Synthesis and thermal decomposition study of some dihydropyridine derivatives

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ABSTRACT

Some new dihydropyridine derivatives have been synthesized and their characterization was done by FT-IR, ¹H NMR and Mass spectral data. Thermal analysis of these dihydropyridine derivatives have been carried out by thermogravimetric (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques. Further, from thermograms of these compounds, various kinetic parameters such as order of reaction (n), energy of activation (E), frequency factor (A) and entropy change (ΔS) have been evaluated. The obtained results indicates that thermal stability of dihydropyridine derivatives have been depend on the type of substituent present in the compounds.

Keywords: dihydropyridine derivatives; thermo gravimetric analysis; differential scanning calorimetry

1. INTRODUCTION

Thermal analysis is a branch of materials science where with change in temperature, change in properties of materials is studied [1].

There are various thermo analytical techniques have been used for thermal analysis out of which thermo gravimetric (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are most common. These thermal techniques are widely used to
study the properties of various types of products such as dyes [2,3], drugs [4-6], polymers [7], metals [8], minerals [9], clays [10], metal complexes [11,12], coal [13], petroleum coke [14] etc. These techniques have also been used in pharmaceutical industries [15,16] for the identification and characterization of active and inactive ingredients [17], quality control [18, 19], to determine stability, purity and kinetic parameters of drugs [20-22] etc. Further, these thermal techniques are used to determine the composition of multicomponent system [23, 24] and to study interactions between drug and excipients [25]. Thus, these techniques have been used to study various types of physical transformation such as glass transition [26], cold transition and crystallization from melts [27], crystallization disorientation [28].

Dihydropyridine derivatives are known to possess wide range of pharmaceutical and biological activities [29-33] and act as intermediate for synthesized different biological active compounds [34-36]. Hence, it would be interesting to study their thermal properties. The data may be useful for pharmacists to study the therapeutic uses of these compounds.

In the present work, some dihydropyridine derivatives have been synthesized and their structures were confirmed by spectroscopic techniques such as FT-IR, $^1$H NMR and Mass. The thermal analysis of these synthesized compounds was carried out by thermo gravimetric (TG), differential thermal analysis (DTA) and differential scanning calorimetric (DSC) techniques. For all the synthesized compounds, thermal stability, melting points and various kinetic parameters such as order of the degradation ($n$), energy of activation ($E$), frequency factor ($A$) and entropy change ($\Delta S$) have been evaluated by these thermal methods.

2. EXPERIMENTAL

2.1. Material

Different substituted acetophenones, 3-methoxy-4-hydroxy benzaldehyde and cyano ethylacetate used for the synthesis of dihydropyridine derivatives, were supplied from Spectrochem Pvt. Ltd. (Mumbai, India) and was used without further purification.

2.2. Synthesis

An ethanolic solution of different acetophenone (0.01 mol), 4-hydroxy-3-methoxybenzaldehyde (0.01 mol), cyano ethyl acetate (0.01mol) and ammonium acetate (0.04 mol) was refluxed for about 8-10 hrs. The completion of reaction was confirmed by analytical thin layer chromatography (TLC) (Performed on aluminium coated plates Gel 60F_{254} (E. Merck)) using (0.4:0.6 v/v-Hexane: Ethyl acetate) as mobile phase. After completion of reaction, the reaction mass was cooled and obtained solid was stirred with toluene for half an hour. The resultant solid was filtered, washed with methanol to remove unreacted reagents and was dried under vacuum to give crude product.

The reaction scheme is given in Figure 1.

2.3. Spectroscopy study

For the structure confirmation, FT-IR, $^1$H NMR and mass analysis was done. The IR spectra were taken on Furrier Transport Infrared Spectrophotometer (SHIMADZU Model-IRaffinity1S). $^1$H NMR spectra were taken on a Bruker AVANCE III (400 MHz). In all the cases, $^1$H NMR spectra were obtained in deuterated dimethyl sulfoxide (DMSO-d$_6$) using TMS as an internal standard.
The NMR signals are reported in δ ppm. Mass spectra were determined using direct inlet probe on a SHIMADZU GC-MS (Model-QP2010) mass spectrometer.

2.4. Thermal analysis

Thermo gravimetric (TG) thermograms of the compounds were recorded on a SHIMADZU DTG-60H in nitrogen atmosphere with flow rate 100 ml·min⁻¹. For TGA analysis, sample put into open silica pan and heats it from room temperature to 800 °C with empty silica pan as the reference. For all compounds, the heating rate was 10 °C·min⁻¹. The DTG-60H instrument was calibrate with Indium and Zinc metals before experiments.

DSC measurements for all the compounds were done by using SHIMADZU DSC-60 calorimeter in nitrogen atmosphere with flow rate 100 ml·min⁻¹. For that sample is enclosed in an aluminium crucible using crimper and subjected to a temperature scan from room temperature to 400° C with an empty aluminium crucible as the reference.

![Reaction scheme of dihydropyridine derivatives.](image)

3. RESULTS AND DISCUSSION

The physical properties of all the studied compounds are given in Table 1 along with their side substitution. Figures 2 to 4 show FT-IR, ¹H NMR, and Mass spectra of compound DPCE-1 respectively.

<table>
<thead>
<tr>
<th>Compound Code</th>
<th>Substitution</th>
<th>Molecular formula</th>
<th>Molecular weight (g/mol)</th>
<th>R*f Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPCE-1</td>
<td>2-methoxy</td>
<td>C₂₀H₁₆O₄N₂</td>
<td>348</td>
<td>0.58</td>
</tr>
</tbody>
</table>
DPCE-2  4-methoxy  C<sub>20</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub>  348  0.55
DPCE-3  4-bromo  C<sub>19</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>Br  397  0.63
DPCE-4  3,4,5-trimethoxy  C<sub>22</sub>H<sub>14</sub>O<sub>5</sub>N<sub>2</sub>  386  0.49
DPCE-5  4-flouro  C<sub>19</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>F  336  0.62
DPCE-6  4-methyl  C<sub>20</sub>H<sub>16</sub>O<sub>3</sub>N<sub>2</sub>  332  0.60
DPCE-7  2-hydroxy  C<sub>19</sub>H<sub>14</sub>O<sub>4</sub>N<sub>2</sub>  334  0.53
DPCE-8  4-hydroxy  C<sub>19</sub>H<sub>14</sub>O<sub>4</sub>N<sub>2</sub>  334  0.51
DPCE-9  4-chloro  C<sub>19</sub>H<sub>13</sub>O<sub>3</sub>N<sub>2</sub>Cl  352  0.61
DPCE-10  Hydrogen  C<sub>19</sub>H<sub>13</sub>O<sub>3</sub>N<sub>2</sub>  318  0.59

*0.4:0.6 - Hexane: Ethyl acetate

3.1. Spectral data

DPCE-1:

IR (ʋ, cm<sup>-1</sup>): 3524.54 (-CN), 3284.77 (O-H), 2214.28 (-CN), 1737.86 (-C=O), 1629.85, 1587.42 (-NH-), 1456.26 (-CH-), 1388.75 (-CH-), 1286.52, 1230.58, 1022.27 (C-O), 939.33 (-OH).

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) (δ ppm): 3.8372 (s, 6H, 2-OCH<sub>3</sub>), 6.7842 (s, 1H, CH), 6.9308-6.9414 (d, 1H, J = 8.2 Hz, CH), 6.9865-6.9918 (d, 1H, J = 4.2 Hz, CH), 7.2480-7.3487 (m, 2H, CH), 7.6047-7.8259 (m, 6H, CH), 7.9186 (s, 1H, CH), 9.7776 (s, 1H, OH), 12.7288 (s, 1H, NH).

Mass (m/z): 348.

DPCE-2:

IR (ʋ, cm<sup>-1</sup>): 3479.58 (-CN), 2924.09 (O-H), 2222.00 (-CN), 1643.35, 1597.06 (-NH-), 1496.76 1427.3, 21381.03, 13241.01, 1280.73, 1211.30 (C-O), 1118.71, 1087.85, 1018.41 (O-C), 902.69 (O-H).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>) (δ ppm): 3.8437-3.8688 (s, 6H, 2-OCH<sub>3</sub>), 6.7842 (s, 1H, CH), 6.9308-6.9414 (d, 1H, J = 8.24 Hz, CH), 6.9865-6.9918 (d, 1H, J = 4.24 Hz, CH), 7.2480-7.3487 (m, 2H, CH), 7.6047-7.8259 (m, 6H, CH), 7.9186 (s, 1H, CH), 9.7776 (s, 1H, OH), 12.7288 (s, 1H, NH).

Mass (m/z): 348.

DPCE-3:

IR (ʋ, cm<sup>-1</sup>): 3427.19 (-CN), 3087.76 (O-H), 2214.74 (-CN), 1741.39 (-C=O), 1647.27, 1583.59 (-NH-), 1474.46, 1398.49, 1340.53 (-CH-), 1274.95, 1213.25, 1089.78 (C-O), 995.27 (-OH), 682.80 (C-Br).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>) (δ ppm): 3.8321 (s, 3H, -OCH<sub>3</sub>), 6.7639 (s, 1H, CH), 6.8602-6.8689 (d, 1H, J = 3.48 Hz, CH), 6.9865-6.9918 (d, 1H, J = 3.2 Hz, CH), 7.2181-7.3083 (m, 2H, CH), 7.5822-7.5994 (d, 2H, J = 6.8 Hz, CH), 7.9006 (s, 1H, CH), 9.7072 (s, 1H, OH), 12.7208 (s, 1H, NH).
Mass (m/z): 397.

DPCE-4:

IR (v, cm\(^{-1}\)): 3534.19 (-CN), 3082.25 (O-H), 2212.14 (-CN), 1747.51 (-C=O), 1649.14, 1585.49 (-NH-), 1471.69, 1398.39, 1340.53 (-CH-), 1274.95, 1213.25, 1089.78 (C-O), 995.27 (-OH).

\(^1\)H NMR (DMSO-d\(_6\)) (\(\delta\) ppm): 3.8321 (s, 3H, -OCH\(_3\)), 3.8945 (s, 3H, -OCH\(_3\)), 3.4123 (s, 3H, -OCH\(_3\)), 3.4289 (s, 3H, -OCH\(_3\)), 6.3418 (s, 1H, CH), 6.5392 (s, 1H, CH), 6.8608-6.9034 (m, 3H, CH), 7.9016 (s, 1H, CH), 9.7072 (s, 1H, OH), 12.7214 (s, 1H, NH).

Mass (m/z): 387.

DPCE-5:

IR (v, cm\(^{-1}\)): 3331.22 (-CN), 3078.25 (O-H), 2217.14 (-CN), 1742.52 (-C=O), 1644.14, 1582.44 (-NH-), 1476.65, 1395.35, 1344.52 (-CH-), 1278.95, 1215.25, 1084.78 (C-O), 992.22 (-OH), 681.19 (C-F).

\(^1\)H NMR (DMSO-d\(_6\)) (\(\delta\) ppm): 3.8320 (s, 3H, -OCH\(_3\)), 6.7892 (s, 1H, CH), 6.8603-6.8778 (d, 2H, J = 7.00 Hz, CH), 7.2180-7.3080 (m, 2H, CH), 7.5641-7.5801 (d, 2H, J = 6.4 Hz, CH), 7.9301 (s, 1H, CH), 9.7070 (s, 1H, OH), 12.7218 (s, 1H, NH).

Mass (m/z): 337.

DPCE-6:

IR (v, cm\(^{-1}\)): 3434.19 (-CN), 3083.14 (O-H), 2210.44 (-CN), 1716.65 (-C=O), 1649.14, 1598.99 (-NH-), 1490.97, 1471.69 (-CH-), 1367.53, 1334.74 (-CH-), 1288.45, 1234.44, 1074.35 (C-O), 968.27 (-OH).

\(^1\)H NMR (DMSO-d\(_6\)) (\(\delta\) ppm): 3.3843 (s, 3H, -CH\(_3\)), 3.6621 (s, 3H, -OCH\(_3\)), 6.7483 (s, 1H, CH), 6.8605-6.8685 (d, 1H, J = 3.2 Hz, CH), 6.9929-7.0082 (d, 1H, J = 6.12 Hz, CH), 7.1131-7.2033 (m, 2H, CH), 7.4632-7.4706 (d, 1H, J = 6.12 Hz, CH), 7.9046 (s, 1H, CH), 9.7072 (s, 1H, OH), 12.7208 (s, 1H, NH).

Mass (m/z): 332.

DPCE-7:

IR (v, cm\(^{-1}\)): 3324.69 (-CN), 3037.56 (O-H), 2215.14 (-CN), 1746.41 (-C=O), 1579.70 (-NH-), 1450.11 (-CH-), 1393.53 (-CH-), 1256.58, 1019.90 (C-N), 1291.48 (C-O), 929.33 (-OH).

\(^1\)H NMR (DMSO-d\(_6\)) (\(\delta\) ppm): 3.0651 (s, 3H, -OCH\(_3\)), 6.7384-6.7462 (d, 1H, J = 3.12 Hz, CH), 7.1337-7.1425 (d, 1H, J = 3.52 Hz, CH), 7.4386-7.4501 (d, 1H, J = 4.6 Hz, CH), 7.5853-
7.9906 (m, 4H, CH), 8.0056 (s, 1H, CH), 9.7272 (s, 1H, OH), 9.7393 (s, 1H, OH), 12.7106 (s, 1H, NH).

Mass (m/\(\text{z}\)): 334.

DPCE-9:

IR (\(\nu\), cm\(^{-1}\)):
3433.69 (-CN), 3083.44 (O-H), 2213.11 (-CN), 1745.51 (-C=O), 1645.28, 1595.13, 1570.06 (-NH-), 1471.69 (-CH-), 1394.53 (-CH-), 1259.52, 1024.20 (C-N), 1230.58 (C-O), 908.47 (N-H), 889.45 (C-Cl).

\(^1\)H NMR (DMSO-d\(_6\)) (\(\delta\) ppm):
3.8622 (s, 3H, OCH\(_3\)), 6.8806 (s, 1H, CH), 6.9308-6.9514 (d, 1H, \(J = 7.84\) Hz, CH), 7.2436-7.2684 (dd, 1H, CH), 7.3446-7.3487 (d, 1H, \(J = 1.46\) Hz, CH), 7.6047-7.6259 (d, 2H, \(J = 8.48\), CH), 7.9186-7.9389 (d, 2H, \(J = 8.12\) Hz, CH), 9.7776 (s, 1H, OH), 12.7288 (s, 1H, NH).

Mass (m/\(\text{z}\)): 352.

DPCE-10:

IR (\(\nu\), cm\(^{-1}\)):
3424.54 (-CN), 3023.95 (O-H), 2221.00 (-CN), 1737.86 (-C=O), 1649.14, 1591.27 (-NH-), 1473.62 (-CH-), 1377.17 (-CH-), 1249.52, 1022.27 (C-N), 1228.66 (C-O), 910.48 (N-H).

\(^1\)H NMR (DMSO-d\(_6\)) (\(\delta\) ppm):
3.0742 (s, 3H, OCH\(_3\)), 6.7569 (s, 1H, CH), 6.2892-6.3048 (d, 1H, \(J = 6.24\) Hz, CH), 6.9992-7.0111 (d, 1H, \(J = 4.76\) Hz, CH), 7.7427-8.3285 (m, 6H, CH), 9.7932 (s, 1H, OH), 12.7836 (s, 1H, NH).

Mass (m/\(\text{z}\)): 318.

The TG thermogram of DPCE-1 is shown in Figure 5. Various thermal properties such as initial decomposition temperature (IDT), the decomposition temperature range and percentage weight loss are reported in Table 2.

Table 2. Some thermodynamic parameter evaluated from TG thermo grams for the synthesized compounds.

<table>
<thead>
<tr>
<th>Compd. code</th>
<th>Amount (mg.)</th>
<th>Initial decomp. temp. (°C)</th>
<th>Decomp. range (°C)</th>
<th>% Wt. loss</th>
<th>Residual wt. loss (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPCE-1</td>
<td>3.870</td>
<td>308</td>
<td>308-697</td>
<td>77.40</td>
<td>2.180</td>
</tr>
<tr>
<td>DPCE-2</td>
<td>1.962</td>
<td>315</td>
<td>315-790</td>
<td>97.96</td>
<td>1.922</td>
</tr>
<tr>
<td>DPCE-3</td>
<td>3.871</td>
<td>318</td>
<td>318-757</td>
<td>56.20</td>
<td>2.176</td>
</tr>
<tr>
<td>DPCE-4</td>
<td>3.593</td>
<td>288</td>
<td>288-431</td>
<td>77.40</td>
<td>3.552</td>
</tr>
<tr>
<td>DPCE-5</td>
<td>3.704</td>
<td>203</td>
<td>203-393</td>
<td>77.39</td>
<td>2.404</td>
</tr>
<tr>
<td>DPCE-6</td>
<td>4.539</td>
<td>154</td>
<td>154-421</td>
<td>72.84</td>
<td>3.306</td>
</tr>
<tr>
<td>DPCE-7</td>
<td>5.540</td>
<td>123</td>
<td>123-393</td>
<td>51.48</td>
<td>2.852</td>
</tr>
</tbody>
</table>
For all the compounds, degradation is multi step process except DPCE-4. In all studied compounds, DPCE-7 is most unstable and DPCE-3 is most stable. Generally, thermal stability depends on structure of compounds. In the studied compounds, central moiety is same for all the compounds but substitutions are different. Hence, the variation in thermal stability is may be due to nature of different substitutions. Thus, the compound DPCE-7 containing 2-hydroxy group is most unstable whereas DPCE-3 having 4-bromo group is most stable. The effect of different of substituent on stability is: 4-Bromo >4-methoxy >2-methoxy > 4-Chloro >3,4,5-trimethoxy > 4-hydroxy > 4-Flouro >Hydrogen > 4-Methyl >2-hydroxy. This suggests that not only the nature but position of substitution in a compound also affect thermal stability of compound.

Overall, the dominating effect of different group is: positive resonating (+R) > positive hyper conjugation effect (+H) > negative inductive (-I). The more stability of DPCE-3 is may be due to higher inductive effect of 3-bromo group while DPCE-6 is most unstable may be due to lower inductive effect of 2-hydroxyl group.

Further, various kinetics parameters such as order of reaction \( n \), energy of activation \( E \) for the decomposition of studied compounds were evaluated for each step using Anderson-Freeman method [37] and its given as:

\[
\Delta \ln \frac{dw}{dt} = n \Delta \ln W - \frac{E}{R} \Delta \left( \frac{1}{T} \right) \tag{1}
\]

where \( dw/dt \) is the rate of decomposition, \( W \) is the active mass, \( R \) is gas constant and \( T \) is temperature. From the intercept and slope of the plot of \( \Delta \ln dw/dt \) verses \( \Delta \ln W \) (Anderson-Freeman plot), the energy of activation \( E \) and order of reaction \( n \) were evaluated respectively.

The frequency factor \( A \) and the entropy change \( \Delta S \) were evaluated by the equations (2) and (3) respectively.

\[
A = \left( \frac{E \beta}{RT^2} \right) e^{E/RT} \tag{2}
\]

\[
\Delta S = R \ln \left( \frac{Ah}{kT} \right) \tag{3}
\]

where \( \beta \) is heating rate \( (10^5 \text{ C/minute}) \), \( h \) is Planck’s constant and \( k \) is Boltzmann constant.

All these evaluated kinetic parameters are given in Table 3 along with the correlation coefficients. It is evident from Table 3 that order of reaction is quite different in different steps for different dihydropyridine derivatives. For most of the compounds, order of reaction is very small for the second step.
Table 3. The kinetics parameters of the thermal decomposition for all the synthesized compounds derived according to Anderson-Freeman method.

<table>
<thead>
<tr>
<th>Compound Code</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; step</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; step</th>
<th>3&lt;sup&gt;rd&lt;/sup&gt; step</th>
<th>4&lt;sup&gt;th&lt;/sup&gt; step</th>
<th>5&lt;sup&gt;th&lt;/sup&gt; step</th>
<th>6&lt;sup&gt;th&lt;/sup&gt; step</th>
<th>7&lt;sup&gt;th&lt;/sup&gt; step</th>
<th>8&lt;sup&gt;th&lt;/sup&gt; step</th>
<th>9&lt;sup&gt;th&lt;/sup&gt; step</th>
<th>10&lt;sup&gt;th&lt;/sup&gt; step</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>n</strong></td>
<td>1.1296</td>
<td>3.9981</td>
<td>1.2075</td>
<td>0.6852</td>
<td>1.3169</td>
<td>1.6721</td>
<td>0.8467</td>
<td>4.6063</td>
<td>1.0453</td>
<td>1.6681</td>
</tr>
<tr>
<td><strong>E (kJmol&lt;sup&gt;-1&lt;/sup&gt;)</strong></td>
<td>218.66</td>
<td>70.00</td>
<td>194.22</td>
<td>28.43</td>
<td>233.79</td>
<td>122.88</td>
<td>135.19</td>
<td>306.45</td>
<td>202.03</td>
<td>125.38</td>
</tr>
<tr>
<td><strong>A (Sec&lt;sup&gt;-1&lt;/sup&gt;)</strong></td>
<td>4.64 X 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>8.70</td>
<td>5.62 X 10&lt;sup&gt;13&lt;/sup&gt;</td>
<td>3.56 X 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>9.57 X 10&lt;sup&gt;16&lt;/sup&gt;</td>
<td>7.20 X 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>2.84 X 10&lt;sup&gt;8&lt;/sup&gt;</td>
<td>2.99 X 10&lt;sup&gt;31&lt;/sup&gt;</td>
<td>1.17 X 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>5.45 X 10&lt;sup&gt;12&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>ΔS (J·mol&lt;sup&gt;-1&lt;/sup&gt;·K&lt;sup&gt;-1&lt;/sup&gt;)</strong></td>
<td>48.56</td>
<td>-236.74</td>
<td>11.91</td>
<td>-281.64</td>
<td>73.74</td>
<td>-140.75</td>
<td>-89.71</td>
<td>353.60</td>
<td>37.46</td>
<td>-4.47</td>
</tr>
<tr>
<td><strong>Correlation coefficient</strong></td>
<td>0.9979</td>
<td>0.9904</td>
<td>0.9941</td>
<td>0.9959</td>
<td>0.9961</td>
<td>0.9978</td>
<td>0.9967</td>
<td>0.9216</td>
<td>0.9968</td>
<td>0.9977</td>
</tr>
</tbody>
</table>

-311-
The energy of activation (\(E\)) and frequency factor (\(A\)) are found to be maximum for 1\(^{\text{st}}\) step of DPCE-5, while lowest for 3\(^{\text{rd}}\) step of DPCE-8 depending upon the type of substitutions in compounds. Comparison of energy of activation and frequency factor values in Table 3 shows that the values of energy of activation and frequency factor are also minimum for second steps of all the studied compounds.

The change in entropy (\(\Delta S\)) values is quite different for different compounds. These values are both positive and negative for different compounds. The positive values indicate that the transition state is less ordered than the original compound whereas negative value corresponds to an increase in the order of transition state than that of individual molecules.

The \(\Delta S\) value for 1\(^{\text{st}}\) step of DPCE-5 was found to be positive and large in magnitude, which implies randomness in transition state. The \(\Delta S\) for 3\(^{\text{rd}}\) step of DPCE-8 is negative indicating there by more ordered transition state.

Differential thermal analysis (DTA) is similar to DSC in many respects and analogous information about the same range of thermal events is observed. On the DTA curves endothermic peak appeared due to the melting. Some other peaks are also appeared due to small weight loss due to evaporation of molten compounds.

The DSC thermo gram for compound DPCE-1 is given as Figures 6. The sharp endothermic peak is due to melting of compound. The melting points of all the compounds were determined by DSC and are given in Table 4 along with melting points determined by open capillary method. It is observed that there is good agreement between the values evaluated from DSC and those determined by open capillary method. Further, the values of enthalpy obtained directly form instrument DSC-60 is reported in Table 4.

**Table 4.** The melting temperatures (°C) of synthesized compounds by DSC and open capillary methods.

<table>
<thead>
<tr>
<th>Compound Code</th>
<th>DSC (°C)</th>
<th>Open capillary (°C)</th>
<th>(\Delta H) (J·g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPCE-1</td>
<td>342.81</td>
<td>340-343</td>
<td>-277.14</td>
</tr>
<tr>
<td>DPCE-2</td>
<td>293.80</td>
<td>292-294</td>
<td>-123.75</td>
</tr>
<tr>
<td>DPCE-3</td>
<td>320.17</td>
<td>318-321</td>
<td>-122.63</td>
</tr>
<tr>
<td>DPCE-4</td>
<td>233.75</td>
<td>233-236</td>
<td>-29.68</td>
</tr>
<tr>
<td>DPCE-5</td>
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<td>233-236</td>
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<td>-164.16</td>
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<td>DPCE-10</td>
<td>343.12</td>
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Figure 2. IR spectrum of DPCE-2.
Figure 3. $^1$H NMR spectrum of DPCE-2.
Figure 4. Mass spectrum of DPCE-2.
Figure 5. TG (-) and DTA (-) curve of DPCE-1.

Figure 6. DSC curve of DPCE-1.
4. CONCLUSION

For the studied compounds, degradation is multistep step process with different order of reaction. The thermal stability depends upon the nature and position of substituent present. It is observed that presence of 4-bromo substituent increases the stability whereas 2-hydroxy substituent decreases the stability.

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References


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