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Synthesis, spectral, and thermal characterisations of some azo-ester derivatives containing a 4-acryloyloxy group

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Abstract

The azo-ester compounds containing an acryloyloxy group were derived from phenol and 2,6-dimethylphenol; first azobenzene derivatives were prepared by reacting substituted benzenediazonium salts with phenol and 2,6-dimethylphenol then their acryloyloxy derivatives were synthesized in a Schotten–Bauman-type reaction. The characterisation of the synthesized azo-ester dye has been described by IR, UV–vis, ^{1}H NMR, ^{13}C NMR spectroscopic techniques, and elemental analysis. The influence of the substituents and acryloyloxy group on the spectral data of the synthesized compounds has been described. The thermal behaviour of the present compounds has been determined by means of differential thermal analysis (DTA) and thermogravimetry (TG) techniques.

Keywords: Azobenzene; Azo-ester dyes; Acrylate; Acryloyloxy; Diazenes; Spectral characterisation; Thermal analysis

1. Introduction

It is well known for many years that dyes have been most widely used in fields such as dyeing textile fiber, biomedical studies, advanced applications in organic synthesis and high technology areas like lasers, liquid crystalline displays, electro-optical devices, and ink-jet printers [1–3].

Azo colorants are the most versatile class of dyes [4]. Spectral data and thermal analysis play an important role in studying their structure [5]. The literature reported so far on azo-ester compounds containing unsaturated group like acryloyloxy moiety is scarce [6,7]. We have previously reported the spectroscopic and dyeing properties of the acryloyloxy derivatives of *o*, *o′*-dihydroxyazo dyes and their metal complexes [7] and also the spectroscopic, thermal and single-crystal structure of (*E*) 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenyl acrylate dye (3,5-dimethyl-4-acryloyloxy-4′-*tert*-butylazobenzene) [8]. The acryloyloxy derivatives of *p*-hydroxyazo compounds may be important to prepare dyes and pigments that have unsaturated groups in their molecules and can undergo copolymerization with different vinyl monomers [6–8].

In present work, we report the synthesis of the newly synthesized azo-ester compounds which have polymerizable acryloyloxy group, the characterisation was done using IR, UV–vis, ^{1}H and ^{13}C NMR spectroscopic and also thermal analysis (DTA and TG) techniques. Influence of the substituents and polymerizable acryloyloxy group on the spectral and thermal data of these compounds has also been reported. In addition, the spectral data are compared with the values of 4-hydroxyazobenzene derivatives without acryloyl group.

2. Experimental

2.1. General

Melting points were taken with a digital melting point apparatus and were uncorrected. IR spectra were determined in the region 4000–200 cm^{-1} on a FTIR-8900 SCHIMADZU IR spectrometer by preparing KBr pellets. The UV–vis absorption spectra in ethanol, acetone and dimethylformamide

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were recorded with a Unicam UV2-100 UV/VIS spectrometer. The ^{1}H and ^{13}C NMR spectra in DMSO-d_6 were measured at 200 and 50 MHz, respectively, using Bruker AC 200 FT-NMR spectrometer referencing tetramethylsilane as internal standard. Thermal analysis was carried out with a Shimadzu DTG-GOH simultaneous thermal analyser combined with a TAS 100 thermogravimetric analyser under dynamic nitrogen atmosphere at a heating rate of 10 cm min^{-1} from ambient temperature to 600 °C. α-Al_2O_3 was used as a reference material. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK, Marmara Research Center.

Substituted anilines were obtained from Aldrich, Merck, and Sigma.

2.2. Preparation of azo-ester compounds

For the synthesis of azo-ester compounds **1**–**18** containing an acryloyloxy group, first the derivatives of 4-hydroxyazobenzene dyes were prepared by the usual azo-coupling reaction of phenol and 2,6-dimethylphenol with substituted aryldiazonium salts as described in the literature [9] and then their acryloyloxy derivatives were synthesized in a Schotten–Bauman-type reaction similar to the following procedure and by the method described previously [8,10].

To a stirred THF (20 ml) solution of substituted 4-hydroxyazobenzene dye (2.48 mmol) and sodium metal (2.48 mmol), acryloyl chloride (2.48 mmol) were directly added dropwise in an atmosphere of dry nitrogen. After 2 h of stirring, the mixture was filtered and the desired product was precipitated out by adding water. The solid filtered was washed several times with water, and then dried. The product was crystallized from ethyl alcohol/water mixture to give related compound. TLC monitored its purity.

All the other substituted azo-ester compounds were synthesized in a manner similar to that described above.

3. Results and discussion

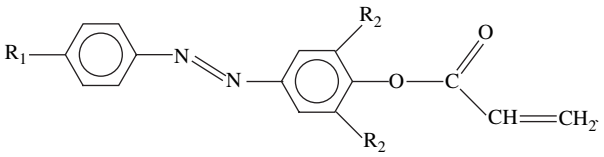
Structures of azo-ester compounds **1**–**18** synthesized by Schotten–Bauman-type reaction of 4-hydroxyazobenzene derivatives and acryloyl chloride are shown in Fig. 1. The spectral investigation of the present compounds is in accord with their structures. The elemental analysis and some physical properties of all these compounds are given in Table 1.

The spectroscopic properties (IR, UV–vis, ^{1}H and ^{13}C NMR), the thermal analysis and single-crystal structure of the azo-ester compound **13** [(*E*) 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenyl acrylate = 3,5-dimethyl-4-acryloyloxy-4′-*tert*-butylazo benzene] have been reported and discussed in our previous paper [8].

3.1. Spectral characterisation

3.1.1. ^{1}H NMR spectra

The ^{1}H NMR chemical shift data of the related azo-ester derivatives containing 4-acryloyloxy group are given in



Azo-esters	R_1	R_2
1	H	H
2	CH_3	H
3	C_2H_5	H
4	$(CH_3)_3C$	H
5	NO_2	H
6	F	H
7	CI	H
8	Br	H
9	OCH_3	H
10	H	CH_3
11	CH_3	CH_3
12	C_2H_5	CH_3
13	$(CH_3)_3C$	CH_3
14	NO_2	CH_3
15	F	CH_3
16	CI	CH_3
17	Br	CH_3
18	OCH_3	CH_3

Fig. 1. The structures of the azo-ester compounds.

Table 2. The typical ^{1}H NMR spectra of the compounds **9**, **18** are shown in Figs. 2 and 3.

In the ^{1}H NMR spectra of the azo-ester compounds recorded in DMSO-d_6, the peaks of the H_a in Z configuration according to >C=O group in an acryloyl moiety are seen at 5.95–6.27 ppm. The peaks of the azo-esters **1**–**9** which have the phenol derivatives are at 6.09–6.25 ppm as asymmetric doublets, in the other esters, **10**–**18**, containing 2,6-dimethylphenol derivatives, these peaks are between 5.95 and 6.27 ppm as doublets. Nevertheless, when the peaks of H_b in E configuration according to >C=O group in phenol derivatives are at 6.47–6.65 ppm as generally doublet of doublets, for the other esters **10**–**18**, these peaks are at 6.45–6.71 ppm as generally doublets. For H_c, the related peaks have been observed at 6.29–6.52 ppm in phenol derivatives and at 6.22–6.57 ppm as quaternets in 2,6-dimethylphenol derivatives. As a result, the peaks of hydrogen (H_a, H_b, H_c) atoms found in acryloyl group are resonated at 5.95–6.71 ppm in agreement with the literature values [6]. The attaching of an acryloyl group was confirmed by the disappearance of the signal at ca. 9.0 ppm in ^{1}H NMR spectra which are typical for hydroxyl protons of the 4-(phenyldiazenyl)phenol derivatives which are the derivatives of the present compounds without acryloyl group [6,8].

The chemical shift values of aromatic protons of the present azo-esters have the effect of deshielding relative to the 4-(phenyldiazenyl)phenol derivatives which are their intermediate compounds. For instance, the values of the compounds **5** and **9** were deshielded according to the literature values [10] of 4-(4-nitrophenyldiazenyl)phenol (at 7.70–8.10 ppm for four protons *ortho* to –N=N–; at 8.10–8.50 ppm, for two protons *ortho* to NO_2; at 6.80–7.10 ppm, for two protons *ortho* to –OH)

Table 1
The elemental analysis and some physical properties of the azo-esters compounds **1**–**18**

Azo-esters	Formula	Yield (%)	Mp (°C)	Analysis (%)	Calculated (found)	
				C	H	N
1	$C_{15}H_{12}N_2O_2$	40	62–64	71.65(71.42)	4.96(4.79)	10.78(11.10)
2	$C_{16}H_{14}N_2O_2$	40	82–84	71.97(72.17)	5.68(5.30)	9.77(10.52)
3	$C_{17}H_{16}N_2O_2$	40	50–52	68.16(68.70)	5.25(5.75)	8.89(9.29)
4	$C_{19}H_{20}N_2O_2$	40	62–64	73.02(74.00)	6.31(6.54)	8.16(9.08)
5	$C_{15}H_{11}N_3O_4$	66	121–124	61.12(60.61)	3.73(3.73)	14.23(14.14)
6	$C_{15}H_{11}N_2O_2F$	58	95–98	66.30(66.66)	3.76(4.10)	9.72(10.37)
7	$C_{15}H_{11}N_2O_2Cl$	58	135–138	62.20(62.84)	3.73(3.87)	9.46(9.77)
8	$C_{15}H_{11}N_2O_2Br$	58	125–130	53.36(54.40)	3.10(3.35)	8.11(8.46)
9	$C_{16}H_{14}N_2O_3$	56	87–90	67.48(68.09)	4.71(5.00)	8.90(9.92)
10	$C_{17}H_{16}N_2O_2$	61	91–92	75.05(72.84)	6.21(5.75)	10.52(9.99)
11	$C_{18}H_{18}N_2O_2$	57	76–77	69.91(70.45)	5.65(6.06)	8.31(8.52)
13	$C_{21}H_{24}N_2O_2$	42	124–125	74.93(74.97)	7.23(7.19)	7.95(8.33)
14	$C_{17}H_{15}N_3O_4$	62	156–159	62.19(62.76)	4.41(4.65)	12.22(12.92)
15	$C_{17}H_{15}N_2O_2F$	68	102–104	66.86(68.45)	4.86(5.07)	8.22(9.39)
16	$C_{17}H_{15}N_2O_2Cl$	58	102–104	63.52(64.87)	4.56(4.80)	8.22(8.90)
17	$C_{17}H_{15}N_2O_2Br$	75	107–109	55.18(56.84)	3.74(4.21)	7.70(7.79)
18	$C_{18}H_{18}N_2O_3$	35	79–81	63.15(63.66)	5.30(5.45)	7.62(8.03)

and 4-(4-methoxyphenyldiazenyl)phenol (at 7.50–8.00 ppm for four protons *ortho* to –N=N–; 6.80–7.20 ppm as quaternets for CH_3O– and OH) [9,10]. The shift values observed for the azo-ester compounds were also similar to the previously discussed literature values of 4-(phenyldiazenyl)phenol derivatives containing acetyl group [10,11].

In compounds **1**–**9** having the phenol derivatives, the *ortho* protons to acryloyloxy group are resonated at ca. 7.33–7.58 ppm as doublets, in the other compounds **10**–**18** containing 2,6-dimethylphenol derivatives resonations are not observed because of the attached methyl groups to both *ortho* sides of the aromatic ring.

The two *ortho* protons to R_1 groups given at ca. 7.09–8.47 ppm are generally doublets as can be seen from Table 2 and also one of which, **17**, is resonated at 7.74 ppm as coupling together with protons *ortho* of –N=N– group.

The phenyl protons *ortho* of –N=N– group according to the acryloyloxy side group are resonated at 7.53–7.76 ppm as singlets for azo-esters **10**–**18** and at 7.86–8.07 ppm for dyes **1**–**9** containing phenol derivatives, whereas the other side protons *ortho* of –N=N– group are resonated at 7.35–8.11 ppm as doublets.

The methyl peaks of the azo-esters containing 2,6-dimethylphenol derivatives are resonated at ca. 2.26–2.12 ppm as singlets. The proton peaks of the other related groups such as methyl, ethyl, and *tert*-butyl are similar to the literature values.

As a result, the aromatic protons of the synthesized azo-esters compounds have the effect of deshielding relative to the compounds in agreement with the literature as phenylazophenol does not have the acryloyl group [9,10].

3.1.2. ^{13}C NMR spectra

The ^{13}C NMR chemical shift data of the azo-ester derivatives containing 4-acryloyloxy group are given in Table 3.

From ^{13}C NMR spectra of the azo-ester compounds, >C=O group signals are observed between 162.83 and 164.46 ppm in agreement with the literature values [8,10]. In the azo-esters **1**–**9** having phenol derivatives, the peaks of C atom of CH moiety found in acryloyl group are resonated at 127.26–127.49 ppm and also at 126.72–126.92 ppm for 2,6-dimethylphenol derivatives, **10**–**18**. The CH_2 peaks of acryloyl group are also seen at 133.69–134.10 ppm for phenol derivatives and at 133.31–136.08 ppm for 2,6-dimethylphenol derivatives. Close similarities among all these values are clearly seen in Table 3.

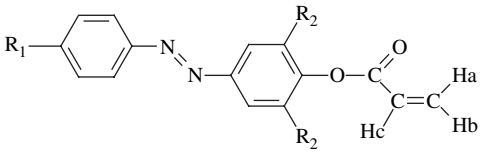
Regarding the phenol derivatives, when the effect of substituted group on the C4 atom was examined, it was found that the chemical shift was in the order of $CH_3O- > F- > Bu^t- > C_2H_5- > NO_2- > CH_3- > H$ depending on the chemical environment of the carbon. Attaching the substituted group to C4 atom of the azo-ester compounds, chemical shift values shielded by ca. 30 ppm as the attached substituted groups. The other C atoms in the groups seemed to have values close to each other (Table 3).

When chemical shift values of C1 atoms attached to the nitrogen of –N=N– group are between 149.45 and 155 ppm, the signals of C5 atoms attached to the other nitrogen appear at 146.07–149.65 ppm depending on the chemical environment of the carbon [12].

On investigation of all the azo-esters as phenol and 2,6-dimethylphenol derivatives, a harmonious chemical shift of C1–C11 atoms for the compound of each series has been detected. For instance, looking at the chemical shift derivatives of C1–C11, close similarities among all the values are obvious compared to the azo-esters **1**,**10**; **2**,**11**; **3**,**12**; **4**,**13**. These values were similar to previously discussed literature values of 4-(phenyldiazenyl)phenol derivatives [12,13].

Chemical shift values in the range between 124.50 and 122.25 ppm at C7 atoms of the phenol derivatives **1**–**9** were shifted upward to the 131.53–130.85 ppm interval in the

Table 2
^{1}H NMR data of azo-ester compounds



No	Four protons *ortho* to –N=N–		Two protons *ortho* to R_1	Two protons *ortho* to acryloyloxy group	H_a	H_b	H_c
	Aniline sides	Phenol sides					
1	7.95–7.92 d	7.90–7.86 t	7.58, 7.57, 7.56 t	7.42–7.38 d	6.19–6.14 d	6.63–6.53 dd	6.48–6.43 to 6.40–6.35
2	7.84–7.80 d	7.97–7.93 d	7.40 s	7.44 d	6.23–6.17 dd	6.65– 6.55 dd	6.51–6.46 to 6.42–6.37
3	7.82–7.78 d	7.94–7.90 d	7.36 s	7.40 s	6.18–6.13 d	6.62–6.53 d	6.48–6.43 to 6.39–6.34
4	7.83–7.79 d	7.94–7.89 d	7.39–7.35 d	7.58–7.54 d	6.18–6.13 dd	6.61–6.53 dd	6.47–6.42 to 6.39– 6.34
5	8.11–8.07 d	8.07–8.03 d	8.47–8.43 d	7.51–7.47 d	6.25–6.19 dd	6.65– 6.57 dd	6.52–6.47 to 6.44– 6.39
6	7.94–7.91 d	7.88–7.87 d	7.41–7.37 d	7.37–7.33 d	6.15–6.09 dd	6.57–6.47 dd	6.43–6.38 to 6.34–6.29
7	8.00–7.96 d	7.94–7.90 d	7.69–7.65 d	7.47–7.42 d	6.24–6.19 d	6.65–6.56 dd	6.52–6.47 to 6.43–6.38
8	7.83 s		8.01–7.96	7.47–7.42 d	6.23–6.17 dd	6.65–6.55 dd	6.51–6.46 to 6.43–6.38
9	7.87–7.86 d	7.92–7.90 d	7.13–7.09 d	7.39–7.35 d	6.20–6.14 dd	6.62–6.53 dd	6.48–6.43 to 6.39–6.35
10	7.89, 7.88, 7.85 t	7.67 s	7.59, 7.56, 7.55 t	–	6.24–6.18 dd	6.69–6.59 d	6.54–6.49 to 6.45–6.40
11	7.75–7.71 d	7.59 s	7.34–7.30 d	–	6.20–6.15 d	6.64–6.55 d	6.49–6.44 to 6.41–6.35
12	7.72–7.69 d	7.53 s	7.19–7.16 d	–	5.99–5.95 d	6.53–6.45 d	6.35–6.30 to 6.22
13	7.86–7.82 d	7.70 s	7.64–7.60	–	6.27–6.22 d	6.71–6.63 d	6.57–6.52 to 6.49–6.44
14	8.05–8.01 d	7.76 s	8.43–8.40 d	–	6.26–6.22 d	6.70–6.62 d	6.55–6.50 to 6.42
15	7.44–7.40–7.35 t	7.65 s	7.95–7.93 to 7.91–7.88	–	6.24–6.18 dd	6.67–6.58 dd	6.52–6.47 to 6.44–6.38
16	7.65–7.61 d	7.67 s	7.89–7.84 d	–	6.24–6.19 d	6.67–6.59 d	6.53–6.48 to 6.44–6.38
17	7.74	7.64 s	7.74	–	6.23–6.18 d	6.67–6.59 d	6.52–6.47 to 6.43–6.39
18	7.89–7.84 d	7.62 s	7.13–7.09 d	–	6.23–6.18 d	6.68–6.60 d	6.53–6.48 to 6.45–6.40

d: Doublet; s: singlet; t: triplet; dd: doublets of doublet.

2,6-dimethylphenol derivatives because of two methyl groups attached to C7 atoms.

The chemical shift values of the other attached groups such as methyl, ethyl, *tert*-butyl can be seen from Table 3.

3.1.3. UV spectra

The UV–vis data of the azo-ester compounds containing 4-acryloyl group are summarized in Table 4. The UV–vis spectra of the compound **15** are shown in Fig. 4 as a typical example.

The UV–vis spectral behaviours of the compounds were investigated in a variety of solvents such as absolute ethyl alcohol, chloroform, and DMF depending on their solubility.

The absorption maxima of the azo-esters in related solvents have shown a hypsochromic shift up to ca. 32 nm relative to the 4-(phenyldiazenyl)phenol derivatives which are the intermediate compounds of the azo-esters but up to ca. 53 nm for those of azo-esters **5** and **14** containing $-NO_2$ groups [10]. For instance, the hypsochromic shift values of the compounds **1** and **10** in DMF are 26 and 32 nm, respectively, according to the literature values of 4-(phenyldiazenyl)phenol (at 357 nm) and 2,6-dimethyl-4-(phenyldiazenyl)phenol (at 364 nm). The other related compounds also have similar values. This may be brought about by the decreasing order of activation of the acryloyloxy moiety instead of the hydroxyl group.

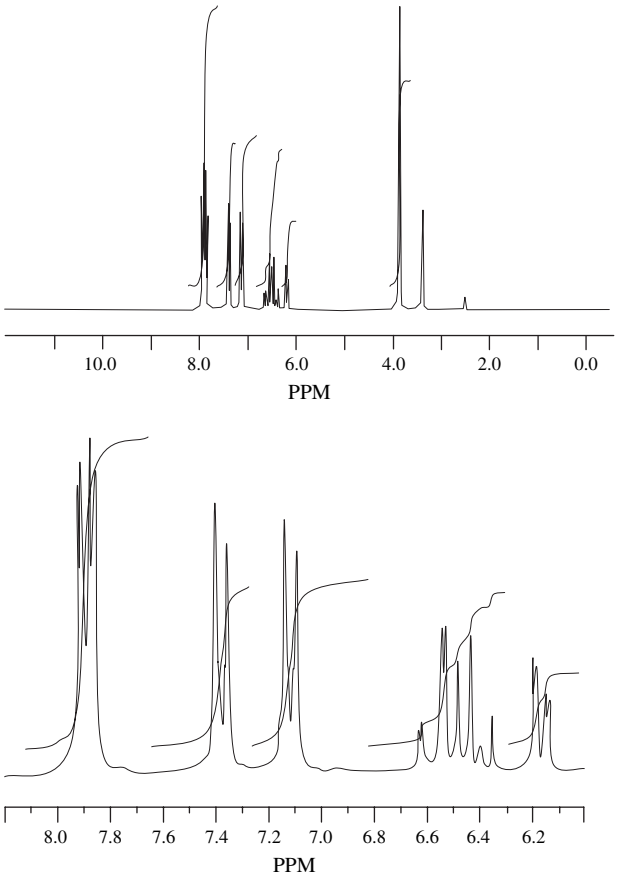


Fig. 2. (a) ^{1}H NMR spectrum of the azo-ester compound **9** containing phenol derivative. (b) Expanded ^{1}H NMR spectrum of the compound.

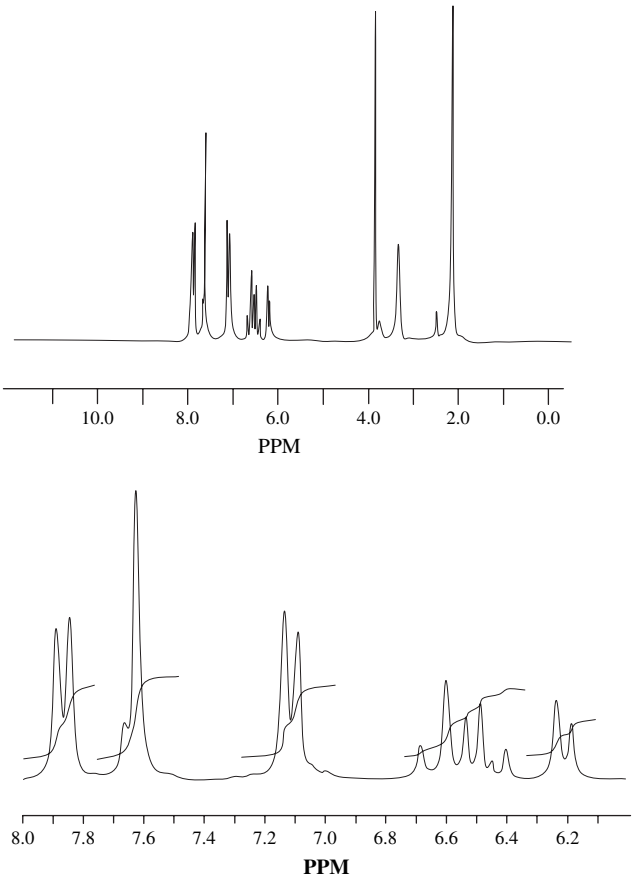
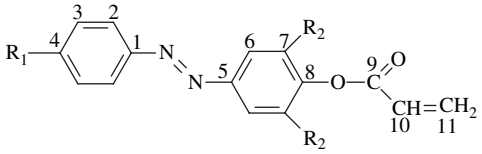


Fig. 3. (a) ^{1}H NMR spectrum of the azo-ester compound **18** containing 2,6-dimethylphenol derivative. (b) Expanded ^{1}H NMR spectrum of the compound.

Table 3
^{13}C NMR data of related azo-ester compounds



No	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	R_1	R_2
1	152.36	123.67	122.42	131.38	149.56	129.27	122.61	151.80	163.68	127.33	133.73	–	–
2	152.14	123.49	122.58	141.71	149.63	129.81	122.43	149.94	163.72	127.35	133.71	20.87	–
3	152.14	123.52	122.56	149.62	147.79	128.58	122.56	150.10	163.70	127.35	133.70	27.95/15.05	–
4	152.14	123.52	122.55	154.48	149.65	126.01	122.25	149.76	163.68	127.34	133.69	30.79/34.61	–
5	155.00	122.85	124.33	148.45	149.50	124.89	123.33	153.32	163.60	127.26	133.90	–	–
6	152.58	123.91	124.90	161.49	148.74	125.09	122.88	149.67	164.46	127.49	134.10		
7	152.60	124.08	122.70	135.97	149.46	129.47	123.81	150.39	163.68	127.32	133.80	–	–
8	152.65	124.83	123.82	132.42	149.47	124.28	122.72	150.71	163.66	127.33	133.81	–	–
9	151.81	122.55	114.51	162.01	146.07	123.32	124.50	149.70	163.79	127.38	133.72	55.55	–
10	151.87	122.28	129.24	131.20	149.36	122.48	131.12	149.81	162.99	126.74	134.01	–	15.79
11	150.18	122.54	129.98	141.76	149.63	122.54	131.28	149.79	163.34	126.92	134.25	21.03	15.99
12	150.29	123.13	128.28	149.66	147.34	122.48	130.85	149.53	162.83	126.76	133.31	15.80/28.02	16.54
13	154.49	122.40	122.16	149.85	149.46	126.08	131.13	149.66	163.08	126.79	134.12	34.66/30.85	15.84
15	150.04	124.76	124.95	161.34	148.78	122.67	131.41	149.46	163.34	126.90	134.36		15.99
16	150.65	124.21	129.67	134.00	149.49	122.83	131.53	150.00	163.35	126.88	136.08		16.00
17	150.68	124.13	124.64	132.30	149.20	122.61	131.17	150.05	162.93	126.72	134.02		15.80
18	149.45	122.13	114.45	161.85	146.11	124.30	130.95	149.24	163.06	126.78	133.93	55.48	15.81

Table 4
The IR and UV–vis data of azo-ester compounds

Azo-ester	Wavelength [λ_{max}(nm)][log ε(l/mol cm)]			pH 1–2 (DMF)	pH 12 (DMF)	IR (cm^{-1})			
	Ethanol	Chloroform	DMF			O–H	>C=O	CH_2=CH–	–C(O)–O
1	327(4.409)	324(4.164)	331(4.547)	338(4.341)	292(3.465)	–	1738	1636	1155, 1200
				444(2.740)	457(4.253)				
2	333(4.536)	335(4.136)	343(4.452)	345(4.545)	284(4.060)	–	1736	1631	1151, 1200
	448(3.272)	444(2.884)		449(3.275)	462(4.615)				
3	335(4.583)	338(4.549)	343(4.598)	298(4.387)	282(4.284)	–	1736	1641	1155, 1202
		443(3.116)		335(4.487)	469(4.820)				
4	234(4.292)	336(4.593)	342(4.367)	339(4.436)	284(3.928)	–	1740	1646	1155, 1196
	336(4.525)				463(4.561)				
5	342(4.705)	349(4.585)	363(4.268)	383(4.247)	299(3.813)	–	1744	1646	1151, 1203
			554(3.198)		542(4.505)				
6	232(4.592)	328(4.203)	343(4.458)	339(4.656)	283(4.167)	–	1744	1636	1161, 1200
	330(4.716)	431(3.382)			468(4.735)				
7	234(4.365)	333(4.230)	346(4.412)	345(4.891)	295(4.231)	–	1748	1636	1161, 1204
	330(4.499)			426(3.684)	496(4.790)				
8	334(4.486)	343(4.208)	343(4.675)	349(4.604)	285(4.213)	–	1746	–	1161, 1202
					484(4.767)				
9	351(4.380)	353(4.258)	359(4.391)	295(4.384)	285(4.114)	–	1734	–	1148, 1199
	441(3.289)	436(1.853)		360(4.608)	470(4.625)				
10	328(4.427)	341(4.337)	332(4.513)	345(4.185)	294(3.756)	–	1736	1646	1163
					480(4.375)				
11	335(4.447)	341(4.123)	344(4.396)	367(4.484)	295(4.027)	–	1736	1630	1151
					489(4.525)				
12	337(4.570)	336(4.536)	333(4.580)	–	–	–	1744	1636	1151
13	334(4.512)	334(4.480)	339(4.518)	341(4.355)	298(4.152)	–	1742	1634	1155
					492(4.750)				
14	347(4.569)	352(4.641)	352(4.403)	365(4.273)	302(3.921)	–	1734	1630	1169
		461(3.466)			596(4.733)				
15	234(4.365)	333(4.230)	340(4.412)	345(4.891)	295(4.231)		1736	1646	1175
	330(4.499)			426(3.684)	496(4.790)				
16	335(4.538)	338(3.863)	342(4.528)	340(4.692)	302(3.280)		1738	1638	1175
			423(3.200)		513(3.919)				
17	336(4.529)	342(4.321)	545(2.751)	343(4.355)	302(4.302)		1736	1646	1175
			340(4.546)		513(4.920)				
18	344(4.469)	349(4.424)	358(4.385)	355(4.509)	298(3.732)		1736	1633	1161
	424(3.393)				489(4.283)				

Further, all azo-ester compounds are hydrolysed with aqueous sodium hydroxide at pH 12 and produces the sodium salts of related 4-(phenyldiazenyl)phenol derivatives and acrylic acid. The absorption values of hydrolysed compounds have shown a large bathochromic shift between 98 and 244 nm, as can be seen from Table 4. This finding indicates that the compounds **1–18** exist in the anion forms of 4-(phenyldiazenyl)phenol derivatives.

Fig. 4 shows the UV–vis spectra of the compound **15** as typical example. The absorption maxima of this compound dissolved in absolute ethyl alcohol, chloroform, DMF, and DMF at pH 12 exhibit one band at 330, 333, 340, and 496 nm, respectively. These bands appear as absorption maxima with high extinction coefficient (4.499, 4.230, 4.412, and 4.790 log ε l/mol cm) and are attributed to the $\pi \rightarrow \pi^*$ transitions of the related compound. The absorption maximum of the compound in DMF demonstrated a hypochromic shift of ca. 24 nm in comparison with 2,6-dimethyl-4-(4-fluorphenyldiazenyl)phenol which is the derivative of the compound **15** without acryloyl group [10]. Further, the absorption value of the compound hydrolysed with aqueous sodium hydroxide at pH 12 is 468 nm (4.735 log ε) and this value is the sodium salt of the 2,6-dimethyl-4-(4-fluorphenyldiazenyl)phenol.

3.1.4. IR spectra

The IR data of the azo-ester compounds containing 4-acryloyl group are summarized in Table 4.

From the IR spectra of the compounds, characteristic vibrational bands observed at ca. 1410 and 1140 cm^{-1} for –N=N– and –C–N= groups were not given because these absorptions are also quite variable and often obscured by phenyl rings' vibrations [4].

As Table 2 shows characteristic stretches and vibrations for hydroxyl groups observed at the range ca. 3200–3500 cm^{-1} in 4-hydroxyazobenzene derivatives do not appear due to the esterification between the hydroxyl group and the acryloyl chloride. This state was confirmed by showing the intensive absorption bands in the range between 1734 and 1748 cm^{-1} which are attributed to the carbonyl groups of the acryloyl moiety.

On investigation of all these compounds as phenol and 2,6-dimethylphenol derivatives, vibrational bands of –C(O)–O– groups in the azo-esters **1–9** having phenol derivatives,

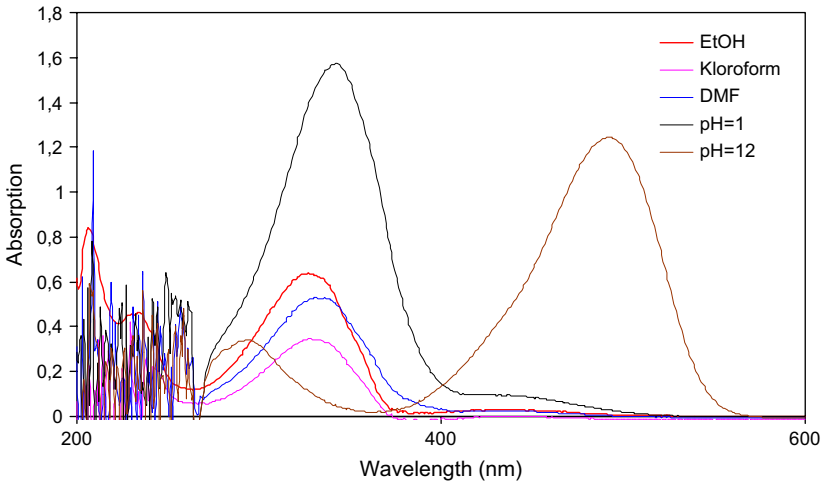


Fig. 4. The UV–vis spectra of the azo-ester compound **15**.

appeared as two sharp peaks at 1148–1161 and 1196–1204 cm^{-1} and also as one sharp peak between 1195 and 1175 cm^{-1} for 2,6-dimethylphenol derivatives **10–18**.

As can be seen from Table 4, the other characterised stretching bands of all the compounds **1–9** and **10–18** are similar to each other.

3.2. Thermal analysis

The typical TG and DTA curves of the dyes **2** and **14** are illustrated in Figs. 5 and 6, respectively. The obtained thermoanalytical results from TG and DTA curves for all these compounds are given in Table 5.

It is clearly seen that considering TG and DTA curves of all the azo-ester dyes from Table 5 the mass losses of all the compounds **1–9** and **10–18** which contain phenol and 2,6-dimethylphenol moieties, respectively, are similar to each other by weakly endothermic process. In all the azo esters, the mass loss in one stage during heating changes from 88 to 98% depending on the substituted groups as Table 5 except **5**, **9**, **14** and **18**. The azo-esters **5**, **14** and **9**, **18** containing nitro and methoxy group lose the mass in two stages, first one of which is from 65–73% and the other 19–28%, respectively.

The thermal mass loss temperatures of these azo-esters starts between 133 and 186 °C and complete in the interval 210–377 °C. For nitro and methoxy substituted compounds, second stage mass loss temperatures start between 372 and 453 °C and in the interval 490–596 °C.

Although the decomposition mechanism of azo compounds is complex, it basically consists of a heterolytic splitting of azo bonds known for the most of the azo dyes [14]. Similar thermal process in the thermal behaviour of some compounds, (2,6-dimethyl-4-(4-nitrophenyldiazenyl)phenol) without acryloyl group has been observed [8].

The thermal mass loss temperature values of 4-(4-nitrophenylazo)phenol have previously been reported from this laboratory and the mass loss temperatures take place sharply between 2120 and 230 °C [15], in the compound **5** being its derivative with an acryloyl group, these values expand from 178 to 304 °C. In addition, the DTA values of the related compounds reduce from 280 [15] to 270 °C. respectively. For the first compound, the mass losses in one stage are from 63% [15] and for second one 96% in two stage. The melting point of 4-(4-nitrophenylazo)phenol is 214 °C but acryloyl derivative of its **5**, is retired to 130 °C. Similar explanations can also be made for 4-(4-nitrophenylazo)-2,6-dimethylphenol which is in the literature [15].

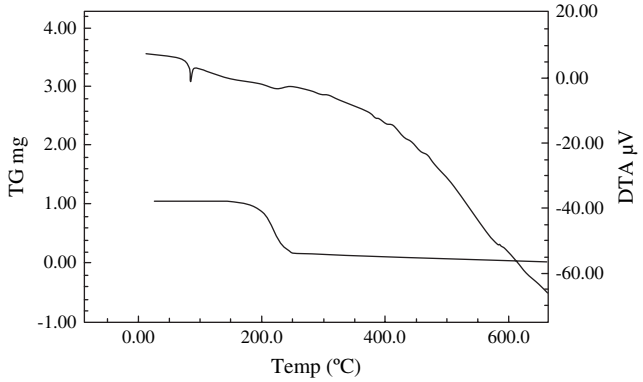


Fig. 5. The DTA and TG curves of the azo-ester compound **2**.

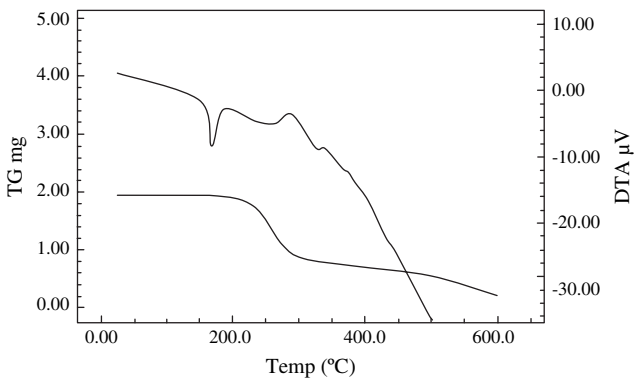


Fig. 6. The DTA and TG curves of the azo-ester compound **14**.

Table 5
Thermoanalytical results of the azo-ester compounds

Azo-esters	Mp[a] (°C)	Mass loss temp. (°C)	Max mass loss (%)	DTA_{max} (°C)
1	68	149–249	90	202 *endo*
2	88	133–268	98	225 *endo*
3	55	158–318	87	220 *endo*
4	100	174–268	76	233 *endo*
5	130	178–304	75	270 *endo*
		453–490	21	
6	106	139–210	92	194 *endo*
7	143	167–235	99	219 *endo*
8	145	167–256	88	227 *endo*
9	98	168–292	65	220 *endo*
		426–557	19	
10	103	142–288	87	234 *endo*
11	83	168–326	88	229 *endo*
13	127	164–381	92	264 *endo*
14	169	149–377	66	258 *endo*
		378–596	28	
15	108	156–268	99	233 *endo*
16	108	175–259	98	245 *endo*
17	112	168–284	97	253 *endo*
18	88	173–344	73	250 *endo*
		372–566	20	

[a] Minimum values in nitrogen atmosphere (from DTA curves).

In the TG curve of the dye **2** Fig. 5 containing phenol moiety and *p*-methyl group, when the mass loss of this compound takes place between 133 and 268 °C at one stage, the weight loss of its is 98% and initial-end mass loss is similar.

From the TG curve (Fig. 6) of dye **14** containing 2,6-dimethylphenol moiety and *p*-nitro group it is seen that when the mass losses in first and second stages during the heating appear at 149–377 and 378–596 °C, respectively, the weight losses of this compound are determined as 66% and 28%, respectively.

The melting process is accompanied by a weakly endothermic change in all the azo-ester dyes. The investigated dyes show considerable differences from 68 to 169 °C in melting points depending on the substituted and acryloyl groups. The maximal mass losses of all the dyes are similar which are average 234 °C from the present DTA results. It is observed that the melting points of the related dyes are higher than the normal values which may be the result of nitrogen atmosphere as shown from Tables 1 and 5. From the data in Table 5, all the derivatives of 4-nitroaniline **5** and **14**, have higher melting points than those of all the other dyes.

4. Conclusion

In present work, we report the synthesis of the azo-ester compounds which have polymerizable acryloyloxy group, and the characterisation using IR, UV–vis, ^{1}H and ^{13}C NMR spectroscopic techniques. The thermal behaviour of these compounds has been determined by means of differential thermal analysis (DTA) and thermogravimetry (TG) techniques.

The attaching of an acryloyl moiety was confirmed by the >C=O group signal appearing at ca. 160 ppm in the ^{13}C NMR spectra, showing an intensive absorption band at ca. 1740 cm^{-1} characteristic of the carbonyl group in the IR, and by the disappearance of the signal at ca. 9.00 ppm in ^{1}H NMR spectra which are typical for hydroxyl protons of the 4-hydroxyazobenzene derivatives.

It is clearly seen considering TG and DTA curves of all the azo-ester dyes from Table 5, that the mass losses of all the compounds **1–9** and **10–18** which contain phenol and 2,6-dimethylphenol moieties, respectively, are similar to each other by weakly endothermic process. The thermal mass loss temperatures of these azo-esters start at 133–186 °C and complete in the internal 210–377 °C.

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References

[1] Peters AT, Freeman HS. Colour chemistry, the design and synthesis of organic dyes and pigments. Barking, Essex: Elsevier Appl Sci Publ Ltd; 1991. p. 193–5.
[2] Gregory P. High-technology applications of organic colorants. New-York and London: Plenum Press; 1991. p. 1–3.
[3] Catino SC, Farris RE. Azo dyes. In: Grayson M, editor. Concise encyclopedia of chemical technology. New-York: John Wiley & Sons; 1985. p. 142.
[4] Venkataraman K. In: The chemistry of synthetic dyes, vol. 3. New-York and London: Academic Press; 1970. p. 303–69.
[5] Griffiths J. Colour and constitution of organic molecules. New-York and London: Academic Press; 1976. p. 193–95.
[6] Shuhaibar K, Pasch FH. The synthesis and characterization of polymerizable azo-naphthols for use in polymeric materials. Dyes and Pigments 1991;15:57–67.
[7] Kocaokutgen H, Özkınalı S. Application of some *o*,*o′*-dihydroxyazo dyes containing a acryloyloxy group and their chromium complexes on nylon and wool. Textile Research Journal 2003;74(1):78–82.
[8] Kocaokutgen H, Gür M, Soylu MS, Lörnnecke P. Spectroscopic, thermal and crystal structure properties of novel (*E*)-2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenyl acrylate dye. Dyes and Pigments, in press.
[9] Kocaokutgen H. Synthesis and investigation of some azo dyes containing the steric hindered group and their dyeing properties. PhD thesis. Samsun, Turkey: OMU; 1995.
[10] Gür M. The synthesis of some azo compounds containing acryloyl group and investigation of their spectroscopic properties. MSc thesis. Samsun, Turkey: OMU; 2004.
[11] Skulsky L, Kleps J. The proton spectra of some *p*,*p′*-disubstituted azobenzenes. On tautomerism of *p′*-substituted, *p*-amino-, and hydroxyazobenzenes. Bull Aca Polanaise Sciences XXI 1973;II:859–71.
[12] Lycka A, Snobl D, Machacek V, Vecera M. ^{13}C-NMR spectra of non-labelled and ^{15}N-monolabelled azo dyes. Organic Magnetic Resonance 1981;15:390–3.
[13] Kocaokutgen H, Gümrükcüoğlu İE. An investigation ^{13}C-NMR spectra of some intramolecular hydrogen bonded and non-bonded azo dyes. Spectroscopy Letters 1996;29(1):185–92.
[14] Wosciechowsky K, Szadowsky J. Thermal analysis of amide derivatives of *N*,*N*-dialkylaminoazobenzene. Journal of the Thermal Analysis 1986;31:297–303.
[15] Kocaokutgen H, Gümrükcüoğlu İE. Thermal characterization of some azo dyes containing intramolecular hydrogen bonds and non-bonds. Journal of the Thermal Analysis and Calorimetry 2003;71:675–9.