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SYNTHESIS AND EVALUATION OF COUPLER 4-ARYL-2-AMINOTHIOPHENE-3-CARBONITRILE AND ITS DERIVATIVES AS POTENTIAL COUPLING COMPONENT IN DYE SYNTHESIS

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ABSTRACT

Thiophene nucleus has been established as the potential entity in the large growing chemical world of heterocyclic compounds possessing promising coupling characteristics. A series of coupler 4-aryl-2-aminothiophene-3-carbonitrile derivatives were synthesized using Gewald's reaction. The Gewald method, involves the reaction of ketones, aldehydes or
1,3-dicarbonyl species with activated nitriles and elemental sulfur in the presence of an amine base. Characterization of these coupling components was carried out by spectra analysis. The synthesized compounds were recrystallized, purified, characterized and evaluated for spectroscopic properties. They were found to possess good coupling properties as well as high degree of brightness and a colour deepening effect compared to other heterocyclic couplers.

Keywords: *Heterocyclic,2-amino-3-cyano-4-phenylthiophene, Synthesis, Absorption spectra and Gewald reaction.*

I. 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 (Zollinger, 2003]. 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 (Egli, 1990).

Thiophene belongs to a class of heterocyclic compounds containing a five membered ring madeup of one sulphur as heteroatom with the formula C_4H_4S. Thiophene and its derivatives exist inpetroleum or coal. Thiophene is taken from the word *theion*, the Greek word for sulfur, and another Greek word *phaino* which means shinning. Thiophene structure can be found in certain natural products and is also incorporated in several pharmacologically active compounds (Jing wang, 2003).

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 fibres (Gewald, 1976).Increasing the electron-withdrawing strength of the substituents on the thiophene ring resulted in bathochromic shifts. Additionally, the sulphur atom plays a decisive role by acting as an efficient electron sink as explained by valence band theory. (Ishatumer 2012)

Synthetic approaches to the construction of thiophene and substituted thiophene have been efficiently developed. Thiophene ring can be constructed from non-heterocyclic precursors by two reaction pathways

- Construction of thiophene ring from appropriately substituted open chain precursors:
  This method involves the introduction of sulphur into a starting material containing the complete carbon skeleton.
- The functionalization at the positions α and β to the sulphur atom of the preconstructedthiophene nucleus(Raghav,2011)

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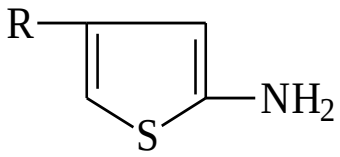

2- amino-4-arylthiophene

II. MATERIALS AND METHOD

All the chemicals used in the synthesis of the coupling components were of analytical grade. They were obtained from sigma Aldrich and molportand were used without further purification. The melting points of the synthesized compounds were determined in open capillary tubes using melting point apparatus expressed in 0C and are uncorrected.

The purity of the compound was checked by TLC on silica gel plates using diethylether:ethanol (75%: 25%) solvent mixture. The Visible absorption spectra were measured using CARY 630 UV-visible spectrophotometer.model: agilent technology . The functional groups that made up the structure of the compound were confirmed by infra-red spectrum on FTIR Nexus 670 spectrometer inKBr disc (thermo nicolet) and absorption bands are expressed in cm^{-1}.

2.1 Synthesis ofcoupler 4-aryl-2-aminothiophene-3-carbonitrile and its derivatives

2.1.1 Synthesis of the coupler 4-aryl-3-cyano-2- aminothiopene AI1.

The starting materials for the synthesis was obtained using the method of Gewald et al, which involves the condensation of corresponding ketone (0.03mol,acetophenone)and malonitrile (0.06mol, 3.96g) in benzene using a heterocatalytic system. The reaction mixture was refluxed in the presence of catalytic amount of acetic acid and ammonium acetate to produce arylidenemalononitrile as an intermediate, followed by the cyclisation with sulphur, using diethylamine as catalysts at 65ºC for 2- 3 hours hours to give the desired products. [Jing wang, 2002].the thick sticky dark product obtained was cooled overnight, filtered ,washed with ethanol, ethanol and water 1:1 and dried (Tumer, 2004). It was purified and recrystallized from hot ethanol. The purity was checked by spotting on a TLC Plate coated with silica gel.

2.2 Synthesis of 2-amino-4-p(chlorophenyl)thiophene-3-carbonitrile AI2

The same procedure as written in (a) above was followed except that the ketone used as starting material was para-chloroacetophenone.

2.3 Synthesis of 2-amino-4-p(aminophenyl)thiophene-3-carbonitrile AI3

The same procedure as written in (a) above was followed except that the ketone used as starting material was para-amino acetophenone.

2.4 Synthesis of 2-amino-3-cyano-4-p(2,4-dichlorophenyl)thiopheneAI4

The same procedure as written in (a) above was followed except that the ketone used as starting material was 2,4-dichloroacetophenone.

2.5 Synthesis of 2-amino-3-cyano-4-p(bromophenyl)thiopheneAI5

The same procedure as written in (a) above was followed except that the ketone used as starting material was para-bromoacetophenone/phenylacylbromide.

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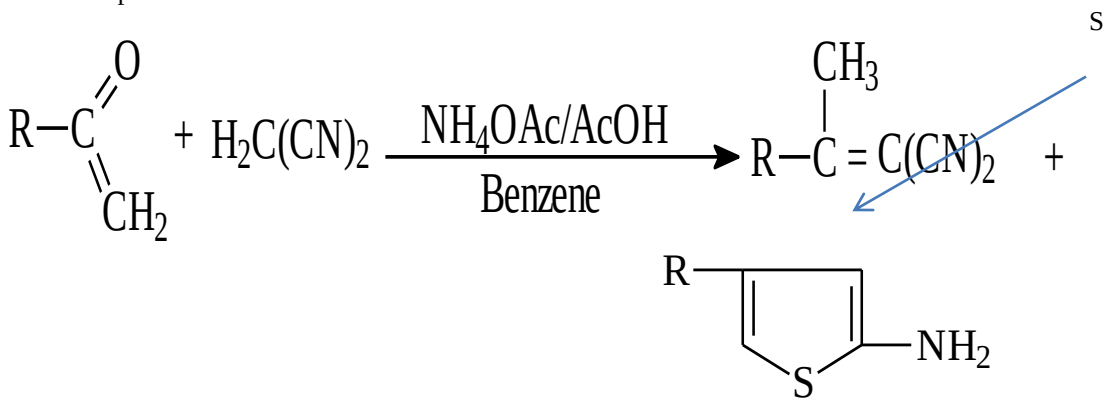
2.6 Synthesis of 2-amino-4-p(2,4-dibromophenyl)thiophene -3- carbonitrileAI6

The same procedure as written in (a) above was followed except that the ketone used as starting material was 2,4-dibromoacetophenone.



Scheme 1: Gewalds synthesis of aminothiophene derivatives

2.7 Recrystallization

All amino thiophene derivatives were purified by 3- 4 recrystallizations from hot ethanol. A known weight of the intermediate was dissolved in small quantity of ethanol and heated up.it was then filtered off using abuchner funnel with asunction pump. The crystals were collected, washed severally with water and dried.after the recrystallization,the purity of each compound was checked by spotting on a thin layer chromatography plate.

III. RESULTS AND DISCUSSION

3.1Synthesis of the coupler 4-aryl-3-cyano-2- aminothiopeneAI$_1$.

Following the stepwise Gewaldsreaction , the dark thick sticky solution obtained was allowed to cool overnight , filtered and washed with ethanol to remove oily substance. A pale orange crystal was obtained, It was purified by recrystallization in hot ehtanol. Melting point 162-164^{o}C, 86%yield which correspond to literature values 161-163,85% yield(yen wang ,2004 dyes and pigment.)Compound AI$_1$FTIR(KBr)/cm^{-1}):1617 (C=C),846,726 (CH – Arbend, double), 2847 (Ali C-H), 3309(NH), 1599 (NH Bnd). 1561 (Ar C=C str), 1349 (C-C), 2202 (C=N),1054 (C-N), 689 (C-S),

3.2 Synthesis of 2-amino-4-p(chlorophenyl)thiophene-3-carbonitrile AI$_2$

The COMPOUND had a yield of product 68%,brown cystals were obtained and recrystallized from hot ethanol. Melting point of 106-108^{o}C, which corresponds to literature values (Jing wang 2003)FTIR(KBr/cm-1): 1617 (C=C), 820,787 (CH bnd, double),3399,3313(NH), 1587 (Ar C=C str), 1289 (C-C), 2214,2206 (C=N),1088 (C-N), 694 (C-S), 1203 (CH Ar).

3.3 Synthesis of 2-amino-4-p(aminophenyl)thiophene-3-carbonitrile AI$_3$

COMPOUND AI$_3$has a yield of product 89%. Black crystals were obtained which was purified by recrystallization in hot ethanol. Melting point is184^{o}C. FTIR(KBr/cm-1): 1606 (C=C), 2922 (Ali C-H str), 831,730 (CH bnd, double), 3451 (NH Str), 1640(NH bnd), 1505 (Ar C=C str), 1334,1292 (C-C), 2214 (C=N), 1058(C-N), 689(C-S), 957 (CH Ar).

3.4 Synthesis of 2-amino-3-cyano-4-p(2,4-dichlorophenyl)thiophene AI$_4$

COMPOUND AI$_4$has a yield of product 72%,pale white crystals were obtained and purified by recrystallization from toluene:acetic acid 60:40.Melting point 188-189^{o}C.FTIR (KBr/cm-1): 1628 (C=C), 2922 (CH)823,670 (CH bnd, double),3306(NH str), 1509 (Ar C=C str), 1386 (C-C), 2214 (C=N), 1028 (C-N), 726(C-S), 1248 (CH Ar).

3.5 Synthesis of 2-amino-3-cyano-4-p(bromophenyl)thiophene AI_5

The COMPOUND AI_5 has a yield of product 70%. Pale yellow crystals were obtained and recrystallized from acetic acid and toluene 60:40. Melting point 190°C.FTIR(KBr/cm-1): 1684 (C=C), 2918 (CH), 827,752 (CH bnd, double),3183(NH str), 1625 (NH bnd), 1490(Ar C=C str), 1359(C-C), 2214 (C=N), 1010 (C-N), 723(C-S), 1185 (CH Ar).

3.6 Synthesis of 2-amino-4-p(2,4-dibromophenyl)thiophene -3- carbonitrile AI_6

The COMPOUND AI_6has a yield of 78%. The Black crystals obtained were purified by recrystallization in acetic acid and ehtanol 20:80. Melting point 203-205°C.FTIR (KBr/cm-1): 1625 (C=C), 827,752 (CH bnd, double),3183(NH str), 1490 (Ar C=C str), 1359 (C-C), 1010 (C-N), 723(C-S), 1233 (CH Ar).

Table 1 : physical characteristics of compounds

Coupler code	Colour of crystals	Melting point(°C)	%yield
AI1	Pale orange	162-164	86
AI2	Crystalline brown	106-108	68
AI3	Black crystal,	184	89
AI4	Pale white	188-190	72
AI5	Pale yellow	191	70
AI6	Pale white	203-205	78

The synthesized compounds were found to be crystalline in nature and easily soluble in ethyl acetate, benzene, toluene , DMSO and DMF but insoluble in hexane. The characteristics data or infra -red spectra of aminothiophene derivatives were recorded in KBr;the compounds AI_1- AI_6 showed two sharp absorption bands of amino group between 3306-3459cm^{-1}and nitrile group around 2206- 2214cm^{-1}and other absorption bands for other derivatives were observed in other region as shown in the result. The functional groups present in the thiophene derivatives showed their various peaks in the corresponding absorption region. They are of bright colour and they give even brighter shade when coupled with a diazo component. Polysubstituted 2-aminothiophenes have also shown to be versatile synthetic building blocks in the dye and other industries. Due to their importance and versatility, the chemistry of 2-aminothiopheneshave received much attention and several synthetic methods have been published. Many of the methods reported involve difficult preparation of starting materials and multi-step synthesis. The most convenient method for preparing 2-aminothiophenes with a high degree of substitution is the Gewald reaction (Scheme 1). This method is an improvement over other existing routes for the synthesis of 2-aminothiophenes. Although the Gewald reaction possesses very good synthetic utility,

IV. CONCLUSION

Using this method of synthesis, a one-step one-pot method for conducting the Gewald synthesis with aryl-alkyl ketones was developed. It further demonstrated that the reaction can be conducted under neat conditions using a heterocatalytic amount of base. This method allows for the safe and easy preparation of a diverse set of aryl-2-aminothiophenes derivatives of coupling components. As shown here, solvent-free methods can have a large impact in organic synthesis, especially with respect to multicomponent reactions.

Gewald reaction is successfully utilized to synthesize the various substituted 2-amino-3-cyano- 4-aminothiophene derivatives as important couplers in the organic or dye synthesis. The analytical and other informational data, available in the results obtained, have rendered thiophenes significantly important class of heterocyclic compounds and their applications in ever challenging dye and organic synthesis. They were found to possess good coupling properties as well as high degree of brigthness and a colour deepening effect compared to other heterocyclic couplers.

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