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Spectroscopic, thermal and crystal structure properties of novel (*E*)-2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenyl acrylate dye

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Abstract

2,6-Dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenyl acrylate ($C_{21}H_{24}N_2O_2$), containing an acryloyloxy group, first 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenol was prepared by reacting 4-*tert*-butylbenzenediazonium salt with 2,6-dimethylphenol and then its acryloyloxy derivative was 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 structure of the present compound has been determined by single-crystal X-ray diffraction. This synthesized azo-ester compound crystallizes in monoclinic system, space group P21/c with $Z = 4$. The thermal behaviour of the compound has been determined by means of differential thermal analysis (DTA) and thermogravimetry (TG) techniques.

Keywords: Acrylate; Azo-ester dyes; Diazenes; Crystal structure; Spectral and thermal analysis

1. Introduction

Colorants have been widely used as dyes owing to their versatility in various fields and high technologies which include textiles, plastics, biological staining, 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, crystal structure, 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 characterisation and synthesis of some *o,o′*-dihydroxyazo dyes containing an acryloyloxy group and their chromium complexes [7]. The acryloyloxy derivatives of *p*-hydroxyazo dyes can 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 present azo-ester compound which have polymerisable acryloyloxy group, the characterisation using IR, UV–vis, ^{1}H NMR and ^{13}C NMR spectroscopic techniques, and we also report here the crystal structure and thermal stabilities in solid state of the related azo-ester dye.

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2. Experimental

2.1. General

The spectrum was recorded on a FTIR-8900 SCHIMADZU IR spectrophotometer calibrated with polystyrene film using the KBr disc. Absorption spectra in ethanol, chloroform, and DMF were determined on a UNICAM UV2 UV–vis spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra in DMSO–d_6 were taken on Brucer AC 200 FT-NMR spectrometer referencing tetramethylsilane as internal standard. The crystal data were collected on Bruker AXS SMART CCD diffractometer. Thermal analysis was carried out with a Shimadzu DTG-GOH simultaneous thermal analyser combined with a TAS 100 thermogravimetric analyser using ca. 3.5 mg samples which were heated at a rate of 10 deg/min from ambient temperature to 600 °C. The measurement was obtained using a flowing nitrogen atmosphere. α-Al_2O_3 was used as a reference material. Elemental analysis was performed by TÜBİTAK, Marmara Research Center.

2.2. Crystal structure analysis

A suitable red crystal of 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenyl acrylate was mounted on a glass fibre. All measurements were made on a Bruker AXS SMART CCD difractometer with plane graphite monochromatic MoKα radiation. The data were collected at a temperature of 210(2) K to a maximum 2θ value of 58.30°. Twelve thousand hundred eighty-nine reflections were collected within the index ranges $-14 \leq h \leq 16$, $-18 \leq k \leq 15$, $-16 \leq l \leq 14$. An absorption correction was applied and resulted in transmission factor at max. 0.9850 and min. 0.9704. A summary of crystallographic data, experimental details, and refinement results for $C_{21}H_{24}N_2O_2$ are given in Table 1, while fractional atomic coordinates with isotopic displacement parameters are listed in Table 2. The structure was solved by direct-methods using SHELXS-97 [9] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [10]. All hydrogen atoms were located in geometric positions and included with a rigid model. Atomic scattering factors were taken from the *International tables for crystallography* [11].

Table 1
Crystal data and structure refinement for c1683fin

Identification code	c1683fin
Empirical formula	$C_{21}H_{24}N_2O_2$
Formula weight	336.42
Temperature	210(2) K
Wavelength	71.073 pm
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	$a = 1214.3(2)$ pm, $\alpha = 90°$ $b = 1351.1(3)$ pm, $\beta = 107.293(3)°$ $c = 1217.8(2)$ pm, $\gamma = 90°$
Volume	1.9077(6) nm^3
Z	4
Density (calculated)	1.171 Mg/m^3
Absorption coefficient	0.076 mm^{-1}
$F(000)$	720
Crystal size	$0.40 \times 0.30 \times 0.20$ mm^3
Theta range for data collection	1.76–29.15°
Index ranges	$-14 \leq h \leq 16$, $-18 \leq k \leq 15$, $-16 \leq l \leq 14$
Reflections collected	12189
Independent reflections	4683 [R(int) = 0.0307]
Completeness to theta = 29.15°	90.9%
Absorption correction	SADABS
Maximum and minimum transmission	0.9850 and 0.9704
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4683/2/330
Goodness-of-fit on F^2	1.018
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.0633$, $wR2 = 0.1508$
R indices (all data)	$R1 = 0.1125$, $wR2 = 0.1748$
Extinction coefficient	0.0033(15)
Largest difference peak and hole	0.224 and −0.200 e Å^{-3}

2.3. Preparation of the azo-ester compound

For the synthesis of 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenyl acrylate containing an acryloyloxy group, first 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)-phenol was prepared by reacting 4-*tert*-butylbenzene-diazonium salt with 2,6-dimethylphenol as described in the literature [12] and then its acryloyloxy derivative was synthesized in a Schotten–Bauman-type reaction similar to the following procedure.

To a stirred THF (20 ml) solution of sodium 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl) phenolate prepared from 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenol (2.48 mmol) and sodium metal (2.48 mmol), acryloyl chloride (2.48 mmol) was 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 the water. The solid filtered and washed several times with water and then dried. The product was crystallized from ethyl alcohol/water mixture to give present compound of m.p. 124–125 °C. Yield 42%. Elemental analysis values for the compound $C_{21}H_{24}N_2O_2$; calcd.: C, 74.97; H, 7.19; N, 8.33%; found: C, 74.93; H, 7.23; N, 7.95%. TLC monitored its purity. The compound was recrystalized from ethyl alcohol to produce crystals of suitable quality for X-ray diffraction analysis.

3. Results and discussion

3.1. Spectral characterisation

The spectral characterisation data of the azo-ester compound synthesized by Schotten–Bauman-type

Table 2
Fractional atomic coordinates with isotopic displacement parameter for the azo-ester compound

	x	*y*	*z*	*U*(eq)
O(1)	−265(1)	2683(1)	−2170(1)	56(1)
O(2)	−1949(2)	2952(2)	−1849(2)	94(1)
N(1)	2538(1)	3341(1)	2977(1)	46(1)
N(2)	2174(1)	3980(1)	2213(1)	48(1)
C(1)	3986(2)	4400(2)	6376(2)	47(1)
C(2)	3585(3)	5063(2)	5473(2)	75(1)
C(3)	3128(2)	4755(2)	4346(2)	71(1)
C(4)	3064(2)	3752(2)	4095(2)	44(1)
C(5)	3484(2)	3086(2)	4971(2)	54(1)
C(6)	3941(2)	3411(2)	6099(2)	54(1)
C(7)	4396(2)	4743(2)	7634(2)	56(1)
C(8)	4732(3)	5839(2)	7743(3)	77(1)
C(9)	5435(5)	4150(4)	8304(4)	133(2)
C(10)	3388(3)	4609(3)	8136(3)	92(1)
C(11)	1578(2)	3584(1)	1105(2)	43(1)
C(12)	1220(2)	2608(2)	919(2)	43(1)
C(13)	585(2)	2290(1)	−170(2)	45(1)
C(14)	334(2)	2990(2)	−1046(1)	43(1)
C(15)	683(2)	3970(2)	−900(2)	44(1)
C(16)	1312(2)	4257(2)	203(2)	47(1)
C(17)	186(3)	1237(2)	−382(2)	66(1)
C(18)	367(2)	4686(2)	−1896(2)	56(1)
C(19)	−1411(2)	2717(2)	−2489(2)	64(1)
C(20)	−1830(4)	2437(3)	−3732(3)	58(1)
C(21)	−2930(4)	2457(3)	−4283(3)	85(2)
C(20F)	−2408(12)	2526(11)	−3508(10)	52(4)
C(21F)	−1951(14)	2232(14)	−4276(15)	67(5)

reaction of 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)-phenol and acryloyl chloride are given in Table 3.

In the IR spectra of the compound, characteristic vibrational bond 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 ring vibrations [4]. The hydroxyl group in the compound does not appear due to the esterification between the hydroxyl group and the acryloyl chloride [6]. This was confirmed by showing an intensive absorption band at 1742 cm^{-1} which is characteristic of the carbonyl group of the acryloyl moiety. The other characterised stretching bands appearing at 1634, 1155, and 2960−2875 cm^{-1} in the spectrum of the compound are attributed to ethenyl ($CH_2{=}CH-$), ester ($>$CO−O), and *tert*-butyl/methyl groups ($(CH_3)_3C-$, CH_3-), respectively.

The UV−vis spectra of the azo-ester compound investigated in absolute ethyl alcohol, chloroform, and DMF exhibit one band at 334, 334, and 339 nm, respectively. These bands appear as absorption maxima with high extinction coefficient (4.512, 4.480, and 4.518 log ε l/mol cm) and are attributed to the $\pi \rightarrow \pi^*$ transitions. The absorption maxima of the compound in ethyl alcohol, demonstrated a hypochromic shift ca. 28 nm in comparison with 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenol [8]. This may be brought about by decreasing order of activation of the acryloyloxy moiety instead of the hydroxyl group. Further, the compound is hydrolysed with aqueous sodium hydroxide at pH 12 and produces the sodium salts of the 2,6-dimethyl-4-(4-*tert*-butylphenil)phenol and acrylic acid.

In ^{1}H NMR spectra of the azo-ester compound recorded in DMSO−d_6, when the peak of hydrogen atom in *z* configuration according to $>$C=O group in an acryloyl moiety is seen at 6.22−6.26 ppm as doublet, those of the other two hydrogen atoms in the same moiety at 6.52−6.66 ppm as multiplets in agreement with the literature values [6]. The attachment of an acryloyl group was confirmed by disappearing of the signal at 9.07 ppm in ^{1}H NMR spectra which are typical for hydroxyl proton of the 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenol which is the derivative of the present compound without acryloyl group [6,8]. The spectra for the compound exhibit a sharp singlet signal at 1.26 ppm (s, 9H) for *tert*-butyl, and 2.19 ppm (s, 3H) for methyl group. The multiples peaks appearing at 7.60−7.86 ppm (m, 6H), are also attributed to aromatic protons.

From the ^{13}C NMR spectra of the azo-ester compound, it is clearly seen that acryloyl group attaches to the oxygen of hydroxyl group because of $>$C=O group signal at 163.08 ppm in agreement with the literature value. The peaks appearing at 126.79 and 134.12 ppm in the spectra of the compound are attributed to CH and CH_2 fragments of the $CH_2{=}CH$ group, respectively, as expected. These values are in accordance with the literature [6]. Attaching the acryloyloxy group to C14 atom of the compound shifted by 7.65 ppm according to its derivative (156.65 ppm for 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenol). When the chemical shift values of C4 atom attached to nitrogen is 154.49 ppm, the signal of C11 atom attached to the other nitrogen appears at 149 ppm, approximately. Some chemical shift values were determined regarding the similar compound without acryloyloxy group in the literature [6,13] and the NMR values of the

Table 3
Spectral characterisation data for the azo-ester compound

UV−vis λ_{max} nm (log ε)			IR cm^{-1} in KBr			^{1}H NMR ppm in DMSO−d_6		^{13}C NMR ppm in DMSO−d_6	
In DMF	In chloroform	In ethanol	O−H	C=O	$CH_2{=}CH-$	OH	$CH_2{=}CH-$	C=O	$CH_2{=}CH-$
339(4.518)	334(4.48)	334(4.512)	−	1742	1634	−	6.22−6.72	163.08	126.79 and 134.12

compound are as shown below: 15.84, 30.84, 34.66, 122.16, 122.40, 126.08, 126.79, 131.13, 134.12, 149.46, 149.66, 149.86, 154.40, 163.08.

3.2. Thermal analysis

The present anhydrous compound was subjected to TG and DTA analysis from ambient temperature to 600 °C in flowing nitrogen atmosphere. Temperature ranges, phase transition temperature, experimental weight loss can be seen from the TG and DTA curves in Fig. 1. From the DTA curve of the compound, the melting process is accompanied by an endothermic phase change at 127 °C. The initial decomposition temperature taken as a parameter of thermal stability is 164 °C and then following the plateau in the TG curve is the endothermic decomposition in the temperature range 164–382 °C. Although the decomposition mechanism of the compound is complex, it basically consists of a heterolytic splitting of azo bonds known as 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 [15].

3.3. Description of the crystal structure

A view of the molecule of 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenyl acrylate with the atom labelling, and molecular packing are shown in Figs. 2 and 3, respectively. The selected bond distances and angles are given in Table 4.

The dihedral angle, θ_1 between the main planes of the 4-*tert*-butylphenyl ring and the C4–N1=N2–C11 azo bridge is 5.93(4)° and the angle θ_2 between the C4–N1=N2–C11 azo group and the 3,5-dimethyl-4-acryloyloxyphenyl ring is 12.46(9)°. The angle θ_3 between the planes of these rings is 17.12(5)°. The value of θ_3 is a little larger than those in (E)-2,6-dimethyl-4-(4-chlorophenyldiazenyl)phenol [($\theta_3 = 5.48(10)$] as reported previously [16]. The methyl groups in *ortho*-positions will probably cause the acryloyloxy moiety to rotate out conjugation with the benzene ring, thus leading to a loss of planarity. As a result, the two phenyl rings which adopt a *trans*-configuration according to the diazene double bond, are nearly in the same plane with the angle 17.12(5)°.

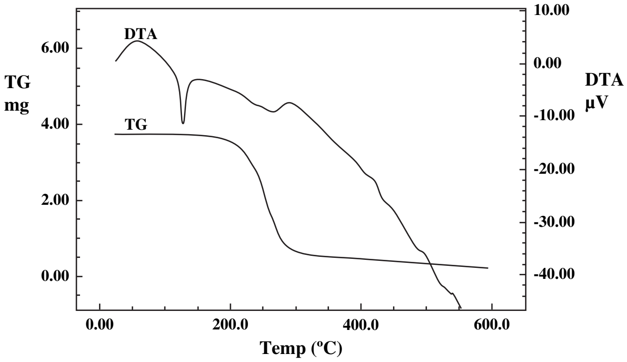

Fig. 1. The TG and DTA curves for the azo-ester compound.

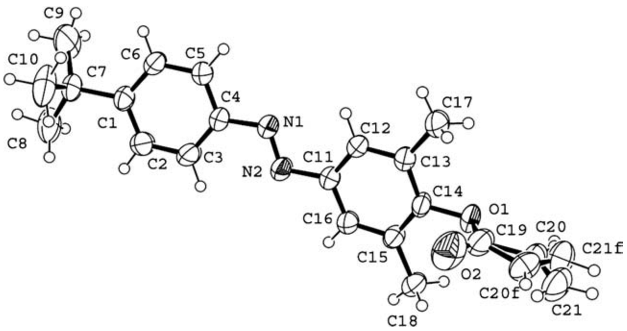

Fig. 2. A view of structure for the azo-ester compound.

In the crystal structure of the present compound, C20 is observed at two different positions due to an orientational disorder. It is indicated in Fig. 2 as C20f. Their ratios are %80 and %20, respectively. Similarly C21 is observed at two positions (C21f) where their ratios are %20 and %80, respectively.

The N1–C4 and N2–C11 bond lengths of 1.432(2) and 1.431(2) Å, respectively, indicate single-bond character, a result consistent with those found for similar 4,4-disubstitutedazobenzene derivatives containing intermolecular hydrogen bond studied recently [16,17]. The –N=N– bond length of 1.250(1) Å indicates significant double-bond character. There are no intermolecular interactions other than van der Waals

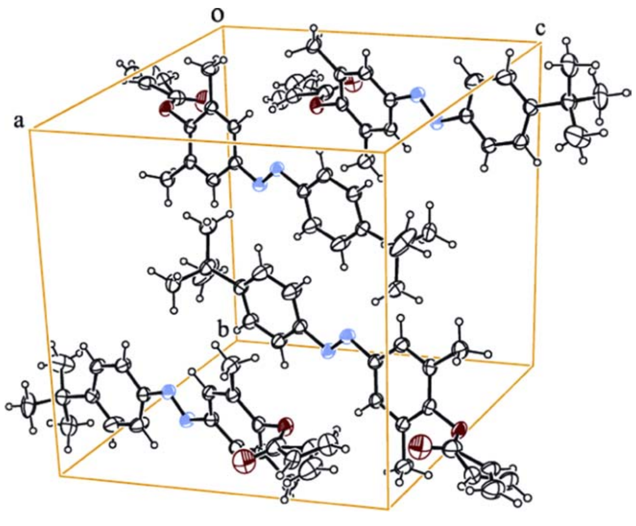

Fig. 3. Molecular packing for the azo-ester compound.

Table 4
Selected bond distances and angles (Å, °)

O1–C19	1.331(3)	C9–C7–C8	107.9(3)
O1–C14	1.408(2)	C12–C11–N2	123.79(17)
O2–C19	1.199(3)	C16–C11–N2	115.74(17)
N1–N2	1.250(2)	C11–C12–C13	120.54(17)
N1–C4	1.432(2)	O2–C19–O1	122.9(2)
N2–C11	1.431(2)	O2–C19–C20F	97.1(6)
C19–C20F	1.475(11)	O1–C19–C20F	139.9(6)
C19–C20	1.494(5)	O2–C19–C20	129.7(3)
C20–C21	1.305(5)	O1–C19–C20	107.4(3)
C20F–C21F	1.284(16)	C20F–C19–C20	32.6(5)
C4–C5	1.373(3)	C21–C20–C19	120.3(5)
C11–C12	1.386(3)	C21F–C20F–C19	104.0(13
C1–C7	1.534(3)		
C7–C8	1.531(4)	C4–N1–N2–C11	−176.10(15)
C13–C17	1.501(3)	N2–N1–C4–C3	3.0(3)
		N1–N2–C11–C12	12.5(3)
C19–O1–C14	117.87(17)	N1–N2–C11–C16	−170.90(17)
N2–N1–C4	113.56(16)	C14–O1–C19–O2	−3.5(3)
N1–N2–C11	114.30(16)	C19–O1–C14–C15	−93.3(2)
C5–C4–N1	116.27(18)	C19–O1–C14–C13	89.8(2)
C3–C4–N1	124.63(18)	C17–C13–C14–O1	−3.1(3)
C4–C5–C6	120.5(2)	C18–C15–C14–O1	3.6(3)

contacts between the molecules which are therefore present as isolated individuals within the crystal.

4. Conclusion

In present work, we report the synthesis of the azo-ester compound which have polymerisable acryloyloxy group, and the characterisation using IR, UV–vis, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. The related structure shown by X-ray diffraction reports here the crystal structure and thermal stabilities in solid state of the related azo-ester dye.

The attachment of an acryloyl moiety was confirmed by the $>$C=O group signal appearing at 163.08 ppm in the ^{13}C NMR spectra, showing an intensive absorption band at 1742 cm^{-1} characteristic of the carbonyl group, and by disappearing of the signal at 9.07 ppm in ^{1}H NMR spectra which are typical for hydroxyl proton of the 2,6-dimethyl-4-(4-*tert*-butylphenyldiazenyl)phenol.

The synthesized azo-ester compound crystallizes in monoclinic system; space group P21/c with $Z = 4$. In the structure of the compound, two phenyl rings which adopt a *trans*-configuration, are nearly in the same plane. The C20 and C21 atoms are founded at two different positions because of an orientational disorder.

The thermal behaviour of this compound has been determined by means of differential thermal analysis (DTA) and thermogravimetry (TG) techniques. From the DTA and TG curves of the present compound, the melting process is accompanied by an endothermic phase change at 127 °C. The compound is stable up to 164 °C and then decomposes in 164–382 °C temperature interval at one stage.

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