COMMUNICATIONS

DE LA FACULTE DES SCIENCES
DE L'UNIVERSITE D'ANKARA

FACULTY OF SCIENCES
UNIVERSITY OF ANKARA

Series B: Chemistry and Chemical Engineering

VOLUME : 32 NUMBER : 1–2 YEAR : 1986

Faculty of Sciences, University of Ankara
06100 Ankara - Turkey

ISSN 0570 - 1414

COMMUNICATIONS

DE LA FACULTE DES SCIENCES
DE L'UNIVERSITE D'ANKARA

FACULTY OE SCIENCES
UNIVERSITY OF ANKARA

Journal is published twice a year by the Faculty of Sciences, University of Ankara. Articles and any other material published in this journal represent the opinions of the author(s) and should not be construed to reflect the opinions of the Editor(s) and the Publisher(s).

Correspondence addresse:
COMMUNICATIONS SECRETARY
Faculty of Sciences, University of Ankara 06 100,
Ankara, TURKEY, Tel. 41 13 17 22

COMMUNICATIONS

DE LA FACULTE DES SCIENCES
DE L'UNIVERSITE D'ANKARA

FACULTY OF SCIENCES
UNIVERSITY OF ANKARA

Series B: Chemistry and Chemical Engineering

VOLUME : 32 NUMBER : 1–2 YEAR : 1986

Faculty of Sciences, University of Ankara
06100 Ankara - Turkey

ISSN 0570 - 1414

ANKARA ÜNİVERSİTESİ BASIMEVİ ANKARA — 1986

Commun. Fac. Sci. Üniv. Ank. Serie B
V. 32. pp. 1-18 (1986)

SYNTHESIS AND INVESTIGATION OF SUBTITUTED 2-AMINOTHIOPHENES FROM SULPHUR AND ACTIVE METHYLENE BEARING NITRILES

VEDİA ERTÜZÜN

Faculty of Science. University of Ankara, Turkey

(Received in June 1986, Accepted in September 1986)

ABSTRACT

β - Benzyl - α - cyano cynnamic acid, a nitrile with active methylene group has been synthesized. The reaction of this compound with sulphur in the presence of diethylamine gave 2-Amino-4,5-diphenyl-3-cyanothiophene. In addition, a similar compound, 2-amino 4-ethyl-5-methyl-3-cyanothiophene has been obtained from sulphur and malonic acid dinitrile using the same amine as catalyst. The both thiophenes and their Schiff's bases with salicylaldehyde and β-Hydroxynaphtaldehyde have been investigated by uv, ir and ^{1}H-nmr spectroscopy and pKa measurements in terms of substituent and heteroatom effects on various characteristics.

INTRODUCTION

Several studies on the synthesis of substituted heteroaromatic amines from active methylene-bearing nitriles have appeared in the literature. Karl Gewald and co-workers have synthesized some substituted 2-aminothiophenes (Gevald, 1961) 2-aminopyroles (Gewald, 1966) and 2-aminofuranes (Gewald, 1961) using a technique based on a spesific version of Knoevenagel condensation.

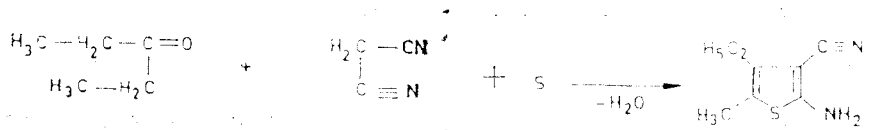
RESULTS AND DISCUSSION

This study is aimed at the synthesis of some novel substituted 2-aminothiophenes through a reaction that is a specific form of Knoevenagel condensation by introducing electron-releasing and electron-withdrawing substituents at the 4- and 5- positions of the subs-

ISSN 0570-1414 A. Üniv. Basımevi

tituted heteroaromatic ring and investigation of the effects of the substituents and the heteroatom on the basıcıty, and uv, ır, 'H-nmr spectroscopic properties of the amines. Elucidation of the structures, by instrumental techniques, and establishing how the above-mentioned effects and properties change during the formation of the new Schiff's bases that are the condensation products of the amines synthesized and salicylaldehyde and β – hydroxy – α – naphtaldehyde are also aimed.

One of the subject amines, 2-amino-4-ethyl-5-methyl-3-cyanothiophene, a compound with electron-releasing alkyl groups, is obtained from the condensation of diethylketon and malonic acid dinitrile with sulphur in the presence of diethylamine as catalyst, (Eq. 1).



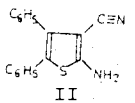
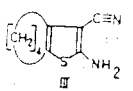
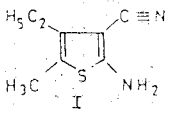
Equation 1

UV, ir and nmr spectra and pKa value of compound (I), synthesized for placing alkyl groups at 4-and 5-positions in 2-amino-3-cyanothiophene have been examined. On the comparison of these values with those obtained for 2-amino-4,5-tetramethylene-3-cyanothiophene, it has been shown that uv, ir and 'H-nmr spectra remain essentially the same whether the substituent is an alkyl or a cycloalkyl. The pKa values have also been found to be the same (pK'a = 20.7) for compound (III) and compound (I) (see: table 1). Notwithstanding that the synthesis of compound (III) had appeared in the literature already, we have recorded its uv, ir and 'H-nmr spectra and pKa' value for the first time.

In the uv spectra, the respective λ_{max} values for NH, C≡N and NH_2 groups for compound (III), (230 nm, log∈ = 4.15; 271 nm, log∈ = 3.93; 320 nm, log∈ = 4.01) were found to be higher than corresponding values for compound (I). This has been explained on the basis of the fact that conjugation in compound (III) is deeper than in compound (I).

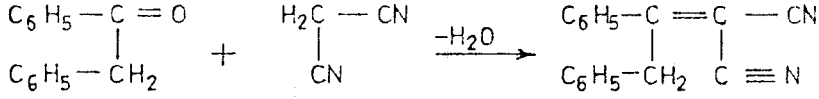
In the ir spectra of compound (III) and compound (I), vibration bands due to the characteristic groups (C≡N, NH and NH_2) have been found to fit well with those aperred in the literature (C.N.R,

Table 1: The UV, IR, HNMR and pka' values of substituted heteroaromatic amines

Compound	pK'_a	UV λ_{max} nm (log ∈)	IR (KBr)			HNMR ($CDCl_3$)	
		CH_3OH	C≡N	NH	NH_2	NH_2	Heteroarom.
 II	19,5	230(5,60), 303(4,78), 335(4,76)	2210	3435-3300 3200	1630	6,1(2 H),	7,80(m) fenil
 III	20,7	230(4,15), 271(3,93) 320(4,01)	2220	3460-3215	1630	4,82(2H), 2,56(4H) homoalil	1,78(4H)
 I	20,7	221(4,53),296(3,84) 211(4,46),298(3,83)	2220	3440-3220	1640	4,80(2H) 1,18(3H)(t), 2,58(2H)(q)	2,22(3H)(s)

1963; Fleming, 1968; Spectra charts. 1959), H-nmr spectra of the two compounds does not appear to have a significant difference.

The other substituted heteroaromatic amine we have synthesized was 2-amino-4,5-diphenyl-3-cyanothiophene. To achieve the synthesis of compound, it is necessary to introduce electron withdrawing phenyl groups at the 4-and 5-positions in 2-amino-3-cyanothiophene. For this purpose, 2-phenylacetophenon is condensed acid dinitrile, and a vinylcyano species with active methylene group on it, namely, α - cyano - β - benzylcynnamic acid nitrile (X) is obtained. (Eq. 2).



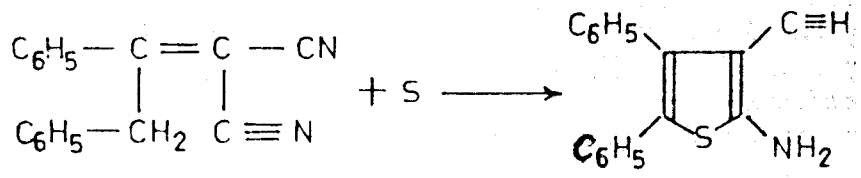
X

Equation 2

The molecular structure of compound (X) has been elucidated on the basis of elemental analysis and uv, ir and 'H-nmr spectroscopic evidence. 2.5×10^{-5} Molar ethanolic solution of compound (X) absorb appreciably in the uv region. Where $\pi \leftrightarrow \pi^*$type electronic transitions are involved. Maximum absorbtion wavelengths of the phenyl groups that are bound to the double bond (296 nm, $\log\epsilon = 4.63$ and 295 nm, $\log\epsilon = 3.98$) fit well with those given in the literature.

In the ir spectrum of compound (X), characteristic group bands can be sorted out. In the 'H-nmr spectrum ($CDCl_3$) CH_2 protons appear to have shifted downfield ($\delta = 4.25$ ppm) due to the presence of an adjacent phenyl group. Integration curve for this peak corresponds to two protons, reaffirming that it belongs to CH_2 protons. The complex multiplets between δ=7.70-6.80 are apparently due to phenyl protons and this is compatible with the fact that the integration curve corresponds to ten protons for these multiplets alltogether. Results of the elemental analysis also confirm the structure based on uv, ir and 'H-nmr evidence. Therefore, the the structure proposed for compound (X) is precise.

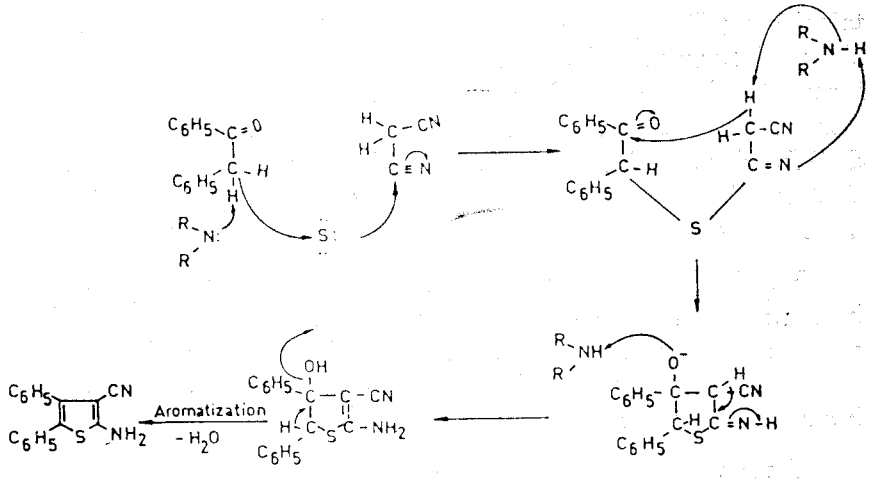
The reaction of compound (X) with sulphur in the presence of diethylamine as catalyst, through a cyclo-addition, led to the formation of 2-amino-4,5-diphenyl-3-cyanothioplene (II). (Eq 3).



X II

Equation 3

Here, the mechanism of ring formation (shown below) can be thought of as the addition of the elemental sulphur to the nitrile component (X) after being dissolved with the aid of the catalyst (diethylamine).



The compound obtained is a stable amine purifiable by recrystallization. When the effect of electron withdrawing groups on the properties of compound II was considered, it was seen that, after the introduction of the oxochromes, λ_{max} values of NH, NH_2 and C≡N groups have shifted towards longer wavelengths in the com-

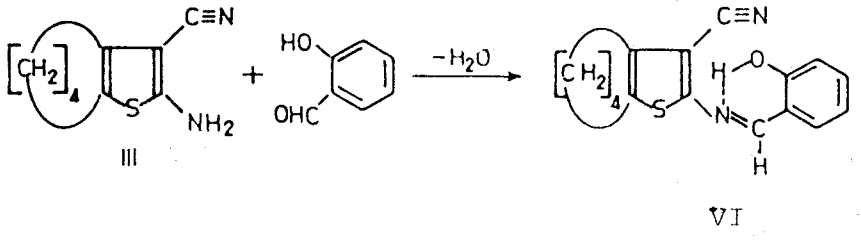
pounds (III) and (I). Ir spectral evidence support this result. As to 'H-nmr spectrum, the peak due to the NH_2 protons in (I) (δ=4.80 ppm) appear to have shifted downfield in compound (II) (δ= 6.1 ppm) under the influence of the new substituents. Potentiometric titration with tetrabutylammonium hydroxyde in pyridine gave a pK'a value of 19.5. Apparently, the basicity power of NH_2 in compounds (III) and (I) must have decreased in compound (II). This evidence, once again, brings forward the well-known fact that electron-withdrawing phenyl groups tend to increase the acidity.

To investigate the effect of the heteroatom on the properties of the amines concerned, two compounds with the same substituent groups but different heteroatoms, namely, 2-amino-4,5-diphenyl 3-cyanofurane and 2-amino-4,5-diphenyl-3-cyanothiophene (II) have been compared. λ_{max} values of NH_2 and C≡N groups shift to longer wavelengths under the influence of sulphur (see: table 1). Conjugation increase, and in the ir spectrum, vibrational bands due to-C≡N, NH_2 and-NH groups behave in a way parallel to this conclusion. In the 'H-nmr spectrum, NH_2 protons give rise to a peak at 4,9 ppm for furane whereas the corresponding NH_2 peak for thiophene (II) appear at a lower field (δ = 6.1 ppm). Inductive effects of oxygene and sulphur atoms are different and this difference is reflected in the nmr data for NH_2 protons. The pK'a value for compound furane is 18.6 compared to the value of 19.5 for compoun d (II). Here again, the inductive effect of oxygen decreases the electron density on the nitrogen and renders the protons to leave more easyly.

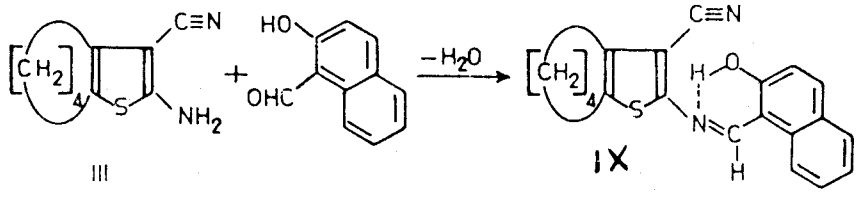
For the investigation of the above-mentioned effects in Schiff's bases, the synthesized amines (compounds I, II and III) have been condensed with salicylaldehyde and β- hydroxy-α-naphtaldehyde and the corresponding Schiff's bases have been prepared. These Schiff's bases are stable compounds that can be purified by recrystallization.

From the condensation of the amine (III) (2-amino-4,5-tetrametilen-3-cyanothiophene) and salicylaldehyde (Equation 4) 2-salicylideneamino-4,5-tetramethylene-3-cyanothiophene(VI) is obtained. (Eq. 4).

The condensation of the same amine (III) with β- hydroxy-α-naphtaldehyde gives the compound, 2-(β-hydroxy-α-naphtilidene) -amino-4,5-tetramethylene-3-cyanothiophene (IX) (eq 5.)



Equation 4

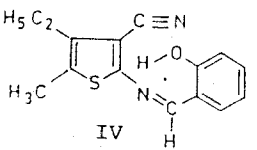
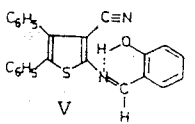
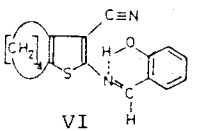


Equation 5

When the uv-vis. spectra of these Schiff bases are examined, it is seen that the different oxochromic effects of phenyl and naphtly groups on the aldehyde proups is reflected on the deepening of the conjugation and thereby the shift of the λ_{max} value of the azometyn group to longer wavelengths. This chromophere absorbs at 296 nm in compound (VI) whereas it absorbs at 433 nm in compound (IX). Again, the effect of the conjugation comes under consideration in the interpretation of the ir band of -C≡N group at 2220 cm^{-1} for compound (VI) compared to the corresponding wave number for compound (IX) (2215 cm^{-1}).

Since the compound 2-(β-hydroxy-α-naphtilidene)-amino- 4,5-tetrametilen-3-cyanothiophen (IX) was insoluble in all the common solvents, 'H-nmr spectrum was not possible. On the other hand, in the 'H-nmr spectrum of 2-Salicylidene-amino-4,5-tetramethylene 3-cyanothiophene, the peak atδ=8.43 ppm (s) due to the azomethyn proton and the OH peak at δ=11,86 ppm are compatible with the values expected from the structures (table 2). The peak at δ=11,86 ppm dissappears after the solution of the compound is shaken with D_20, confirming that this peak has given rise to by the OH proton. Protons of the tetramethylene group at the-4,5-positions of the thi-

Table 2: The UV, IR, HNMR and pka' values of salicylaldehyde Schiff's bases

Compound	pK'_a	UV ($CH_3COOC_2H_5$)	IR (KBr)			HNMR ($CDCl_3$)
		λ_{max} nm (logϵ)	OH	C≡N- , -C=N-		OH, H-C=N- , Arom. ve Heteroarom. halka
 IV	14,7	286(4,61), 393(5,01)	2980	2240	1610-1550	12,46(s). 8,82(s)
 V	14,8	405(4,40) 285(4,27) 251(4,28)	3500-3200	2210	1620-1450	12,40(s) 8,80(s).
 VI	15,2	296(4,39)	3500-3200	2220	1640-1450	11,86(s) 8,43(s) 2,66 CH_2 homoalil 1,86 CH_2 7,96-6,95(m) fenil

ophene ring of compound (VI) (see: figure-a) appear at different fields in the 'H-nmr spectrum. When figure-a is considered, the protons $H_A$and H_B, that are adjacent to the thiophene ring can be assumed as homoallylic protons. $H_A$protons allylic protons. H_A

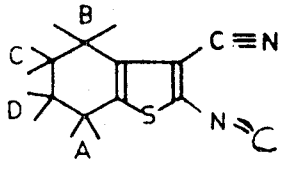
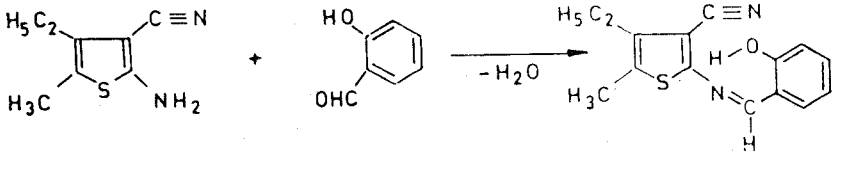


Figure-a

protons appear at lower fields under the inductive effect of the S atour. The broad signal at $\delta = 2{,}66$ ppm can be attributed to these protons. As to H_C and $H_D$protons, they are responsible for the broad signal around $\delta = 1{,}86$ ppm. The substituent effects have not been investigated because compound (IX) was impossible to disolve. The pK'a values for compound (VI) and compound (IX) have been found to be 15,2 and 13,6 respectively. When the pK'a values for salicylaldelyde and β-hydroxy-α-naphtaldelyde (15,0 and 13,4 respectively) are considered, acidity is understood to have been lowered by 0,2 pKa unit in compounds (VI) and (IX) From these observation, the conclusion that some electron transfer from the electron-releasing alkyl groups to the aldehydic group has occured can be drawn.

When the spectroscopic characteristics of the Schiff's base obtained from the condensation of amine (I) with salicylaldehyde, namely, 2-salicylidene-amino-4-ethyl, 5-methyl-3 cyanothiophen (IV) is compared with those of the compound (VI), it is seen in the UV spectra that the absorbtion band of the (Eq. 6) azomethyn groups are essentially the same in the both compounds. On the other hand, in the

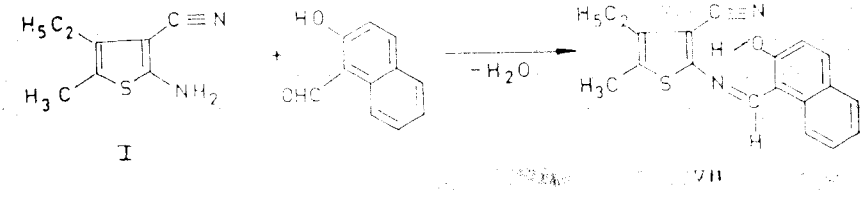


I IV

Equation 6

ir spectra, the azomethyn group absorbs in 1640-1450 cm^{-1}region in compound (VI) whereas, in compound (IV), it appears in 1610 1550 cm^{-1}region. Increased conjugation in compound IV can be deduced from these observations. As to the 'H-nmr spectra, the azomethyn protons that give a signal at $\delta=8.43$ ppm in compound (VI) and at $\delta=8.82$ ppm in compound (IV) is clearly seen to have been effected by the substituents. We beleive that the effect of the cyclohexyl subtituent can reach the azomethyn protons whereas the effect of the alkyl groups is smaller. Therefore, azomethyn protons appear at higher field for compound (VI) and at lower field for compound (IV). For compound (VI), pK'a = 15.2 whereas for compound (IV), pK'a=14,7. Since pK'a=15.0 for electron transfer the cyclohexyl group to the aldehyde group can be deduced for the Schiff base bearing cy$_t$clohexyl group. On the contrary in the Schiff's base 2-Salicilidene-amino-4-ethyl-5-methyl-3-cyanothiophene, alkyl groups appear to be withdrawing electrons from the aldehyde group, resulting in an increase in the acidic power of Salicylaldehyde. Therefore, the existance of substituent effects in the Schiff base formation can be contemplated (see: table-2).

In the Schiff base 2-(β-hydroxy-α-naphtylidene) -amino-4-ethyl 5-methyl-3-cyanothiophene (VII), that has been the condensation product of 2-amino-4-ethyl-5-methyl-3-cyanothiophene (I) and β-hydroxy-α-naphtaldehyde, (equation-7), conjugation is deepened with the substitution of the naphtyl ring and thereby, in the uv spectrum, λ_{max} value of the azomethyn groups is Shifted to longer wavelengths (434 nm).

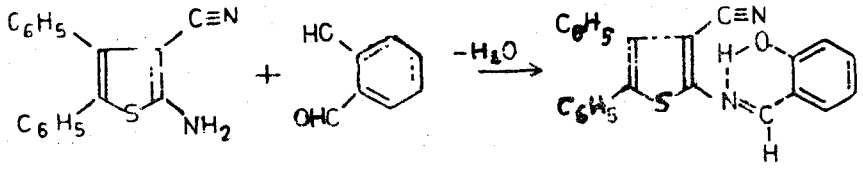


Equation - 7

When the spectrum of the compound (IV) is compared with the ir spectrum, the effect of the conjugation can be noticed although, the difference is not so significant. In the 'H-nmr spectra, the fact

that the peak due to the azomethyn proton appear downfield at δ=9,53 ppm (s) compared to the corresponding signal for compound (IV) can be explained on the basis of naphthyl group substitution. The pK'a value for compound (VII) is 13.1 Since the pK'a value for β-hydroxy-α-naphtaldehyde is 13,3 it is apparent that electron is withdrawn from the group on the formation of the Schiff base. This conclusion is compatible with the fact that the naphtaline ring is an electron withdrawing substituent.

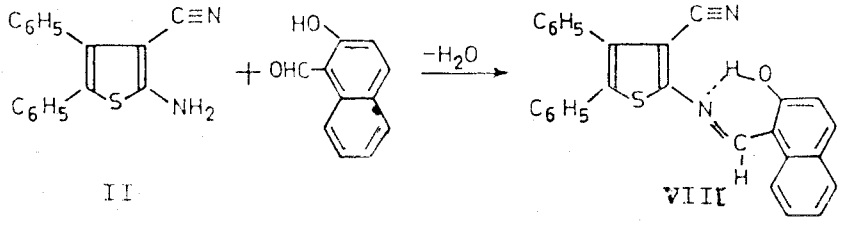
As to the Schiff bases carrying phenyl groups on the 2-aminothiophene ring, they are the condensation products of the amine 2-amino-4,5-diphenyl-3-cyanothiophene (II) and the two aldehydes salicylaldehyde and β-hydroxy-α-naphtaldehyde. The first Schiff's base 2-salicylidene-amino-4,5-diphenyl-3-cyanothiophene (V) is formed by the reaction shown in equation-8 and the Schiff's base 2-(β-hydroxy-α-



II

Equation-8

naphtylidene)-amino-4,5-diphenyl-3-cyanothiophene (VIII) is formed according to equation-9.



II VIII

Equation-9

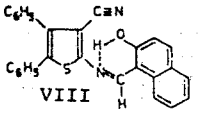
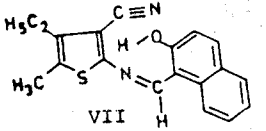
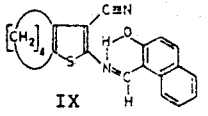
uv Monitoring during the formation of compound (VI) it was shown that substitution of the phenyl rings deepens the conjugation. In the ir spectra, the vibration band of the CN group appear at 2240 cm^{-1}

for compound (IV) whereas, for compound (VI), it shifts to 2210 cm^{-1}under the influence of the conjugation. In the 'H-nmr spectra, the position of the peak due to the azomethyn proton are approximately the same for the compounds (IV) and (VI) (δ=8.82 ppm and δ=8.80 ppm respectively). The pK'a values for the compounds (IV) and (V) are found to be 14.7 and 14,8 respectively. These values have been determined in pyridine medium by potentiometric titration with tetrabutylammonium hydroxyde as titrant. The difference of 0.1 pKa unit in between the pKa values of compound (IV) and compound (VI) can not be explained on the basis of substituent effects. Because, aromatic substituents in compound (V) is expected to increase the acidity that is, a lower pK'a value should be measured, for compound (V). Heteroatom effect can be used as an explanation. For this purpose, the pK'a values of the compounds 2-salicylidene-amino-4,5 diphenyl-3-cyanofurane have been compared. The lower electronegativity of the sulphur atom in compound (VI) leads to an electronic thiophene ring, therefore, a lower acidity (higher pK'a value) is expected In the other compound, the oxygen atom in the furane ring is more electronegative than sulphur and a lower pK'a value (14.2 unit for this compound) is expected (see: table-2).

Substituent effects in the compound 2-(βhydroxy-α-naphtylidene) -amino-4,5-diphenyl-3-cyanothiophene (VIII) are apperant in the increased λ_{max} values in the uv spectrum due to deeper conjugation and the shift of the 'H-nmr signal of the azomethyn proton downfield

For pK'a value for β-hydroxy-α-naphtaldehyde is 13.6 whereas for compound (VIII), pK'a value is found to be 12.6. This means that the formation of the Schiff's base led to electron-withdrawal from the aldehyde group and thereby increased the acidity of the aldehydic proton. The heteroatom effect is also in that direction (see: table 3). In the Schiff bases 2-(β-hydroxy-α-naphtylidene)-amino-4,5-diphenyl-3-cyanothiophene (VIII) and 2-(β-hydroxy-α-naphtylidene) - amino-4,5-diphenyl-3-cyanofurane, where the only difference lies with the heteroatoms, comparison of the pK'a values (pK'a = 12.6 and 12.5 respectively) shows that the furane derivative is a stronger acid (see: table - 3) This conclusion is compatible with the fact that the oxygen atom is more electronegative than the sulfur atom, that is, the compound (VIII) is a weaker acid.

Table 3: The UV, IR, HNMR and pka' values oj β-hydroxy-α-naphthaldehyde schiff's bases

Compound	pK'_a	UV ($CH_3COO_2H_5$)		IR (KBr)			HNMR ($CDCl_3$)
		λ_{max} nm	(log∈)	OH	-C≡N-	-C=N-	OH, H-C=N-, Arom ve Heteroarom. halka
 VIII	12,6	443 nm	4,45	3500-3300	2220	1640-1450	13,90(s) 9,68(s) 8,40-7,40(m) fenil ve naftil
 VII	13,1	434	4,59	2990	2240	1615-1540	11,93(s) 9,53(s)
 IX	13,6	433 nm	4,27	3500-3200	2215	1640-	Çözünmediğinden HNMR spektrumu alınamamıştır.

EXPERİMENTAL

The Apparatus used during this study

Hitachi model 200-2O Double Beam UV-VİS spectrophothometer, Perkin-Elmer-337 IR spectrophotometer, Varian-T-60A, 60 mHZ and Perkin-Elmer-R-32 90mHZHNMR spectrophotometer, Orion 801 A PH meter and electrocapilary melting point determination instrument.

2-Amino-4-Ethyl-5-Methyl-3-Cyanothiophene (I)
(From Diethylketone)

In a three necked flask of 250 ml capacity 8.6 g (0,1 mole) of diethylketone, 6,6 g (0,1 mole) of malonic acid dinitrile, 3,5 g (0,11 atom-gram) of finely-powdered sulphur and 25 ml of ethyl alcohol are mixed throughly using a magnetic stirrer. To this mixture, 10 ml of diethyl-amine is added dropwise through a dropping funnel. When this mixture is heated in a water bath, elemental Sulphur dissolves gradually. Taking care for the temperature not to exceed 60°C, the solution is heated for another 1 hour. Crystallization begins during cooling down. The mixture is kept in a refrigerator for 2 hours. Then, about twice as much water as the volume of the mixture is added and mixed throughly. The mixture is left aside for some time for the completion of the crystallization. The mixture is filtered by suction, the solid residue is dried and recrystallized twice, from alcohol. The needle -shaped crystals melt at 104°-105°C. The product is 13,20 g (0,080 mol) and the yield is 80 %.

Elemental Analysis:

Calculated from $C_8H_{10}N_2S$: C 57,83 H 6,02 N 16,86 S 19,27
Found : C 57,31 H 6,12 N 17,02 S 19,20
UV (C_2H_5OH) λ_{max}nm (logϵ), 221 (4,53), 297 (3,84) $2.5.10^{-5}$M.
IR (KBr) $\upsilon_{max}(cm^{-1})$, 3440-3220 (NH), 1640 (NH_2), 2220 (C≡N)
HNMR ($CDCl_3$)$_i\delta$ (ppm), 4,80 (2H), 1,18 (t) (3H), 2,22 (s) (3H), 2,58 (q) 2H).
PKa' 20.7 (Table 1)

2- Amino-4,5-Diphenyl-3-Cyanothiophene (II) (From Substituted Cinnamic Acid Dinitrile)

In a three necked flask of 50 ml capacity, 2,44g (0,01 mol) of α-cyano-β-benzyl cinnamic acid nitrile, 0.32 g (0,01 atom-gram)

of sulphur and 25 ml of ethanol are mixed with a magnetic stirrer. While mixing, 4 ml of diethylamine is added dropwise. The mixture is heated in a water bath under 50°C. Formation of a cream-coloured precipitate commence after half an hour. Completion of the precipitation is achieved by mixing the mixture at room temperature for some time. The mixture is left aside without mixing for half an hour. Then, twice as much water of its volume is added. A chunky solid is obtained after filtration by suction. This solid is dried and recrystallized from alcohol. The melting point of the bright coloured crystals is 192°C. The product is 2.27g (0,0082 mole) and the yield is 82 %. The material is insoluble in water, slightly soluble in alcohol and very soluble in ether, acetone and chloroform.

Elemental Analysis:

Calculated from $C_{17}H_{12}N_2S$: C73, 91 H4. 35 N10, 15 S11, 59

Found : C74, 05 H4, 49 N10, 22 S11, 36

UV (C_2H_5OH) λ_{max}nm (logϵ), 230 (5.60), 303 (4,78), 335 (4.76). $2.5.10^{-6}$M.

IR (KBr) $\upsilon_{max}(cm^{-1})$, 3435-3300 (NH), 1630 (NH_2) 2210 (C≡N).

HNMR ($CDCI_3$)$_1\delta$ (ppm), 6,1 (2H), 7,8 (m) (phenyl).

pKa′ = 19,5 (Table 1).

Aldimines of Cyanothiophene

2-Salicylidene-Amino-4,5Tetramethylene

-3-Cyanothiophene (VI)

The light green, needle-shaped crystals obtained from 2-amino-4,5-Tetramethylene-3-Cyanothiophene and salicylaldehyde have a melting point of 205°C. The product is 4.04 g (0.014 mole) and the yield is 72 %. The compound is insoluble in water, alcohol and ether, but soluble in chloroform and ethyl acetate.

Elemental Analysis:

Calculated from $C_{16}H_{14}N_2OS$: C68, 08 H4,96N9.92 S11.34

Found : C67,54 H4.31N9.84 S11.69

UV ($CH_3COOC_2H_5$) λ_{max}nm (logϵ), 396 (4,39), $3{,}54.10^{-5}$M.

IR (KBr) $\upsilon_{max}(cm^{-1})$, 3500-3200 (OH), 2220 (C≡N), 1640-1450 (C=N). HNMR ($CDCl_3$)δ(ppm), 11, 86 (s) (OH), 8,43 (s) (H–C=N), 2,66 (4H) (homoallil), 1,86 (CH_2).

pKa′= 15,2 (Table: 2).

2- (β- Hydroxy-α-Napthylidene)-amino-4,5-Tetramethylene-3-Cyano-thiophene (IX)

The deep yellow-coloured needle-like crystals obtained from the amine (III) and β- hydroxy-α-naphtaldehyde have a melting point of 290°C. The product is 4.65 g (0.014 mol) and the yield is 70 %. The compound is not soluble in water, alcohol and ether, but soluble slightly in chloroform and ethyl acetate.

Elemental Analysis:

Calculated from $C_{20}H_{16}N_2OS$: C72.22 H4.82 N8.43 S9.63

Found: C72,20 H4. 73 N8.61 S9, 92

UV ($CH_3OOC_2H_5$) λ_{max}nm (log∈), 433 (4.27), 4.10^{-5}M

IR (KBr) $\upsilon_{max}(cm^{-1})$, 3500, 3200 (OH), 2215 (C≡N), 1640 (C=N).

HNMR spectrum was not available due to low solubility.

pKa′= 13.6 (Table: 3)

2- Salicylidene-Amino-4-Ethyl-5- Methyl -3-Cyanothiophene (IV)

The yellow-coloured, needle-like crystals that have been obtained from 2-amino-4-ethyl-5-methyl-3-cyanothiophene and salicylaldehyde have a melting point of 159°C. The product is 2.15 g (0.0079 mole) and the yield is 80 %. The compound is not soluble in alcohol and ether, but soluble in chloroform and ethyl acetate.

Elemental Analysis:

Calculated from $C_{15}H_{14}N_2OS$: C66.63 H5.18 N10.37

Found: C66,52 H5.21 N10.92

UV ($CH_3COOC_2H_5$) λ_{max}nm (log∈), 393 (5.01), 286 (4,61), $2.5.10^5$M.

IR (KBr) $\upsilon_{max}(cm^{-1})$, 2990 (OH), 2240 (C∈N), 1615 (C=N).

HNMR ($CDCl_3$) δ (ppm) 12,46 (s) (OH), 8.82 (s) (H-C=N)

PKa′= 14.7 (Table: 2).

2- (β-Hydroxy-α-Naphtylidene) -Amino-4-Ethyl-5-Methyl-3- Cyano-thiophene (VII)

The dark red-coloured, needle-like crystals that have been from amine (1) and β-hydroxy-α-naphtaldehyde have a melting point

of 228 °C. The product is 2.72 g (0.0085 mole) and the yield is %. 85 The compound is insoluble in water, alcohol and ether, but slightly Soluble in chloroform and ethyl acetate.

Elemental Analysis:

Calculated from $C_{19}H_{16}N_2OS$: C 71.25 H 5.00 N 8.75
Found : C 70.39 H4.98 N 8.69

UV ($CH_3COOC_2H_5$) λ_{max}nm (logϵ), 434 (4.59) $2.5.10^{-5}$ M

IR (KBr) $\upsilon_{max}(cm^{-1})$, 2990 (OH), 2240 (C = N), 1615 (C = N), HNMR ($CDCl_3$+ CF_3CO_2H); δ (ppm); 11,93 (s) (OH), 9,53 (s) (H-C=N)

1,20 (t) (3H) H_2C-C, 2-24 (s) (3H) (H_2C-Ar), 2,70 (q) (2H)

-Ar 7,20-7,50 (m) phenyl, PKa'= 13,1 (Table: 3)

2- Salicylidene-Amino-4,5-Diphenyl
3-Cyanothiophene (V)

The cinnamon-coloured, needle-like crystals that are obtained from 2-amino-4,5-diphenyl-3-cyanothiophene and salicyl-aldehyde have a melting point of 155°C. The product is 1.48 g (0.0039 mole) and the yield is 70 %. The compound is not soluble in water, alcohol and ether, but soluble in ethyl acetate and chloroform.
Elemental Analysis:

Calculated from $C_{24}H_{16}N_2OS$ C75.79 H4.21N 7.37 S8.42

Found: C76,01 H4.25N8.05 S9.37

UV ($CH_3COO\ C_2H_5$) λ_{max} nm (logϵ), 405 (4.40), 285 (4.27) 251 (4.28.) $3.75.10^{-5}$M.

IR (KBr) $\upsilon_{max}(cm^{-1})$, 3500-3200 (OH), 2210 (C$\equiv$N), 1620-1450 (C=N).

HNMR ($CDCl_3$)$_1\delta$ (ppm), 12,40 (s) (OH, 8.80 (s) (H-C=N), 7,70-7.10 (m) Phenyl.

pKa'= 14,8 (Tabla: 2)

2- (β-Hydroxy-α-Naphthylidene)-Amino-4,5-Diphenyl
3-Cyanothiophene (VIII)

The orange-coloured, needle-like crystals that are obtained from amine (III) and β-hydroxy-α-Naphtaldehyde have a melting point of 192°C. The product is 2.1 g (0.0048 mole) and the yield is 83 %.

The compound is not soluble in water, alcohol and ether, but soluble in chloroform and ethyl acetate.

Elemental Analysis:

Calculated from: $C_{28}H_{18}N_2OS$: C78.41 H4.18 N6.51,S7.44

Found: C78.51 H4.62 N7.82 S7.61

UV ($CH_3COO\ C_2H_5$) λ_{max} nm (logϵ), 443 (4.45), $1.86.10^{-5}$M.

IR (KBr) $\upsilon_{max}(cm^{-1})$, 3500-3300 (OH), 2220 (C≡N), 1640 (C=N).

HNMR ($CDCl_3$): δ (ppm), 13,90 (s) (OH), 9,68 (s) (H-C=N), 8,40-7,40 (m) Phenyl, Naphtlyl.

pKa'= 12.6 (Table: 3).

ACKNOWLEDGEMENT

I would like to express my gratitute to Prof. Dr. Celal TÜZÜN for his invaluable suggestion throughout the course of this study. I would also like to thank Prof. Dr. Turgut GÜNDÜZ and his colleagues for their great help to estimate the pK'a values.

I am also very grateful to Varian-company (Switzerland) for ta king HNMR spectra.

REFERENCES

C.N.R. RaO, 1963. Chemical Applications of luf.ared Spectrascopy. *Academic Press.* New York and London.

GEWALD K., 1961 a. *Angew. Chem.* 73, 114.

GEWALD K., 1966. *Chem., Ber.* 99, 1002.

GEWALD K., 1961 b. *Z. Chem.* 1, 349.

FLEMING I, Spektroskopische Methoden Inder Organischen Chemie s. 29-33. Georg Thieme *Verlagstutgard* 1968.