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SYNTHESIS OF N-(4-HEXYLBENZOYL) DITHIENO[3,2-b:2',3'-d]PYRROLE AS A NEW BUILDING BLOCK TOWARD APPLICATION IN DONOR – ACCEPTOR CONJUGATED POLYMERS

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ABSTRACT

A new derivative of bridged bithiophene based N-(4-hexylbenzoyl) dithieno[3,2-b:2',3'-d]pyrrole (HBDP) has been successfully synthesized from 3,3'-dibromo-2,2'-bithiophene and 4-hexylbenzamide via Ullmann-type C-N coupling amidation using 20 mol% CuI and 40 mol% DMEDA in 24 hours. A conversion of the HBDP monomer has obtained around of 35%. The structure of main product HBDP was characterized via the nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) and fourier transform infrared (FT-IR). The HBDP monomers will be used as potential moieties for direct arylation polycondensation to synthesize the donor-acceptor conjugated polymers.

Keywords: *N*-acyl dithieno[3,2-b:2',3'-d]pyrrole (DTP), Donor-acceptor (D-A) conjugated polymers, polymeric solar cells, Ullmann reaction.

TÓM TẮT

Tổng hợp hợp chất mới n-(4-hexylbenzoyl) dithieno[3,2-b:2',3'-d]pyrrole làm đơn vị mắt xích ứng dụng trong polymer liên hợp cho – nhận điện tử

Một dẫn xuất mới của họ bithiophene có cầu nối, N-(4-hexylbenzoyl) dithieno[3,2-b:2',3'-d]pyrrole (HBDP) đã được tổng hợp thành công từ 3,3'-dibromo-2,2'-bithiophene và 4-hexylbenzamide bằng phản ứng ghép đôi amide hóa theo kiểu Ullmann. Hiệu suất chuyển hoá tốt nhất của HBDP đạt được là 35% với hệ xúc tác gồm 20 mol% CuI và 40 mol% DMEDA trong thời gian 24 giờ. Cấu trúc hoá học của HBDP đã được khảo sát bằng phổ cộng hưởng từ hạt nhân (^{1}H-NMR, ^{13}C-NMR) và phổ hồng ngoại (FT-IR). Monomer HBDP sẽ được sử dụng làm nguyên liệu chính cho phản ứng trùng ngưng aryl hoá trực tiếp để tổng hợp nhiều loại polymer liên hợp cho – nhận điện tử.

Từ khóa: N-acyl dithieno[3,2-b:2',3'-d]pyrrole (DTP), polymer liên hợp cho – nhận điện tử, pin mặt trời hữu cơ, phản ứng Ullmann.

1. Introduction

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Nowadays, there are great anxieties in both academic and industry about polymer solar cells (PSCs) on account of their benefits containing flexibility, solution process ability, lightweight, economic efficiency, short-time energy payback [1]. However, PSCs still have a limitation for commercialization due to low stability, low power conversion efficiency (PCE), voltage loss, short lifetime and large scale fabrication [2]. Consequently, several endeavors have been presented to solve these disadvantages as well as to improve efficiency of PSCs. Among them, narrowing PSCs materials band gaps is a sufficient solution lead to formation of donor-acceptor polymer feature which is to alternatively combine an electron-rich moiety (D) and an electron-deficient unit (A) into a same polymer molecular [3]. The magnitude of the band gap of D-A polymers will be reduced because of push-pull driving forces between donor and acceptor building blocks to form a new higher HOMO level and a lower LUMO level. The strength of donor and acceptor has a substantial impact on the degree of band gap reduction. Therefore, the selection of building blocks pave the way to obtain D-A polymer with expected band gap magnitude. It is practically recognized that the narrower the optical band gap, the stronger the electron-withdrawing ability of acceptor unit in the copolymer [4]. In addition, the incorporations of medium/strong donor units and medium/strong acceptor units usually result in sufficient photovoltaic performances (PCE > 5 %) [5-11]. Based on that point, medium and strong acceptor segments are believed to be a superior decision for effective D-A conjugated polymer [12, 13].

Bridged bithiophene-based building blocks incorporating into D-A conjugated polymers have achieved high performance in PSCs. In 2010, Rasmussen and co-workers reported second generation of DTP, N-acyl-substituted DTP, with carbonyl group adjacent to nitrogen bridging atom possesses inductive effect led to the lowered HOMO level and consequently the devices acquired high V_{oc} [14]. Recently, the *N*-acyl dithieno[3,2-b:2',3'-d]pyrrole (DTP) building blocks have been received considerable concern due to their good planar crystal structure, strong electron-withdrawing ability and symmetrical chemical structure with the side chain at the bridging unit [15]. Abovementioned priorities lead to low band gap and high mobility materials. These structures can be combined into various polymeric, oligomeric and molecular materials with a great properties to produce different high performance D-A conjugated polymers which are useful in a wide range of applications such as OLED, OFET and photovoltaic cells [16-19].

In this article, we report the synthesis and characterization of an emerge moiety, 4-hexylbenzoyl dithieno[3,2-b:2',3'-d]pyrrole (HBDP) with an attached long *n*-hexyl chain on benzoyl group to increase its solubility without disturbing the planarity of polymer backbone which could be used as acceptor units in D-A conjugated polymers.

2. Experiment

2.1. Materials

3,3’-dibromo-2,2’-bithiophene (98 %); N’,N-dimethylethylene diamine (DMEDA, 99%), copper(I) iodide (CuI, 98 %) were purchased from AK Scientific and used as received. 4-hexylbenzoyl chloride (99 %) was purchased from Sigma Aldrich. Ammonium hydroxide solution 25% (NH_3 25%) was purchased from Merck. Chloroform ($CHCl_3$, Fisher Scientific, 99 %), tetrahydrofuran (THF, Fisher Scientific, 99 %), toluene (Merck, 99 %), *n*-heptane (Labscan, 99 %) and ethyl acetate (Merck, 99 %) were used as received. All reactions were carried out in oven-dried flask under purified nitrogen.

2.2. Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated chloroform ($CDCl_3$) with tetramethylsilane as an internal reference, on a Bruker Avance 500 MHz. Fourier transform infrared (FTIR) spectrum, collected as the average of 64 scans with a resolution of 4 cm^{-1}, were recorded from KBr disks on the FTIR Bruker Tensor 27.

2.3. Synthesis of 4-hexylbenzamide

The 4-hexylbenzoyl chloride (10 mmol, 2.25 g) was dissolved in 3 mL dry tetrahydrofuran and 5 mL of an aqueous ammonium hydroxide solution (25 %) was added dropwise at 0 ^{0}C. The mixture was stirred for 4 h and then it was extracted with ethyl acetate (100 mL). The resulting precipitate was filtered off, washed with H_2O and recrystallized from CH_3OH, yielding a white solid (1.89 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.72 (d, 2H), 7.24 (d, 2H), 6.11 (b, 1H), 5.93 (b, 1H), 2.65 (t, 2H), 1.62 (m, 2H), 1.31 (m, 6H), 0.88 (t, 3H).

2.4. Synthesis of N-(4-hexylbenzoyl) dithieno[3,2-b:2’,3’-d]pyrrole

In an exemplary experiment, to a 50 mL rounded-bottomed flask equipped with a magnetic stirrer was added copper(I) iodide (0.191 g, 1mmol), DMEDA (0.215 mL, 2 mmol), potassium carbonate (2.07 g, 15 mmol), followed by evacuation and backfilling with nitrogen. Then, toluene (15 mL) was added to the reaction mixture and the solution was stirred for 30 minutes. 4-hexylbenzamide (1.23 g, 6mmol) was added, followed by 3,3’-dibromo-2,2’-bithiophene (1.62 g, 5 mmol). The reaction mixture was stirred at 110 ^{o}C. The reaction was cooled to the room temperature in the next step, washed with distilled water (3 x 50 mL) and extracted with chloroform (100 mL). The organic phase was dried by anhydrous K_2CO_3. The solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography with the eluent as following *n*-heptane/ethyl acetate (*v/v = 4/1*) to give the isolated products.

4-hexylbenzoyl dithieno[3,2-b:2’,3’-d]pyrrole (HBDP). Yellowless crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.93 (d, 1 H), 7.79 (d, 2 H), 7.39 (d, 1H), 7.29 (d, 2H), 7.19 (d, 1H), 7.14 (d, 1H), 2.66 (t, 2H), 1.63 (m, 2H), 1.31 (m, 6H), 0.88 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 172. 36, 147.39, 133.75, 132.24, 128.76, 128.03, 127.03, 126.06, 123.99, 35.85, 31.67, 31.13, 28.92, 22.66, 14.14.

4H-dithieno[3,2-b:2',3'-d]pyrrole (4H-DTP). White solid. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.31 (b, 1H), 7.13 (d, 2H), 7.03 (d, 2H). Exactly match with the report of Bäuerle [20].

3. Results and discussion

4-hexylbenzamide was synthesized through nucleophilic substitution of 4-hexylbenzoyl chloride and NH_3 in THF at 0°C for 4h with high conversion of 92%. Figure 1 showed ^{1}H NMR spectrum of 4-hexylbenzamide, which exhibited similarity in chemical shifts and integrations of protons with product reported by Stephens and co-workers [21].

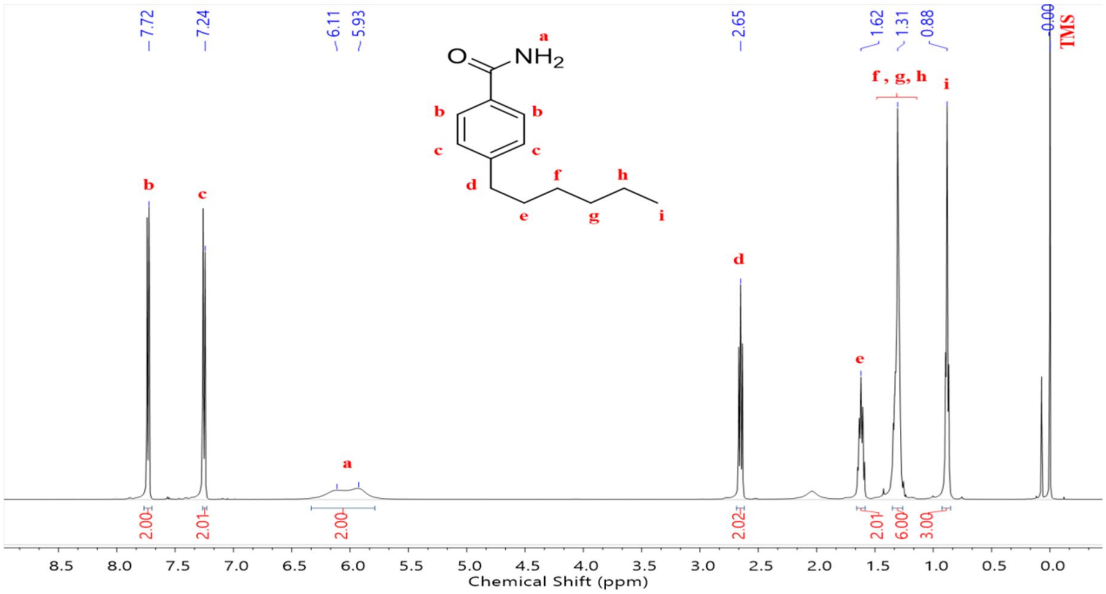
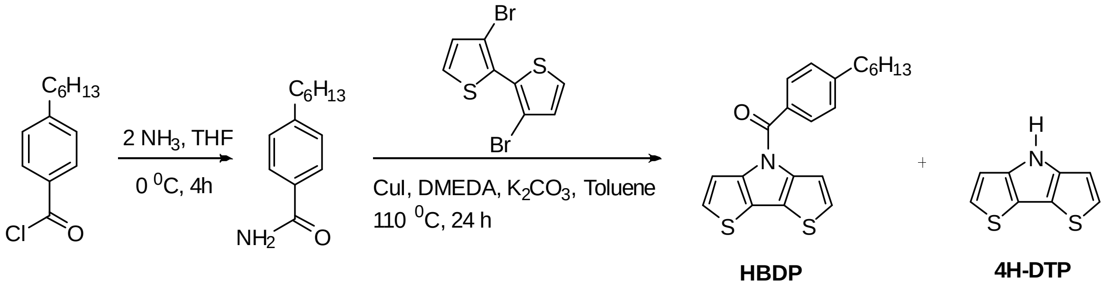


Figure 1. *^{1}H NMR spectrum of 4-hexylbenzamide*

The reaction between 4-hexylbenzamide and 3,3'-dibromo-2,2'-dithiophene *via* Ullmann-type C-N coupling under Cu(I)-catalysis to generate HBDP as the major product as shown in Scheme 1. Besides HBDP, 4H-DTP formation as by-product through an *in situ* hydrolysis of HBDP by the formed water was revealed by Bäuerle [20]. The reaction was conducted in presence of CuI as active catalyst, DMEDA as ligand and K_2CO_3 as base. After completion of reaction, both products were attained by extracting with chloroform, washing with distilled water and purification via column chromatography using the eluent of *n*-heptane and ethyl acetate (v/v:4/1).



***Scheme 1.** Synthesis routes of HBDP monomer*

Following this protocol, three factors of catalytic system comprise CuI, DMEDA and reaction time were studied to achieve the optimized parameters for highest conversion of HBDP (Table 1).

***Table 1.** Investigated catalytic conditions for the production of HBDP*
K_2CO_3 base (3 equiv), toluene solvent (0.2 M), temperature (110 ^{0}C)

Entry	**Catalyst CuI (mol%)**	**Ligand DMEDA (mol%)**	**Time (hour)**	**% Yield**
				HBDP
1	10	20	24	18
2	10	40	24	23
3	10	60	24	20
3	20	40	24	35
4	30	40	24	24
5	20	40	36	17
6	20	40	30	27
7	20	40	18	25

Firstly, we explored the influence of ligand DMEDA loadings on the generation of HBDP (Entry 1-4). The reaction was performed in toluene at 110°C for 24h with 10 mol% CuI catalyst and 20 mol%, 40 mol%, 60 mol% DMEDA. The reaction executed at 20 mol% DMEDA offered 18% yield of the expected product and by-product was 15% after 24h. Meanwhile, the yield of HBDP could be increased slightly to 23% after 24h when using 40 mol% DMEDA but reduced to 20% with 60 mol% DMEDA pointed out the optimized concentration ligand was 40 mol%.

Afterwards, the amounts of CuI were investigated and shown a critical effect on the conversion of main product (Entry 5-7), and the yield reached 35% with 20 mol% CuI employed comparing to 10 mol% showed a significant improvement of conversion. However, the yield of HBDP decrease to 24% with 30 mol% CuI. By contrast, the yield of 4H-DTP raised to 29%. These results indicated the best CuI ratio was 20 mol%.

Last approach was aimed at reaction time. The reaction was examined for 18h, 24h, 30h and 36h. The 18h reaction provide HBDP with the yield of 25% and reached the highest point of 35% at 24h. Nevertheless, the conversion reduced in 30h and 36h with 4H-DTP yield went up simultaneously. It was revealed that the longer reaction times than 24h caused augmentation of side-product by hydrolysis process.

As a consequence of due to abovementioned experiments, optimized parameters of Ullmann-type catalytic system were determined. For the best result, the reaction should be operated in toluene at 110°C and K_2CO_3 as base with 20 mol% CuI, 40 mol% DMEDA for 24h. Consequently, structures of HBDP was determined by FT-IR and NMR method.

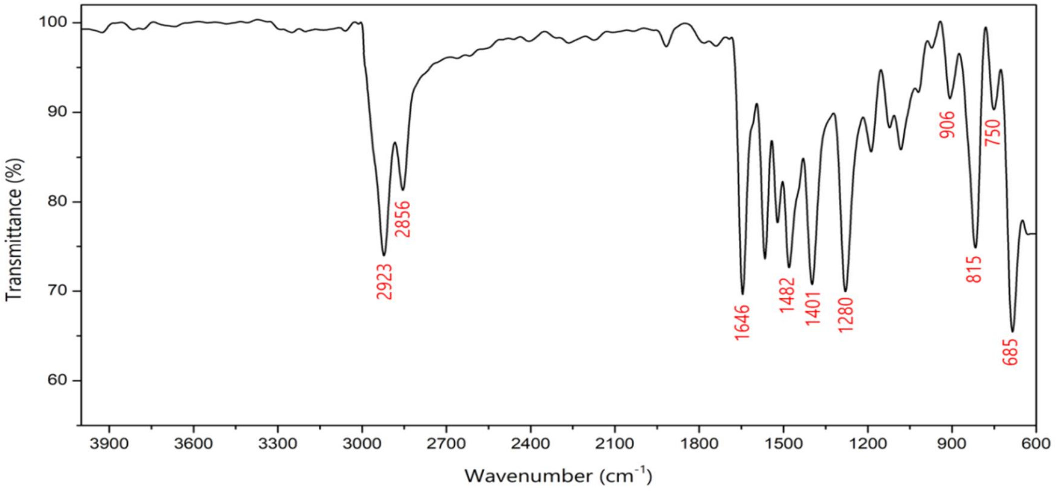


Figure 2. *FT-IR spectrum of HBDP*

The FT-IR spectrum of HBDP (Figure 2) displayed several peaks between 2856 and 2923 cm^{-1} which were responsible for C-H stretching modes of n-hexyl groups and ring C-H stretching vibrations. The peak at 1646 cm^{-1}, which was ascribed to the C=O stretching vibrations precisely proved for the existence of the N-acyl group in this structure. The peaks at 1482/1401 cm^{-1} and the bands in range of 750 to 906 cm^{-1} are assigned to the aromatic C-C stretching vibrations and aromatic C-H deformation vibrations, respectively. In addition, the band of 1280 cm^{-1} is assigned to the aromatic C-N stretching vibration of the pyrrole units. In addition, the peak at 615 cm^{-1} pointed out the thiophene S-C stretching vibrations.

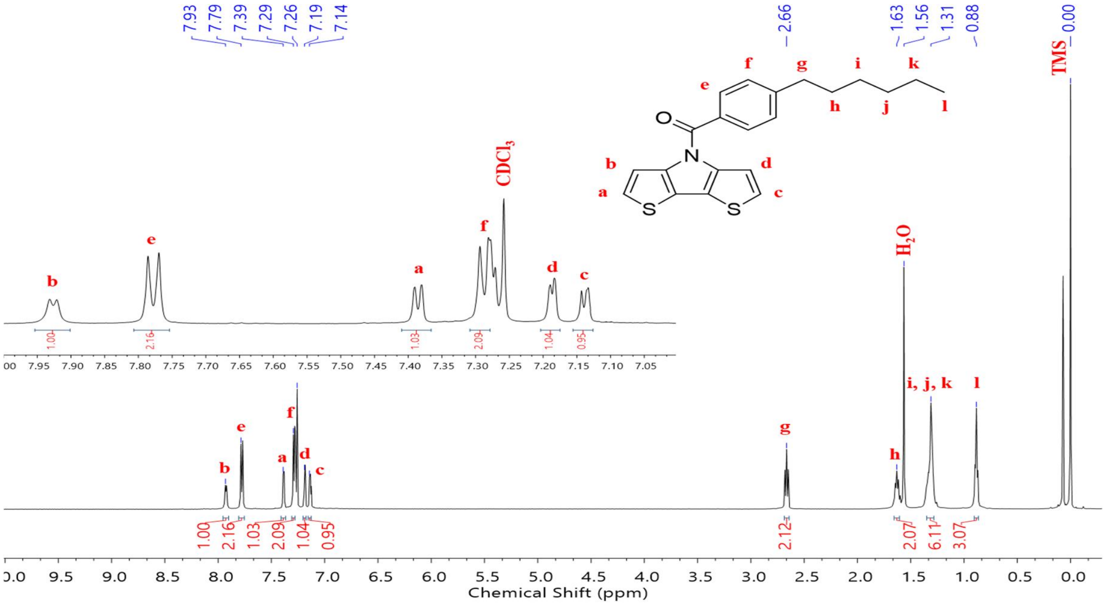


Figure 3. *^{1}H NMR spectrum of HBDP in CDCl$_3$*

In the ^{1}H NMR spectrum of HBDP (Figure 3), the doublet peak at 7.79 ppm and 7.29 ppm respectively corresponded to the four protons of *ortho* and *meta* positions on the benzene ring, in detail, two at positions ‘e’ and two at positions ‘f’. Obviously, peaks of thiophene ring are asymmetric due to strong hydrogen bond generated between C=O bond and thiophene β-proton on one side demonstrated two doublet peaks shifted to low-magnetic field region at 7.93 and 7.39 ppm which were respectively responsible for positions ‘a’ and ‘b’. This phenomenon also affected peaks of the remaining side. The doublet peaks at 7.19 and 7.14 ppm corresponded to the two protons on the non-affected side at positions ‘c’ and ‘d’. Several peaks in range of 0.88 and 2.66 was assigned to protons on *n*-hexyl side chain. The chemical shifts along with the integrals of obtained signals were suitable with the structural formula of HBDP. Moreover, the HBDP monomer chemical structure of HBDP is similar to the chemical structure of *N*-acyldithieno[3,2-b:2′,3′-d]pyrroles was confirmed by ^{1}H NMR spectrum [14].

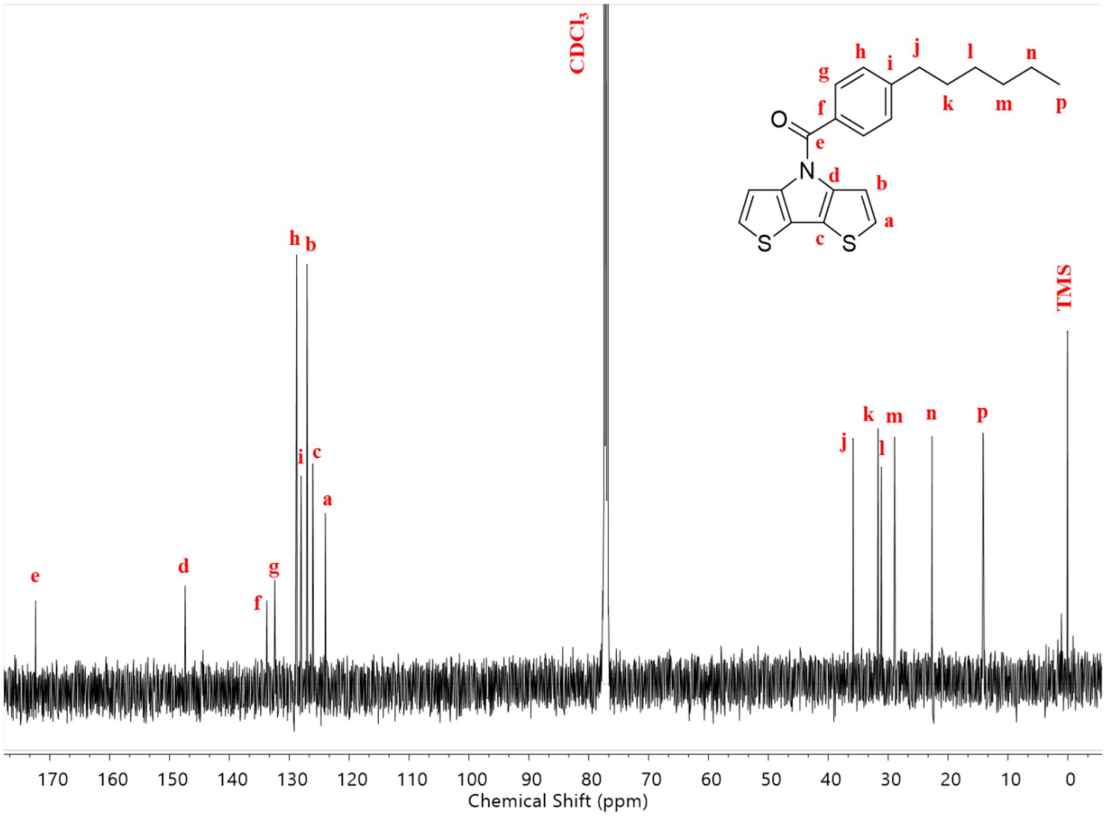


Figure 4. *^{13}C NMR spectrum of HBDP monomer*

^{13}C NMR spectrum presented characteristic carbon positions to clearly determined HBDP structure (Figure 4). It exhibited C=O bond at 172.3 ppm. Meanwhile, peaks from 147.4 to 124 ppm were corresponded to carbons on benzene and thiophene rings. Moreover, peaks in range of 35.8 to 14.1 ppm were assigned to carbons of *n*-hexyl side chain. These results indicated that Cu(I)-catalyzed Ullmann reaction successfully produced the main product HBDP.

4. Conclusion

In conclusion, the new derivative of bridged bithiophene DTP incorporating with N-acyl group, particularly N-(4-hexylbenzoyl) DTP monomer, has been achieved as expected product via copper(I)-catalyzed Ullmann-type amidation reaction. The chemical structures of these compounds were characterized by ^{1}H NMR, ^{13}C NM and FT-IR analysis. In next generation, these monomers will be used to synthesize the novel D-A conjugated polymers.

❖ ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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