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# Benzopyrazinoisoindigo or Its Reduced Form? Synthesis, Clarification, and Application in Field-Effect Transistors

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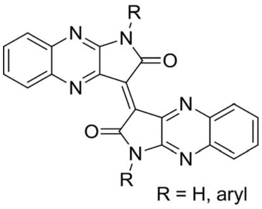
**Abstract:** Benzopyrazinoisoindigo, a pigment reported 40 years ago, should be a good candidate for n-type semiconductors if the reported structure is correct. Reinvestigation of this molecule revealed that it is actually (4*H*,4′*H*)-benzopyrazinoisoindigo, which could be considered as the reduced form of benzopyrazinoisoindigo, and hence, it is a good candidate for p-type semiconductors. The route toward the synthesis of this molecule was optimized, and a mechanism was accordingly proposed. A field-effect transistor based on this material showed a hole mobility up to $2.5 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$.

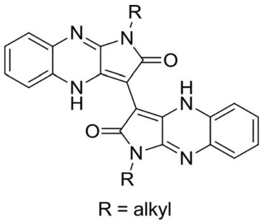
## Introduction

Small molecular organic field-effect transistors (SM-OFETs) have attracted much attention in the past decade owing to the existence of a large pool of tailorable conjugated molecules, the versatile methods towards their synthesis, and their uniform structure and performance.[1] Although great progress has been achieved for SM-OFETs,[2] there is still a need to discover novel organic semiconductors that can be synthesized from commercially affordable starting materials in an easy and scalable way to lower the costs of SM-OFETs.[3] Recently, isoindigo[4] and its derivatives[5] were used to construct polymeric OFETs.[6] It is believed that strong dipolar interactions between the adjacent isoindigo units favor close packing of the polymer chains, which improves the performance. Theoretically, such a strong interaction would also favor charge-carrier transport in small molecules based on the isoindigo core, provided that the length of conjugation in such small molecules was long enough. However, SM-OFETs based on the isoindigo core structure are less studied. Recently, it was reported that a cyanated isoindigo SM-OFET exhibited ambipolar charge-transfer behavior with electron and hole mobilities of 0.11 and 0.045 cm$^2$ V$^{-1}$ s$^{-1}$, respectively,[7] which implies potential room for further improvement.

In our continuous efforts to design novel derivatives based on the isoindigo core,[8] we noticed a report published in the 1970s stating the successful synthesis of benzopyrazinoisoindigo,[9] namely, [3,3′-bipyrrolo[2,3-*b*]quinoxalinylidene]-2,2′(1*H*,1′*H*)-dione (Figure 1, compound **1**), and related compounds. We realized that the combination of the electron-deficient character of both the pyrazine and isoindigo cores would make it an even better candidate for electron transport. However, owing to the poor solubility of those pigments, they were not well characterized (only mass spectroscopic data and elemental analysis data of N atom were provided), and the actual structure remains in question. We envisioned that the synthesis of the alkylated derivatives would cast light on its real structure, and also, its OFET performance could be tested. Herein, we clarify the structure of compound **1**, which is actually its reduced form (compound **2**, Figure 1), namely, alkylated (4*H*,4′*H*)-benzopyrazinoisoindigo. Starting from abundant maleic anhydride, a fast and efficient synthesis route toward this conjugated molecule is developed and the mechanism is discussed. Contrary to isoindigo, this small molecule exhibits p-type semiconductivity, and SM-OFETs based on this material show a hole mobility up to $2.5 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$.


R = H, aryl

Compound 1


R = alkyl

Compound 2

Figure 1. The structure of the reported benzopyrazinoisoindigo derivative (compound **1**) and the actual structure (compound **2**).

## Results and Discussion

In the reported procedure,[9] compound **1a** was synthesized in three steps (Scheme 1, route A): the reaction of dichloromaleic

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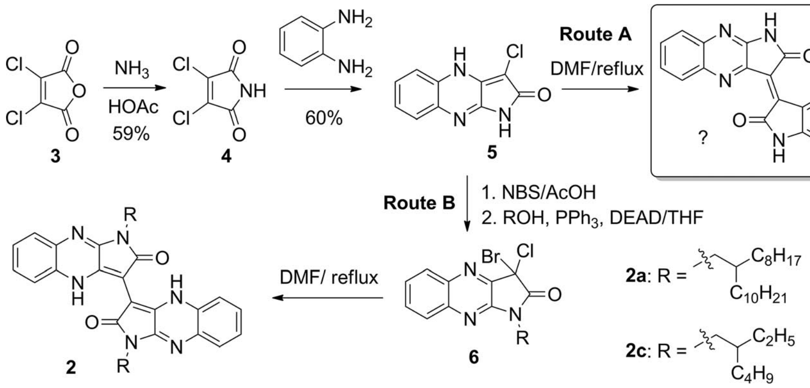


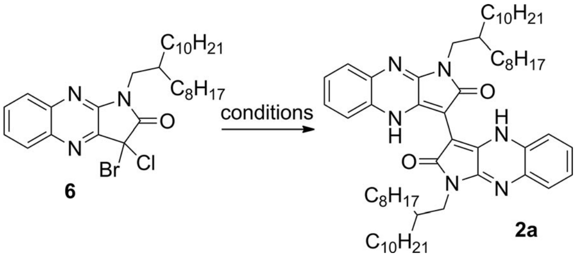
Scheme 1. Synthetic route toward the target molecule; NBS = *N*-bromosuccinimide, DEAD = diethyl azodicarboxylate.

anhydride (**3**) with ammonia afforded 1*H*-pyrrole-2,5-dione **4**, which upon treatment with 1,2-diaminobenzene gave an incompletely characterized compound, 3-chloro-1*H*-pyrrolo-[2,3-*b*]quinoxalin-2(4*H*)-one (**5**). Compound **5** was then heated at refluxed in DMF to effect dimerization to give compound **1a** in 21 % yield. However, the last step is questionable: at first glance, the oxidation of the enamine-like moiety followed by homocoupling accounts for the formation of **1a**, but it is unclear how this process could be realized only by heating **5** in DMF. This procedure was repeated in our laboratory, and the structure of compound **5** was confirmed. Unfortunately, heating compound **5** in DMF gave a purplish-red powder, which was impure and difficult to characterize even after sublimation.

To solve this problem, alkylation of compound **5** was attempted. Unfortunately, alkylation with an alkyl bromide gave a mixture, as alkylation of the undesired N atom could not be avoided. Alkylation under Mitsunobu conditions also failed as a result of the poor solubility of compound **5**. Alternatively, bromination of compound **5** afforded the geminal halogenated compound, which was soluble under Mitsunobu conditions and was successfully alkylated to give compound **6** in good yield (Scheme 1, route B). However, subjecting compound **6** to reflux conditions in DMF resulted in a complex mixture; one of the products was identified as **2a**, but it was afforded in only low yield (ca. 5 %). The $^1$H NMR spectrum of **2a** clearly shows a signal at $\delta = 12.98$ ppm, which is assigned to the N–H proton of the enamine, and high-resolution mass spectrometry explicitly gave the mass of the protonated molecule ($m/z = 929.7337$, see the Supporting Information). Other side products failed to be purified by flash chromatography and could not be identified.

The formation of **2a** was surprising, as it seemed that the corresponding product was formed by the reduction of compound **6** followed by homocoupling, without any reducing reagents. To improve the yield and also to cast light on the mechanism, various conditions were tested, as listed in Table 1. Simply switching to other solvents did not seem to lead to any improvements (Table 1, entries 1 to 4). Inspired by a patent,[10] NBu$_3$ was then added, and the yield increased to 48 % (Table 1, entry 5). NBu$_3$ was also used in more polar solvents such as *N*-methylpyrrolindone (NMP), and the yield was further improved to 65 % (Table 1, entry 6). Other amines such as 1,2-diaminobenzene also worked (Table 1, entry 7). It is clear that amines promote this reaction, but their role is unclear. However, we can confirm that they do not act as a base, as there is no proton to abstract in compound **6**. Upon heating the starting material under acidic conditions (Table 1, entry 8), the same product was obtained in 51 % yield, which further testified to the fact that a base was not necessary for this reaction. Given that amines are prone to oxidation, it is possible for them to act as an electron donor under heating conditions. Thus, other compounds that could act as an electron donor were tested (Table 1, entries 9–11). Upon treating the substrate with PPh$_3$ at room temperature, the desired product was obtained in 10 % yield. The yield was improved to 40 % under reflux conditions. The use of P(NEt$_2$)$_3$, a more powerful one-electron donor, gave a satisfactory yield of the product at room temperature. Reac-

Table 1. Optimization of the synthesis of **2a**.

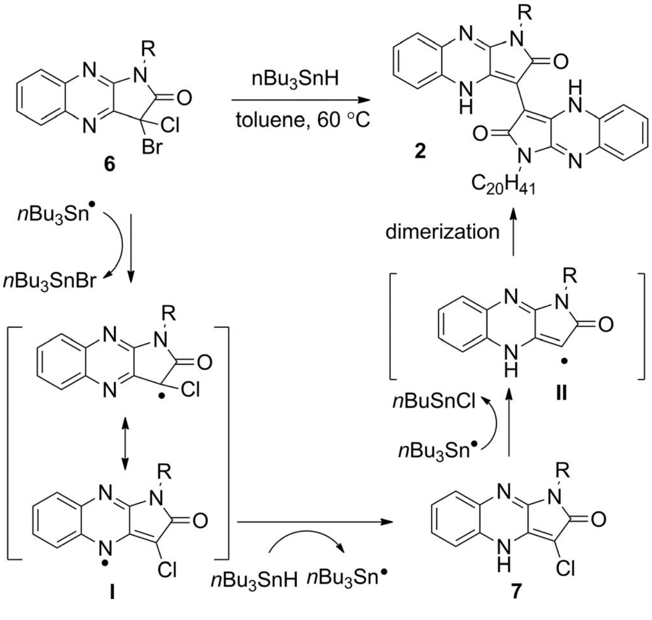


| Entry | Conditions | Yield [%] |
|---|---|---|
| 1 | DMF, 140 °C, 5 h | <5[a] |
| 2 | DMSO, 140 °C, 24 h | decomposition |
| 3 | xylene, Ar, 110 °C, 12 h | no reaction |
| 4 | xylene, 110 °C, 24 h | no target molecule[a] |
| 5 | xylene, NBu$_3$, 110 °C, 12 h | 48[a] |
| 6 | NMP, NBu$_3$, 130 °C, 12 h | 65 |
| 7 | xylene, 1,2-diaminobenzene, Ar, 110 °C, 3 h | 69 |
| 8 | AcOH/THF/H$_2$O, 125 °C; then, evaporate to dryness | 51[a] |
| 9 | PPh$_3$, THF, r.t., 48 h | 10 |
| 10 | PPh$_3$, THF, reflux | 40 |
| 11 | P(NEt$_2$)$_3$, CH$_2$Cl$_2$, –78 °C to r.t., 48 h | 58 |
| 12 | Cu powder, DMSO, r.t., 24 h | 10 |
| 13 | CuI, THF/DMF, ascorbic acid, r.t., 24 h | 37 |
| 14 | *n*Bu$_3$SnH/toluene, 60 °C, 24 h | 71 |

[a] Reaction was performed in an open system.

tions involving $Cu^0$ were also tested (Table 1, entry 12 and 13), and the product was obtained in moderate yield in each case. All these results imply that a one-electron reduction process or radical species is involved in this reaction. With this assumption in mind, a radical initiator, tributyltin hydride ($nBu_3SnH$), was introduced into the reaction. To our delight, the reaction occurred at room temperature and the rate was increased at an elevated temperature (60 °C) to deliver the product in a satisfactory yield (71 %; Table 1, entry 14).

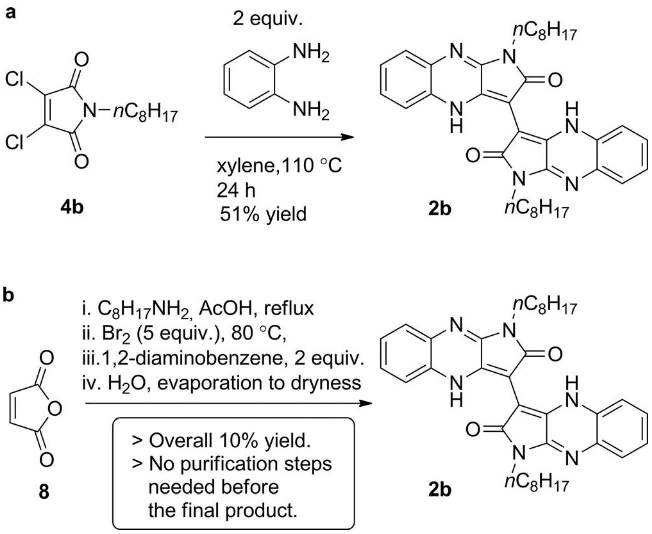
The mechanism became clear at that point, as shown in Scheme 2, by using $nBu_3SnH$ as an example. The organotin radical abstracts the bromine atom from compound **6** to afford radical intermediate **I**, which grabs a hydrogen atom from $nBu_3SnH$ to give compound **7** with regeneration of the organotin radical. The chlorine atom of compound **7** is then abstracted by the tin radical to form radical intermediate **II**. Dimerization of **II** affords the final product. During this process, at least 2 equivalents of $nBu_3SnH$ is needed. In reality, an excess amount of $nBu_3SnH$ was needed, which is in accordance with the proposed mechanism. Although compound **7** could not be directly prepared from compound **5**, we managed to synthesize octylated derivative **7b** in an alternative way (see the Supporting Information, p. S6), which was converted into dimerized product **2b** upon treatment with $nBu_3SnH$. This confirmed that compound **7** was the intermediate involved in the reaction.



Scheme 2. Proposed mechanism of the reaction.

Other conditions (e.g., amines, phosphines, $Cu^0$) also promote this radical process. At first glance, the role of the trialkylamine in this reaction is not clear, as the redox ability of trialkylamines is quite weak. However, it is known that trialkylamines can abstract the iodine atom from alkyl iodides to generate an alkyl radical and initiate a living radical polymerization.[11] The formation of an iodine radical–trialkylamine complex and/or a more complicated complex is the driving force. Although abstraction of a bromine atom by $NBu_3$ is more difficult, we postulate that it could be initiated at elevated temperatures and, thus, goes through a similar process to give the desired compound, as described in Scheme 2. It is also understandable that switching to more reductive 1,2-diaminobenzene improves the yield, and a more powerful reducing reagent such as $P(NEt_2)_3$ even allows this reaction to be performed as room temperature. However, at this stage we are not sure why this process can still occur upon heating in acidic solutions.

With the clarified mechanism in mind, we further optimized the reaction conditions. To circumvent the problematic alkylation of compound **5**, dichloromaleic anhydride (**3**) was converted into *N*-alkylated pyrrole-2,5-dione **4b**. Upon treatment with 1,2-diaminobenzene (2 equiv., added portionwise) in xylene at 110 °C, compound **4b** was converted into final product **2b** in 51 % yield, as shown in Scheme 3 (a). Furthermore, given that this reaction is not sensitive to solvents, the product was even obtained in a "quasi-one-pot" manner from one of the most abundant chemicals, maleic anhydride (**8**), as shown in Scheme 3 (b). Treatment of compound **8** with an alkylamine gave the corresponding *N*-alkylated pyrrole-2,5-dione, which was then treated with $Br_2$ to afford 3,4-dibromo-1-octyl-1*H*-pyrrole-2,5-dione. The excess amounts of $Br_2$ and HBr generated in situ were then evaporated, and without isolation, 1,2-diaminobenzene (2 equiv.) was added portionwise to the mixture, and the mixture was heated to reflux. Finally, an adequate amount of water was added to the mixture, and the solvent was slowly evaporated. The residue was then crystalized in MeOH to give **2b** in an overall 10 % yield. No isolation or chromatography was needed before the final crystallization step, which makes this route suitable for scale up.



Scheme 3. Optimized synthetic conditions.

Compounds **2a** and **2b** are deep-red crystalline powders, which show a maximum UV/Vis absorption band at around 506 nm, as shown in Figure 2 (a) and Table 2. Relative to that observed for isoindigo, which shows $\lambda_{max}$ = 496 nm, the intensity of the band is largely increased, which reflects the effect of extending the chromophore. Contrary to isoindigo, which is an electron acceptor, **2a** and **2b** are good electron donors, as shown by the cyclic voltammetry diagrams (Figure 2, b) Two reversible oxidation peaks located at 0.54 and 0.95 eV are observed. No reductive peak is observed upon scanning towards negative potentials. Thus, **2a** and **2b** can be considered the reduced forms of benzopyrazinoisoindigo (**1**). Notably, **2a** is very stable under electrochemical conditions. Even after 500 scans, little decay of its electrochemical activity is detected, as shown in Figure 2 (b). However, all attempts to convert compounds **2a**/**2b** into **1a**/**1b** by using various oxidants failed [organic oxidants such as $PhI(OAc)_2$, 7,7,8,8-tetracyanoquinodimethane, 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone; inorganic oxidants such as $PbO_2$, $I_2$, $MnO_2$, $AgNO_3$], and we then came to the conclusion that compound **1** reported in the literature is actually reduced form **2**.

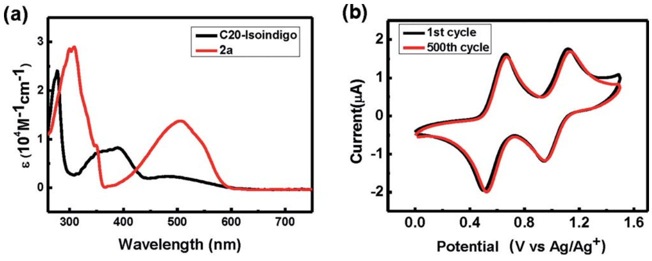


Figure 2. (a) UV/Vis absorption spectra of isoindigo (black line) and **2a** (red line) in $CH_2Cl_2$ solution ($1 \times 10^{-5}$ M); (b) cyclic voltammetry diagrams of **2a** in $nBu_4NPF_6/CH_2Cl_2$ solution (scan rate: 0.1 V $s^{-1}$, vs. Ag/AgCl), the 1st cycle (black line) and 500th cycle (red line) are shown.

Table 2. Optical (UV/Vis) properties and electrochemical data.[a]

| | $\lambda_{max}$ [nm] in solution | $E_{onset}^{ox}$ [eV] | $E_g^{opt}$ [eV] | LUMO [eV] | HOMO [eV] |
|---|---|---|---|---|---|
| **2a** | 506 | 0.54 | 2.05 | –2.89 | –4.94 |

The HOMO energy level of compound **2** was calculated by using the equation $E_{HOMO} = -(E_{onset}^{ox} - \text{ferrocene}) - 4.8$ eV, in which $E_{onset}^{ox}$ is the onset of the oxidation potential. The LUMO energy level was deduced from the equation $E_{LUMO} = E_{HOMO} + E_g^{opt}$, in which $E_g^{opt}$ is the optical band gap. The HOMO/LUMO levels of **2a** are –4.94 and –2.89 eV, respectively. The suitable HOMO level and its excellent electrochemical stability indicate that **2a** is an idea material to fabricate p-type OFETs.

To evaluate the OFET performance, (4*H*,4′*H*)-benzopyrazinoisoindigo with three different alkyl chains (branched $C_{20}$, *n*-$C_8$, and branched $C_8$; compounds **2a**–**c**) were synthesized, and top-gate/bottom-contact OFET devices were fabricated (Table 3). Representative transfer and output curves are given in Figure 3. Films of **2a** gave the best performance, with the highest hole mobility ($\mu_h$) of $2.5 \times 10^{-2}$ $cm^2 V^{-1} s^{-1}$, the lowest threshold voltage ($V_T$) value of 3 V, and the highest on/off current ratio ($I_{on}/I_{off}$) of $10^6$, which indicate that side-chain engineering also has an important influence on device performance.

Table 3. OFET performance of **2a**–**c** thin films under ambient conditions.

| | $\mu_h$ [$cm^2 V^{-1} s^{-1}$] | $V_T$ [V] | $I_{on}/I_{off}$ |
|---|---|---|---|
| **2a** | 0.025 | 3 | $10^6$ |
| **2b** | 0.0057 | –40 | $10^6$ |
| **2c** | 0.004 | –23 | $10^5$ |

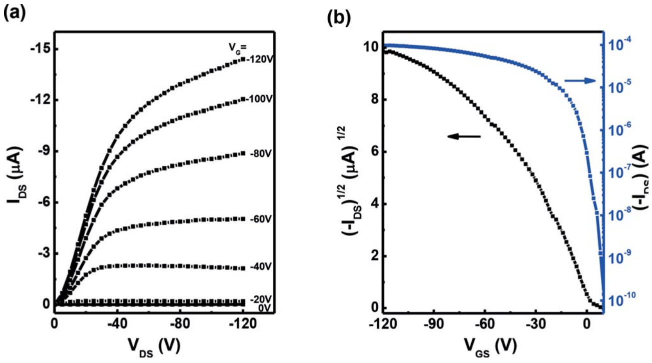


Figure 3. (a) Output characteristics and (b) transfer characteristics of **2a** OFET devices; $V_{DS}$ = drain-to-source voltage; $V_{GS}$ = gate-to-source voltage; device dimensions: ratio of channel width to channel length: 175; device was measured under ambient conditions.

## Conclusions

In conclusion, aiming at alkylated benzopyrazinoisoindigo, (4*H*,4′*H*)-benzopyrazinoisoindigo, was unexpectedly obtained. The reaction conditions were optimized, and $C_8$-(4*H*,4′*H*)-benzopyrazinoisoindigo could even be obtained in a "quasi-one-pot" manner from maleic anhydride, one of the most abundant chemicals, which may lower the cost of producing such conjugated molecules for OFETs. A mechanism involving a one-electron reduction/radical process was accordingly proposed. This work also clarified the structure of an long-known pigment reported 40 years ago. Contrary to isoindigo, (4*H*,4′*H*)-benzopyrazinoisoindigo is a p-type semiconductor with excellent electrochemical stability, and its HOMO energy level matches well with the work function of Au and is suitable to fabricate p-type OFETs. A field-effect transistor based on this material showed a hole mobility up to $2.5 \times 10^{-2}$ $cm^2 V^{-1} s^{-1}$.

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**Keywords:** Conducting materials · Dyes/Pigments · Organic field-effect transistors · Semiconductors · Synthetic methods

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