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# Extensive Substituent Scrambling in Substituted Diphenylacetylenes on Electron Impact

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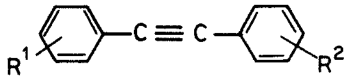
**Extensive randomization of the substituents is found in mono- and disubstituted diphenylacetylenes under electron impact conditions. The study of diphenylacetylenes with a variety of substituents indicates that the electron-withdrawing groups favour the substituent scrambling. All the substituted diphenylacetylenes give an ion at *m/z* 176, having a common ion-structure, arising as a result of the expulsion of a hydrogen radical and the substituent in monosubstituted diphenylacetylenes and the expulsion of both the substituents in disubstituted diphenylacetylenes. A ring-expanded structure is postulated for this common fragment.**

## INTRODUCTION

Electron impact randomization of hydrogen atoms and substituents in aromatic compounds is a well-known phenomenon although the precise mechanisms of these rearrangements have not been well established. In the case of benzene,[1] halogenobenzenes,[2] pyridines,[3] benzonitrile,[4] nitrosobenzene[5] and phenylpropynes,[6] hydrogen scrambling occurs in the molecular ion prior to fragmentation. It has been shown[7] that hydrogen scrambling between the two phenyl rings in diphenylacetylene occurs to an extent of 65% in the decomposing molecular ions. It has been suggested[8] by comparison of the metastable peak ratios that complete chlorine randomization occurs over fourteen carbon atoms of the diphenylacetylene nucleus upon electron impact prior to elimination of HCl from monochloro-, and $Cl_2$ from dichlorodiphenylacetylenes. In the present study the electron impact induced fragmentations of substituted diphenylacetylenes (**1** to **17**) (Scheme 1) have been investigated to evaluate the possible occurrence of substituent scrambling, rearrangements, and also to examine the substituent effect on the scrambling process.



| Compound № | $R^1$ | $R^2$ |
|---|---|---|
| 1 | H | H |
| 2 | H | *o*–Cl |
| 3 | H | *p*–Cl |
| 4 | H | *p*–$NO_2$ |
| 5 | H | *p*–$OCH_3$ |
| 6 | H | *m*–Cl |
| 7 | *o*–Cl | *o*–Cl |
| 8 | *o*–Cl | *p*–Cl |
| 9 | *o*–Cl | *p*–$NO_2$ |
| 10 | *m*–Cl | *o*–Cl. |
| 11 | *p*–$CH_3$ | *p*–$CH_3$ |
| 12 | *p*–$CH_3$ | *p*–$NO_2$ |
| 13 | *p*–$OCH_3$ | *p*–$OCH_3$ |
| 14 | *p*–$OCH_3$ | *p*–$NO_2$ |
| 15 | *p*–Cl | *p*–Cl |
| 16 | *p*–Cl | *p*–$OCH_3$ |
| 17 | *p*–Cl | *p*–$NO_2$ |

**Scheme 1**

## RESULTS AND DISCUSSION

The mass spectra of a variety of monosubstituted and disubstituted (one substituent on each of the phenyl rings) diphenylacetylenes have been studied. The chief fragment ions found in the mass spectrum of diphenylacetylenes (**1**) are due to loss of two hydrogen radicals and expulsion of $C_2H_2$ from the molecular ion in parallel fragmentation pathways to produce the fragment at *m/z* 176(17% relative abundance) and an ion *a*

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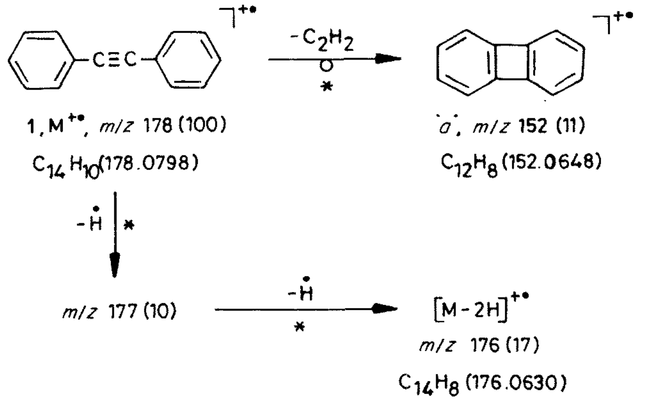


**Scheme 2**

at m/z 152(11%), respectively, (see Scheme 2). The elemental compositions $C_{14}H_8$ (176.0630) for the ion at m/z 176, and $C_{12}H_8$ (152.0648) for the ion '*a*' at m/z 152, as obtained by the high-resolution technique, support the proposed elimination of two hydrogen radicals and $C_2H_2$ from the molecular ion, respectively, during the formation of these ions. It has further been established through *B/E* linked-scan spectra of the $M^{+\bullet}$ ion of **1** (Table 1) that the ion at m/z 176 is formed by the loss of two hydrogen radicals in a step-wise process and the ion at m/z 152 is produced directly from the molecular ion by the expulsion of $C_2H_2$. Based on these facts a biphenylene radical cation structure is assigned to *a* at m/z 152 in **1** (Scheme 2). The envisaged structure of *a* is supported by the comparison of the collision-induced dissociation (CID) mass-analysed ion kinetic energy (MIKE) spectrum of *a* with that of the ion at m/z 152, (for which a biphenylene radical cation structure is proposed) derived from anthraquinone[9] (Fig. 1).

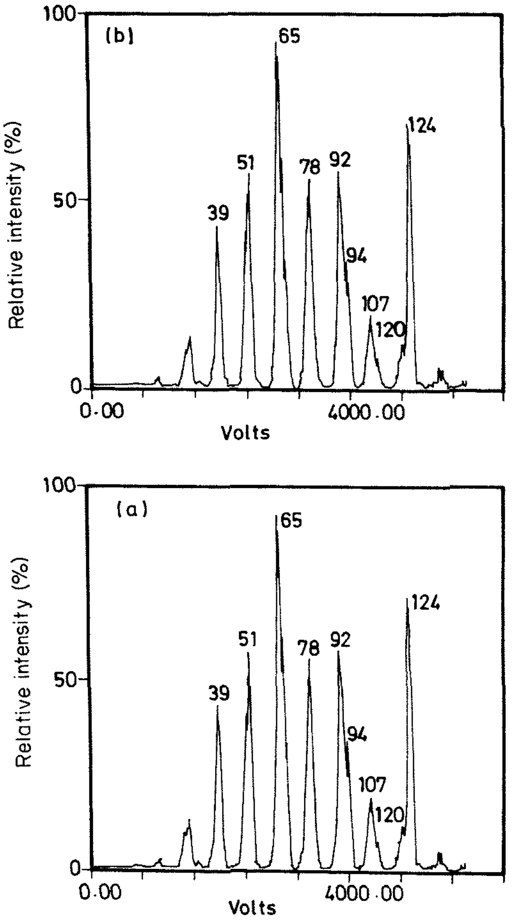


**Figure 1.** CID-MIKE spectra of ions at m/z 152 from (a) diphenylacetylene, and (b) anthraquinone.

Many of the compounds isomeric with diphenylacetylene such as phenanthrene,[10] anthracene,[10] 9-methylenefluorene[11] and benz(*a*)azulene[12] give rise to identical electron impact mass spectra as that of diphenylacetylene (Fig. 2). Furthermore, the CID-MIKE spectra of the molecular ions at m/z 178 of phenanthrene, anthracene and diphenylacetylene are compared (Fig. 3) and are found to be identical. Hence it appears that, under electron impact conditions, all these compounds isomerize to a common structure before fragmentation. Furthermore, it can be inferred from the *B/E* linked-scan spectra of the relevant ions from **1**, **2**, **9**, **15** and **17** (Table 1) that the mono-substituted diphenylacetylenes lose the substituent and the hydrogen radical whilst the disubstituted diphenylacetylenes (similar substituents with one substituent on each of the phenyl rings) lose both the substituents in a concerted as well as step-wise process, and the disubstituted diphenylacetylenes with different substituents on each of the phenyl rings lose both the substituents, irrespective of their positions, in a step-wise process to give rise to the common ion at m/z 176 with varying abundances (Table 2). Loss of a single substituent from the $M^{+\bullet}$ ion is insignificant in all the compounds studied. It can be noticed from the abundances (Table 2) of the common fragment at m/z 176 in the compounds studied that the electron-withdrawing substituents such as chloro and nitro groups favour the formation of this ion. In contrast the formation of this ion at m/z 176 is less favoured when electron-releasing substituents such as methyl and methoxyl are present. This view is supported by the fact that the ratios of the intensities of the ions at m/z 176 with respect to the intensities of the corresponding molecular ions are found to be larger (Table 3) for those compounds having chloro and nitro substituents than those for compounds having methyl and methoxyl substituents. Furthermore, it can be seen from Table 3 that compounds containing similar substituents, but at different positions, present

**Table 1. *B/E* Linked-scan spectral data**

| Compound no. | Parent ion | m/z values of daughter ions with relative abundances in parentheses |
|---|---|---|
| 1 | $M^{+\bullet}$, m/z 178 | 177 (32), 152 (10) |
| | m/z 177 | 176 (40), 152 (5) |
| 2 | $M^{+\bullet}$, m/z 212 | 211 (5), 177 (25), 176 (15) |
| | m/z 211 | 176 (75), 152 (5) |
| | m/z 177 | 176 (40), 151 (5) |
| 9 | $M^{+\bullet}$, m/z 257 | 227 (25), 211 (15) |
| | m/z 211 | 176 (28) |
| 15 | $M^{+\bullet}$, m/z 246 | 245 (5), 211 (22), 176 (15) |
| | m/z 211 | 176 (80), 175 (10) |
| 17 | $M^{+\bullet}$, m/z 257 | 256 (2), 227 (12), 211 (10) |
| | m/z 211 | 176 (34) |

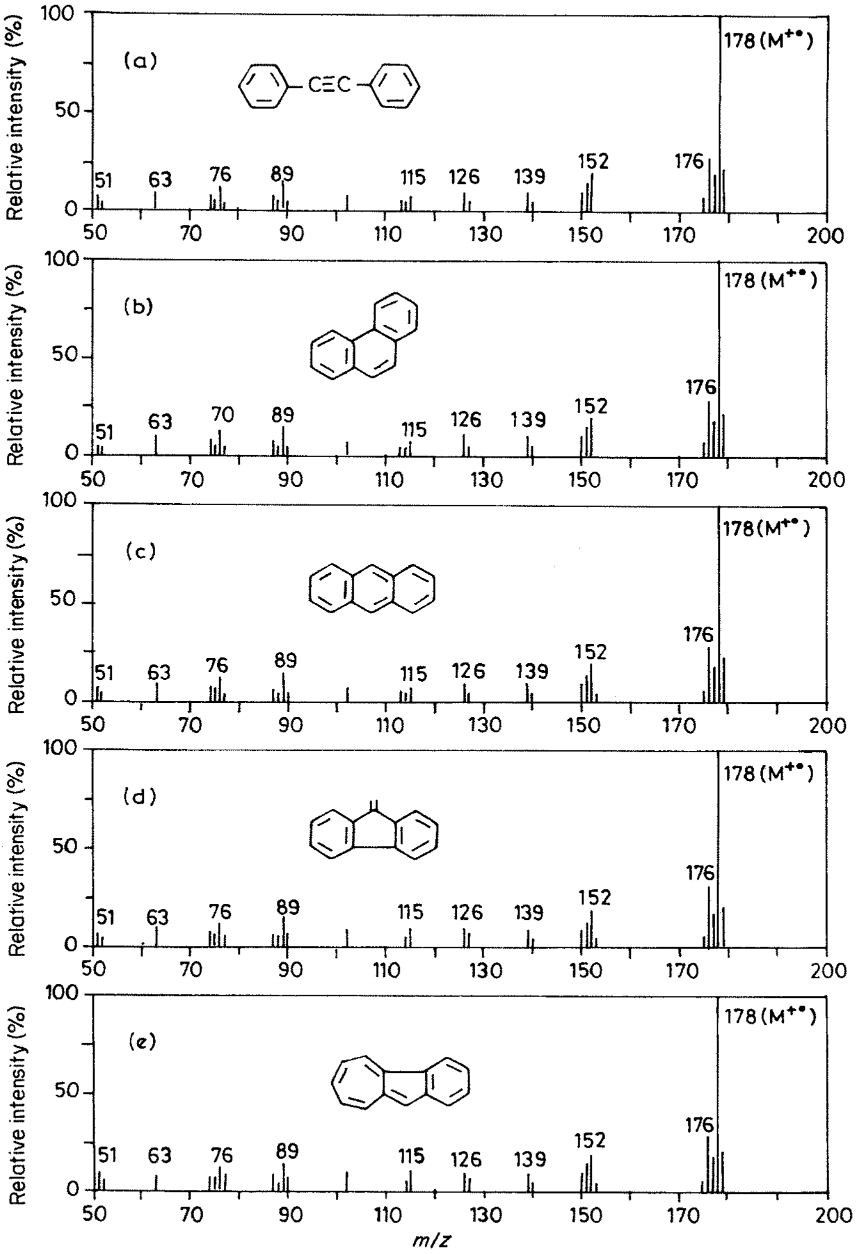


**Figure 2.** Electron impact mass spectra of (a) diphenylacetylene, (b) phenanthrene, (c) anthracene, (d) 9-methylenefluorene, and (e) benz(*a*)azulene.

**Table 2. Partial mass spectra of compounds 1 to 17**

| Compound no. | R¹ | R² | $M^{+\cdot}$ | $[M-R^1R^2]^{+\cdot}$ (*m/z* 176) | $[M-C_2H_2]^{+\cdot}$ | *m/z* 152 |
|---|---|---|---|---|---|---|
| **1** | H | H | 178 (100[a]) | 17[a] | 152 (11[a]) | 11[a] |
| **2** | H | *o*-Cl | 212 (100) | 56 | 186 (4) | 3 |
| **3** | H | *p*-Cl | 212 (100) | 25 | 186 (3) | 2 |
| **4** | H | *p*-NO$_2$ | 223 (100) | 69 | – | – |
| **5** | H | *p*-OCH$_3$ | 208 (100) | 3 | – | – |
| **6** | H | *m*-Cl | 212 (100) | 70 | 186 (4) | 6 |
| **7** | *o*-Cl | *o*-Cl | 246 (100) | 45 | – | 2 |
| **8** | *o*-Cl | *p*-Cl | 246 (100) | 45 | – | – |
| **9** | *o*-Cl | *p*-NO$_2$ | 257 (100) | 85 | – | – |
| **10** | *m*-Cl | *o*-Cl | 246 (100) | 40 | – | – |
| **11** | *p*-CH$_3$ | *p*-CH$_3$ | 206 (100) | 3 | – | 4 |
| **12** | *p*-CH$_3$ | *p*-NO$_2$ | 237 (100) | 12 | – | 6 |
| **13** | *p*-OCH$_3$ | *p*-OCH$_3$ | 238 (100) | – | – | 18 |
| **14** | *p*-OCH$_3$ | *p*-NO$_2$ | 253 (100) | 6 | – | 6 |
| **15** | *p*-Cl | *p*-Cl | 246 (100) | 43 | – | – |
| **16** | *p*-Cl | *p*-OCH$_3$ | 242 (100) | 4 | – | – |
| **17** | *p*-Cl | *p*-NO$_2$ | 257 (100) | 82 | 231 (3) | – |

[a] Relative abundance.

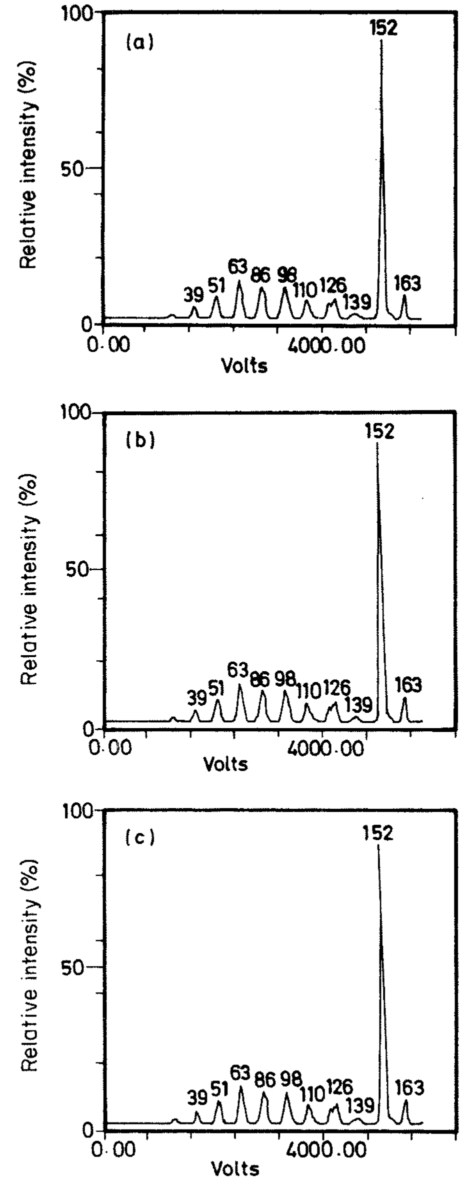


*Figure 3.* CID-MIKE spectra of ions at (a) $M^{+\cdot}$, $m/z$ 178 of phenanthrene, (b) $M^{+\cdot}$, $m/z$ 178 of anthracene, and (c) $M^{+\cdot}$, $m/z$ 178 of diphenylacetylene.

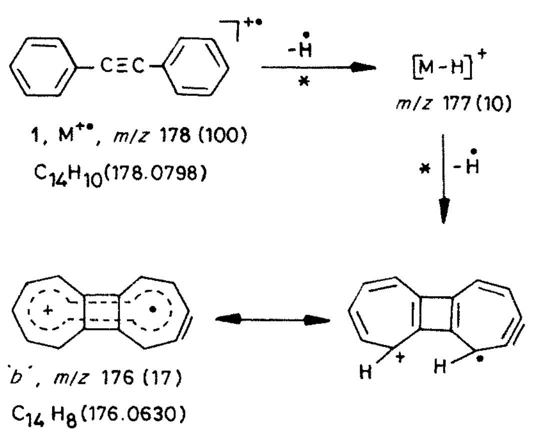
similar ratios implying that the positions of the substituents in the parent compounds are not important for the formation of the ion at $m/z$ 176. It can be inferred from this observation that extensive randomization of the substituents is occurring in the molecular ions before fragmentation.

The CID-MIKE spectra of the ions at $m/z$ 176 from diphenylacetylene (**1**), 2-chlorodiphenylacetylene (**2**), 4,4′-dichlorodiphenylacetylene (**15**) and 4-chloro-4′-nitrodiphenylacetylene (**17**) are compared (Fig. 4) and are found to be exactly identical. It is clear from this observation that the hydrogen and the substituent scrambling in diphenylacetylenes lead to the formation of the ion at $m/z$ 176, having a common ion-structure.

Based on these facts it is proposed in this work that loss of two hydrogens in unsubstituted diphenylacetylene, loss of a substituent and a hydrogen in monosubstituted derivatives, and loss of both the substituents in disubstituted compounds give rise to a common ion *b* at $m/z$ 176 for which a dehydrobitrophenylene radical-cation structure is envisaged (see Scheme 3). The ion structure assigned to *b* is a reasonable postulate based upon the observations made in this work, although no definite evidence is produced. From the fact that the substituents are lost irrespective of their positions in diphenylacetylenes, it is reasonable to expect that the substituents undergo extensive scrambling and that the molecular ions take part in a ring-expansion process; through which substituents eventually lose their positional integrity.

**Table 3. Ratio of the intensity of the ion at *m/z* 176 with respect to the intensity of the molecular ion for compounds 1 to 17**

| Compound no. | $R^1$ | $R^2$ | $m/z$ 176/$M^{+\cdot}$ |
|---|---|---|---|
| **1** | H | H | 0.17 |
| **2** | H | *o*-Cl | 0.56 |
| **3** | H | *p*-Cl | 0.25 |
| **6** | H | *m*-Cl | 0.76 |
| **7** | *o*-Cl | *o*-Cl | 0.45 |
| **8** | *o*-Cl | *p*-Cl | 0.45 |
| **10** | *m*-Cl | *o*-Cl | 0.40 |
| **15** | *p*-Cl | *p*-Cl | 0.43 |
| **9** | *o*-Cl | *p*-$NO_2$ | 0.85 |
| **17** | *p*-Cl | *p*-$NO_2$ | 0.82 |
| **4** | H | *p*-$NO_2$ | 0.69 |
| **12** | *p*-$CH_3$ | *p*-$NO_2$ | 0.12 |
| **14** | *p*-$OCH_3$ | *p*-$NO_2$ | 0.06 |
| **11** | *p*-$CH_3$ | *p*-$CH_3$ | 0.03 |
| **13** | *p*-$OCH_3$ | *p*-$OCH_3$ | – |
| **5** | H | *p*-$OCH_3$ | 0.03 |
| **16** | *p*-Cl | *p*-$OCH_3$ | 0.04 |



**Scheme 3**

It is known that hydrogen scrambling does not occur between the two phenyl rings in 1,2-diphenylethane[13] under electron impact conditions whilst such a process is observable in stilbene.[14,15] But in the case of diphenylacetylene,[7] extensive scrambling of hydrogen atoms between the two rings does occur. It can be concluded that hydrogen scrambling is aided by the presence of extensive conjugation within the system. The

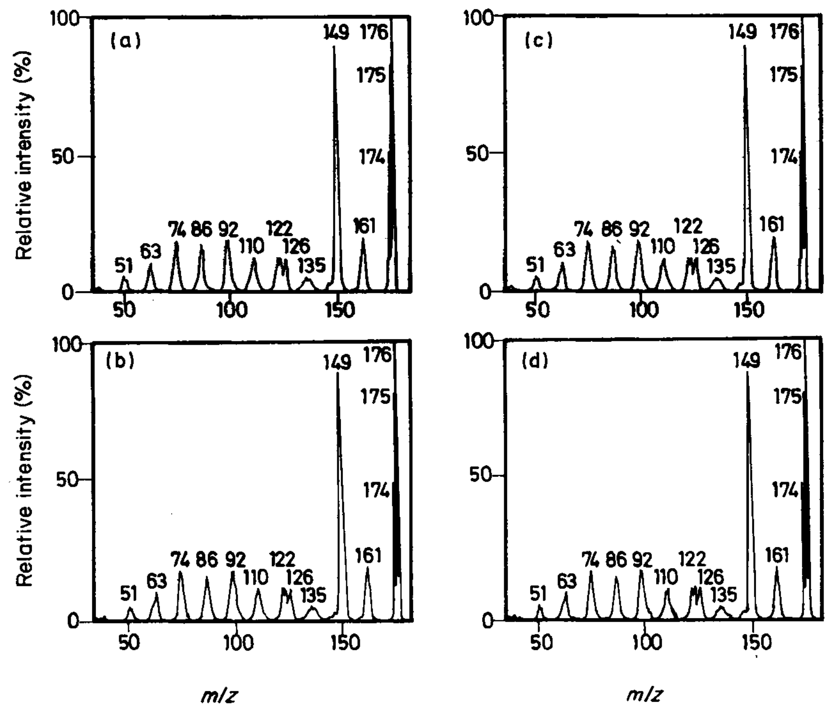


Figure 4. CID-MIKE spectra of ions at *m/z* 176 from (a) diphenylacetylene, (b) 2-chlorodiphenylacetylene, (c) 4,4′-dichlorodiphenylacetylene, and (d) 4-chloro-4′-nitrodiphenylacetylene.

present study reveals that different substituents present on the phenyl rings in disubstituted diphenylacetylenes experience extensive randomization, the electron-withdrawing substituents favour extensive scrambling whilst the electron-releasing substituents show this tendency to a lesser degree.

## EXPERIMENTAL

Compounds **1** to **17** were prepared from the appropriately substituted copper(I) phenylacetylide and the corresponding iodobenzene by refluxing for 10–12 h in dry pyridine solvent under a nitrogen atmosphere according to the general procedure reported in the literature.[16,17] All the compounds studied were recrystallized to constant melting point and their purity was checked by thin-layer chromatography. The structures were confirmed by nuclear magnetic resonance and infrared spectral data. Table 4 gives the yield, melting point (uncorrected) and micro-analytical data for the hitherto unreported compounds discussed in this work.

**Table 4. Characterization data for unknown compounds**

| Compound no. | Yield (%) | m.p.[a] (°C) | Microanalytical data Calculated (%) C | H | Observed (%) C | H |
|---|---|---|---|---|---|---|
| **7** | 80 | 84–85 | 68.29 | 3.25 | 68.12 | 2.89 |
| **9** | 71 | 114–115 | 65.36 | 3.11 | 64.97 | 3.33 |
| **10** | 80 | 150–151 | 68.29 | 3.25 | 68.26 | 3.28 |
| **17** | 88 | 160–161 | 65.36 | 3.11 | 64.86 | 2.98 |

[a] The solvent used for crystallization was benzene–hexane.

The mass spectra were taken on Varian MAT CH-7 and Finnigan MAT 8230 mass spectrometers. The spectra were run at 70 eV with an emission current of 100 μA. All the compounds were introduced into the mass spectrometer through the direct probe insertion at probe temperatures varying between 30 and 110 °C.

Accurate mass measurements were carried out at a resolution of 7000 (10% valley) with a Finnigan MAT 8230 double focusing mass spectrometer using the peak-matching technique and PFK as reference. The CID-MIKE spectra were measured using a VG ZAB 2F double-focusing mass spectrometer with the following conditions: electron energy = 70 eV; electron trap current = 200 μA; accelerating voltage = 6 kV and ion source temperature = 200–230 °C. The ions of interest were focused magnetically into the 2nd field-free region (2nd FFR) and the MIKE spectra were obtained by scanning the ESA voltage. The collision-induced dissociation spectra were obtained by introducing helium gas into the collision cell of the 2nd FFR at such a rate that the intensity of the main beam was reduced to 50% of its original value. The linked-scan measurements (*B*/*E* scan in the 1st FFR) were made on a Finnigan MAT 8230 mass spectrometer with a PDP 11 data system at an ionization energy of 70 eV and an accelerating voltage of 3 kV.

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