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N-Alkylation Of 6,6'-Dibromoisoindigo via Tosylate: An Economical Pathway

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This paper introduces a substantial and price reasonable pathway to N-alkylate the 6,6'-dibromoisoindigo. The conventional method for this N-alkylation involves the usage of alkyl bromides, which are available in the commercial with high-priced and limited amount. In this research, the price to purchase 7-(bromomethyl) pentadecane is four-fold than the cost to synthesize the relevant tosylate from 2-hexyl-1-decanol. The most suitable reaction condition to N-alkylate this 6,6'-dibromoisoindigo is by refluxing it with potassium carbonate in dried DMF under nitrogen atmosphere. After characterization, it can be concluded that 6,6'-dibromoisoindigo has been successfully N-alkylated with tosylate without involved the expensive alkyl bromide.

Keywords: N-alkylation, tosylate, isoindigo, electron acceptor, conjugated polymer

I. INTRODUCTION

The well-known indigo compound was introduced in the mid-20th century [1]. It is an indigoid pigment which could be found naturally from the woad leaves named *isatis tinctoria*, *polygonum tinctorium*, and *indigofera tinctoria*. This pigment has been applied as dyestuffs for centuries [2–4]. Isoindigo is structurally isomeric with this famous indigo, as shown in Figure 1. This isoindigo was first to be introduced as electron accepting monomer for conjugated polymer in 20th century [5]. The chemical structures for both indigo and isoindigo were illustrated in Figure 1.

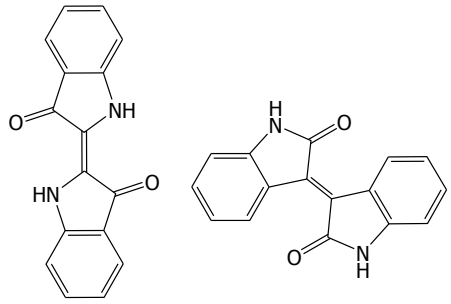

Figure 1. The chemical structure of indigo and isoindigo.

II. LITERATURE REVIEW

From the past research papers regarding the synthesis of conjugated polymers for the photovoltaic application, isoindigo has been extensively studied and found to be a promising candidate for electron acceptor along the polymeric backbone [6]. Based on the previous studies, this isoindigo applied as the acceptor is generally presented as 6,6'-dibromoisoindigo

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with two bromine atoms attached at the 6th- and 6th'- positions, which is synthesized from 6-bromoisatin [7] and 6-bromo-2-oxindole [8], before polymerized with other monomers through either Suzuki's or Stille's coupling reaction [9–17][18][19]. However, isoindigo can also be directly polymerized without the present of bromine substituents through direct arylation[20–25]. The chemical structure for 6,6'-dibromoisoindigo was shown in Figure 2.

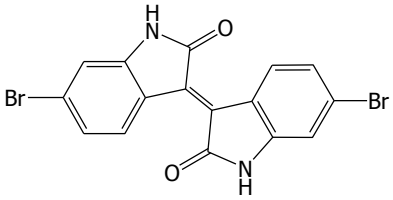


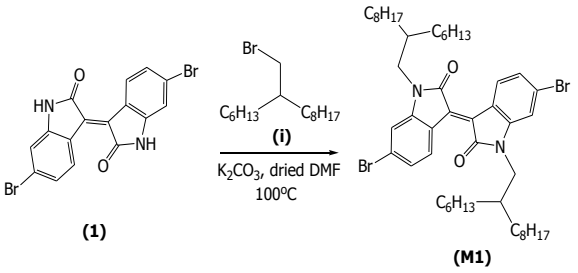
Figure 2. The 6,6'-dibromoisoindigo **(1)**

The secondary amine group present in this 6,6'-dibromoisoindigo **(1)** is an interesting functional group for the researchers as the present of N-alkyl chains are known to be able to enhance the solubility and have significant impacts on the molecular, electrical, and optical properties of the resulting conjugated polymers [26]. There are several pathways to incorporate the desired alkyl chains on the amine groups of **(1)**. Amongst the existing pathways, the commonly used method is refluxing the compound **(1)** with the chosen either alkyl bromide (R-Br) [5,10,27–33] or alkyl iodide (R-I) [9,34–38] in the present of potassium carbonate (K_2CO_3) under inert atmosphere. For the fluorinated compound **(1)**, R-I with potassium hydroxide (KOH) in 1:1 DMSO/THF is the suitable condition for N-alkylation [39]. These alkyl halides have been applied as the alkyl source to N-alkylate the compound **(1)** since 2010. Tosylation is the synthesis of desired tosylates by reacting the appropriated alcohols with p-toluenesulfonyl chloride [40]. After that, the synthesized tosylates are used to N-alkylate the amine groups of the targeted compounds. There are several papers reported the synthesis method to N-alkylate the amine group present in carbazole from tosylates in the present of KOH [41–45], yet there have no paper mentioned about N-alkylation of compound **(1)** through tosylates. Thus, some trials have been done and the most suitable reaction condition and base is reported in this paper.

III. METHODOLOGY

All the chemicals and solvents mentioned in these procedures were purchased from the commercial suppliers and used without further purification, except for the DMF solvent which was dried in advance by distillated over calcium hydride.

A. The Conventional Pathway



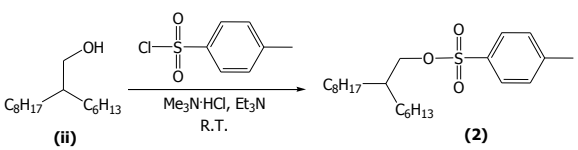
Scheme 1. N-alkylation through alkyl bromide.

The 6,6'-dibromoisoindigo **(1)** (1.00 g, 2.38 mmol, 1.00 equiv.) and anhydrous potassium carbonate (1.65 g, 11.90 mmol, 5.00 equiv. to **1**) were added into 50 mL of dried DMF, after which the reaction mixture was heated up to

100 °C under nitrogen atmosphere. Next, 7-(bromomethyl) pentadecane (1.82 mL, 1.82 g, 5.95 mmol, 2.50 equiv. to (**1**) was then injected into the solution mixture through a syringe. The reaction mixture was continue to stir and reflux for 24 hours at 100°C. After that, the resulting mixture was dropped into 100 mL distilled water and extracted three times with 250 mL of dichloromethane (DCM). The combined organic layer was washed with brine (8 w/v% NaCl), water, and dried over Na_2SO_4. The DCM solvent was then removed under reduced pressure, the resulting deep-red oil was purified through column chromatography (SiO_2, 1:1 n-Hexane/DCM, Rf =0.84) [5,10,32,33]. The first yellowish outflow was removed while the second bright reddish outflow was collected and dried overnight. After that, the reddish product was passed through the column chromatography (SiO_2, 11:9 n-Hexane/Toluene, Rf =0.99) once again and only the reddish outflow was collected and dried. Finally, the purity of the product was double confirmed with the aids of TLC. The product **(M1)** yielded 527 mg (0.606 mmol, ɣ= 25.46 %).

B. The Economical Pathway

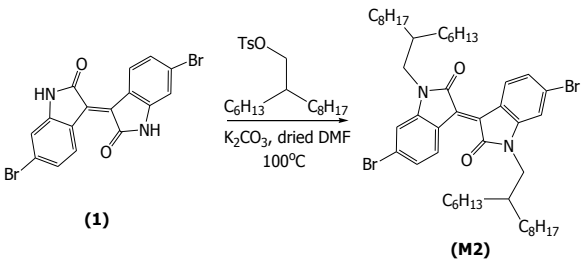
Step 1:



Scheme 2. Synthesis of tosylate

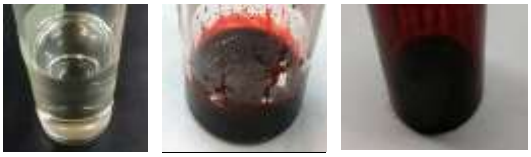
First of all, two portions of reaction mixture were prepared. For the first portion, 2-hexyl-1-decanol **(ii)** (5 mL, 4.18 g, 17.24 mmol, 1.00 equiv.), trimethylammonium monohydrochloride, $Me_3N{\cdot}HCl$ (1.24 g, 12.93 mmol, 0.75 equiv. to **ii**), and triethylamine, Et_3N (7.40 mL, 5.38 g, 53.20 mmol, 3.09 equiv. to **ii**) were added subsequently into a stirring 17.25 mL of DCM. The second portion consisted of p-toluenesulfonyl chloride, p-TsCl (6.00 g, 31.46 mmol, 1.83 equiv. to **ii**) in 17.25 mL of DCM. The first portion was then placed into an ice bath. After that, second portion was added dropwisely into the cold stirring mixture, and the resulting reaction mixture was stirred for 3 hours with the temperature maintained in the range of 0-5°C. Next, distilled water was added and the solution mixture was extracted three times with DCM. The combined DCM layer was then washed with distilled water and brine (8%w/v NaCl) solution, before dried over Na_2SO_4. Finally, the DCM was evaporated off under reduced pressure and the resulting residue was purified through column chromatography (SiO_2, 9:1 n-hexane/ethyl acetate, Rf=0.52) [41,42,46]. The obtained transparent oily liquid **(2)** was yielded 6.82 g (17.19 mmol, ɣ= 99.71 %).

Step 2:



Scheme 3. N-alkylation through tosylate

First of all, 6,6'-dibromoisoindigo **(1)** (1.00 g, 2.38 mmol) and K_2CO_3 (1.65 g, 11.90 mmol, 5.00 equiv. to (**1**) was added into 30 mL of dried DMF. The reaction mixture was stirred and heated up to 60°C under nitrogen atmosphere until the precursor **(1)** was completely dissolved. After that, another set of solution mixture which contains 2-hexyl-1-decane p-toluenesulfonate **(2)** (2.83 g, 7.14 mmol, 3.00 equiv. to **1**) in 20 mL of dried DMF was dropwisely added into the former reaction mixture. The resulting mixture was then heated up to 100 °C for 24 hours under nitrogen atmosphere. Next, the reaction mixture was cooled down to room temperature and dropped into 200 mL of distilled water, followed by the extraction with 300 mL of ethyl acetate three times. The collected organic layers were combined, washed with water, and dried over Na_2SO_4. The solvent was then removed under reduced pressure, the resulting deep-red oil was purified through column chromatography (SiO_2, 1:1 n-Hexane/DCM, Rf =0.84). The reddish outflow was collected, dried, and purified again through column chromatography (SiO_2, 11:9 n-Hexane/Toluene, Rf =0.99). Only the red outflow was collected, dried and the yielded was 503 mg (0.579 mmol, ɣ= 24.33 %).



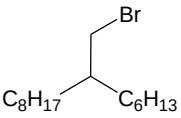
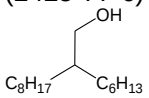
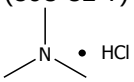
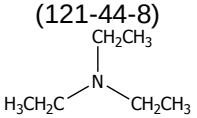
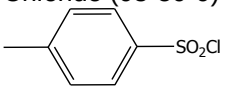
(2) **(M1)** **(M2)**

Figure 3. The synthesized products.

C. Price Comparison

The price comparison was done according to the price stated in the online catalog portal of the Millipore Sigma® and TCI chemicals® by October 2017. All the prices were clearly tabulated in Table 1.

Table 1. The price comparison for the precursors of alkyl chain.

Conventional pathway	Economical Pathway
7-bromomethylpentadecane (52997-43-0)  ➢ 25 mL: 418 USD[2]	2-hexyl-1-decanol (2425-77-6)  ➢ 25 mL: 29.80 USD[1] ➢ 25 mL: 29.00 USD[2]
	Trimethylamine hydrochloride (593-81-7)  ➢ 25 g: 14.90 USD[1]
	Triethylamine (121-44-8)  ➢ 100 mL: 29.30 USD[1]
	p-Toluenesulfonyl Chloride (98-59-9)  ➢ 25 g: 16.00 USD[2]
418 USD	89.20 USD*

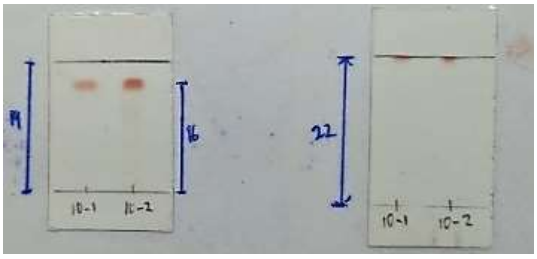
[1]Millipore Sigma®, [2]TCI chemicals®, [3]Fischer Scientific®
*Sum of the lowest prices

From the Table 1, we could know that the price for an alkyl bromide is far more expensive than the price for all the precursors needed to synthesize a suitable tosylate for N-alkylation.

Meanwhile, the price of the salt, NaCl and the solvents involved in the economical pathway, i.e. dichloromethane, n-hexane, and ethyl acetate are not inputted in the Table 1 as these solvents are purchased in large amount, yet only a small quantity were used for one cycle of the alternative pathway.

IV. RESULTS AND DISCUSSIONS

The 6,6'-dibromo-(N,N'-2-hexyldecyl) isoindigo obtained through the conventional (M1) and economical (M2) pathways were then further characterized with FTIR and NMR. The melting points for both M1 and M2 are lied in the range of 49-52 ^{o}C. In addition, only the first reddish outflow was collected during the purification process, as the other reddish portions with Rf value <0.70 were found to be the by-products with aromatic ring deformation. This is also the reason for the low product yield for both M1 and M2. The purified Rf values of the TLC were calculated as shown in Figure 4.



(a) (b)

Figure 4. The TLC for (a) 1:1 DCM/n-hexane, and (b) 11:9 n-hexane/toluene.

During the experiment, it was discovered that the precursor (1) cannot be N-alkylated with the tosylate (2) in the present of KOH base at room temperature, even though this reaction condition is commonly used to N-alkylate the carbazole. For the alkylation of precursor (1), 100^{o}C reflux and K_2CO_3 are the most suitable reaction condition with reasonable cost for the time being. Besides that, the solubility of precursor (1) in DMF is much better than DMSO. Hence, DMF is the most suitable solvent for this reaction.

A. Fourier Transform Infrared (FTIR) Spectroscopy

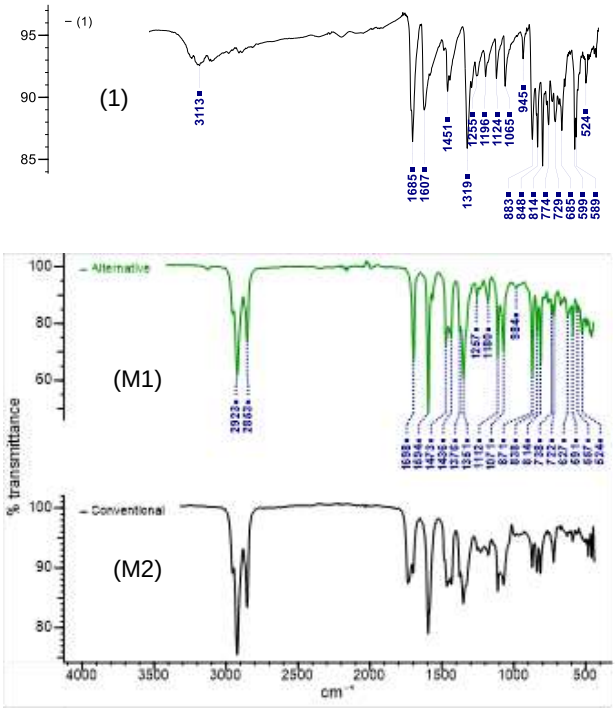


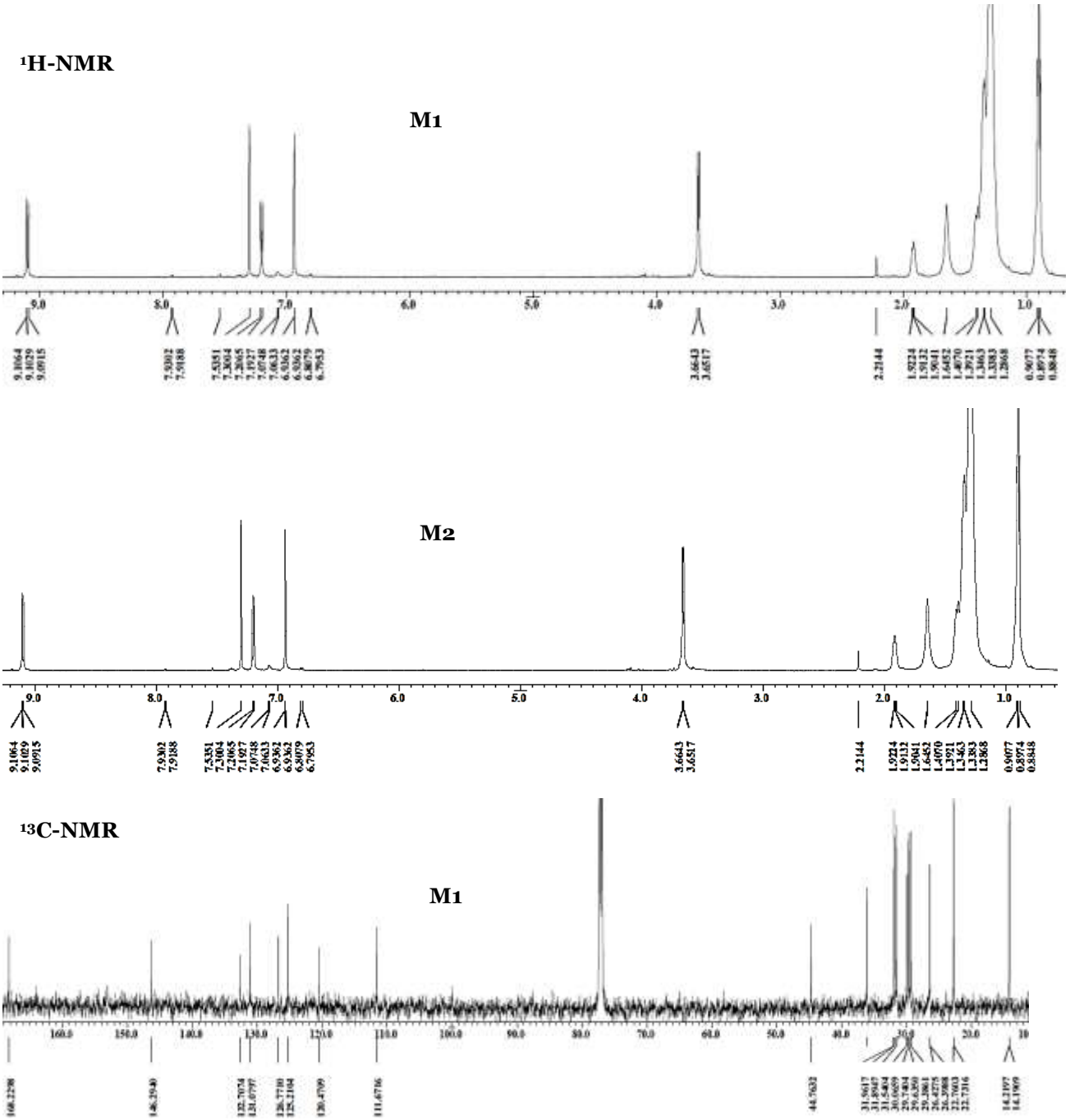
Figure 5. The FTIR spectra of (M1) and (M2) versus (1)

From the FTIR spectra shown in Figure 5, it can be concluded that both M1 and M2 consist of same functional groups as they have similar absorption frequencies. The two strong absorption bands located in the range of 2850-2990 cm^{-1} represent the stretching vibration of $-CH_3$ and $-CH_2$, which indicate the present of alkyl chains in both M1 and M2. On the other hand, the band located at 3113 cm^{-1} in the spectrum of precursor (1) represents the present

of secondary amine group. The vanishing of secondary amine band and emergence of alkyl bands denoted that the N-alkylation has been successfully carried out via both conventional and economical pathways as mentioned in section 3.0.

B. Nuclear Magnetic Resonance (NMR)

The ^{1}H-NMR and ^{13}C-NMR spectra of M1 and M2 shown in Figure 6 have similar peaks, which indicated that both M1 and M2 are analogous with each other.



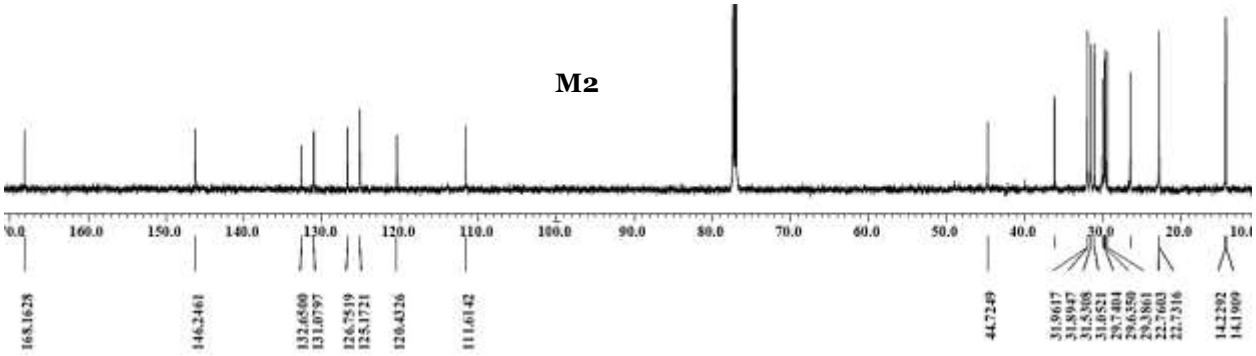


Figure 6. The ^{1}H-NMR and ^{13}C-NMR spectra of M1 and M2

V. SUMMARY

N-alkylation of 6,6'-dibromoisoindigo can be done by using tosylates, which is a low-cost pathway. The commercial price for alkyl bromide is four-fold higher than to synthesize the relevant tosylate from alcohol.

VI. ACKNOWLEDGMENT

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