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Synthesis and Application of Disperse Dyes Derived from 2-Aminothiophene Using Acetoacetanilide as the 1, 3-Dicarbonyl Compound

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Abstract:

Disperse dyes derived from 2-aminothiophene diazo components was synthesized using via Gewald reaction, the intermediate were diazotized, coupled and the dyes were purified by re-crystallization. The melting points were found to span from 163°C- 209°C and spectroscopic assessment such as FT-IR spectroscopy and GC-MS were carried out to elucidate their structures. The vibrational frequency obtained for the synthesized dyes shows the characteristics absorption peaks due to stretching frequency of the NH-group in the region 3097-3365cm⁻¹. An absorption peak in the region 2217.8, 2221.5, 2214.0, 2206.6cm⁻¹ was observed for dye A, A1, B and B1 due to the presence of cyano group. The IR spectra of the prepared azo dye also showed an absorption peak in the region 1438.8-1599cm⁻¹ ascribed to $\nu_{N=N}$, while the observed vibrational frequency in the region 1602.8-1736.9 was due to $\nu_{C=O}$. The disperse dye A, A1, B and B1 were applied at 2% depth on polyester and nylon 6,6 fabric and gave purple, deep purple and deep pink hues with brighter and deeper shades, tinctorial strength and excellent levelness on the fabric. All the dyes show good to excellent fastness to washing on polyester fabric and fair to very good fastness to washing on nylon 6,6 fabric respectively. The remarkable degree of levelness and brightness after washing indicate good penetration and excellent affinity of the dyes to the fabric. However, dye C and dye C1 gave yellowish to deep yellowish hues with excellent tinctorial strength and brightness on the nylon 6,6 fabric. However, the light fastness ratings of the dyed polyester and nylon 6,6 fabric shows moderate to very good light fastness.

Keywords: Disperse dyes, 2-aminothiophene, Nylon 6, 6 and Polyester fabric

1. Introduction

Interest in the design of azo dyes containing heterocyclic moieties stems from their high degree of brightness compared to azo dyes derived from anilines (Town, 1999). The 2-aminothiophene based azo dyes are known as disperse dyes with excellent brightness of shade. This class of dyes was established as an alternative to more expensive anthraquinone dyes. The thiophene-containing azo dyes have many advantages including a colour deepening effect as an intrinsic property of the thiophene ring and small molecular structure leading to better dye ability. The heterocyclic nature of the thiophene ring has also allowed for excellent sublimation fastness on the dyed fibers increasing the electron withdrawing strength of the substituents on the thiophene ring resulted in bathochromic shifts. Additionally, the sulfur atom plays a decisive role by acting as an efficient electron sink as explained by valence band theory. (Godon and Gregory, 1983)

The use of heterocyclic diazo components is now becoming a prime area of research by dye chemist and remarkable successes have been recorded. The colour range of these dyes extends to blue and blue green, hitherto the exclusive domain of the anthraquinones. Although hydroxyl groups are known to be electron donors, they are less efficient

in arylazo phenol versus aryazo naphthol structure. This is because the naphthol system does not lose full aromatization when electron delocalization occurs. Therefore, p-N, N-dimethylaminobenzaldehyde couplers generally give dyes that are more bathochromic than phenol-based dyes. The two main thrusts of dyestuffs research have been improved technical excellence and greater cost effectiveness. One long-term aim had been to combine the brightness and high fastness properties of anthraquinone dyes with the strength and economy of azo dyes, (Maradiya and Patel, 2002a).

2. Materials and Methods

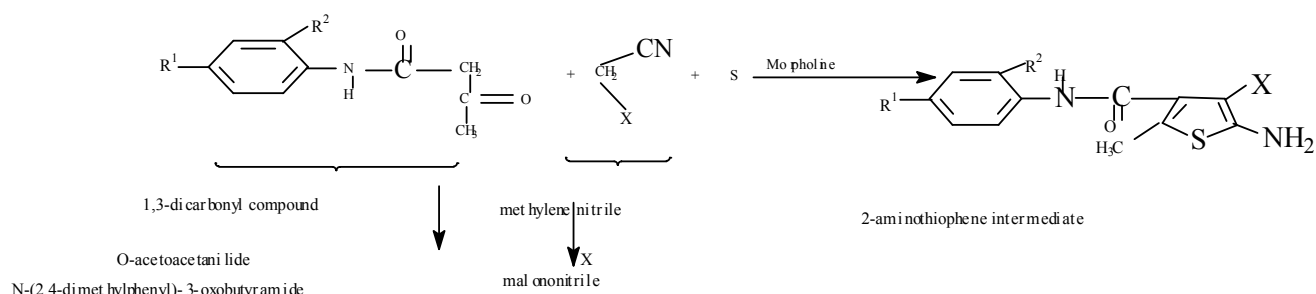
2.1. Materials

o-acetoacetanilide, N-(2,4-dimethylphenyl)-3-oxobutyramide, N,N-dimethylaniline, p-N,N-dimethylaminobenzaldehyde, malononitrile, morpholine, propionic acid, acetic acid, dimethylformamide (DMF), dimethylsulfoxide (DMSO), sodium nitrite, concentrated sulphuric acid, mueller hinton agar, potato dextrose agar, nutrient agar, Magnetic stirrer, oven, reflux condenser, melting point apparatus, Uv-visible spectrophotometer, Fourier transform infra-red spectrophotometer, GC-MS.

3. Methods

3.1. Synthesis of Intermediates

The aminothiophene intermediate was synthesized by following methods reported in the literature (Alaa and Tarek, 2006).



3.1.1. Aminothiophene Intermediate 1

o-acetoacetanilide (21.16g, 0.1mol), malononitrile (6.96g, 0.1mol) and sulphur (3.37g, 0.1mol) in ethanol were stirred in the presence of morpholine (8.97g, 0.1mol) at 60-70°C for 3hrs, followed by filtration, washing with ethanol and then ethanol/water (1:1) solution and was dried. The light brown powder obtained was crystallized from ethanol.

3.1.2. Aminothiophene Intermediate 2

N-(2,4-dimethylphenyl)-3-oxo-butyramide (20.72g, 0.1mol), malononitrile (6.96g, 0.1mol) and sulphur (3.37g, 0.1mol) in ethanol were stirred in the presence of morpholine (8.7g, 0.1mol) at 60-70°C for 3hours. Followed by washing with ethanol and then ethanol/water solution and dried. The dark brown obtained powder was recrystallized from ethanol.

3.2. Structures of Synthesized Intermediate

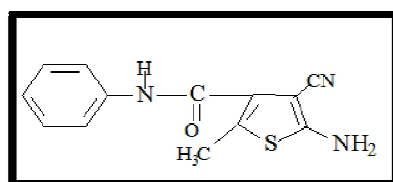


Figure 1: Intermediate 1

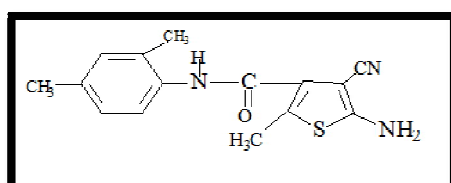
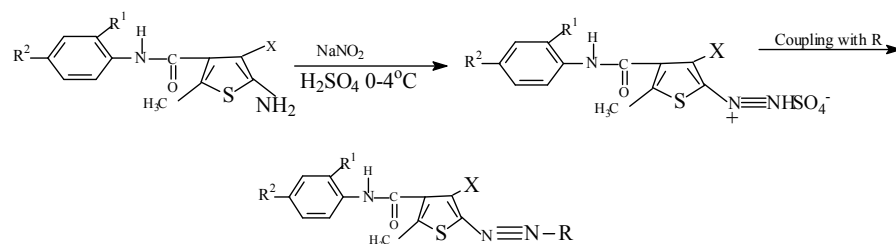


Figure 2: Intermediate 2

3.3. Procedure for Diazotization and Coupling

Sodium nitrite (1.38g, 0.02mol) was added portion wise to 10ml of concentrated sulphuric acid at 10°C and heated to 60°C with stirring for 15min. The solution was then cool to 5°C and a mixture of acetic acid and propionic acid (17:3) was then added to the mixture below 30°C. The finely ground aminothiophene intermediate 1-2 (4.90g, 0.02mol) was added within 30min below 5°C and the whole mixture was stirred at 0-5°C for 2-4hrs. The associated steps are illustrated in the reaction scheme 3.4.



where R¹ and R² are H or methyl group and R is the coupling component

Scheme 3.4: Diazotization and Coupling of 2-aminothiophene.

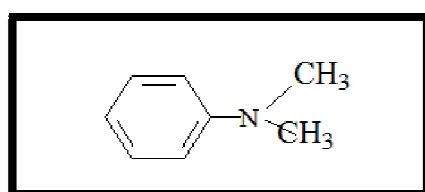


Figure 3: N, N-dimethylaniline

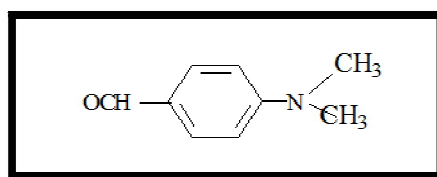
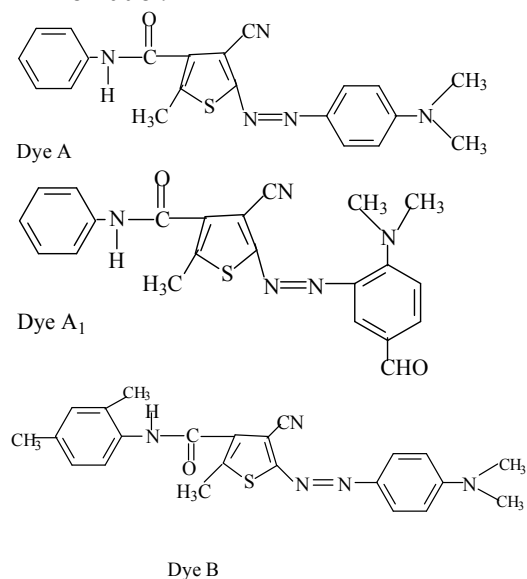
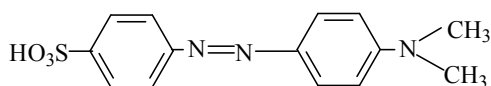


Figure 4: p-N, N-dimethylaminobenzaldehyde

3.4. Coupling Reaction

The coupling component, N, N-dimethylaniline, p-N, N-dimethylaminobenzaldehyde couplers was dissolved separately in acetic acid and cooled to 0°C by adding ice. The diazonium solution of the intermediate 1 and 2 that was prepared was then added for 30-40min with vigorous stirring (Maradiya and Patel, 2010). The resulting product was collected by filtration, wash with water and dried. The crude product was purified by recrystallizing it from ethanol and DMF of ratio 9:1.





Dye C

3.5. Characterization of the Intermediates and the Dyes

The physicochemical properties of the intermediates and synthesized dyes were carried out and spectroscopic properties such as FT-IR and GC-MS.

3.6. Dyeing of Fabric with Synthesized Dyes

Polyester and Nylon 6.6 fabrics were dyed using the synthesized dyes. The fastness properties of the dyes were examined using standard method.

3.6.1. Application of Dyes

1% stock solution of each dye was prepared, a aliquot ratio of 50:1 was used, 2% shade on weight of fabric (o.w.f) and 1g of fabric each of nylon and polyester. The volume required from each stock solution was calculated based on the formula:

$$V = \frac{P \times W}{C}$$

Where:

P = percentage shade

W = weight of fabric

C = percentage concentration of stock solution.

For the polyester a carrier (phenol) and dispersing agent (anionic detergent) was used to facilitate the dyeing process. The fabric was wetted and thoroughly squeezed to remove excess water. It was then immersed into the bath at 40°C and allowed to reach the boil within 15minutes. Dyeing was carried out for one hour at a temperature of 100°C with agitation. At the end of the dyeing process the substrate was removed, squeezed and rinsed thoroughly under running tap and allowed to dry at room temperature (Giles and Rahman, 1992; Nkeoye, 1987; Miah and Ahmed, 2013).

3.6.2. Measurement of Dye Exhaustion

Dye uptake was determined by measuring the absorbance of diluted dyebath samples at the wavelength of maximum absorption of each dye. The bath was sampled before and after dyeing. A 1ml aliquote was taken from the bath and diluted in 20ml acetone. This is to ensure that the absorbance falls within the readable range of 1.5. The percentage of dyebath exhaustion (%E) was calculated using the equation below, (Jae-Hong Choi *et.al.*, 2008; Ozan Avinc *et.al.*, 2006).

$$\%E = \frac{A_0 - A_i}{A_0} \times 100$$

where A_0 and A_i are the absorbance at λ_{max} of the dyebath prior to dyeing and after dyeing respectively.

3.6.3. Wash Fastness Test

The dyed samples were subjected to I.S.O.2 wash fastness test by the following procedures: The specimens were prepared by cutting the dyed fabrics into 5cm x 2cm dimensions; they were then made into composites by stitching the test specimen made of the dyed sample place in between white cotton of dimensions 10cmx4cm. The composite was agitated in solution made up of the following:

Soap solution 5g/l

Liquor ratio 50:1

The washing was maintained at 50°C for 45minutes with continuous agitation in the automated test machine. At the end of the washing test the composite specimen was rinsed in cold water, squeezed to remove excess water and dried. The change in colour of the dyed samples and the staining of adjacent undyed cloths were assessed using the standard grey scale and the results are shown in Table 4.12 and 4.13. (SDC, 1965).

3.6.4. Light Fastness Test (Nunn, 1979)

The dyed samples and blue wool standard were exposed facing due south and inclined at an angle to the horizontal approximately equal to the latitude of the place where the exposure is being made. Adequate ventilation of the samples during exposure was ensured. The partly covered samples were exposed to Ultra-violet radiation. As exposure proceeded for 3days, the samples under test and the blue wool standard were examined at interval and the change in colour of the samples compared visually with the changes that occur in the standards. The light fastness of the sample is the number of the standard that shows a similar visual contrast between the exposed and unexposed part of the samples. The exposure was terminated when the blue wool standard seven fades or when fully exposed and non-exposed test samples is equivalent to grade 3 on the grey scale. The result are shown in Table 4.12 and 4.13

4. Result and Discussion

4.1. Physical Properties of the Synthesized Intermediates

Intermediate	Molecular Formular	Molecular Weight G/Mol	Melting Point °C	% Yield	Colour Of The Crystal
1	C ₁₃ H ₁₁ N ₃ OS	257	199-204	47	Light brown
2	C ₁₅ H ₁₅ N ₃ OS	285	163-171	51	Dark brown

Table 1: Physical Properties of Amino thiophene Intermediates

The colour of the diazo compounds ranges from light brown to dark brown for the intermediate 1 and 2 respectively. The molecular mass of the intermediate is from 257-285g/mol while the melting point were 163-204°C as shown in the Table 1. The yield of the intermediate can also be described as fair to good. This is not surprising in view of the result from previous and similar works. (Sabnis *et al.*, 1999), reported the fact that 1,3-dicarbonyl compound generally pose a problem of low yield and difficult purification process when compared to other ketones and aldehyde. One of the methods mentioned as a way of overcoming this is a prolonged reaction time.

Dyes	Molecular Formula	Molecular Weight(g/mol)	Melting Point(°C)	% Yield	Colour of the Dyes
A	C ₂₁ H ₁₉ N ₅ OS	389	204-209	58	Dark magenta
A1	C ₂₂ H ₁₉ N ₅ O ₂ S	417	201--205	41	Margenta
B	C ₂₃ H ₂₃ N ₅ OS	417	174-178	42	Maroon
B1	C ₂₄ H ₂₃ N ₅ O ₂ S	445	167-170	31.50	Dark purple
C	C ₁₄ H ₁₅ N ₃ O ₃ S	305	180-183	74.63	Deep red
C1	C ₁₅ H ₁₄ N ₃ O ₄ S	332	187-191	62.	Red

Table 2: Physical Properties of the Synthesized Dyes

Table 2 shows the physical properties of the synthesized azo dyes. All the purified dyes exhibited fairly well-defined melting points characteristics of a pure compound. Thus, dyes from low-melting diazo components tended to have low melting points themselves and the factors determining high melting points were generally preserved in the dyes from high-melting heteroaryl amine as shown in Table 2 above. Thienyl-2-azo dyes with 3-cyano groups had higher melting points than their analogues with alkyl esters, which Hallas and Towns (1996a, 1996b) had earlier observed, may be as result of increased polarity and / or the rod like shape of the cyano group being more conducive to efficient packing in the crystal structure. For instance, dye A, A1, B and B1 had melting point of 204-209, 201-205, 174-178, and 167-170°C respectively. These figures are close in magnitude to that of amino thiophene intermediate 1 and intermediate 2 with melting point of 199-204°C and 163-171°C respectively.

Intermediate and Dyes	IR Vmax (cm ⁻¹)
Intermediate 1	3421.7, 3276.3(NH), 2199(CN), 1625, 1662, 1695(C=O)
Intermediates 2	3354, 3317, 3198(NH), 2206(CN), 1647, 1631, 1602(C=O)
Dye A	3309(NH), 2217.8(CN), 1666.1, 1695.9(C=O), 1528(N=N)
Dye A1	3328(NH), 2221.5(CN), 1736.9, 1602.8, 1662(C=O), 1528.2(N=N)
Dye B	3369.5(NH), 2214.0(CN), 1651.2(C=O), 1498, 1438.8(N=N)
Dye B1	3313.6, 3354.6(NH), CN(2206.6), 1651.2(C=O), 1599.0, 1520.8(N=N)
Dye C	3220, 3097(NH), 2803.0(CH), 1599, 1543(N=N)
Dye C1	3365(NH), 1654.9(C=O), 1513.3(N=N)

Table 3: IR-Vibrational Frequencies of the Synthesized Dyes and Intermediates

Table 5 shows the IR-vibrational frequencies of the synthesized dyes and its intermediates and the result obtained indicates that amino thiophene intermediate 1 and 2 show absorption peaks in the range 2199-2206cm⁻¹ due to the presence of cyano group. The amino group absorption for the two intermediate appeared in the range 3198-3421.7cm⁻¹ while the carbonyl absorption showed up in the range 1602-1695cm⁻¹. However, the vibrational frequency obtained for the synthesized dyes shows the characteristics absorption peaks due to stretching frequency of the NH-group in the region 3097-3365cm⁻¹. An absorption peak in the region 2217.8, 2221.5, 2214.0, 2206.6cm⁻¹ was observed for dye A, A1, B and B1 due to the presence of cyano group. The IR spectra of the prepared azo dye also showed an absorption peak in the region 1438.8-1599cm⁻¹ attributed to $\nu_{N=N}$, while the observed peak in the region 1602.8-1736.9 was due to $\nu_{C=O}$ as outline in Table 5

Dyes/Intermediate	Mass (m/z)
Intermediate 1	(C ₆ H ₅ SN ₂) ⁺ = 140 (C ₇ H ₇ NO) ⁺ = 123
Intermediate 2	(C ₇ H ₅ N ₂ SO) ⁺ = 165, (C ₈ H ₁₀ N) ⁺ = 117
Dye A	(C ₆ H ₆ N) ⁺ = 81.1, (C ₇ H ₃ N ₃ SO) ⁺ = 177, (C ₈ H ₁₁ N) ⁺ = 129
Dye B	(C ₈ H ₁₀ N ₃) ⁺ = 149, (C ₇ H ₄ N ₂ SO) ⁺ = 179, (C ₈ H ₉) ⁺ = 91

Table 4: GC- MS Fragmentations of the Synthesized Dyes and Intermediates

Thus intermediate 1 and 2 showed intense molecular ion peaks at m/z 259±2 and 282±3, consistent with the molecular formulae C₁₃H₁₁N₃OS and C₁₅H₁₅N₃OS respectively. The molecular ion of the intermediate 1 shown in Table 4 underwent

fragmentations to produce peaks at m/z 139 and 123 corresponding to its molecular mass. While the intermediate 2 underwent fragmentation to produce peaks at m/z 117 and 165 respectively. However, Dye A and B showed molecular ion peaks at m/z 394.2 ± 5 and 414.6 ± 3 , consistent with the molecular formulae $C_{21}H_{19}N_5OS$ and $C_{23}H_{23}N_5OS$ respectively.

Polyester Fabric					
Dyes	Change	Staining	Light Fastness	% Exhaustion	Colour on Fabric
A	5	5	6	74	Deep pink
A1	4-5	4-5	4	70	Deep purple
B	4-5	4	5	63	Purple
B1	4	4-5	4	61	Purple

Table 5: Wash Fastness and Light Fastness of the Synthesized Dyes on

Dyes	Change	Staining	Light Fastness	% Exhaustion	Colour on Fabric
A	4-5	4	4	82	Deep Purple
A1	4	4	5	80	Purple
B	4-5	4	4	74	Purple
B1	3	4-5	4	75	Purple
C	3	4	3	86	Yellowish
C1	3	4	4	84	Deep Yellowish

Table 6: Wash and Light Fastness of the Synthesized Dyes on Nylon 6, 6 Fabrics

The disperse dye A, A1, B and B1 were applied at 2% depth on polyester and nylon 6,6 fabric. Their dyeing properties are given in Table 4.12 – 4.13. These dyes gave purple, deep purple and deep pink hues with brighter and deeper shades, tinctorial strength and excellent levelness on the fabric. The variation in the shade of dyed fabric results from alteration in the diazo and coupling component. Thus from Table 6 and 4.13 all the dyes show good to excellent fastness to washing on polyester fabric and fair to very good fastness to washing on nylon 6,6 fabric respectively. The remarkable degree of levelness and brightness after washing indicate good penetration and excellent affinity of the dyes to the fabric. However, dye C and dye C1 gave yellowish to deep yellowish hues with excellent tinctorial strength and brightness on the nylon 6,6 fabric. In addition the result obtained showed that the dyed fabrics have excellent fastness level to washing which may be due to the absence of solubilizing group, which affect solubility and washing ability of the dye-out of the fabric. Also, the fastness properties are interrelated since they depend, among other things such as the rate of diffusion of the dyes on fabric. This rate is a function of the geometry of dye molecule, the concentration of the dye in the fabric which appeared to be the most influential factor in the fastness of dyeing. (Dawson, 1991). However, the light fastness ratings of the dyed polyester and nylon are shown in Table 4.11-4.12 showing moderate to very good light fastness. Light fastness value of 6, 4, 5 and 4 for Dye A, A1, B and B1 respectively can be attributed to the introduction of acetamido group ortho to the azo group resulting in a significant improvement in light fastness (Patel *et al.*, 2003). Also the intramolecular hydrogen bonding between acetamido and azo group can also be ascribed to be responsible for higher value of light fastness as compared to dye C and dye C1 (Divyesh *et al.*, 2014). In a related work by (Evans and Stapleton, 1978). It was also observed by Maradiya, 2010, that there is no absolute value for the light fastness of a dye.

5. Conclusion

Disperse dyes derived from 2-aminothiophene diazo components was synthesized and the intermediate was diazotized, coupled and the dyes were purified by re-crystallization and was characterized using FT-IR spectroscopy and GC-MS. The dyes gave mostly deep purple, orange and yellow shades on the polyester and nylon 6,6 fabric and exhibited good to excellent washing fastness properties on substrate and moderate to very good light fastness indicating that the dyes were good on both substrate.

6. Reference

- Alaa.S and Tarek.H. Dyes and Pigments. (2006). Vol 70, pp 80.
- Maradiya, H.R and Patel V.S. (2010). Synthesis and Dyeing Performance of Some Novel Thiazole Azo Disperse Dyes. Journal of Saudi Chemical Society.
- Alaa and Tarek. Dyes and Pigments. (2006). Vol 70, pp 80
- Divyesh.P. R, Naitic. P. B, Bhavesh. P.M and Keshav. P.C. (2014). Synthesis and Dyeing Properties of Some New Monoazo Disperse Dyes Derived from 2-amino-4-(2, 4-dichlorophenyl) – 1-3-Thiazole. Journal of Saudi Chemical Society, vol 7, pp 12-16.
- Dixit B.C, Patel N.M and Desai D.J. (2007). Synthesis and Application of New Mordant and Disperse Azo Dyes Based on 2, 4-dihydroxybenzophenone. J. Serb. Chem. Soc Vol 72: 119-
- Patel P.S, Patel S.K and Patel K.C. (2003). Synthesis of Heteroaryazo Disperse Dyes and Their Dyeing Performance on Various Fibres. 14(1), 420-426.
- Evans, N.A. and Stapleton I.W. (1978). The Chemistry of Synthetic Dyes. Venkataraman, Academic Press, New York, vol VIII pp 236-238.
- Sabnis.R. W, Rangnekar. D. W and Sonawane. N. D. (1999). 2-Aminothiophenes by the Gewald Reaction. Journal of Heterocyclic Chemistry. Vol (36), pp 333-345.
- Hallas. G and Choi. J. H. (1999a). Synthesis and Properties of Novel Aziridinyl Azo Dyes from 2-aminothiophenes Part 1: Synthesis and Spectral Properties. Dyes and Pigments 40 (2-3); 99-117.