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PII:	S0040-4039(19)30241-2	
DOI:	https://doi.org/10.1016/j.tetlet.2019.03.035	
Reference:	TETL 50676	
To appear in:	Tetrahedron Letters	
Received Date:	5 February 2019	
Revised Date:	8 March 2019	
Accepted Date:	12 March 2019	



Please cite this article as: Iwanaga, T., Asano, N., Yamada, H., Toyota, S., Synthesis and photophysical properties of dinaphtho[2,3-*b*:2',3'-*i*]-dihydrophenazine derivatives, *Tetrahedron Letters* (2019), doi: https://doi.org/10.1016/j.tetlet.2019.03.035

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Tetrahedron Letters

journal homepage: www.elsevier.com

Synthesis and photophysical properties of dinaphtho[2,3-*b*:2',3'-*i*]dihydrophenazine derivatives

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Dedicated to Emeritus Prof. Takahiko Inazu in celebration of his 81th birthday.

ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

Keywords: Dinaphtho[2,3-*b*:2',3'-*i*]dihydrophenazine Photophysical property Electrochemical property Intramolecular charge-transfer interaction

ABSTRACT

A dinaphtho[2,3-*b*:2',3'-*i*]dihydrophenazine (DNP) derivative was synthesized by Buchwald-Hartwig cross-coupling, and its electronic spectrum was compared with that of dinaphtho[*b*,*i*]dihydrophenazine-5,18-dione (DNP-dione) as an anthraquinone analog. An absorption band of DNP is attributed to extension of π -conjugation over the entire molecule via the N atom. DNP-dione showed a broad absorption band in the range 450–490 nm due to intramolecular charge-transfer interactions. Additionally, the absolute fluorescence quantum yield of DNP was larger than that of DNP-dione. DNP-dione exhibited reversible oxidation peaks and a similar oxidation potential to DNP, since there are very weak electronic interactions between the anthracene and anthraquinone units across the N atoms with the 4-octyloxyphenyl substituent.

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1. Introduction

As an electron-sufficient moiety, the phenazine framework has proven an attractive building unit for the molecular design of new π -conjugated functional materials.¹ Particularly, π -extended phenazine derivatives, including aza analogs² of pentacenes and heptacenes, have been extensively applied to developing new organic dyes and devices,³ such as organic field-effect transistors.⁴ Dibenzo[*b*,*i*]dihydrophenazine is also a promising candidate for constructing different functional molecules,⁵ while anthraquinone-based dihydrophenazine derivatives such as indanthrone have been used as organic dyes.⁶ Recently, Shinokubo et al. reported the facile synthesis of π -extended dinaphtho[*a*,*h*]dihydrophenazines with zigzag structure by oxidation using DDQ.⁷



Figure 1. Molecular structures of dinaphtho[2,3-*b*:2',3'-*i*]-dihydrophenazine derivatives **1** and **2**.

However, to the best of our knowledge, linear-type dinaphtho[2,3-b:2',3'-i]dihydrophenazine derivatives and

anthraquinone analogs have not yet been reported in the literature. Thus, we designed dinaphtho[2,3-b:2',3'i]dihydrophenazine 1 and dinaphtho[2,3-b:2',3'i]dihydrophenazine-5,18-dione 2 possessing a anthraquinone unit, in which the nitrogen atoms derived from 4-octyloxyaniline function as connecting groups (Figure 1). These derivatives were diaza analogs of 7,16-diphenylheptacene, which is an extremely weak photo-oxidation.8 Herein, we report the synthesis and spectroscopic data of dinaphtho derivative 1 and its quinone analog 2, and their photophysical and electrochemical properties are compared to assess the electronic interactions via nitrogen atoms.

2. Results and Discussion

2.1. Synthesis



Scheme 1. Synthesis of 2,3-dibromoanthraquinone **3** and 2,3-dibromoanthracene **4**.





Scheme 2. Synthesis of 2,3-diaminoanthracene derivative 6.



Scheme 3. Synthesis of dinaphtho[*b*,*i*]dihydrophenazine derivatives 1 and 2.

To synthesize the target phenazine derivatives, 2,3dibromoanthracene 4^9 was used as a key intermediate for amination via cross-coupling.¹⁰ This precursor was produced according to **Scheme 1**. Friedel-Crafts reaction of phthalic anhydride with 1,2-dibromobenzene in the presence of AlCl₃ yielded the adduct, which was then dehydrated with conc. H₂SO₄ to afford 2,3-dibromoanthraquinone **3** via the known method.¹¹ Reduction of **3** with NaBH₄ gave 2,3-dibromoanthracene **4** in a stepwise manner. Compound **4** was produced in 17% overall yield from 1,2-dibromobenzene.

Conventional Buchwald-Hartwig coupling of 4 with 4octyloxyaniline **5** $(2 \text{ equiv.})^{12}$ gave compound **6** as a yellow solid in 64% yield (**Scheme 2**). The reaction conditions were optimized for synthesizing 1 from dibromide 4 and diamine 6 (Scheme 3). We reacted 4 and 6 in the presence of Pd(X-Phos_G1) in xylene under reflux for 48 h, this reaction gave a complicated mixture which is not including the target compound. The reaction with 10 mol% of $Pd(t-Bu_3P)_2$ gave the desired compound in 3% yield. This yield was further increased to 5% by adding $Pd(dba)_2$ and $t-Bu_3PHBF_4$ rather than $Pd(t-Bu_3P)_2$; this tetrafluoroborate salt easily generates fresh Pd(0) catalyst in this reaction system. Anthraquinone analog 2 was prepared by same coupling using $Pd(t-Bu_3P)_2$ catalyst 2,3cross of dibromoanthraquinone 3 and diamine 6 (3% yield).

These compounds showed good stability under ambient conditions and were reliably characterized by NMR and mass spectroscopy. Molecular ion peaks of **1** and **2** were observed at m/z 790.45 ($C_{56}H_{58}N_2O_2$) and 820.43 ($C_{56}H_{56}N_2O_4$), respectively, in the mass spectra. In the ¹H NMR spectrum of **1**, two singlets were observed in the aromatic region at δ 7.7 and 6.3, while in the ¹³C NMR spectrum, compound **2** gave a signal due to carbonyl carbons at δ 182.0. Compounds **1** and **2** gave 11 and 17 aromatic carbon signals, respectively, which was consistent with their molecular symmetry.

2.2. Structures

We obtained a single crystal of compound **1** suitable for X-ray analysis from a hexane/CH₂Cl₂ solution (**Figure 2**).¹³ As expected, compound **1** has a planar framework with C_{2h} symmetry. To avoid steric hindrance, the two 4-octyloxyphenyl groups are twisted from the naphthophenazine plane as indicated



Figure 2. X-ray structure (a) and packing diagram (b) of compound 1 (solvent molecules are included).

by the dihedral angles (θ) between the two planes (+81.1° and -75.6°). In the crystal packing, intermolecular C-H··· π contacts (2.8 Å) between the anthracene and phenyl groups rather than π ··· π contacts (3.5 Å) between the anthracene units are dominant. The molecules have no significant intermolecular contacts as they are sterically protected by the two 4-octyloxyphenyl groups. Because we could not obtain single crystals suitable for X-ray analysis for 2, the molecular structure of model compound 2' possessing methoxy groups in place of octyloxy groups was optimized at the B3LYP/6-31G(d) level (Figure S1). In the global minimum structures, compound 2' has a planar framework with a large surface area.



Figure 3. UV-vis (solid line) and FL (dotted line) spectra of compounds 1 and 2 in CH₂Cl₂.

2.3. Electronic Spectra

The absorption spectra of compounds 1 and 2 were recorded in CH₂Cl₂ (**Figure 3**). The spectroscopic data are summarized in Table 1. These compounds showed absorptions at λ_{max} 474 nm (1) and 431 nm (2). An absorption band for 1 is attributed to extension of π -conjugation over the entire molecule via the N atom, while compound 2 exhibited a characteristic broad shoulder band extending to ca. 490 nm in the longest wavelength

Table 1. UV-vis absorption and fluorescence data for compounds **1** and **2** in CH₂Cl₂.

	$\lambda_{\rm max}/{\rm nm}$	calcd $\lambda_{\rm max}$ /nm (f) ^a	$\lambda_{\rm em}/{\rm nm}$	
	(8)	[composition of band]	$({oldsymbol{ \Phi}}_{\! F})^{ m b}$	
1	474	443 (0.65)	483 (0.72)	
	(59600)	[H-1->L, 45%; H->L+2, 3%]		
2	431 (68000)	646 (0.02) [H->L, 49%]		
		553 (0.08)	N. D. ^c	
		[H-1->L, 48%; H-1->L, 2%]		

^aTD-DFT calculations (TD/B3LYP/6-31G(d)) were performed by using optimized structures of compounds **1'** and **2'** at the B3LYP/6-31G(d) level; f = oscillator strength.

^bAbsolute fluorescence quantum yields.

°Not measured due to weak fluorescence.



Figure 4. Energy levels (eV) and calculated MOs of **1**' and **2**' (octyloxy groups were replaced to methoxy groups) using the B3LYP/6-31G(d) level of theory.

region. This broad band of **2** was assigned to the HOMO-1 to LUMO transition based on TD-DFT calculations using model compound **2'** as described above. The calculated MOs of **2'** suggested that the HOMO-1 and LUMO levels were mainly located on the anthracene and anthraquinone units, respectively (**Figure 4**). Thus, the shoulder absorption peak of **2** at 450-490 nm is attributed to an intramolecular charge-transfer interaction.

The fluorescence spectra were measured in CH₂Cl₂ (**Figure 3** and **Table 1**). An emission peak for compound **1** was observed at 483 nm, while compound **2** showed a weak emission. The absolute fluorescence quantum yield $\Phi_{\rm F}$ of **1** was 0.72. The non-fluorescence of **2** was attributed to efficient photoinduced intramolecular electron-transfer from anthracene to the anthraquinone unit.¹⁴

2.4. Electrochemical Properties

Finally, the redox properties of 1 and 2 were explored by cyclic voltammetry in CH_2Cl_2 (Figure 5). The redox potentials

and calculated energy levels are given in Table 2. Compound 1 gave irreversible reduction potentials, while compound 2 gave reversible reduction potentials at -1.48 and -1.71 V due to the formation of a radical anion and a dianion species of the anthraquinone unit, respectively. The first oxidation peak of 1 was observed at +0.24 V, and that of 2 at a similar potential (+0.26 V). There are very weak electronic interactions between the anthracene and anthraquinone units through the N atoms of the *p*-alkoxyphenyl substituent. This tendency is consistent with the calculated HOMO energies given in Table 2.

Table 2. Electrochemical	data for compounds 1 and 2.

	$E^{1/2}_{ox}$ /V ^a	$E^{1/2}_{ m red}$ /V ^a	НОМО	LUMO
			level /eV ^b	level /eV $^{\rm b}$
1	+0.24	_c	-4.52	-1.45
2	+0.26	-1.48, -1.71	-4.74	-2.37

^a Measured in CH₂Cl₂ (1.00 mmol L^{-1}) with *n*-Bu₄NBF₄ (0.10 mol L^{-1}) as the supporting electrolyte and Ag/Ag⁺ as the reference electrode.

 $^{\rm b}$ Calculated at the B3LYP/6-31G(d) level for model compounds 1' and 2'.

^c Only the first redox potential is shown due to irreversible waves.



Figure 5. Cyclic voltammograms of **1** (black) and **2** (red) in CH_2Cl_2 with 0.10 mmol L^{-1} *n*-Bu₄NPF₆ as supporting electrolyte, Ag/Ag⁺ as reference electrode, a glass carbon disk as working electrode, a Pt wire as counter electrode, and a scan rate of 0.10 V s⁻¹.

3. Conclusion

In conclusion, we synthesized dinaphtho[b,i]dihydrophenazine derivatives via Buchwald-Hartwig coupling. The X-ray crystallographic analysis of 1 indicated a planar structure. The photophysical properties were influenced by nitrogen atoms, resulting in extended π -conjugation for 1 and intramolecular donor–acceptor interactions for 2. The oxidation potentials of 1 and 2 were similar due to the independence of the 2,3-diaminoanthracene unit. Further studies involving the synthesis of π -extended heteroacene analogs and their application to the design of efficient hole transport materials are in progress.

Supplementary data

Supplementary data associated with this article is available in the online version under http://dx.doi.org/##.####.

Acknowledgments

This work was partly supported by JSPS KAKENHI Grant-in-Aid for Young Scientists (B) (Grant Number 16K17874) and Grant for Promotion of OUS Research Project (OUS-PR-29-1). The authors gratefully thank the Research Instruments Center,

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Okayama University of Science for provision of NMR and MALDI-TOF mass spectra. The authors also thank Prof. Kan Wakamatsu of Okayama University of Science for their useful suggestions.

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- 13. Crystal data of 1: formula $C_{56}H_{58}N_2O_2 \cdot 2CH_2Cl_2$, M = 960.90, triclinic, space group *P*-1, a = 7.534(3), b = 10.172(4), c = 16.405(6) Å, $\alpha = 88.9308(10)$, $\beta = 78.941(8)$, $\gamma = 85.465(8)$ °, V = 1230.0(8) Å³, Z = 1, $D_c = 1.297$ g cm⁻³, μ (Mo K α) = 0.286 mm⁻¹, T = 123(2) K, 19754 reflections, R1 = 0.0439 ($I > 2.0\sigma(I)$), wR2 = 0.1188, GOF 1.058. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1890893.
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Highlights

 π -Extended phenazine derivatives and its quinone analog were prepared.

An absorption band of phenazine derivatives is attributed to π -extension.

Acceleration A broad absorption of quinone analog is attributed to intramolecular CT interactions.