

**SYNTHETIC APPROACHES TO
2-SUBSTITUTED PYRAZINES AND
2-SUBSTITUTED QUINOXALINES AND THEIR
FLUORESCENCE CHARACTERISTICS**

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**DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
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KUALA LUMPUR**

2009

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AZILA MOHD IDRIS

**A DISSERTATION SUBMITTED IN FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE**

**DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2009

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ABSTRACT

Treatment of 2-chloropyrazine and 2-chloroquinoxaline with piperidines, anilines, phenoxy and cresols gave 2-*N*-piperidinopyrazine (**37**), 2-*N*-(3-methyl)piperidinopyrazine (**38**), 2-*N*-(4-methyl)piperidinopyrazine (**39**), 2-*N*-anilinopyrazine (**46**), 2-*N*-(*m*-methyl)anilinopyrazine (**47**), 2-*N*-(*p*-methyl)anilinopyrazine (**48**), 2-*N*-(*m*-methoxy)anilinopyrazine (**49**), 2-*N*-(*p*-methoxy)anilinopyrazine (**50**), 2-*N*-(*p*-chloro)anilinopyrazine (**51**), 2-phenoxy pyrazine (**55**), 2-(*m*-methyl)phenoxy pyrazine (**56**), 2-(*p*-methyl)phenoxy pyrazine (**57**), 2-*N*-piperidinoquinoxaline (**59**), 2-*N*-(3-methyl)piperidinoquinoxaline (**60**), 2-*N*-(4-methyl)piperidinoquinoxaline (**61**), 2-*N*-anilinoquinoxaline (**62**), 2-*N*-(*m*-methyl)anilinoquinoxaline (**63**), 2-*N*-(*p*-methyl)anilinoquinoxaline (**64**), 2-*N*-(*m*-methoxy)anilinoquinoxaline (**65**), 2-*N*-(*p*-methoxy)anilinoquinoxaline (**66**), 2-*N*-(*p*-chloro)anilinoquinoxaline (**67**), 2-phenoxyquinoxaline (**68**), 2-(*m*-methyl)phenoxyquinoxaline (**69**) and 2-(*p*-methyl)phenoxyquinoxaline (**70**). The structures of the compounds prepared were confirmed by spectroscopic methods such as ¹H NMR, ¹³C NMR, IR, GCMS spectra and X-Ray Diffraction method.

All *N*-alkylamino, *N*-arylamino and phenoxy derivatives of pyrazine and quinoxaline showed fluorescence properties. Out of 24 compounds prepared, 17 of the compounds showed highest fluorescence intensity in polar aprotic solvent with higher dielectric constant. The study also shows that the fluorescence intensity of capped samples is higher than the uncapped samples. 2-*N*-piperidinopyrazine (**37**), 2-*N*-anilinopyrazine (**46**), 2-*N*-piperidinoquinoxaline (**59**) and 2-*N*-anilinoquinoxaline (**62**) showed higher intensity in neutral and alkaline conditions whereas reduced fluorescence intensity was observed in acidic condition. 2-Substituted quinoxalines tend

to fluoresce at a higher wavelength compared to the respective of 2-substituted pyrazines.

ABSTRAK

Tindakbalas bagi 2-kloropirazina dan 2-klorokuinozalina dengan piperidina, analina, fenoksi dan kresol memberikan 2-*N*-piperidinopirazina (**37**), 2-*N*-(3-metil)piperidinopyrazina (**38**), 2-*N*-(4-metil)piperidinopirazina (**39**), 2-*N*-anilinopirazina (**46**), 2-*N*-(*m*-metil)anilinopirazina (**47**), 2-*N*-(*p*-metil)anilinopirazina (**48**), 2-*N*-(*m*-metoksi)anilinopirazina (**49**), 2-*N*-(*p*-metoksi)anilinopirazina (**50**), 2-*N*-(*p*-kloro)anilinopirazina (**50**), 2-fenoksipirazina (**55**), 2-(*m*-metil)fenoksipirazina (**56**), 2-(*p*-metil)fenoksipirazina (**57**), 2-*N*-piperidinokuinozalina (**59**), 2-*N*-(3-metil)piperidinokuinozalina (**60**), 2-*N*-(4-metil)piperidinokuinozalina (**61**), 2-*N*-anilinokuinozalina (**62**), 2-*N*-(*m*-metil)anilinokuinozalina (**63**), 2-*N*-(*p*-metil)anilinokuinozalina (**64**), 2-*N*-(*m*-metoksi)anilinokuinozalina (**65**), 2-*N*-(*p*-metoksi)anilinokuinozalina (**66**), 2-*N*-(*p*-kloro)anilinokuinozalina (**67**), 2-fenoksikuinozalina (**68**), 2-(*m*-metil)fenoksikuinozalina (**69**), 2-(*p*-metil)fenoksikuinozalina (**70**). Struktur sebatian yang diperolehi dikenalpasti dengan menggunakan kaedah X-Ray.

Kesemua terbitan *N*-alkilamino, *N*-arilamino, fenoksi pirazina dan kuinozalina menunjukkan keamatan pendafluoran yang tinggi dalam larutan polar aprotik dan mempunyai pemalar dielektrik tinggi. Kajian juga menunjukkan keamatan pendafluoran bagi sampel tertutup lebih tinggi berbanding sampel terbuka. 2-*N*-piperidinopirazina (**37**), 2-*N*-anilinopirazina (**46**), 2-*N*-piperidinokuinozalina (**59**) dan 2-*N*-anilinokuinozalina (**62**) menunjukkan keamatan pendafluoran yang tinggi dalam keadaan neutral dan berkali manakala keamatan menurun dalam keadaan berasid.

2-Terbitan tertukarganti kuinozalina cenderung untuk berpendafluor pada panjang gelombang yang tinggi berbanding 2-terbitan tertukarganti pirazina.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge all of individuals who have contributed towards completion of this thesis.

Firstly, I wish to express sincere thanks to my supervisor and co-supervisor, Assoc. Prof. Dr. Azhar Ariffin and Prof. Dr. Zanariah Abdullah for their help and constant support over the whole duration of this research. They were always there when needed to discuss the problem that I encountered and drawing upon their vast knowledge of the subject always had an answer.

The help given by the staff members of the Chemistry Department are greatly acknowledged. I am also indebted to many others who have helped in one way or another in carrying out my research work.

My special thanks also go to all of my friends especially the members from my group for being such wonderful, understanding and supportive friends. They are the reasons for my enjoyable, conducive working and living environment.

I would also like to thank the University of Malaya for the SLAB Scheme, Research Grant (PJP: FS 302/2007C) and The Ministry of Higher Education for their financial assistance throughout the entire course.

Lastly, grateful appreciation is also given to my beloved parents and siblings for their unconditional love and inspiration throughout my education. Through thick and thin, they are always and forever my strongest pillars. Without their support, this work would not have been done smoothly.

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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
ddd	doublet of doublets of doublets
Eq	equivalent
EtOAc	ethyl acetate
EtOH	ethanol
IR	infrared
J	coupling constant
M	mole per litre
m	multiplet
m.p.	melting point
min	minute
MW	molecular weight
NMR	nuclear magnetic resonance
s	singlet
t	triplet
THF	tetrahydrofuran
TLC	thin layer chromatography
λ	wavelength
ν	stretching vibration
δ	chemical shift