

ABSTRACT

2-*N*-(3-methyl)piperidinoquinoline (**25**), 2-*N*-(4-methyl)piperidinoquinoline (**26**), 2-*N*-anilinoquinoline (**28**), 2-*N*-(*m*-methyl)anilinoquinoline (**30**), 2-*N*-(*p*-methyl)anilinoquinoline (**32**), 2-*N*-(*m*-ethyl)anilinoquinoline (**34**), 2-*N*-(*p*-ethyl)anilinoquinoline (**36**), 2-*N*-methylanilinoquinoline (**38**), 2-*N*-ethylanilinoquinoline (**40**), 2-*N*-(*m*-methoxy)anilinoquinoline (**42**), 2-*N*-(*p*-methoxy)anilinoquinoline (**44**), 2-*N*-(*m*-chloro)anilinoquinoline (**46**), and 2-*N*-(*p*-chloro)anilinoquinoline (**48**) were prepared by reacting 2-chloroquinoline (**22**) with 3-methylpiperidine (**23**), 4-methylpiperidine (**24**), aniline (**27**), *m*-toluidine (**29**), *p*-toluidine (**31**), *m*-ethylaniline (**33**), *p*-ethylaniline (**35**), *N*-methylaniline (**37**), *N*-ethylaniline (**39**), *m*-anisidine (**41**), *p*-anisidine (**43**), *m*-chloroaniline (**45**) and *p*-chloroaniline (**47**) respectively. The structure of these compounds were confirmed using ¹H NMR, ¹³C NMR, infra-red and GCMS. The fluorescence properties were recorded using Luminescence Spectrophotometer. Almost all compounds prepared showed highest fluorescence intensity in less polar solvents and lowest fluorescence intensity in polar protic solvents. Compound **30**, **34** and **48** showed higher fluorescence intensity in alkaline and neutral conditions while lower fluorescence intensity was recorded in acidic condition.

ABSTRAK

2-*N*-(3-metil)piperidinoquinolina (**25**), 2-*N*-(4-metil)piperidinoquinolina (**26**), 2-*N*-anilinoquinolina (**28**), 2-*N*-(*m*-metil)anilinoquinolina (**30**), 2-*N*-(*p*-metil)anilinoquinolina (**32**), 2-*N*-(*m*-etil)anilinoquinolina (**34**), 2-*N*-(*p*-etil)anilinoquinolina (**36**), 2-*N*-metilanilinoquinolina (**38**), 2-*N*-etilanilinoquinolina (**40**), 2-*N*-(*m*-metoksi)anilinoquinolina (**42**), 2-*N*-(*p*-metoksi)anilinoquinolina (**44**), 2-*N*-(*m*-kloro)anilinoquinolina (**46**), dan 2-*N*-(*p*-kloro)anilinoquinolina (**48**) disediakan melalui tindakbalas 2-kloroquinolina (**22**) dengan 3-metilpiperidina (**23**), 4-metilpiperidina (**24**), anilina (**27**), *m*-toluidina (**29**), *p*-toluidina (**31**), *m*-etilanilina (**33**), *p*-etilanilina (**35**), *N*-metilanilina (**37**), *N*-etilanilina (**39**), *m*-anisidina (**41**), *p*-anisidina (**43**), *m*-kloroanilina (**45**) and *p*-kloroanilina (**47**). Struktur sebatian ini ditentukan menggunakan ^1H NMR, ^{13}C NMR, infra-merah and GCMS. Ciri pendafluoran telah direkod menggunakan Spektrometer Pendafluoran. Hampir semua sebatian yang disediakan menunjukkan keamatan pendafluoran paling tinggi dalam pelarut kurang berkutub dan keamatan pendafluoran yang rendah dalam pelarut protik berkutub. Sebatian **30**, **34** dan **48** menunjukkan keamatan pendafluoran tinggi dalam keadaan berbes dan neutral dan keamatan pendafluoran yang rendah direkodkan dalam keadaan berasid.

ACKNOWLEDGEMENT

Firstly, sincere and deep gratitude goes to my supervisors, Professor Dr. Zanariah Abdullah and Dr. Hairul Anuar Tajuddin as always giving guidance and support during this work. Their understanding, encouraging and personal guidance have provided a good basic for this thesis.

Thanks you to all my friends for a lot of help in completing the laboratory work and provide moral support to complete this task. My warm thanks to the staff members of Chemistry Department for their kind support throughout this work.

My special gratitude goes to my parents, Hasan Md. Ali and Aminah Mustaffa for their concern and loving support. Special thanks to my siblings for their care and understanding to complete my work.

Finally, I'm grateful to University of Malaya for the Fellowship and Research Grant for their financial assistance throughout the entire course.

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ABSTRAK	iii
ACKNOWLEDGEMENT	iv
TABLE OF CONTENTS	v
APPENDICES	ix
LIST OF FIGURES	x
LIST OF TABLES	xii
LIST OF SCHEMES	xii
LIST OF SYMBOLS AND ABBREVIATIONS	xiv

CHAPTER ONE: SYNTHESIS AND REACTIVITY OF QUINOLINE

1.0	Introduction of Quinoline	1
1.2	Synthesis of Quinoline	2
1.2.1	Skraup synthesis	2
1.2.2	Doebner-von Miller synthesis	2
1.2.3	The Combes synthesis	3
1.2.4	The Friedländer synthesis	3

1.3	Reactivity of Quinoline	4
1.3.1	General features of the chemistry of quinolines	4
1.3.2	Reactions with nucleophilic reagents	5
1.3.2.1	Nucleophilic substitution with hydride transfer	5
1.3.2.2	Nucleophilic substitution with displacement of halide	6

CHAPTER TWO: FLUORESCENCE SPECTROSCOPY

2.0	Introduction	7
2.1	Historical development	7
2.2	Theory of fluorescence	8
2.3	Factors that effect the fluorescence characteristic	11
2.3.1	Environmental effects	11
2.3.1.1	Solvent effects	11
2.3.1.2	Influence of pH	13
2.3.1.3	Effect of oxygen	15
2.3.2	Chemical structure	16
2.3.2.1	Carbon skeleton	16
2.3.2.2	The geometrical arrangement of the molecules	17
2.3.2.3	The type and positions of substituents	18

2.4	Instrumentation of fluorescence spectroscopy	19
2.4.1	Light sources	20
2.4.2	Monochromators	20
2.4.3	Slits	21
2.4.4	Sample cells	22
2.4.5	Detectors	22
2.5	Objectives of the project	23

CHAPTER 3: RESULTS AND DISCUSSION

3.1	Synthesis of Quinoline Derivatives	24
3.1.1	2- <i>N</i> -(3-methyl)piperidinoquinoline (25) and 2- <i>N</i> -(4-methyl)piperidinoquinoline (26)	25
3.1.2	Reactions of 22 with Various Amines.	27
3.3	Fluorescence Characteristics	37

CHAPTER 4: CONCLUSION

CHAPTER 5: EXPERIMENTAL DETAILS

5.0	General procedures	52
5.1	Preparation of quinoline derivatives	53
5.1.1	Preparation of 2- <i>N</i> -(<i>m</i> -methyl)piperidinoquinoline (25)	53

5.1.2	Preparation of 2- <i>N</i> -(<i>p</i> -methyl)piperidinoquinoline (26)	54
5.1.3	Preparation of 2- <i>N</i> -anilinoquinoline (28)	55
5.1.4	Preparation of 2- <i>N</i> -(<i>m</i> -methyl)anilinoquinoline (30)	56
5.1.5	Preparation of 2- <i>N</i> -(<i>p</i> -methyl)anilinoquinoline (32)	57
5.1.6	Preparation of 2- <i>N</i> -(<i>m</i> -ethyl)anilinoquinoline (34)	58
5.1.7	Preparation of 2- <i>N</i> -(<i>p</i> -ethyl)anilinoquinoline (36)	59
5.1.8	Preparation of 2- <i>N</i> -methylanilinoquinoline (38)	60
5.1.9	Preparation of 2- <i>N</i> -ethylanilinoquinoline (40)	61
5.1.10	Preparation of 2- <i>N</i> -(<i>m</i> -methoxy)anilinoquinoline (42)	62
5.1.11	Preparation of 2- <i>N</i> -(<i>p</i> -methoxy)anilinoquinoline (44)	63
5.1.12	Preparation of 2- <i>N</i> -(<i>m</i> -chloro)anilinoquinoline (46)	64
5.1.13	Preparation of 2- <i>N</i> -(<i>p</i> -chloro)anilinoquinoline (48)	65
5.2	Fluorescence Measurements	66
5.2.1	Fluorescence Measurement of quinoline derivatives	66

REFERENCES	69
-------------------	----

LIST OF PUBLICATIONS

CONFERENCE PROCEEDINGS

APPENDICES

Appendix 1: ¹H, ¹³C, IR, GCMS spectra for all compounds prepared

Appendix 2: Fluorescence spectra for all compounds prepared in various solvents

Appendix 3: Publications

LIST OF FIGURES

	Page
Figure 1.1: Structure and numbering of quinoline	1
Figure 1.2: Skraup synthesis of quinoline	2
Figure 1.3: Doebner-von Miller synthesis of quinoline	3
Figure 1.4: Combes synthesis of quinoline	3
Figure 1.5: Friedländer synthesis of quinoline	4
Figure 1.6: Addition reactions initiated by electrophilic attack at nitrogen	5
Figure 1.7: Alkylation and arylation of quinoline	5
Figure 1.8: Amination of quinoline	6
Figure 1.9: Nucleophilic substitution with displacement of halide of quinoline	6
Figure 2.1: Transition giving rise to absorption and fluorescence emission spectra	9
Figure 2.2: Schematic representation of equilibrium and Franck-Condon (F-C) electronic states	12
Figure 2.3: Overall excitation-reaction sequence of phenol	14
Figure 2.4: Schematic diagram of a typical fluorescence measuring devices	19
Figure 3.1: Reactions of 2-chloroquinoline with various piperidine	25
Figure 3.2: Reactions of 2-chloroquinoline with anilines derivatives	28
Figure 3.3: Ortep diagram of 2- <i>N</i> -(<i>p</i> -chloro)anilinoquinoline (48)	37
Figure 3.4: Fluorescence intensity of 28 , 36 and 48 in different solvent	38
Figure 3.5: The formation of a complex with the solvent through hydrogen bonding	39
Figure 3.6: The formation of a complex with the solvent through hydrogen bonding	40
Figure 3.7: Proton transfer to the ring nitrogen	40

Figure 3.8: Intramolecular charge transfer transitions via hydrogen bonding	41
Figure 3.9: Fluorescence graph of 2- <i>N</i> -anilinoquinoline (28) in different time in chloroform (4.5399×10^{-4} M)	42
Figure 3.10: Fluorescence graph of 2- <i>N</i> -(<i>p</i> -methyl)anilinoquinoline (32) in different time in chloroform (4.2680×10^{-4} M)	42
Figure 3.11: Fluorescence graph of 2- <i>N</i> -(<i>p</i> -chloro)anilinoquinoline (48) in different time in chloroform (3.9260×10^{-4} M)	43
Figure 3.12: Fluorescence intensity of 2- <i>N</i> -anilinoquinoline (28) at different concentration in ethyl acetate	44
Figure 3.13: Fluorescence intensity of 2- <i>N</i> -(<i>p</i> -ethyl)anilinoquinoline (36) at different concentration in ethyl acetate	45
Figure 3.14: Fluorescence intensity of 2- <i>N</i> -(<i>p</i> -chloro)anilinoquinoline (48) at different concentration in ethyl acetate	45
Figure 3.15: Fluorescence intensity of 2- <i>N</i> -(<i>m</i> -methyl)anilinoquinoline (30) in pH 5, 7 and 9	48
Figure 3.16: Fluorescence intensity of 2- <i>N</i> -(<i>m</i> -ethyl)anilinoquinoline (34) in pH 5, 7 and 9	48
Figure 3.17: Fluorescence intensity of 2- <i>N</i> -(<i>p</i> -chloro)anilinoquinoline (48) in pH 5, 7 and 9	49
Figure 3.18: The proton transfer to the ring nitrogen of 2- <i>N</i> -(<i>m</i> -methyl)anilinoquinoline (30) and 2- <i>N</i> -(<i>m</i> -ethyl)anilinoquinoline (34)	50
Figure 3.19: The proton transfer to the ring nitrogen of 2- <i>N</i> -(<i>p</i> -chloro)anilinoquinoline (48)	50

LIST OF TABLES

	Page
Table 3.1: Crystal data and structure refinement of 48	36
Table 3.2: Fluorescence characteristic of 28 , 36 and 48 in different solvents	38
Table 3.3: Fluorescence characteristic of 28 , 36 and 48 in different concentrations	44
Table 3.4: Fluorescence characteristic of 30 , 34 and 48 in acetonitrile with variation of pH.	47

LIST OF SCHEMES

	Page
Scheme 3.1: Proposed reaction of nucleophilic substitution between 2-chloroquinoline and amines at position-2 of quinoline system	25

LIST OF SYMBOLS AND ABBREVIATIONS

The following symbols and abbreviations have been used throughout this thesis.

CDCl_3	deuterated chloroform
CH_3CN	acetonitrile
d	doublet
dd	doublet of doublets
EtOAc	ethyl acetate
EtOH	ethanol
IR	infrared
J	coupling constant
M	mole per liter
m	multiplet
m.p	melting point
min.	minute
MW	molecular weight
NMR	nuclear magnetic resonance
q	quartet
s	singlet
t	triplet
td	triplet of doublets
THF	tetrahydrofuran
TLC	thin layer chromatography
δ	chemical shift
λ	wavelength
ν	stretching vibration