

**TOWARDS THE TRANSFER OF CHIRALITY FROM
MOLECULAR MOTORS TO BIARYLS VIA NON-COVALENT
INTERACTIONS**

THESIS

**As a pre-requisite
to obtain Master Degree from
Insitut Teknologi Bandung**

By

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INSTITUT TEKNOLOGI BANDUNG

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ABSTRACT

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Chirality is a property of molecules which plays a big role in many aspects of living systems. Since its discovery by Louis Pasteur in 1848, much research on the chirality of both natural and synthetic compounds has been carried out. One of the most interesting topics in this field is the chiral induction, in which chirality is transferred from a chiral molecule to an achiral molecule. In this research, a series of complexes was designed for chirality transfer from a chiral ‘first-generation’ biphenol molecular motor to conformationally flexible biaryls, such as 3,3'-bipyridine, 4,4'-biisoquinoline, 1,1'-dimethyl-4,4'-biisoquinoline, and 1,1'-diphenyl-4,4'-biisoquinoline through hydrogen bonding. The biphenol molecular motor was successfully synthesized in three reaction steps, namely Friedel-Crafts alkylation and subsequent acylation, McMurry homocoupling, and deprotection of methoxy groups in good yield for each step (59–74%). Both enantiomers of the biphenol motor were obtained in high enantiomeric excess (>99%) from resolution of the synthesized motor with (8*S*,9*R*)-*N*-benzylcinchonidinium chloride using either ethyl acetate or acetonitrile as the solvent. Each of the four biaryls was synthesized in one reaction step, either Pd-catalyzed cross coupling, Ni-catalyzed homocoupling, or 1,4-functionalization in low to moderate yields (5–49%). Furthermore, photochemical and thermal isomerization steps of bismethoxy motor, an intermediate in the synthesis of biphenol motor, were studied by means of UV-Vis and ¹H NMR spectroscopy. The results showed that the introduction of the methoxy group in the motor does not have a significant influence on the thermal isomerization steps. NMR study revealed that there were no hydrogen bonding between the biphenol motor with either 3,3'-bipyridine or 4,4'-biisoquinoline. Similar result was obtained when the biaryl was substituted with chiral aliphatic diamines. A new design of complex for chirality transfer employing a pyridine-based molecular motor was constructed, but attempts on the synthesis of the motor scaffold were unsuccessful.

Keywords: chirality transfer, biphenol, molecular motor, biaryls, hydrogen bonding.

ABSTRAK

**KAJIAN TRANSFER KIRALITAS DARI
MOTOR MOLEKUL KE SENYAWA BIARIL MELALUI
INTERAKSI NON-KOVALEN**

Oleh

Jefri

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Kiralitas adalah sifat molekul yang memiliki peranan besar dalam berbagai aspek kehidupan. Sejak penemuannya oleh Louis Pasteur pada tahun 1848, banyak penelitian tentang kiralitas senyawa bahan alam dan sintetik telah dilakukan. Salah satu topik yang paling menarik dalam bidang ini adalah induksi kiralitas, dimana kiralitas ditransfer dari suatu molekul kiral ke molekul akiral lain. Dalam penelitian ini, serangkaian molekul kompleks dirancang untuk transfer kiralitas dari motor molekul bifenol ‘generasi pertama’ yang kiral ke senyawa biaril yang fleksibel secara konformasi, seperti 3,3’-bipiridin, 4,4’-biisokuinolin, 1,1’-dimetil-4,4’-biisokuinolin, dan 1,1’-difenil-4,4’-biisokuinolin melalui pembentukan ikatan hidrogen. Senyawa motor molekul bifenol berhasil disintesis melalui tiga tahap reaksi, yaitu reaksi alkilasi Friedel-Crafts diikuti asilasi, homokupling McMurry, dan deproteksi gugus metoksi dengan rendemen yang baik untuk setiap tahap (59–74%). Kedua enansiomer motor molekul bifenol diperoleh dalam *enantiomeric excess* tinggi (>99%) dari resolusi motor molekul hasil sintesis dengan (8*S*,9*R*)-*N*-benzilcinchonidinium klorida menggunakan etil asetat atau asetonitril sebagai pelarut. Masing-masing senyawa biaril disintesis melalui satu tahap reaksi, yaitu reaksi kupling-silang-terkatalisis-Pd, homokupling-terkatalisis-Ni, atau fungsionalisasi-1,4 dengan rendemen rendah hingga sedang (5–49%). Selanjutnya, tahap isomerisasi fotokimia dan termal motor molekul bismetoksi, intermediat dalam sintesis motor molekul bifenol, dipelajari menggunakan spektroskopi UV-Vis dan ¹H NMR. Hasilnya menunjukkan bahwa gugus metoksi dalam motor molekul tidak memiliki pengaruh signifikan dalam tahap isomerisasi termal. Studi NMR menunjukkan tidak adanya pembentukan ikatan hidrogen antara motor molekul bifenol dengan 3,3’-bipiridin maupun 4,4’-biisokuinolin seperti yang diharapkan. Hasil serupa juga diperoleh ketika senyawa biaril diganti dengan senyawa diamina alifatik kiral. Sebuah kompleks baru untuk transfer kiralitas menggunakan motor molekul berbasis piridin dirancang, tetapi upaya untuk mensintesis kerangka motor tersebut belum berhasil.

Kata kunci: transfer kiralitas, bifenol, motor molekul, biaril, ikatan hidrogen.

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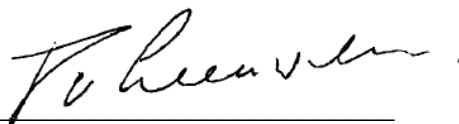
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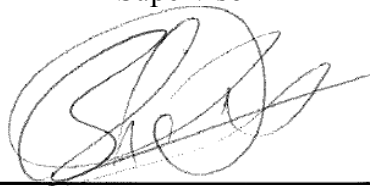


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GUIDELINE FOR USING THIS THESIS

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Dedicated to my father, my mother, and my brothers.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATION	FULL FORM	First time used in page
DNA	Deoxyribonucleic Acid	1
CD	Circular Dichroism	3
NMR	Nuclear Magnetic Resonance	3
CAHB	Charged-Assisted Hydrogen Bond	3
UV-Vis	Ultraviolet-Visible	7
MeLi	Methylithium	8
PhLi	Phenyllithium	8
HRMS	High Resolution Mass Spectroscopy	8
SFC	Supercritical Fluid Chromatography	8
PSS	Photostationary State	8
kJ	kilo Joule	15
s	second	15
min	minute	15
K	Kelvin	15
TS	Transition State	16
BINOL	1,1'-Bi-2-naphthol	18
R _f	Retention factor	19
CPL	Circularly Polarized Light	20
L-CPL	Left-handed Circularly Polarized Light	20
R-CPL	Right-handed Circularly Polarized Light	20
T	Temperature	23
H	Host	24
G	Guest	24
C	Complex	24
M	Molar	26
TLC	Thin Layer Chromatography	28
PMA	Phosphomolybdic Acid	28
ESI	Electrospray Ionization	28

APCI	Atmospheric Pressure Chemical Ionization	28
μm	micrometer	28
nm	nanometer	28
MHz	Mega Hertz	28
ppm	parts per million	28
eq	equivalent	29
cm	centimeter	29
g	gram	29
mL	milli Liter	29
h	hour	29
Et ₂ O	Diethylether	29
PPA	Polyphosphoric Acid	29
EtOH	Ethanol	30
lit	literature	30
calcd	calculated	30
THF	Tetrahydrofuran	30
EtOAc	Ethylacetate	30
mmol	millimol	31
PPh ₃	Triphenylphosphine	32
Et ₄ NI	Tetraethylammonium iodide	32
DME	1,2-Dimethoxyethane	33
DDQ	2,3-Dichloro-5,6-dicyano- <i>p</i> -benzoquinone	33
DCM	Dichloromethane	34
DMF	<i>N,N</i> -dimethylformamide	34
<i>ee</i>	enantiomeric excess	36
d	day	42
rt	room temperature	49
Phen	1,10-Phenantroline	51
MeOH	Methanol	56
Et ₃ N	Triethylamine	69
cat	catalytic	70
GC-MS	Gas Chromatography-Mass Spectroscopy	73
EI	Electron Impact	73

LDA	Lithium Diisopropylamide	74
n-BuLi	normal-buthyllithium	75

SYMBOL

pK_a	Acid dissociation constant at logarithmic scale	3
$\Delta H^\ddagger$	Enthalpy of activation	8
$\Delta S^\ddagger$	Entropy of activation	8
$\Delta G^\ddagger$	Gibbs free energy of activation	8
τ	Half-life	15
$^\circ\text{C}$	Celcius degree	15
%	Percent	16
$\Delta\varepsilon$	Difference of molar absorptivity	20
A_L	Absorbance of left-handed circularly polarized light	20
A_R	Absorbance of right-handed circularly polarized light	20
ε_L	Molar absorptivity of left-handed circularly polarized light	20
ε_R	Molar absorptivity of right-handed circularly polarized light	20
[J]	Molar concentration of sample	20
l	Path length of sample	20
$k^\ddagger$	Rate constant of activation	23
κ	Transmission coefficient	23
ν	Vibrational frequency of relevance	23
k	Rate constant	23
k_B	Boltzmann constant	23
h	Planck's constant	23
R	Gas constant	23
A	Arrhenius constant	23
E_a	Energy of activation	23
K	Binding constant	24
$[\text{H}]_t$	Total concentration of host at initial stage	24

$[G]_t$	Total concentration of guest at initial stage	24
$[C]_t$	Total concentration of complex at initial stage	24
$[H]$	Concentration of host at equilibrium	24
$[G]$	Concentration of guest at equilibrium	24
$[C]$	Concentration of complex at equilibrium	24
δ	Chemical shift	25
c	Concentration	29
J	Coupling constant	30
$[\alpha]_D^{20}$	Specific rotation using D line of sodium spectrum at 20 °C	36
λ	Wavelength	37
π	Phi bond	51