

## **Simple Synthesis and Analysis of 3,6 and 2,7-dibromo-9-dodecylcarbazole by Direct Probe-Atmospheric Pressure Chemical Ionization Mass Spectrometry (DP-APCI-MS)**

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### **Abstract**

Isomeric 3,6-dibromo-9-dodecylcarbazole (3,6-diBrCz) and 2,7-dibromo-9-dodecylcarbazole (2,7-diBrCz) as a starting materials for conjugated materials were synthesized by Alkylation and Bromination reaction. This work reports a new and simple eco-friendly alkylation method for synthesis of 3,6-diBrCz and 2,7-diBrCz. All synthesized carbazole were purified by a silica gel with column chromatography, and were examined by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FTIR, and DP-APCI-MS. Comparison of DP-APCI mass spectrum for 3,6-diBrCz and 2,7-diBrCz shows fragmentation routs are different. DP-APCI mass spectrum for 3,6-diBrCz shows the ions with  $mz^{-1}$  496.3047, 325.8983, and 168.0786 were assigned as  $C_{24}H_{32}Br_2N^+$ ,  $C_{12}H_8Br_2N^+$ , and  $C_{12}H_{10}N^+$ , respectively, in which firstly the dodecyl at N position and then bromine at C-3 and C-6 position were eliminated. DP-APCI mass spectrum for 2,7-diBrCz shows the ions with  $mz^{-1}$  496.3036, 336.2671, and 168.0789 were assigned as  $C_{24}H_{32}Br_2N^+$ ,  $C_{24}H_{34}N^+$ , and  $C_{12}H_{10}N^+$ , respectively, in which firstly bromine at C-2 and C-7 position and then the dodecyl at N position were eliminated.

**KEYWORDS:** 3,6-substituted carbazole; 2,7-substituted carbazole; DP-APCI-MS

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### **Introduction**

Carbazole is the aromatic heterocyclic molecule with two six-membered benzene rings and a five-membered nitrogen in intramolecular conjugate compound [1]. Carbazole is an important starting material for the synthesis of hole transporters [2 – 4], emitters [5], dyes [6], pharmaceuticals [7, 8] and polymers [9]. Often, carbazole compounds were studied as uminescent Materials in organic light-emitting diodes [5, 10, 11]. The carbazole derivatives are designed by improvement at 3,6, 2,7, 1,8 and N positions of carbazole [12]. The synthesis of 2,7-substituted carbazoles is complicate, while 3,6-functionalized carbazoles can be easily synthesized by electrophilic aromatic substitution [9]. 3,6 and 2,7-dihalo-9-alkylcarbazole as a starting materials for conjugated materials. There is demand for alkylated carbazoles due to their emphasis as synthesis, separation and fabrication. Previously, a number of methods have been developed for the alkylation of carbazole leading to alkylated products. For instance, alkylation of carbazoles with bromoalkane in the presence of sodium

hydride (NaH) in N, N-Dimethylformamide (DMF) at 70 °C for 24 h [13], bromoalkane in the presence of NaH in DMF at room temperature for 18 h [14], bromoalkane in the presence of NaH in DMF at 0 °C for overnight [15], bromoalkane in the presence of sodium hydroxide (NaOH) and phase transfer catalyst in toluene and water at 70 °C for 10 h [16], bromoalkane in the presence of NaOH in toluene and water [17], bromoalkane in the presence of tetrabutylammonium bromide and NaOH for 10 h [18], bromoalkane in the presence of NaH in DMF at 70 °C for 20 h [19], bromoalkane in the presence of tetra-n-butylammonium hydrogen sulfide and NaOH in acetone at reflux for 5 h [20], bromoalkane in the presence of potassium carbonate ( $K_2CO_3$ ) in DMF at 80 °C for 16 h, bromoalkane in the presence of potassium hydroxide (KOH) in dimethyl sulfoxide (DMSO) at 80 °C for 16 h, and tosylate in the presence of KOH in DMSO at room temperature for 20 h [21].

Nevertheless, to the finest of information, the straightway alkylation of *N*-alkylcarbazoles has not been reported. This work reports a new and simple alkylation method for synthesis of

carbazoles with 1-bromododecane in the presence of NaH in DMF at room temperature for 3 h resulting 3,6-dibromo-9-dodecylcarbazole (3,6-diBrCz) and 2,7-dibromo-9-dodecylcarbazole (2,7-diBrCz) compounds in excellent yield, short process time, low-cost and low-energy process. Isomeric 3,6-diBrCz and 2,7-diBrCz were characterized by Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ), Carbon-13 nuclear magnetic resonance ( $^{13}\text{C-NMR}$ ), Fourier Transform infrared Spectroscopy (FTIR) and Direct probe-atmospheric pressure chemical ionization mass spectrometry (DP-APCI-MS). Differences between isomeric 3,6-diBrCz and 2,7-diBrCz determinations with alterable physical properties due to their different compositions. DP-APCI capacitated the identification of isomeric 3,6-diBrCz and 2,7-diBrCz because DP-APCI-MS can be analyzed solid and liquid samples within seconds by heating at slowly increasing temperatures for physical separation of the thermally desorbed ingredients and thermal degradation compounds, depended on their bond stabilities and volatilities [22 – 26].

## Materials and Methods

### Materials

All reagents and solvents were purchased from Aldrich, Acros, Fluka, Thai suppliers and used without further purification and distillation. Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F254. Column chromatography was carried out using gravity feed chromatography with Merck silica gel mesh 60 Å. The solvent mixtures are used and the portions are given by volume.

### Synthesis of 9-dodecylcarbazole (2)

To a solution of carbazole (1) (10.00 g, 59.80 mmol) and 1-bromododecane (15.00 g, 89.70 mmol) in DMF (93 ml) was added followed by NaH (2.15 g). The reaction mixture was stirred at room temperature for 3 h. Water (100 ml) was added and the mixture was extracted with methylene chloride (50 ml  $\times$  3). The combined organic phases were washed with a dilute HCl solution (50 ml  $\times$  2), water (100 ml), and brine solution (50 ml), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with hexane gave 2 (18.65 g, 93%) as a yellow viscous oil.  $R_F$  0.44;

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09 (d,  $J$  = 2.40 Hz, 2H), 7.44 (m, 4H), 7.25 (d,  $J$  = 2.40 Hz,

4.30 (t,  $J$  = 2.10 Hz, 2H), 1.88 (t,  $J$  = 2.10 Hz, 2H), 1.33 (m, 18H), and 0.89 (t,  $J$  = 2.10, 3H) ppm;

$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ): 140.57, 125.67, 122.98, 120.45, 118.82, 108.77, 43.15, 32.09, 29.77, 29.66, 29.56, 29.51, 29.09, 27.45, 22.86, and 14.19 ppm;

HRMS  $mz^{-1}$ : 336.2680 (calcd for  $\text{C}_{24}\text{H}_{33}\text{N}$ , 335.2613).

### Synthesis of 3,6-diBrCz

A solution of 9-dodecylcarbazole (0.07 g, 0.21 mmol) in  $\text{CHCl}_3$  (15 ml) was added followed by NBS (0.07 g, 0.42 mmol). The reaction mixture was stirred at room temperature for 3 h. Water (15 ml) was added and the mixture was extracted with methylene chloride (20 ml  $\times$  3). The organic layer was separated and dried in  $\text{Na}_2\text{SO}_4$ . The solvent was removed in vacuum. The pure product was obtained by column chromatography over silica gel eluting with hexane as an eluent gave 3,6-diBrCz (0.09 g, 92%) as a white pearl solid. m.p.: 50 °C;  $R_F$  0.52;

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 (s, 2H), 7.56 (d,  $J$  = 0.60 Hz 2H), 7.26 (d,  $J$  = 0.90 Hz, 2H), 4.24 (t,  $J$  = 0.90 Hz, 2H), 1.82 (t,  $J$  = 0.90 Hz, 2H), 1.43 (m, 18H), and 0.87 (t,  $J$  = 2.10 Hz, 3H) ppm;

$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ): 139.32, 129.00, 128.18, 123.45, 123.24, 111.94, 110.38, 108.93, 43.35, 31.90, 29.58, 29.52, 29.44, 29.32, 28.83, 27.20, 22.68, and 14.11 ppm;

FTIR (KBr) 2919, 2847, 1469, 1434, 1288, 1224, 1148, 1057, 1017, 870, 831, 802, 785, 724, 648, and 564  $\text{cm}^{-1}$ ;

HRMS  $mz^{-1}$ : 496.3047 (calcd for  $\text{C}_{24}\text{H}_{31}\text{Br}_2\text{N}$ , 493.0803).

### Synthesis of 2,7-diBrCz

A solution of 2,7-dibromocarbazole (2.00 g, 6.15 mmol) and 1-bromododecane (1.99 g, 7.99 mmol) in DMF (20 ml) was added followed by NaH (0.29 g, 12.30 mmol). The reaction mixture was stirred at room temperature for 3 h. Water (100 ml) was added and the mixture was extracted with methylene chloride (100 ml  $\times$  3). The combined organic phases were washed with a dilute HCl solution (100 ml  $\times$  2), water (100 ml), and brine solution (100 ml), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with hexane gave 2,7-diBrCz (2.70 g, 89%) as white solid. m.p. 78 °C;  $R_F$  0.57;

$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (s, 1H), 7.79 (s, 1H), 7.44 (d,  $J$  = 1.2 Hz, 2H), 7.25 (dd,  $J$  = 8.1 Hz,

$J = 1.5$  Hz, 2H), 4.09 (t,  $J = 7.2$  Hz, 2H), 1.77 – 1.72 (m, 2H), 1.17 (m, 18H), and 0.80 (t,  $J = 7.5$  Hz, 3H) ppm;

$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ) 141.38, 122.53, 121.47, 121.29, 119.69, 112.02, 43.36, 31.92, 29.61, 29.49, 29.33, 28.77, 27.18, 22.70, and 14.13 ppm;

FTIR (KBr) 3054, 2927, 2855, 1712, 1656, 1481, 1441, 1365, 1265, 1226, 1054, 889, 800 and 739  $\text{cm}^{-1}$ ;

HRMS  $mz^{-1}$ : 496.3036 (calcd for  $\text{C}_{24}\text{H}_{31}\text{Br}_2\text{N}$ , 493.0803).

#### Instruments

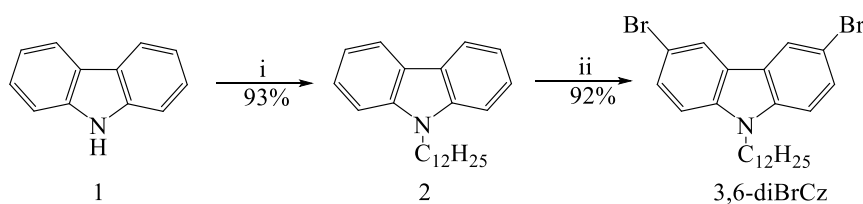
$^1\text{H}$ -NMR (Proton Nuclear Magnetic Resonance) spectra were recorded on a Bruker AVANCE (300 and 600 MHz) spectrometer using  $\text{CDCl}_3$  as solvent in all cases.  $^{13}\text{C}$  NMR (Carbon Nuclear Magnetic Resonance) spectra were recorded on Bruker AVANCE (75 and 150 MHz) spectrometer and were fully decoupled. Chemical shifts ( $\delta$ ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants ( $J$ ) are given in Hertz (Hz). Multiplicities are quoted as singlet (s), broad (br), doublet (d), triplet (t), and multiplet (m). High resolution mass spectrometry (HRMS) analysis was measured on Direct Probe-Atmospheric Pressure Chemical Ionization Mass Spectrometry (DP-APCI-MS). Melting points were reported in

degree Celsius by BIBBY Stuart Scientific melting point apparatus SMP3 in open capillary method. The IR spectrum was recorded on a Perkin-Elmer FTIR spectroscopy as KBr disks. The absorption peaks are quoted in wavenumber ( $\text{cm}^{-1}$ ).

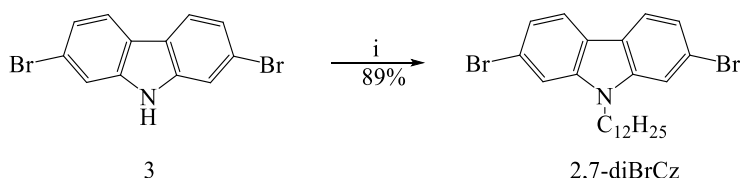
## Results and Discussion

#### Synthesis and characterization

For synthesis of the desired 3,6-diBrCz in Fig. 1, start with alkylation of carbazole (1) by 1-bromododecane in the presence of NaH as a base in DMF as a solvent at room temperature gave 2 in 93% yield. The solubility of molecule in common organic solvent is pretty excellent owing to the long alkyl chain attached to N position of carbazole. The Alkyl peaks were observed in  $^1\text{H}$ -NMR spectrum (measured in  $\text{CDCl}_3$ ) of 2 to confirm successful introduction of alkyl group to N position of carbazole. The  $^1\text{H}$ -NMR of 2 shows triplet signal at chemical shift 4.24 ppm ( $J = 0.90$  Hz, 2H) assigning as proton of alkyl group. NBS bromination of 2 in  $\text{CHCl}_3$  as a solvent at room temperature afforded 3,6-diBrCz in excellent yield. The structure of 3,6-diBrCz was confirmed by  $^1\text{H}$ -NMR spectrum (measured in  $\text{CDCl}_3$ ) which exhibit very clear singlet signal of aromatic proton of C-4 and C-5 carbazole at chemical shift 8.15 ppm (2H).



**Fig. 1** Synthesis route to the desired 3,6-diBrCz (overall yield: 85%), Reagents and conditions; i)  $\text{C}_{12}\text{H}_{25}\text{Br}$ , DMF, NaH, rt; ii) NBS,  $\text{CHCl}_3$ , rt.



**Fig. 2** Synthesis route to the desired 2,7-diBrCz, Reagents and conditions; i)  $\text{C}_{12}\text{H}_{25}\text{Br}$ , DMF, NaH, rt.

For synthesis of the desired 2,7-diBrCz in Fig. 2, start with alkylation of 2,7-dibromocarbazole (3) by 1-bromododecane in the presence of NaH in DMF at room temperature gave of 2,7-diBrCz in 89% yield. The Alkyl peaks were observed in  $^1\text{H-NMR}$  spectrum (measured in  $\text{CDCl}_3$ ) of 2,7-diBrCz to confirm successful introduction of alkyl group to N position of carbazole and aromatic proton of C-1 and C-8 carbazole. The  $^1\text{H-NMR}$  of 2,7-diBrCz shows triplet signal at chemical shift 4.09 ppm (2H,  $J = 7.2$  Hz) assigning as proton of alkyl group, singlet signal chemical shift 7.80 (1H) and 7.79 ppm (1H) assigning as aromatic proton of C-1 and C-8 carbazole.

#### DP-APCI-MS results

Isomeric 3,6-diBrCz and 2,7-diBrCz were heated at gently increasing temperatures on a DP-APCI source of a quadrupole ion trap mass spectrometer. Slow heating of the DP allowed for physical separation of the thermally desorbed ingredients and thermal degradation compounds, based on bond stability and volatility of them. DP-APCI mass spectrum for 3,6-diBrCz shows the molecular ion peak at  $mz^{-1}$  496.3047 as  $\text{C}_{24}\text{H}_{32}\text{Br}_2\text{N}^+$  peak of 3,6-diBrCz is intense. Loss

of the alkyl group gives a moderately intense M -  $\text{C}_{12}\text{H}_{25}$  peak at  $mz^{-1}$  325.8983 as  $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}^+$  peak followed by loss of two bromine atom give prominent peak at  $mz^{-1}$  168.0786 as  $\text{C}_{12}\text{H}_{10}\text{N}^+$  peak in Fig. 3. DP-APCI mass spectrum for 2,7-diBrCz shows the molecular ion peak at  $mz^{-1}$  496.3047 as  $\text{C}_{24}\text{H}_{32}\text{Br}_2\text{N}^+$  peak of 2,7-diBrCz is intense. Loss of two bromine atom give prominent peak at  $mz^{-1}$  336.2671 as  $\text{C}_{24}\text{H}_{34}\text{N}^+$  peak followed by loss of the alkyl group gives a moderately intense peak at  $mz^{-1}$  168.0789 as  $\text{C}_{12}\text{H}_{10}\text{N}^+$  peak in Fig. 5. It was noted above that cleavage of alkyl carbazole occurs with rearrangement involving cleavage of C-N bond that is the heteroatom controls cleavage, cleavage of the C-N bond is dominant. The M-Br peak is large for all compounds in which Br is attached directly to the ring. Comparison of DP-APCI mass spectrum for 3,6-diBrCz and 2,7-diBrCz shows fragmentation routs are different in Fig. 4 and 6. The C-Br bond in the 3,6-diBrCz is more stable than the C-Br bond in the 2,7-diBrCz because of resonance stability. The DP-APCI mass spectra depend on temperature additionally presents information about the thermal and bond stability of the different properties within isomeric 3,6-diBrCz and 2,7-diBrCz.

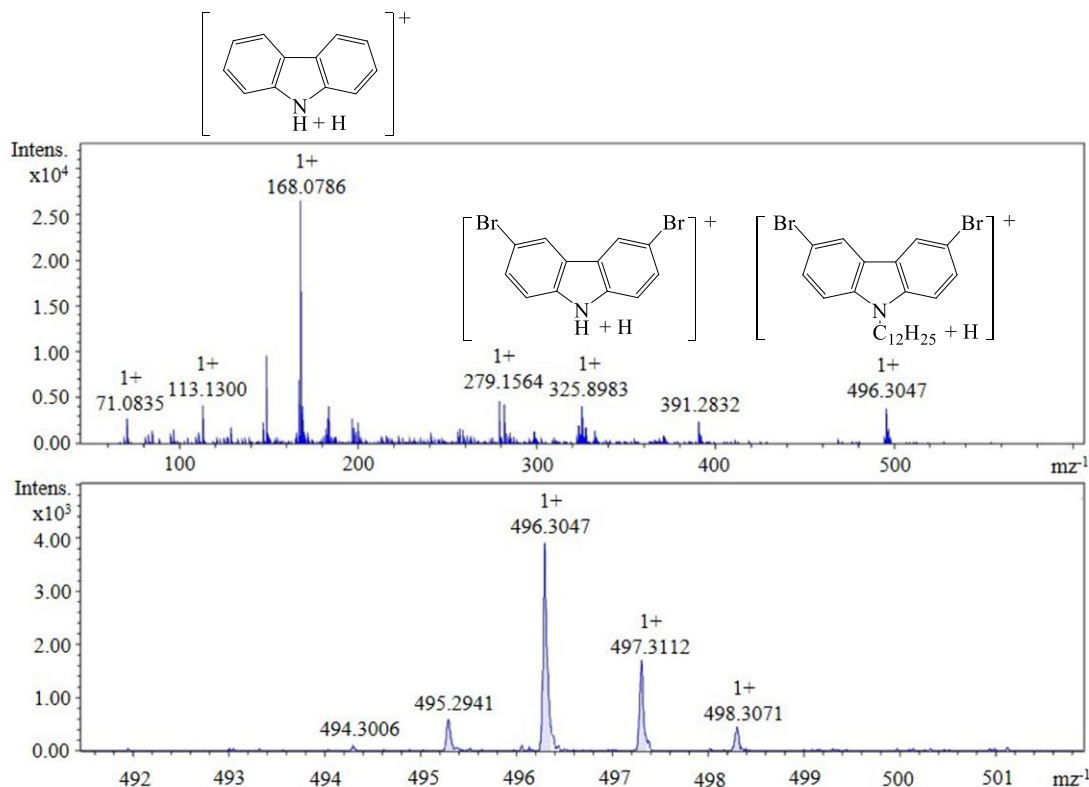


Fig. 3 DP-APCI mass spectrum for 3,6-diBrCz.

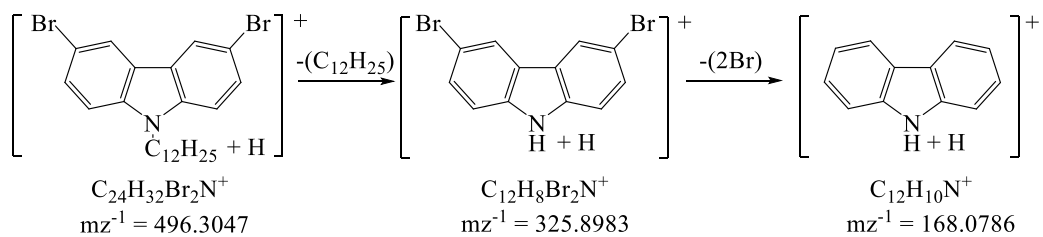


Fig. 4 Possible fragmentation routs of 3,6-diBrCz.

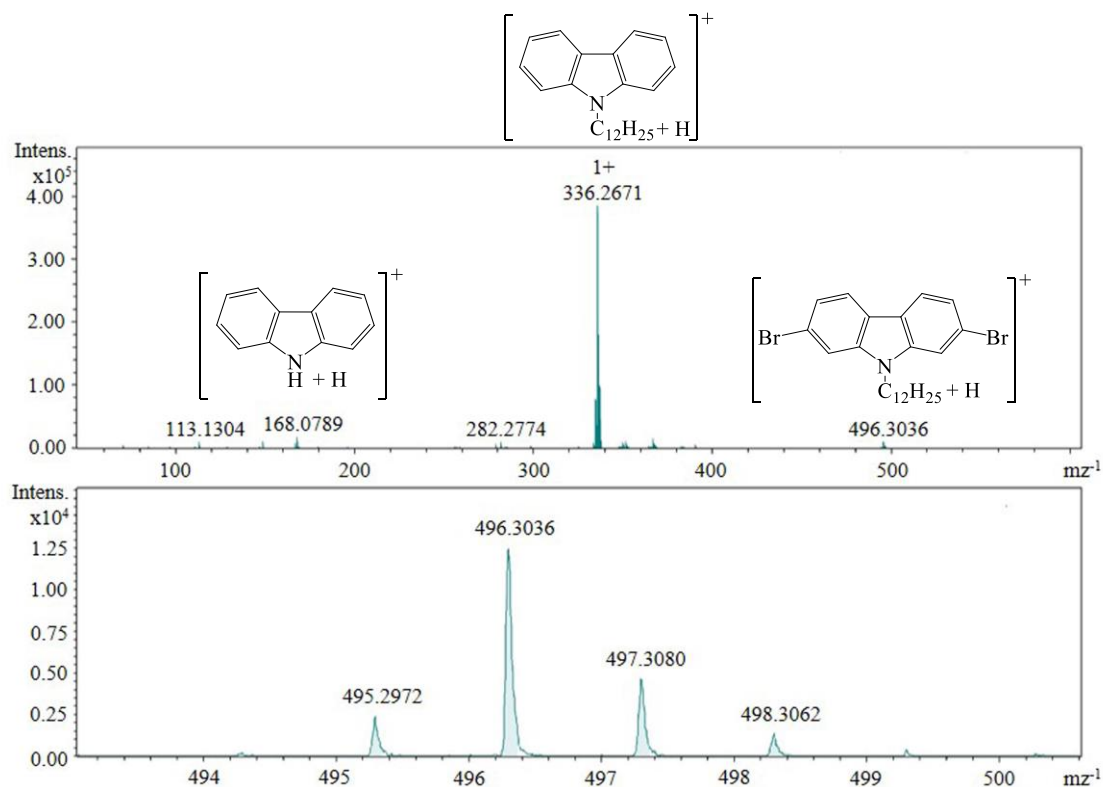


Fig. 5 DP-APCI mass spectrum for 2,7-diBrCz.

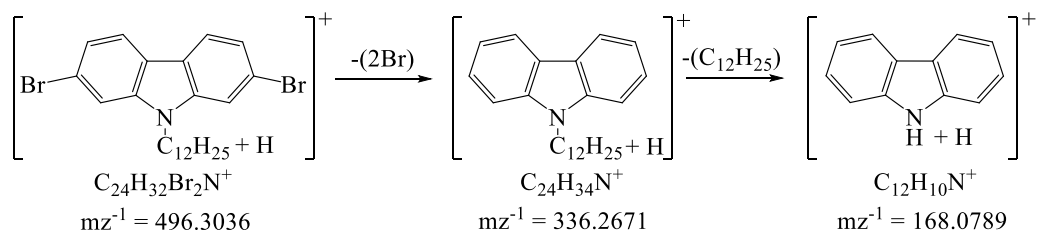


Fig. 6 Possible fragmentation routs of 2,7-diBrCz.

## Conclusion

Isomeric 3,6-diBrCz and 2,7-diBrCz as a starting materials for conjugated materials were synthesized by Alkylation and Bromination reaction. This work reports a new and simple alkylation method for synthesis of carbazoles with 1-bromododecane resulting 3,6-diBrCz and 2,7-diBrCz compounds in excellent yield, short process time, low-cost and low-energy process. All synthesized carbazole were purified by a silica gel with column chromatography, and were examined by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FTIR, and DP-APCI-MS. Comparison of DP-APCI mass spectra for 3,6-diBrCz and 2,7-diBrCz show fragmentation routs were different. DP-APCI mass spectrum for 3,6-diBrCz shows the ions with  $mz^{-1}$  168.0786, 325.8983, and 496.3047 were assigned as C<sub>12</sub>H<sub>10</sub>N<sup>+</sup>, C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub>N<sup>+</sup>, and C<sub>24</sub>H<sub>32</sub>Br<sub>2</sub>N<sup>+</sup>, respectively, in which bromine at C-3 and C-6 position and the dodecyl at N position were eliminated. DP-APCI mass spectrum for 2,7-diBrCz shows the ions with  $mz^{-1}$  168.0789, 336.2671, and 496.3036 were assigned as C<sub>12</sub>H<sub>10</sub>N<sup>+</sup>, C<sub>24</sub>H<sub>34</sub>N<sup>+</sup>, and C<sub>24</sub>H<sub>32</sub>Br<sub>2</sub>N<sup>+</sup>, respectively, in which the dodecyl at N position and bromine at C-2 and C-7 position were eliminated. The C - Br bond in the 3,6-diBrCz is more stable than the C-Br bond in the 2,7-diBrCz because of resonance stability. The DP-APCI mass spectra depend on temperature additionally presents information about the thermal and bond stability of the different properties within isomeric 3,6-diBrCz and 2,7-diBrCz.

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