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Dyes and Pigments 64 (2005) 271–278

DYES and PIGMENTS

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The investigation of crystal structure, spectroscopic and thermal properties of *p*-(*p*-acetylphenylazo)-*o*-allylphenol and *p*-(*p*-bromphenylazo)-*o*-allylphenol

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Received 5 February 2004; received in revised form 21 April 2004; accepted 2 June 2004

Abstract

The two new azo dyes *p*-(*p*-acetylphenylazo)-*o*-allylphenol (compound **I**) and *p*-(*p*-bromphenylazo)-*o*-allylphenol (compound **II**) have been synthesized and studied by FT-IR, UV–VIS, ^{1}H NMR, ^{13}C NMR techniques, elemental analysis, X-ray structure analysis and TG, DTG, and DTA analyses. Compound **I** crystallizes in the monoclinic space group P21/c with $a = 19.6130(15)$ Å, $b = 7.3586(6)$ Å, $c = 21.4752(15)$ Å, $\alpha = 90.00°$, $\beta = 101.413(6)°$, $\gamma = 90.00°$, $Z = 8$, $V = 3038.1(4)$ Å^3 and the molecules are linked by two intermolecular O···O hydrogen bonds. There are two independent molecules in the asymmetric unit of compound **I**. Compound **II** crystallizes in the monoclinic space group Cc with $a = 4.7194(7)$ Å, $b = 24.597(2)$ Å, $c = 12.2241(16)$ Å, $\alpha = 90.00°$, $\beta = 96.509(11)°$, $\gamma = 90.00°$, $Z = 4$, $V = 1409.9(3)$ Å^3 and the molecules are linked by O···N and C–H···O intermolecular hydrogen bonds. They are characterized by UV–VIS, FT-IR, ^{1}H NMR, ^{13}C NMR techniques, elemental analysis, TG, DTG, and DTA analyses.

Keywords: Azo dyes; X-ray; UV–VIS; IR; NMR; Thermal analysis

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1. Introduction

Azo compounds have caused great interest in organic synthesis. In the class of the dye molecule, azo compounds are an important kind of organic colorants and consist of at least a conjugate chromophore azo group and two or more aromatic rings. The color of azo dyes is mainly due to the interaction of the azo group and incident light. Azo dyes are widely used in textiles, printing, cosmetics, drugs, foods coloring, and other consumer goods [1,2]. They are also used extensively in laboratories as either biological stains or *pH* indicators [2]. They can also be used as materials for non-linear optics and for storage of optical information in laser disks [3]. Recently, many noteworthy studies have shown that some azo compounds possess excellent optical memory and photoelectric properties [4,5]. The X-ray and spectroscopic investigations are revealing the relationship between molecular structure, solid state packing arrangements and dye performance characteristics.

In this study, the molecular and crystal structure of *p*-(*p*-acetylphenylazo)-*o*-allylphenol and *p*-(*p*-bromphenylazo)-*o*-allylphenol were identified by the spectroscopic techniques such as UV–VIS, IR, ^{1}H NMR, ^{13}C NMR, determined by X-ray diffraction method, elemental and thermal analysis techniques.

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0143-7208/$ - see front matter
doi:10.1016/j.dyepig.2004.06.004

2. Experimental

2.1. Synthesis

The *p*-phenylazo-*o*-allylphenol dyes synthesized with azo-coupling reactions of substituted benzenediazonium salts and *o*-allylphenol are shown in Scheme 1. Substituted anilines were diazotized using sodium nitrite in the presence of hydrochloric acid followed by coupling with *o*-allylphenol substrate to produce *p*-phenylazo-*o*-allylphenol dyes **I** and **II** in good yield.

The diazotization reactions were carried out in an identical manner, and one representative description of the method will be given [6]. *p*-Acetylaniline (1.64 g, 0.012 mol) was dissolved in water (50 mL) containing 6 mL of 5 N HCl. The clear solution was cooled to 0 °C in an ice bath. To this solution was added dropwise $NaNO_2$ (0.83 g, 0.012 mol) dissolved in water (15 mL) at 0 °C maintaining the temperature of the mixture below 5 °C. This mixture was stirred for 1 h at 0 °C and *o*-allylphenol (3.00 g, 0.02 mol) dissolved of aqueous NaOH (0.80 g, 0.02 mol) was added dropwise to this prepared solution. The addition was accomplished quickly and the temperature was not permitted to rise above 5 °C. Following the addition of *o*-allylphenol, the solution became bright red and a red precipitate was collected by suction filtration. Red solid was washed with water (50 mL) and ethanol (50 mL). It was then recrystallized from hot ethanol and dried under vacuum at 50 °C for 6 h and its purity was examined by thin-layer chromatography. Single crystals were grown by slow evaporation of reaction mixture at room temperature. Elemental analyses are in good agreement with the molecular formula proposed for these compounds. *Caution*: prolonged heating in excess of 90 °C may lead to the decomposition of diazo linkage. Yield for compound **I**: 68%. Mp.113 °C. Elemental analysis, found (calculated for $C_{17}H_{16}N_2O_2$, compound **I**), C: 72.42% (72.86%), H: 5.07% (5.71%), N: 9.34% (9.99%). Yield for compound **II**: 78%. Mp.105 °C. Elemental analysis, found (calculated for $C_{15}H_{13}BrN_2O$, compound **II**): 55.76% (56.78%), H: 3.95% (4.10%), N: 8.20% (8.83%).

2.2. Physical measurements

IR spectra of compounds **I** and **II** were recorded in the region of 4000–400 cm^{-1}, using a Mattson 1000 FT-IR Spectrometer (KBr pellets). Absorption spectra in chloroform were determined on a Unicam UV–VIS Spectrometer. ^1H NMR and ^{13}C NMR data were acquired on a Bruker AC 200 Spectrometer. TG, DTG and DTA curves were recorded simultaneously on Rigaku TG 1810 thermal analyzer combined with a TAS 100 thermogravimetric analyzer. The experiments were performed in nitrogen atmosphere (80 mL/min) with a heating rate of 10 °C/min from room temperature to 1000 °C in platinum crucibles. Elemental analyses were recorded by TUBITAK Atal Laboratories.

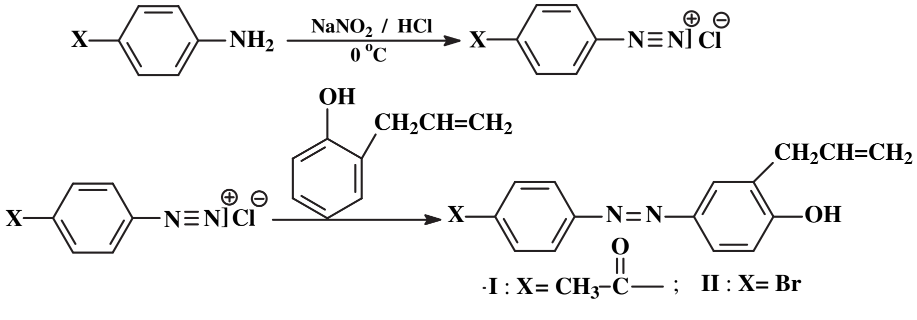
2.3. Crystal structure analysis

Crystals suitable for X-ray work were cut to the size of $0.17 \times 0.44 \times 0.50$ mm for compound **I** and $0.14 \times 0.35 \times 0.50$ mm for compound **II**. X-ray diffraction data were collected on a STOE IPDS II diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. A summary of crystallographic data, experimental details, and refinement results for compounds **I** and **II** are given in Table 1.

3. Result and discussion

3.1. Description of the crystal structure

The molecular structure of compound **I** is shown in Fig. 1 with the atom numbering scheme. The compound consists of two phenyl rings (C1 to C6 and C7 to C12), and an azo frame (C4–N1–N2–C7). The phenyl rings adopt a *trans*-configuration about the azo functional group as observed in crystals of the other azo compounds. The *p*-(*p*-acetylphenylazo)-*o*-allylphenol **I** molecules are linked into zigzag chains by O1B–H1B··· O2A and O1A–H1A···O2B hydrogen bonds, with O···O distances of 2.713(3) Å and 2.717(3) Å, respectively (Table 2). There are two independent molecules



Scheme 1.

Table 1
Summarized crystallographic data for compounds **I** and **II**

p-(*p*-Acetylphenylazo)-*o*-allylphenol (compound **I**)	
Empirical formula	$C_{17}H_{16}N_2O_2$
Formula weight	280.32
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	$a = 19.6130(15)$ Å
	$b = 7.3586(6)$ Å
	$c = 21.4752(15)$ Å
	$\alpha = 90.00°$
	$\beta = 101.413(6)°$
	$\gamma = 90.00°$
Volume	3038.1(4) $Å^3$
Z	8
Density (calculated)	1.226 $g\,cm^{-3}$
F_{000}	1184
Absorption coefficient	0.082 mm^{-1}
Crystal size	0.50 × 0.44 × 0.17 mm
Wavelength, λ	Mo Kα, 0.71073 Å
Temperature, T	293(2) K
Measured reflections	22 285
R_{int}	0.1550
h,k,l range	$-21 \rightarrow 21, -7 \rightarrow 7, -22 \rightarrow 23$
θ range for data collection	2.01–22.50
Independent reflections	3957
Reflections with ($I > 2\sigma(I)$)	2460
Goodness-of-fit on F^2	1.028
R, R_w ($I > \sigma(I)$)	0.054, 0.1912
Extinction coefficient	0.0067 (14)
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/$Å^3$)	0.240, −0.215
p-(*p*-Bromphenylazo)-*o*-allylphenol (compound **II**)	
Empirical formula	$C_{15}H_{13}BrN_2O$
Formula weight	317.18
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	$a = 4.7194(7)$ Å
	$b = 24.597(2)$ Å
	$c = 12.2241(16)$ Å
	$\alpha = 90.00°$
	$\beta = 96.509(11)°$
	$\gamma = 90.00°$
Volume	1409.9(3) $Å^3$
Z	4
Density (calculated)	1.494 $g\,cm^{-3}$
F_{000}	640
Absorption coefficient	2.909
Crystal size	0.50 × 0.35 × 0.14
Wavelength, λ	Mo Kα, 0.71073 Å
Temperature, T	293(2) K
Measured reflections	5907
Reflections with ($I > 2\sigma(I)$)	1058
R_{int}	0.1404
h,k,l range	$-6 \rightarrow 6, -31 \rightarrow 31, -15 \rightarrow 15$
θ range for data collection	1.66–27.23
Independent reflections	1574
Reflections with ($I > 2\sigma(I)$)	1058
Goodness-of-fit on F^2	0.944
R, R_w ($I > \sigma(I)$	0.0652, 0.1496
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/$Å^3$)	0.686, −0.764

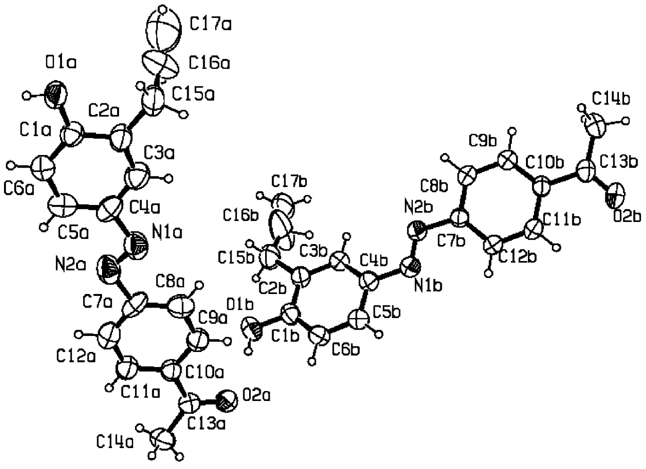


Fig. 1. Molecular structure and atom-labeling scheme for compound **I**.

(labeled as **IA** and **IB**) in the asymmetric unit as depicted in Fig. 1. The dihedral angle between the phenyl rings C1B–C6B of **IB** and C7A–C12A of **IA** is 69.80(9)°. The dihedral angle between the phenyl rings of **IA** is 0.31(12)°, which is less than in 2-(4-methoxyphenylazo)-4-phenylphenol, (2.7°) [8], and 2-hydroxy-5-*tert*-butylazobenezene, (3.4°) [9]; but this value is unexpectedly large [26.74(14)°] for **IB**, that is to say **IA** is planar but **IB** is not. The loss of planarity in **IB** is doubtless as a consequence of the packing form in the crystal (Fig. 2). The allyl group is twisted out of the plane of its attached phenyl ring by 81.48(1)° in **IA** and 10.76(1)° in **IB**.

The N1=N2 bond distances are 1.158(4) Å in **IA** and 1.247(3) Å in **IB**, which are shorter than those observed in the azo compounds with no intramolecular hydrogen bonds cited in literature: 1.250(1) Å [10], 1.256(1) Å [11], 1.267(3) Å [12] and 1.278 Å [13]. While the same N–C bond lengths [N1A–C4A = N2A–C7A = 1.542(5) Å] in **IA** correspond to the same degree of π-conjugation resulting from the planarity of the phenyl rings, the differences in N–C bond lengths [N1B–C4B = 1.420(4) Å and N2B–C7B = 1.425(4) Å] in **IB** correspond to a different degree of π-conjugation of the –N=N– group resulting in this case from the non-planar alignment of the phenyl rings.

The angularly symmetric form of the C4 atom of the phenyl ring is distorted after substitution, [C5–C4–N1 = 127.7(4)° and 115.6(3)°, C3–C4–N1 = 112.7(4)° and 125.0(3)° in **IA** and **IB**, respectively]. This asymmetry seems to be caused by the π-conjugation of the central azo system with C1–C6 ring and steric hindrance involving the C5A–H5A group with N2A [C5A···N2A = 2.681(5) Å and H5A···N2A = 2.470(5)], and

Table 2
Hydrogen bonds for compound **I** (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O1B–H1B···O2A	0.820	1.909	2.713(3)	166.35
O1A–H1A···O2B[a]	0.820	1.902	2.717(3)	172.12

[a] Symmetry transformations used to generate equivalent atoms: $x + 1, -y + 1/2, z + 1/2$.

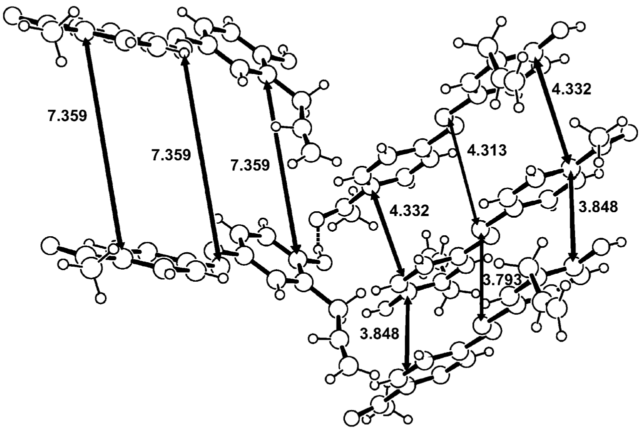


Fig. 2. Stacking of the phenyl rings in the molecules **IA** and **IB**. (The rings with the contact distance of 7.359 Å are referred as **IB** and the others as **IA**.)

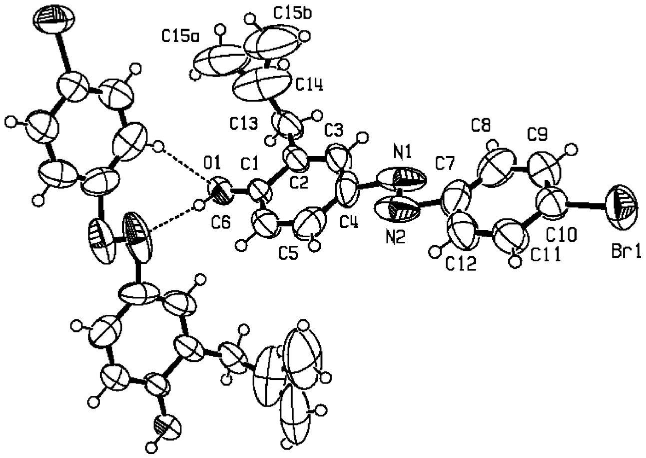


Fig. 3. Molecular structure and atom-labeling scheme for compound **II**.

C3B–H3B group with N2B [C5B···N2B = 2.746(4) Å and H3B···N2B = 2.492(4)]. Due to the similar effect, the same angular asymmetry was observed on the C7 and C10 atoms of C7–C12 ring (Table 3). The C2A atom is nearly angularly symmetric but C2B is not, because of the more steric hindrance of C16B–H16B group with C3B, [C3A···C16A = 3.331(5) Å and H16A···C3A = 3.011(5), C3B···C16B = 2.948(4) Å and H16B···C3B = 2.354(4)]. The same kind of asymmetry is observed for the exocyclic angles at C1 (Table 3), which is common

Table 3
Selected bond lengths (Å) and angles (°) and torsion angles (°) for compound **I**

O1A–C1A	1.357(4)	O1B–C1B	1.359(4)
C13A–O2A	1.223(4)	C13B–O2B	1.223(4)
N1A–N2A	1.158(4)	N1B–N2B	1.247(3)
C4A–N1A	1.542(5)	C4B–N1B	1.420(4)
N2A–C7A	1.542(5)	N2B–C7B	1.425(4)
C2A–C3A	1.371(5)	C2B–C3B	1.376(4)
C3A–C4A	1.349(5)	C3B–C4B	1.378(4)
C4A–C5A	1.379(6)	C4B–C5B	1.384(4)
C5A–C6A	1.393(5)	C5B–C6B	1.368(4)
C6A–C1A	1.377(4)	C6B–C1B	1.375(5)
C7A–C8A	1.398(6)	C7B–C8B	1.380(4)
C8A–C9A	1.385(5)	C8B–C9B	1.377(4)
C9A–C10A	1.378(4)	C9B–C10B	1.381(4)
C10A–C11A	1.385(5)	C10B–C11B	1.390(4)
C11A–C12A	1.355(5)	C11B–C12B	1.368(4)
C12A–C7A	1.351(5)	C12B–C7B	1.383(4)
C10A–C13A	1.479(4)	C10B–C13B	1.474(4)
O1A–C1A–C6A	122.6(3)	O1B–C1B–C6B	122.7(3)
O1A–C1A–C2A	116.1(3)	O1B–C1B–C2B	116.4(3)
C1A–C2A–C15A	121.4(3)	C1B–C2B–C15B	118.8(3)
C3A–C2A–C15A	121.3(4)	C3B–C2B–C15B	123.4(3)
C3A–C4A–N1A	112.7(4)	C3B–C4B–N1B	125.0(3)
C5A–C4A–N1A	127.7(4)	C5B–C4B–N1B	115.6(3)
N2A–N1A–C4A	104.8(4)	N2B–N1B–C4B	115.1(3)
N1A–N2A–C7A	104.4(4)	N1B–N2B–C7B	113.6(3)
C8A–C7A–N2A	125.9(4)	C8B–C7B–N2B	116.1(3)
C12A–C7A–N2A	112.9(4)	C12B–C7B–N2B	124.0(3)
C9A–C10A–C13A	120.0(3)	C9B–C10B–C13B	122.4(3)
C11A–C10A–C13A	121.3(3)	C11B–C10B–C13B	119.6(3)
N1A–N2A–C7A–C8A	0.1(5)	N1B–N2B–C7B–C8B	−164.6(3)
N1A–N2A–C7A–C12A	178.6(3)	N1B–N2B–C7B–C12B	16.6(4)
C7A–N2A–N1A–C4A	179.6(3)	C7B–N2B–N1B–C4B	−178.0(2)
C3A–C4A–N1A–N2A	−178.3(3)	C3B–C4B–N1B–N2B	9.7(4)
C5A–C4A–N1A–N2A	0.2(5)	C5B–C4B–N1B–N2B	−171.0(3)

Table 4
Selected bond lengths (Å) and angles (°) and torsion angles (°) for compound **II**

C1–O1	1.347(9)	C6–C1	1.386(11)
N1–N2	1.087(12)	C7–C8	1.403(18)
N1–C4	1.614(16)	C8–C9	1.376(16)
C7–N2	1.680(14)	C9–C10	1.354(15)
C1–C2	1.409(9)	Br1–C10	1.897(8)
C2–C3	1.372(12)	C10–C11	1.401(14)
C3–C4	1.365(16)	C11–C12	1.364(17)
C4–C5	1.445(16)	C12–C7	1.337(16)
C5–C6	1.371(12)	C13–C2	1.486(14)
O1–C1–C2	115.7(7)	C8–C7–N2	134.2(10)
O1–C1–C6	122.8(6)	C12–C7–N2	107.8(9)
C3–C4–N1	111.8(9)	C9–C10–Br1	119.4(7)
C5–C4–N1	128.8(10)	C11–C10–Br1	120.3(7)
N2–N1–C4	92.9(11)	C1–C2–C13	120.7(7)
N1–N2–C7	92.8(11)	C3–C2–C13	121.2(7)
C4–N1–N2–C7	179.8(6)	N2–N1–C4–C3	−179.6(8)
C12–C7–N2–N1	177.0(9)	N2–N1–C4–C5	4.3(11)
C8–C7–N2–N1	−7.4(13)		

Table 5
Hydrogen bonds for compound **II** (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O1–H1···N1	0.8196	2.0409	2.852(12)	170.32
C8–H8···O1[a]	0.9302	2.3862	3.260(11)	156.47

[a] Symmetry transformations used to generate equivalent atoms: x, $-y+1$, $z+1/2$.

with phenols. The torsion angles C4A–N1A–N2A–C7A and C4B–N1B–N2B–C7B in the azo moiety are 179.6(3)° and −178.0(2)°, respectively.

An ORTEP [14] view of compound **II** and its numbering scheme are shown in Fig. 3 and selected bond distances and bond angles are listed in Table 4. The phenyl rings C1–C6 and C7–C12 adopt a *trans*-configuration about the azo functional group, as observed in compound **I** and crystals of the other azo compounds. The *p*-(*p*-bromphenylazo)-*o*-allylphenol (compound **II**) molecules are linked to each other by O1–H1···N1 [O···N = 2.852(12) Å] and C8–H8···O1 [C8···O1 = 3.260(11) Å] hydrogen bonds (Table 5) through the formation of seven-membered hydrogen bonded rings (N1–N2–C7–C8–H8–O1–H1). The molecule **II** is planar with 2.3(6)° dihedral angle between the phenyl rings, which is approximately equal to the value of 2-(4-methoxyphenylazo)-4-phenylphenol, (2.7°) [8]. The allyl group is twisted out of the plane of the C1–C6 ring by 58(3)°. X-ray structure determination reveals that the C15 atom is distorted about the C14 atom making a fillip-flop motion between the C15A and C15B positions with occupation factor of 0.71 and 0.29, respectively.

3.2. Spectral characteristics

IR frequencies of various diagnostic bands in the solid state (KBr) are collected in Table 6. The IR spectra of compounds **I** and **II** are shown in Fig. 4. The IR spectra show characteristic bands for the coupling components, which were assigned in accordance with literature data [15]. At 1675 cm^{-1}, there is a characteristic band for ν(C=O) of the acetyl group in compound **I** and the medium bands at 1637 cm^{-1} (for compound **I**) and 1646 cm^{-1} (for compound **II**) were assigned to $\nu(\mathrm{C{=}C_{allyl}})$. The absorption bands assignable to the stretching of ν(N=N) bond for compounds **I** and **II** were observed at frequencies of 1412 cm^{-1} and 1425 cm^{-1} and these values conform with that reported in the IR spectrum for unsubstituted phenolic azo dyes which possesses the formulation of $\mathrm{XC_6H_4N{=}NC_6H_4OH}$. The azo compounds without intramolecular hydrogen bonds display IR spectra characteristic to $\nu(\mathrm{C_{aryl}{-}N{=}})$ at 1145–1425 cm^{-1} region [15]. A band assignable to the stretching of O–H bond is found to be broadened within the frequency range of 3530–3125 cm^{-1} and at 1220–1240 cm^{-1} region, δOH phenolic. This observation implies that the H atom from the O–H group in compounds **I** and **II** have intermolecular hydrogen bonding.

The assignment of all bands has not been attempted. However, a comparison of the IR data with those of the X-ray data obtains useful information. The azo moiety stretching are observed at 1412 cm^{-1} ν(N–N) and 1145 cm^{-1} $\nu(\mathrm{C_{aryl}{-}N{=}})$ in compound **I**, but at 1425 cm^{-1} ν(N–N) and 1135 cm^{-1} $\nu(\mathrm{C_{aryl}{-}N{=}})$ in compound **II**. According to compound **I**, the N=N stretching is shifted to higher energy region but the C–N stretching is shifted to lower energy region in compound **II**. The reason for this shift is the O1–H1···N1 and C8–H8···O1 hydrogen bonds which are hinder to vibration of azo moiety and make conjugation of *n* electrons of N atom with aromatic ring difficult. This type of H bond is not observed in compound **I**. Furthermore, the effect of hydrogen bonds is supported

Table 6
Infrared frequencies (cm^{-1}) of compounds **I** and **II** in the solid state (KBr)

Compounds	ν_{OH}	δ_{OH}	ν(C=O)	$\nu(\mathrm{C{=}C_{allyl}})$	ν(N=N)	$\nu(\mathrm{C_{aryl}{-}N{=}})$
I	3530–3272 bs	1225	1675 s	1637 m	1412 w	1145 s
II	3460–3125 bs	1240	–	1646 m	1425 w	1135 s

Abbreviations: s, strong; bs, broad strong; m, medium; w, weak.

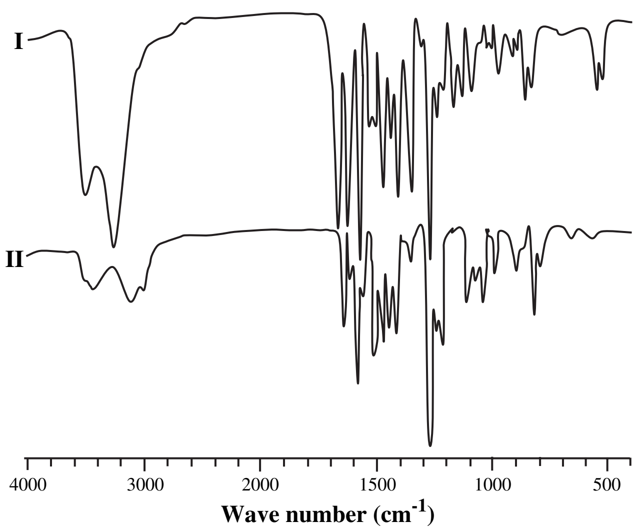


Fig. 4. FT-IR spectra of compounds **I** and **II** in the solid state (KBr).

by the UV–VIS spectra. UV–VIS spectrum of *p*-(*p*-acetylphenylazo)-*o*-allylphenol (compound **I**) shows an absorption of $n \rightarrow \pi^*$ at 471 nm ($\epsilon_{max} = 2620$) and $\pi \rightarrow \pi^*$ at 368 nm ($\epsilon_{max} = 33\,430$), but *p*-(*p*-bromphenylazo)-*o*-allylphenol (compound **II**) exhibits an absorption at 457 nm ($\epsilon_{max} = 2430$) and $\pi \rightarrow \pi^*$ at 358 nm ($\epsilon_{max} = 27\,390$) (Fig. 5). It is clearly seen that the transition in compound **II** shifts to shorter wavelengths and to less ϵ value. The solution spectra were recorded in 800–200 nm in chloroform and assigned on the basis of literature data [15,17].

The ^{1}H and ^{13}C NMR data recorded in acetone-d_6 solutions are shown in Tables 7 and 8, respectively. The NMR spectral analysis was carried out for each of the two dyes synthesized which provided further evidence for the structural characteristics of the dyes. The ^{1}H NMR and ^{13}C NMR spectra for compound **I** are shown in Figs. 6 and 7, respectively. In the ^{1}H NMR spectrum of compound **I**, a single peak observed at $\delta = 9.34$ was assigned to OH group. As expected, the allyl group showed three signals at δ 6.09 (ddt, 1H, H_C), δ 5.16 (dd, 1H, H_A), δ 5.08 (dd, 1H, H_B) and δ 3.50 (d, 2H, CH_2). At δ 8.14 (dd, 2H, H3′ and H5′), δ 7.94 (dd, 2H, H2′ and H6′), δ 7.83 (d, 1H, H6), δ 7.76 (dd, 1H, H2) and δ 7.07 (d, 1H, H3) were assigned to the aromatic protons and the upfield signal at δ 2.64 (s, 3H) was assigned to CH_3. Compound **II** showed similar characteristic signals as those discussed in compound **I**.

The aliphatic region of the ^{13}C NMR spectra of *p*-(*p*-acetylphenylazo)-*o*-allylphenol (compound **I**) showed two peaks as seen in Fig. 7. The medium intense peak CH_3 (26.83 ppm) was conveniently assigned to the methyl carbon of the acetyl group. The peak $-CH_2-$ (34.72 ppm) is due to methylene carbons according to the chemical shift. In the aromatic region of the ^{13}C NMR spectrum of compound **I**, the peaks C2 (123.12 ppm), C3 (116.20 ppm), C6 (124.49 ppm), C2′ and C6′ (128.60 ppm), C3′ and C5′ (130.18 ppm) were

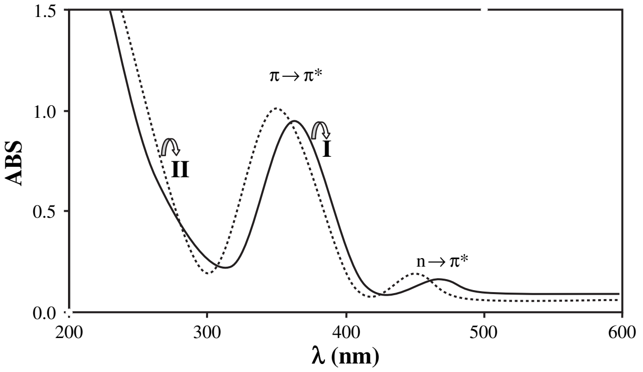
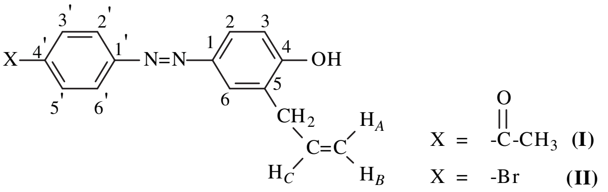


Fig. 5. UV–VIS spectra of compounds **I** and **II** in chloroform.

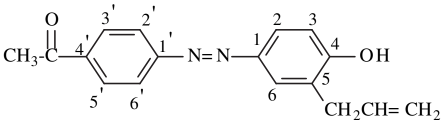
Table 7
^{1}H NMR chemical shifts (ppm) of azo dyes **I** and **II** in acetone-d_6



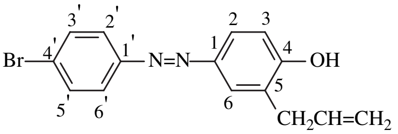
Chemical shifts (ppm)	Compounds	
	I	**II**
OH	9.34 (s)	9.30 (s)
H_A	5.16 (dd) $J_{A,B} = 1.91$ $J_{A,C} = 17.04$	5.16 (dd) $J_{A,B} = 1.92$ $J_{A,C} = 17.05$
H_B	5.08 (dd) $J_{B,A} = 1.91$ $J_{B,C} = 10.21$	5.07 (dd) $J_{B,A} = 1.92$ $J_{B,C} = 10.07$
H_C	6.09 (ddt) $J_{C,CH_2} = 6.62$ $J_{C,A} = 17.04$ $J_{C,B} = 10.21$	6.05 (ddt) $J_{C,CH_2} = 6.64$ $J_{C,A} = 17.05$ $J_{C,B} = 10.07$
$-CH_2-$	3.50 (d) $J_{CH_2,C} = 6.62$	3.49 (d) $J_{CH_2,C} = 6.64$
CH_3-	2.64 (s)	–
H2	7.76 (dd) $J_{2,3} = 8.40$ $J_{2,6} = 1.96$	7.52 (dd) $J_{2,3} = 8.39$ $J_{2,6} = 1.90$
H3	7.07 (d) $J_{3,2} = 8.40$	7.05 (d) $J_{3,2} = 8.39$
H6	7.83 (d) $J_{6,2} = 1.96$	7.77 (d) $J_{6,2} = 1.90$
H2′,H6′	7.94 (dd) $J_{2',3'} = 8.55$ $J_{2',6'} = 2.00$	7.81 (dd) $J_{2',3'} = 8.99$ $J_{2',6'} = 2.00$
H3′,H5′	8.14 (dd) $J_{3',2'} = 8.55$ $J_{3',5'} = 2.00$	7.72 (dd) $J_{3',2'} = 8.99$ $J_{3',5'} = 2.00$

s = singlet, d = doublet, dd = double doublets, ddt = double double triplets. TMS used as internal standard.

Table 8
^{13}C NMR chemical shifts (ppm) of azo dyes **I** and **II** in acetone-d_6



(I)



(II)

Chemical shifts (ppm)	Compounds	
	I	**II**
C=O	197.34	–
CH_2=	116.37	116.33
–CH_2–	34.72	34.73
–CH=	137.33	137.37
CH_3^-	26.83	–
C1	147.40	147.16
C2	123.12	124.18
C3	116.20	116.15
C4	159.87	159.53
C5	125.89	125.66
C6	124.49	124.89
C1′	156.15	152.66
C2′	128.60	133.18
C3′	130.18	124.61
C4′	138.99	128.51
C5′	130.18	124.61
C6′	128.60	133.18

TMS used as internal standard.

assigned to the proton carrying carbons and the peaks C1 (147.40 ppm), C4 (159.87 ppm), C5 (125.89 ppm), C1′ (156.15 ppm), C4′ (138.99 ppm) were assigned to the quaternary carbons. The others peaks (116.37 and 137.33 ppm) were assigned olefinic carbons of allyl group.

In the carbonyl region of the ^{13}C NMR spectrum of compound **I**, there is one peak at 197.34 ppm and this peak was assigned to the carbonyl carbon of the acetyl group. The peaks were then tentatively assigned by matching the observed and calculated chemical shifts. The spectroscopic data obtained in this work are agreed well with previous works [7,15–17].

3.3. Thermal behaviour

The TG–DTG and DTA curves of *p*-(*p*-acetylphenylazo)-*o*-allylphenol (compound **I**) and *p*-(*p*-bromphenylazo)-*o*-allylphenol (compound **II**) are shown in Figs. 8 and 9. As seen in the Fig. 8, three different decomposition steps have been observed for the thermal decomposition of compound **I**. The endothermic peak at 113 °C, obtained without any weight loss, clearly

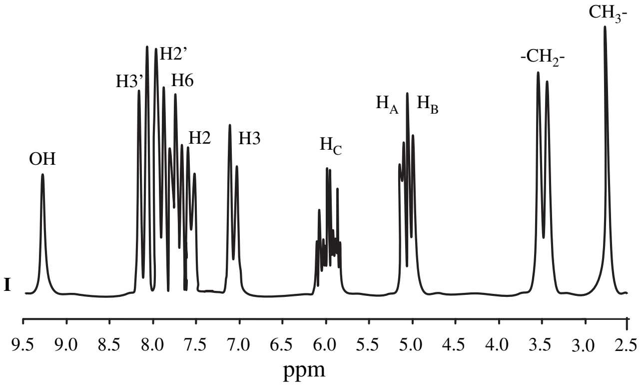


Fig. 6. ^{1}H NMR spectra of compound **I** in acetone-d_6.

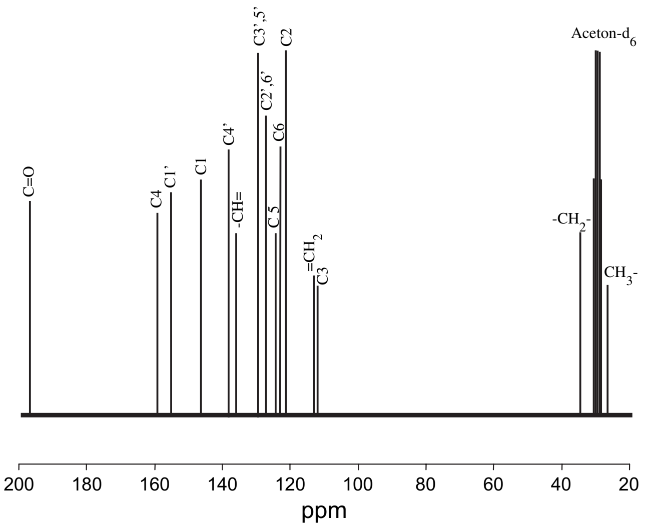


Fig. 7. ^{13}C NMR spectra of compound **I** in acetone-d_6.

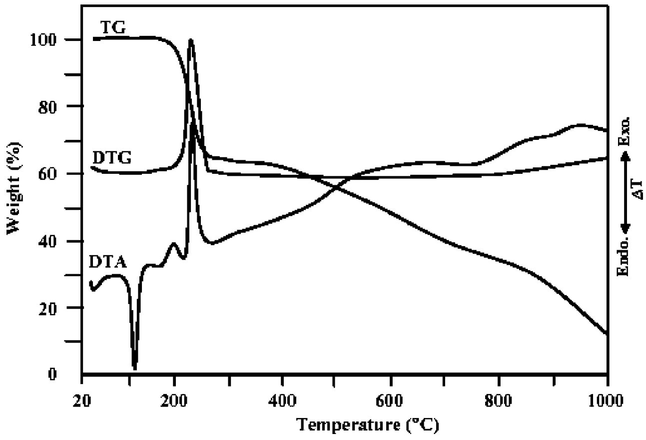


Fig. 8. DTA, TG, and DTG curves of compound **I**.

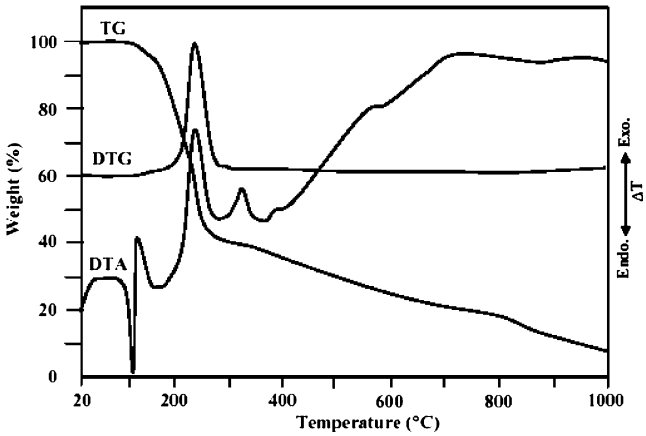


Fig. 9. DTA, TG, and DTG curves of compound **II**.

represents a physical process and is attributed to the melting of compound **I**. The weight loss starts at 174 °C and continuous to well above to 900 °C. In the first and second steps occurring between 174 °C and 268 °C, calculations indicate that the weight loss might be due to exothermic allyl and N_2 groups' loss (exp. 26.20%; calc. 24.64%). Similar decompositions have been observed by different researches [18,19]. The third step observed in 269 °C–1000 °C in the TG curve might be due to decomposition of the remaining hydrocarbon parts of compound **I**.

Three decomposition steps have been observed for compound **II** (Fig. 9). The first exothermic step at 113 °C–97 °C corresponds to the removal of N_2 (exp. 8.20%; calc. 8.83%). The second exothermic decomposition at 198 °C–280 °C indicates that the weight loss might be due to allyl group and bromine losses (exp. 42.95%; calc. 41.86%). As in compound **I**, the third step observed at 281 °C–1000 °C in the TG curve might also be due to the decomposition of the remaining hydrocarbon parts of compound **II**. The endothermic peak at 105 °C, without any weight loss, clearly is attributed to the melting of compound **II**.

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