Asian Journal of Chemistry Vol. 22, No. 3 (2010), 1944-1948

Optical and Printability Properties of 2-[[4-(Aminosulfonyl)-phenyl]hydrazono]-N-(4-ethoxyphenyl)-3-oxobutanamide

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The synthesis and characterization of 2-[[4-(aminosulfonyl)phenyl]-hydrazono]-N-(4-ethoxyphenyl)-3-oxobutanamide (**SM1**) for a potential use in the formulations of printing inks were employed. Following this, **SM1** was applied to an ink formulation and its printability together with densitometric and spectrophotometric colour values were examined by comparison with PY3 as a standard pigment. It was observed that the proposed dye had reasonable gloss, colour direction, transparency, mass colour, rub resistance, light fastness, densitometric and spectro-photometric values (CIE L* a* b*). These results indicated that the proposed compound could be used in oil based offset ink production as a pigment.

Key Words: Optical properties, Yellow pigment, Hydrazo compound, Printability, Rub resistance, Printing ink.

INTRODUCTION

The azo/hydrazo chromophores are of great importance in organic chemistry because of their usage as colouring agents in a large number of products such as food, cosmetics, textile, paper, *etc.*[1-4]. Many azo and hydrazo compounds are also used in the manufacturing of printing inks. Yellow organic pigments are used in many industrial print and ink applications. Pigments of acetoacetanilide derivatives such as yellow 74 and PY3 are commonly used pigments in ink preparation (Fig. 1). In present study, a compound derived from this class, 2-[[4-(aminosulfonyl)phenyl]-hydrazono]-N-(4-ethoxyphenyl)-3-oxobutanamide (**SM1**) was planned to synthesize a pigment with lower toxicity for the printing ink formulation and its printability was evaluated. 2-[[4-(Aminosulfonyl)phenyl]hydrazono]-N-(4-ethoxyphenyl)-3-oxobutanamide was then characterized by elemental analysis, UV, IR, ^{1}H NMR and mass spectroscopic methods.

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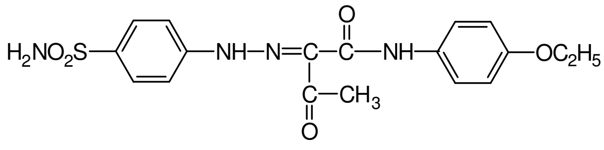
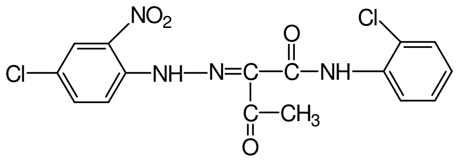
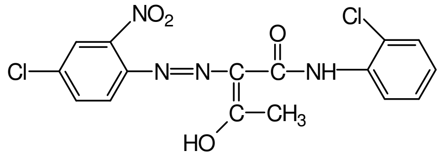


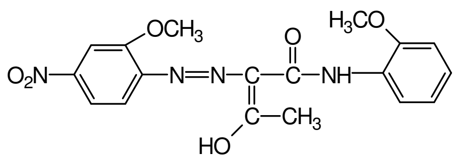
SM1



PY3 (Hydrazo form)



PY3 (Azo-enol form)



Yellow 74 (Azo-enol form)

Fig. 1. Structural formula of **SM1** and related pigments

EXPERIMENTAL

Synthesis and characterization of SM1: To a cooled aqueous solution of sulfanilamide (0.01 mol) in 2 mL of hydrochloric acid (37 %) an ice-cold solution of sodium nitrite (10 %) was added. The reaction mixture was then poured into a mixture of acetoacetyl-4-phenetidide (0.01 mol) and 60 g of sodium acetate in (50 % ethanol) by stirring[5]. The precipiated yellow solid is filtered and recrystallized from ethanole. Yield = 3.8 g (90 %). m.p. 200-210 °C (decomposed). UV (Shimadzu UV-2100s spectrophotometer) (EtOH) λ_{max} (nm): 377 (ε:50217), 251 (ε:25735), 205 (ε:25896). IR Spectrum (Perkin-Elmer 577 spectrophotometer) (KBr) ν_{max} (cm^{-1}): 3335, 3235 (sulphanilamide -NH); 3068 (hydrazone -NH); 1662 (ketone C=O); 1615 (amide C=O); 1597, 1557, 1529, 1474 (hydrazone C=N, aromatic C=C); 1333, 1157 (O=S=O); 850 (1,4-disubstituted benzene). ^{1}H NMR (Bruker AVANC-DPX 400 spectrometer; 400 MHz, DMSO-d_6/TMS) δ ppm: 1.32 (3H, t, -CH_2-CH_3); 1.74 (3H, s, -CH_3); 4.00 (2H, q, -CH_2-CH_3); 6.90 (2H, d, *m*-protons to the -SO_2-NH_2); 7.28 (2H, br. s., -SO_2-NH_2); 7.59 (2H, d, *o*-protons to the -O-CH_2-CH_3); 7.61 (2H, d, *m*-protons to the -O-CH_2-CH_3) ; 7.81 (2H, d, *o*-protons to the -SO_2-NH_2); 11.93 (1H, br, s., amide -NH). Anal. (Perkin-Elmer 240C): found: C 53.45; H 4.98; N 13.85. $C_{18}H_{20}N_4O_5S$ requires: C 53.31; H 4.86 ; N 13.65. Mass (Agilent 1100 MSD spectrometer; API-ES, m/z): 404 (M^+), 403 (M^+-1), 339 (M^+-64), 255, 241, 277, 220, 137, 113, 89,75, 59.

Preparation of the ink dispersions and the printing experiment: The ink formulations from both the synthesized pigment (**SM1**) and the standard pigment used in the offset process ink formulations (PY3, the colour index number of 11710) were prepared separately in the following recipies. Ingredients of ink (total 100 %) are test varnish (phenolic resin based) 62, alkyd resin (linseed oil based isophthalic alkyd) 10, drier (cobalt and manganese octoate) 1.5, skin preventer (hydroquinone) 0.5, PE wax (micronized polyethylene powder wax) 1, pigment 15 and mineral oil.

In the preparation of the inks, the pigment particles were dispersed in a triplicate cylinder in about 10 micron size. The track value was adjusted in between 7.0-7.5 by the addition of the mineral oil.

Printing technique: The printability test of the ink was carried out using a Prüfbau/Peissenberg multipurpose printability tester and a test print equipment from IGT. The printing was accomplished using 3 g/m^2 ink on glossary paper of 135 g/m^2. When the test prints were dried completely, the following tests were employed.

Gloss test: A gardner glossmeter with micro reflectance mirror was used. The gloss parameter was measured photoelectrically with a ± 0.3 linearity by the light exposed to print sample with an angle of 60º.

Densitometric measurements: The densitometric measurements were taken using a D 19 C Gretag Macbeth Reflection Densitometer. The calibration was done over the unprinted surface of the paper. The CMYK colour values (cyan-magenta-yellow and black, respectively) were obtained from the measurement of the printed paper.

Spectrophotometric measurements: The colorimetric values of the print were measured using light source corresponding to the 5000 K daylight with a Spectro Eye Gretag-Macbeth spectrophotometer.

Light fastness test: The fastness degree of the pigment was evaluated by a Solarbox equipment according to the Blue Wool Scale by allowing it to stand for 192 h under a xenon light with a power of 1500 w/m^2 in a closed environment.

Rub resistance test: This was carried out using a Sutherland rub tester with a 924 g weight. The test was done with 30 oscillation for the coated gloss paper.

RESULTS AND DISCUSSION

2-[[4-(Aminosulfonyl)phenyl]hydrazono]-N-(4-ethoxyphenyl)-3-oxobutana-mide (**SM1**) was synthesized according to the Fig. 2 as described in the text[5]. The UV, IR, ^{1}H NMR and mass analysis confirmed the proposed structure and the results from analysis are in accordance with previous studies[6]. The coupling products may have azo or hydrazo tautomeric form according to the chemical nature of the active hydrogen component used in the synthesis[7]. The printability tests showed that the proposed compound could meet the demands of reasonable gloss, colour direction, transparency, mass colour, rub resistance, light fastness, densitometric and spectrophotometric values (Commission Internationale de I'Eclairage CIE L* a* b* and c, h values) by comparison with the standard pigment PY3 (Table-1). Finally, this compound

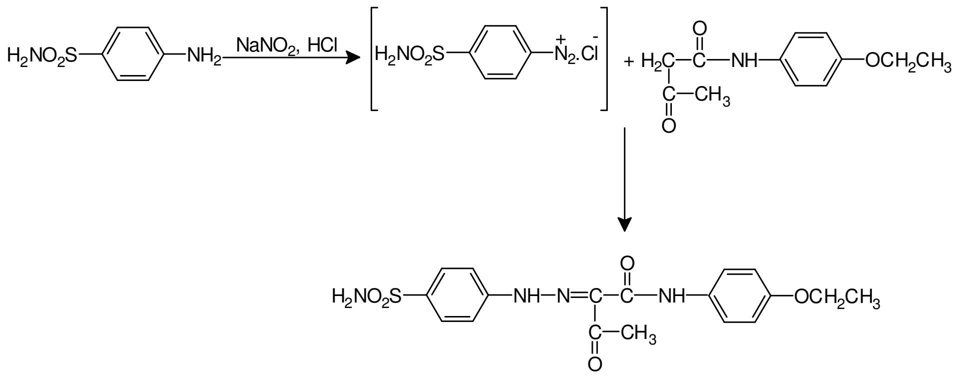


Fig. 2. Synthesis of **SM1**

TABLE-1
TEST VALUES OBTAINED WITH PY3 AND **SM1**

Tests		PY3	**SM1**
Gloss		44.5	44.8
Colour direction*		Standard	Dark yellow
Transparency*		Standard	More transparent
Mass colour*		Standard	Dark yellow
Rub resistance* (in coated gloss paper)		Standard	Reasonable
Densitometric values (in coated gloss paper)	D_Y	0.46	0.33
	D_M	0.01	0.02
	D_C	0.02	0.01
	D_K	0.02	0.02
Spectrophotometric values (in coated gloss paper)	L	89.19	90.11
	a	-10.12	-15.60
	b	47.82	65.85
	c	48.88	67.68
	h	101.95	103.33
Light fastness		6-7	3-4

where PY3 and **SM1** are standard and test pigments; and D_Y, D_M, D_C and D_K are densities of yellow, magenta, cyan and black, respectively.
*These characteristics were evaluated visually.

could be suggested for the use in oil based ofset printing ink formulations. On the other hand, the synthetic procedure employed was quite simple and cheap which could also be another advantage for the bulk production. The potential toxicity and mutagenity of azo dyes are well known property[8,9]. Azo dyes are reported to be more toxic compared to hydrazones[10]. Therefore, this compound can be suggested in a safe pigment in the ink production. The metabolic and toxicologic studies on **SM1** are currently investigated in our laboratory.

Conclusion

A novel hydrazone pigment, 2-[[4-(aminosulfonyl)phenyl]hydrazono]-N-(4-ethoxyphenyl)-3-oxobutanamide (**SM1**), was synthesized with a high yield. **SM1** can be used in oil based offset ink production as a pigment.

ACKNOWLEDGEMENT

The authors acknowledge Müge Mengüberti, Research Engineer from DYO Printing Ink Company, Izmir for her enormous help for the printability experiment of this compound.

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(*Received*: 28 April 2009; *Accepted*: 25 November 2009) AJC-8079