

## Spectroscopic, Thermal and Crystal Structure Properties of 4-Nitro-4'-[N-Ethyl-N-(2-Hydroxyethyl)-Amino]azobenzene Acrylate Dye

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**Abstract:** 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene acrylate (C<sub>19</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>) containing an acryloxy group, first 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene was prepared by reacting 4-nitrobenzenediazonium salt with N-ethyl-N-hydroxy ethyl aniline and then its acryloxyloxy derivative was synthesized in a Schotten-bauman type reaction. The characterization of the synthesized azo-ester dye has been described by IR, UV-vis, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopic techniques. The structure of the present compound has been determined by single-crystal X-ray diffraction. The synthesized azo-ester compound crystallizes in orthorhombic, space group P212121 with Z=4. The thermal behavior of compound has been determined by Differential Scanning Calorimetry (DSC) technique.

**Key words:** Acrylate · Azo-ester dyes · Diazenes · Crystal structure · Spectral and thermal analysis

### INTRODUCTION

Colorants have been widely used as dyes owing to their versatility in various field and high technologies which include textiles, plastics, biological staining and lasers. Liquid crystalline displays, electro-optical devices and ink jet printers [1, 2].

Azo colorants are the most versatile class of dyes [3]. Spectral data, crystal structure and thermal analysis play an important role in studying their structure [4]. The literature reported so far on azo-ester compounds containing unsaturated group like acryloyloxy moiety is scarce [5]. It have been previously reported the characterization and synthesis of some o,o'-dihydroxyazo dyes containing an acryloyloxy group and their chromium complexes [5]. 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]. In present work, we report the synthesis of the present azo-ester compound which have polymerisable acryloyloxy group, the characterization using IR, UV-vis, <sup>1</sup>H NMR and <sup>13</sup>C NMR

spectroscopic techniques and we also report here the crystal structure and thermal properties of the related azoester dye.

### Experimental

**General:** The spectrum was recorded on a FTIR-8101 M-Shimadzu IR spectrophotometer calibrated with polystyrene film using the KBr disc. Absorption spectrum in ethanol and was determined on a Perkin Elmer Lambda 15 spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were taken on Broker 2500 FT-NMR spectrometer referencing tetramethylsilane as internal standard. The crystal data were collected on a STOE IPDS-II diffractometer. Thermal analysis was carried out with the Perkin-Elmer (DSC-4). 4.4mg sample was heated at a rate of 5 deg/min from ambient temperature to 140°C.

**Crystal Structure Analysis:** A suitable red crystal of 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene acrylate was mounted on a glass fiber. All measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-K<sub>α</sub> radiation. Data were collected at a temperature of 120(2) K to a maximum  $\theta$  value of 27.94°.

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Table 1: Crystal data and structure refinement for Kh45-abs1

Identification code Empirical	Kh45-abs1
formula	C <sub>19</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub>
Formula weight	368.39
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system Space group Unit cell dimensions	Orthorhombic, P212121 a=8.1518(9) Å alpha= 90 deg b=10.6651(11) Å beta=90 deg c=20.6782(19) Å gamma=90
Volume	1797.8(3) Å <sup>3</sup>
Z Density (calculated)	4, 1.361 Mg/m <sup>3</sup>
Absorption coefficient	0.098 mm <sup>-1</sup>
F(000)	776
Crystal size	0.5 x 0.2 x 0.06 mm
Theta range for data collection	1.97 to 27.94 deg
Limiting indices	-10<=h<=10, -14<=k<=14, -27<=l<=26
Reflections collected / unique	15596 / 4331 [R(int)= 0.0441]
Completeness to theta	27.94 99.2%
Absorption correction	Numerical
Max. and min. transition	0.994 and 0.977
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4331 / 0 / 244
Goodness-of-fit on F <sup>2</sup>	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0806
R indices (all data)	R1 = 0.0346, wR2 = 0.0819
Absolute structure parameter	-0.1 (7)
Largest diff. peak and hole	0.214 and -0.215 e.Å <sup>-3</sup>

Fifteen thousand fifty nineteen six reflections were collected within the index ranges  $-10 \leq h \leq 10$ ,  $-14 \leq k \leq 14$ ,  $-27 \leq l \leq 26$ . An absorption correction was applied and resulted in transmission factor at max. 0.994 and min. 0.977. A summary of crystallographic data, experimental details and refinement results for C<sub>19</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub> have been given in Table 1, while fractional atomic coordinates with isotopic displacement parameters are listed in Table 2. The structure was solved by direct methods and subsequent difference Fourier maps and then refined on F<sup>2</sup> by a full-matrix least-squares procedure using anisotropic displacement parameters [7]. All of hydrogen atoms were located in a difference Fourier map and then after refined isotropically. Atomic scattering factors were taken from the International tables for crystallography [8].

**Preparation of the Azo-Ester Compound:** For the synthesis of 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene acrylate dye containing an acryloyloxy group, 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene was prepared by reacting 4-nitrobenzenediazonium salt with N-ethyl-N-hydroxyethyl aniline as described in the literature [9] and then its acryloyloxy derivative was synthesized in a Schotten-

Table 2: Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for Kh45-abs1

	x	y	z	U(eq)
C(1)	8463(2)	755(1)	1285(1)	19(1)
C(2)	8210(2)	1881(2)	1607(1)	21(1)
C(3)	6730(2)	2057(1)	1929(1)	21(1)
C(4)	5541(2)	1120(1)	1925(1)	19(1)
C(5)	5829(2)	-1(1)	1590(1)	24(1)
C(6)	7297(2)	-192(1)	1266(1)	23(1)
C(7)	1633(1)	633(1)	2631(1)	18(1)
C(8)	1223(2)	1705(1)	2991(1)	19(1)
C(9)	-264(2)	1780(1)	3304(1)	19(1)
C(10)	-1444(2)	796(1)	3267(1)	17(1)
C(11)	-976(2)	-305(1)	2929(1)	19(1)
C(12)	516(2)	-365(1)	2617(1)	19(1)
C(13)	-4126(2)	-128(1)	3565(1)	22(2)
C(14)	-3749(2)	-1062(1)	4104(1)	31(1)
C(15)	-3504(2)	2118(1)	3808(1)	20(1)
C(16)	-3071(2)	2231(1)	4520(1)	21(1)
C(17)	-3026(2)	3847(1)	5292(1)	22(1)
C(18)	-3578(2)	5121(1)	5479(1)	27(1)
C(19)	-4338(2)	5900(2)	5094(1)	40(1)
N(1)	10046(1)	551(1)	963(1)	22(1)
N(2)	4069(1)	1380(1)	2273(1)	21(1)
N(3)	3099(1)	447(1)	2289(1)	19(1)
N(4)	-2965(1)	920(1)	3537(1)	19(1)
O(1)	11031(1)	1420(1)	946(1)	36(1)
O(2)	10316(1)	-489(1)	726(1)	32(1)
O(3)	-3643(1)	3455(1)	4725(1)	22(1)
O(4)	-2112(1)	3222(1)	5623(1)	30(1)

Bauman-type reaction similar to the following procedure. To a stirred THF (15 ml) solution of sodium 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene salt prepared from 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene (1.5 mmol) and sodium metal (1.5 mmol), acryloyl chloride (1.5 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 to give present compound of m.p. 111-112°C (Yield 63%). TLC monitored its purity. The compound was recrystallized from ethyl alcohol to produce crystals of suitable quality for X-ray diffraction analysis.

## RESULT AND DISCUSSION

**Spectral Characterization:** The spectral characterization data of the azo-ester compound synthesized by Schotten-Bauman-type reaction of 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene and acryloyl chloride have been given in Table 3.

In the IR spectrum of the compound, characteristic vibrational bond observed at ca. 1410 and 1140  $\text{cm}^{-1}$  for N=N- and -C-N= groups were not given because these absorptions are also quite variable and often obscured by phenyl ring vibrations [3]. 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 1728  $\text{cm}^{-1}$  which is characteristic of the carbonyl group of the acryloyl moiety. The other characterized stretching bands appearing at 1603, 1141 and 2979-2875  $\text{cm}^{-1}$  in the spectrum of the compound are attributed to ethenyl ( $\text{CH}_2=\text{CH}$ -), ester (CO-O) and ethyl/methyl groups, respectively.

The UV-vis spectrum of the azo-ester compound investigated in absolute ethyl alcohol, exhibits one band at 460 nm. This band appear as absorption maxima with high extinction coefficient and is attributed to the  $\pi \rightarrow \pi^*$  transition. The absorption of the compound in ethyl alcohol, demonstrated a hypsochromic shift ca. 20 nm in comparison with 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-

amino]azobenzene. This may be brought about by decreasing order of activation of the acryloyloxy moiety instead of the hydroxyl group.

In  $^1\text{H}$  NMR spectrum of the azo-ester compound recorded in  $\text{CDCl}_3$ , when the peak of hydrogen atom in z configuration according to -C=O group in an acryloyl moiety is seen at 6.06-6.17 ppm as doublet of doublet, those of the other two hydrogen atoms in the same moiety at 5.84-5.89 ppm and 6.38-6.46 ppm as doublet of doublet in agreement with the literature values [6]. The attachment of an acryloyl group was confirmed by disappearing of the signal at 1.75 ppm in  $^1\text{H}$  NMR spectra which are typical for hydroxyl proton of the 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino] azobenzene which is the derivative of the present compound without acryloyl group. The spectrum for the compound exhibits a sharp singlet signal at 1.28 ppm (t, 3H) for  $\text{CH}_3$  group, 3.56 ppm (q, 2H) for  $\text{CH}_2-\text{CH}_3$ , 3.75 ppm (t, 2H) for  $\text{CH}_2-\text{N}$ -, 4.4 ppm (t, 2H) for  $\text{CH}_2-\text{O}$ -. The peaks appearing at 6.82-8.35 ppm (6H), are also attributed to aromatic protons.

From the  $^{13}\text{C}$  NMR spectrum 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 167.8 ppm in agreement with the literature value. The peaks appearing at 127.9 and 131.6 ppm in the spectrum of the compound are attributed to CH and  $\text{CH}_2$  fragments of the  $\text{CH}_2=\text{CH}$  group, respectively, as expected. The NMR values of the compound are as shown below: 12.3, 45.9, 49.0, 61.04, 111.8, 122.6, 124.7, 126.8, 127.9, 131.6, 143.9, 147.5, 151.2, 156.8 and 167.8.

**Thermal Analysis:** The DSC traces obtained with a small sample of azo compound at a rate of 5°C/min. The lower curve in Figure 1 corresponds to a heating process. This is followed by a cooling process, represented in the upper curve. During the first heating, the sharp endothermic peak can be seen at 111.55°C, while two phases transition at 49.3, 53.15°C are detected in the cooling cycle. These result shows the acrylate compound has liquid crystal property, probably. One curious aspect of this thermogram is that the freezing point of a sample is much lower than its melting point. This is due to an effect called hysteresis. Hysteresis has two principal causes.

Table 3: Spectral characterization data for the azo-ester compound

UV-vis $\lambda_{\text{max}}$ nm		IR $\text{cm}^{-1}$ in Kbr		$^1\text{H}$ NMR ppm in $\text{CDCl}_3$		$^{13}\text{C}$ NMR ppm in $\text{CDCl}_3$	
In ethanol	O-H	C=O	$\text{CH}_2=\text{CH}$ -	OH	$\text{CH}_2=\text{CH}$ -	C=O	$\text{CH}_2=\text{CH}$ -
460	-	1728	1603,1141	-	5.84-6.17	167.8	127.9-131.6

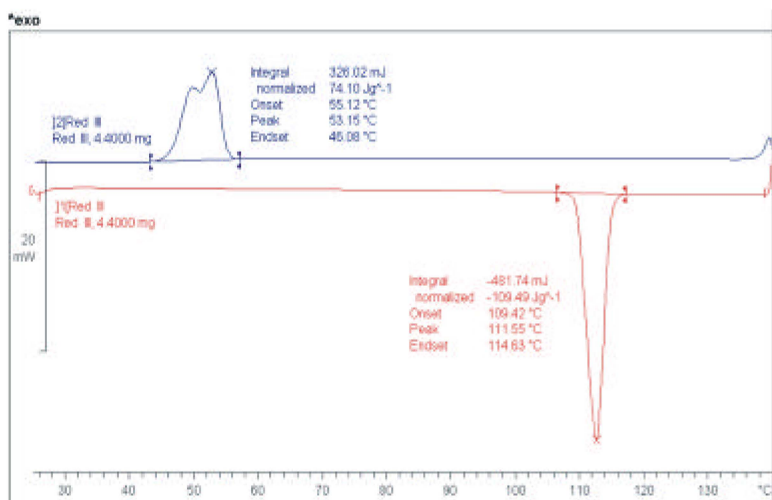


Fig. 1: DSC Thermogram analysis of single crystal azo compound at a rate of 5°C/min

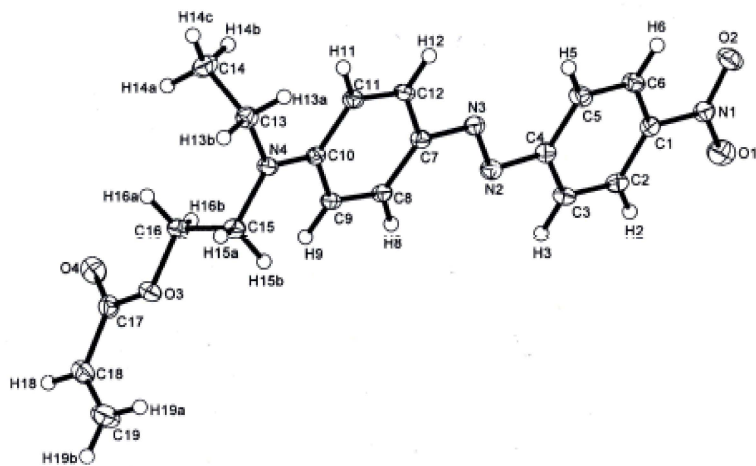


Fig. 2: A view of structure for the azo-ester compound

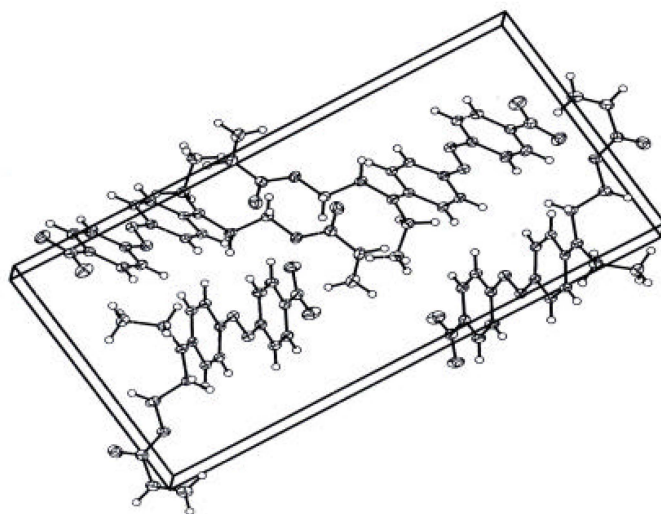


Fig. 3: Molecular of packing for the azo-ester compound

The thermal history of a sample plays a large role. As this sample was heated and cooled repeatedly, hysteresis was obvious. Hysteresis is also an inherent physical property, as solid are more oriented than liquids. Orienting, especially into complex crystalline structures, is more difficult and unpredictable than disordering [10].

**Description of the Crystal Structure:** A view of the molecule of 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene acrylate with the atom Labeling and molecular packing have been shown in Figures 2 and 3, respectively. The selected bond distances and angles have been given in Table 4. The dihedral angle,  $\theta_1$  between the main planes of the 4-nitro-phenyl ring and the C4-N1=N2-C11 azo bridge is  $5.93(4)^\circ$  and the angle  $\theta_2$  between the C4-N1=N2-C11 azo group and the N-ethyl-N-acryloyloxyethyl phenyl ring is  $12.46(9)^\circ$ . The angle  $\theta_3$  between the planes of these rings is  $17.12(5)^\circ$ . The N3-C7 and N2-C4 bond lengths of  $1.4020(15)$  and  $1.4266(16)$  Å $^\circ$ , respectively, indicate single-bond character, a result consistent with those found for similar 4, 4-disubstituted azobenzene derivatives containing intermolecular hydrogen bond studied recently [11]. The -N=N- bond length of  $1.2714(14)$  Å $^\circ$  indicates significant double-bond character. There are no intermolecular interactions other than van der Waals contacts between the molecules which are therefore present as isolated individuals within the crystal (CCDC No.665351).

## CONCLUSION

In present work, we report the synthesis of the azoester compound which have polymerisable acryloyloxy group and the characterisation using IR, UV-Vis,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopic techniques. The related structure has been 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  $167.8$  ppm in the  $^{13}\text{C}$  NMR spectrum, showing an intensive absorption band at  $1728\text{ cm}^{-1}$  characteristic of the carbonyl group and by disappearing of the signal at  $1.75$  ppm in  $^1\text{H}$  NMR spectrum which are typical for hydroxyl proton of the 4-nitro-4'-[N-ethyl-N-(2-hydroxyethyl)-amino]azobenzene. The synthesized azo-ester compound crystallizes in orthorhombic system; space group P212121 with  $Z=4$ . In the structure of the compound, two phenyl rings which adopt a trans-

onfiguration are nearly in the same plane. The thermal behavior of this compound has been determined by differential Scanning Calorimetry (DSC) technique. From the DSC curve of the present compound, the melting process is accompanied by an endothermic phase change at  $111.55^\circ\text{C}$ .

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