone (74·0 g, 0·3 mol) in ethanol (250 cm^3) and sodium bicarbonate (90·0 g, 1·07 mol) in water (400 cm^3) at 5°C over a period of 1 h. After the reaction mixture had been stirred for 16 h, the solid precipitated out was isolated and recrystallized from DMSO and water to give dark red needles of the mono-azo compound 5-(2-nitrophenyl-azo) 2,2′,4,4′-tetrahydroxybenzophenone (110·0 g, 92%) m.p. 232–234°C.

3.3 5-(2-Nitrophenyl-azo-)2,2′,4-trihydroxy-4′-acryloyloxybenzophenone

5-(2-Nitrophenyl-azo-)2,2′,4,4′-tetrahydroxybenzophenone (3·4 g, 0·009 mol) was mixed with sodium hydroxide (0·72 g, 0·018 mol) in water (50 cm^3). Acryloyl chloride (0·81 g, 0·009 mol) in chloroform (30 cm^3) was added dropwise over a period of 1 h. After stirring for 2 h at room temperature, the organic layer was isolated, dried, and evaporated to yield 2·2 g (57%) of product. Recrystallization from aqueous DMSO gave red needles, m.p. 132–134°C. The infra-red spectrum showed absorptions at 1610 and 1740 cm^{-1} ($>$C=O stretching). The ^{1}H NMR chemical-shift data are presented in Table 2 and electronic spectra data in Table 3.

3.4 5-(2-Nitrophenyl-azo-)2,2′,4-trihydroxy-4′-methacryloyloxybenzophenone

5-(2-Nitrophenyl-azo-)2,2′,4,4′-tetrahydroxybenzophenone (3·4 g, 0·009 mol) was mixed with sodium hydroxide (0·72 g, 0·018 mol) in water (50 cm^3). Methacryloyl chloride (0·94 g, 0·009 mol) in chloroform (30 cm^3) was added dropwise over a period of 1 h. After stirring for 2 h at room temperature, the organic layer was isolated, dried, and evaporated, to yield 2·4 g (59%). Recrystallization from aqueous DMSO gave red needles, m.p. 128–130°C. The infra-red spectrum showed absorptions at 1610 and 1740 cm^{-1} ($>$C=O stretching). The ^{1}H NMR chemical-shift data are presented in Table 2 and electronic spectra data in Table 3.

3.5 5-(2H-Benzotriazole-2-YL)2,2′,4,4′-tetrahydroxybenzophenone

5-(2-Nitrophenyl-azo-)2,2′,4,4′-tetrahydroxybenzophenone (30·0 g, 0·75 mol) was dissolved in 2 N sodium hydroxide (200 cm^3). Zinc powder (20·0 g, 0·30 mol) was added with stirring to the solution of the azo compound over a period of 0·5 h, followed by the addition of a solution of sodium hydroxide (40·0 cm^3, 40%) over a period of 1 h at room temperature. The colour of the reaction mixture changed from red to green, indicating that the azo compound had been reduced. After stirring for 16 h at room temperature, the suspension was filtered and the residue extracted twice with sodium hydroxide (10%). The filtrate was combined with the extract and cooled in an ice bath. While keeping the temperature below 5°C, the solution was acidified with concentrated hydrochloric acid and the crude benzotriazole precipitated. The precipitate was filtered, dried, and recrystallized from aqueous ethanol to give yellow needles, 19·3 g (70%), m.p. 226–228°C. The infra-red spectrum showed absorptions at 3000–3400 cm^{-1} (—OH stretching). The ^{1}H NMR chemical-shift data are presented in Table 2 and electronic spectra data in Table 3.

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