

Highly Efficient Ionization of Liquid Crystals by Laser Diode Thermal Desorption-Atmospheric Pressure Chemical Ionization (LDTD-APCI)

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Overview

Purpose: To observe protonated ions $[M+H]^+$ of liquid crystal having Schiff bases and cyano groups.

Methods: Laser diode thermal desorption – atmospheric pressure chemical ionization (LDTD™-APCI) method coupled to a triple stage quadrupole mass spectrometer.

Results: Using an LDTD-APCI method, protonated ions of these liquid crystals, which could not be ionized by API methods, ESI, APCI and APPI, could be observed and structural information could be obtained by tandem mass spectrometry (MS/MS) analysis using a Thermo Scientific TSQ Quantum Ultra triple stage quadrupole mass spectrometer.

Introduction

In recent years, liquid crystal display materials have been the focus of research and development by the leading manufacturers of these technologies in the Asia region. In order to improve quality, they often analyze their competitor's materials as well as impurities included in their materials. APPI has been reported to be useful to ionize lower polarity liquid crystals, where the observed molecular ions were M^+ and/or $[M+H]^+$.^{[1], [2]} However, some classes of liquid crystals having Schiff bases and cyano groups were still difficult to ionize even using APPI, ESI and APCI. We examined the potential of a new LDTD-APCI method, to allow the gaseous neutral samples to react with H_3O^+ directly to produce molecular ions, $[M+H]^+$.

Methods

LDTD-APCI MS/MS analyses was performed using a TSQ Quantum Ultra™ triple stage quadrupole mass spectrometer equipped with an LDTD-APCI source (Phytronix Technologies Inc.). Six liquid crystals having Schiff bases and/or cyano groups, purchased from Tokyo Kasei Co., were dissolved in n-hexane or tetrahydrofuran:

compound (1) 4-(trans-4Amylcyclohexyl)benzoxonitrile; $C_{18}H_{25}N$ (MW. 255.4),

compound (2) 4-Cyano-4'-n-pentylbiphenyl; $C_{18}H_{19}NO$ (MW. 265.4),

compound (3) 4-Cyano-4'-pentylbiphenyl; $C_{18}H_{19}N$ (MW. 249.4),

compound (4) 4'-(Amyloxy)benzylidene-4-cyanoaniline; $C_{19}H_{20}N_2O_2$ (MW. 292.4),

compound (5) 4'-n-Butoxybenzylidene-4-pentylaniline; $C_{22}H_{29}NO$ (MW. 323.5)

compound (6) Terephthalbis(p-phenetidine); $C_{24}H_{24}N_2O_2$ (MW. 372.5).

The chemical structures of each of these compounds is shown in Figure 1. Two μ L of sample solution were spotted into a well of the LazWell™ (Phytronix Technologies Inc.) used for LDTD-APCI measurement. (Figure 2) Figure 3 shows a schematic diagram of the LDTD ion source. LC- (APPI, ESI and APCI) MS measurements were performed using Thermo Scientific Exactive benchtop FTMS, using methanol and water as mobile phases.

FIGURE 1. Chemical Structures of compound (1)-(6)

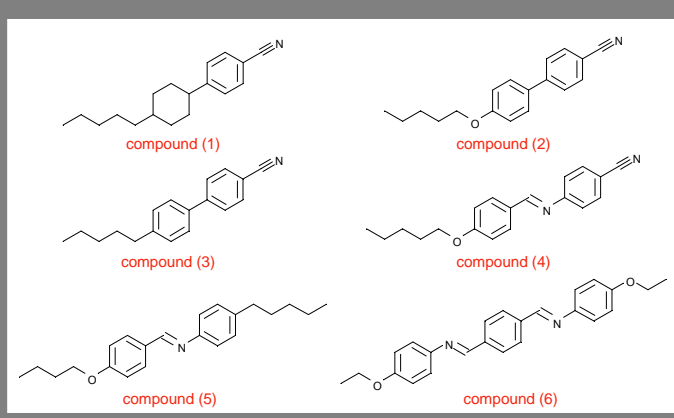
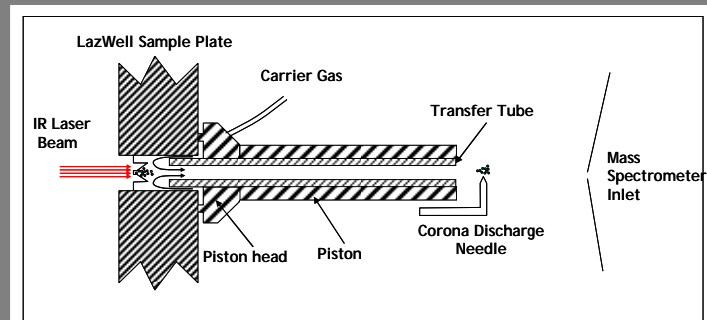


FIGURE 2. Photograph of LDTD-APCI MS system (Left) and LazWell plate (Right)



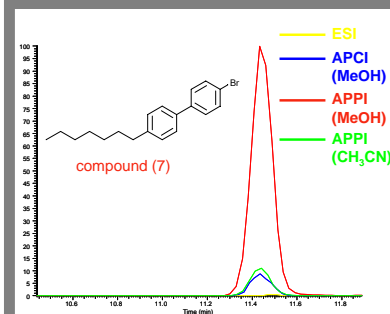
FIGURE 3. Schematic diagram of LDTD ion source



Results

We compared the mass spectra obtained from ionization by LDTD-APCI, LC-ESI, LC-APCI and LC-APPI. Previously, we reported that an LC-APPI using methanol and water as mobile phase was useful for the ionization of lower polarity liquid crystals, such as 4-Bromo-heptylbiphenyl (compound 7; $C_{19}H_{23}Br$) to produce the radical cation, M^+ . The ionization efficiency of lower polarity compounds, such as liquid crystals, was influenced by the proton affinity of solvent used as mobile phases during APPI mechanism. Using methanol, the ion intensity of compound 7 was 10 times higher, compared with that using an acetonitrile. Figure 4 shows the extracted ion chromatogram of compound 7 obtained by LC-ESI, APCI, and APPI using methanol, and APPI using an acetonitrile as mobile phases.

FIGURE 4. Extracted Ion Chromatograms of Compound 7 Obtained by LC-ESI (yellow), APCI (blue), APPI (MeOH) (red) using MeOH and APPI (green) using CH_3CN .



However, in case of liquid crystals having cyano groups (R-CN) such as compound (1)-(3), both the protonated ion, $[M+H]^+$, as well as methanol adduct ions, $[M+H+MeOH]^+$, and lots of fragment ions, were observed by LC-ESI, APCI and APPI. As a result, it was difficult to determine the precursor ions, due to complex spectra. Using LDTD-APCI, the protonated ions, $[M+H]^+$ were mainly observed without fragmentations or solvent adducts (Figure 5). In case of liquid crystals having Schiff bases ($R_1-HC=N-R_2$), such as compounds (4)-(6), their protonated ions were also clearly observed using LDTD-APCI, although no molecular ions were observed using LC-ESI, APCI and APPI (Figure 6).

It was thought that these results depended on differences of the ionization mechanism between LC-API and LDTD-APCI. In LC-API methods including ESI, APCI and APPI, ionized solvent molecules would react with analytes, to produce protonated ions as well as adduct ions and fragment ions. While in the LDTD-APCI, solvent molecules never existed during the ionization process, and the gaseous neutral samples react with H_3O^+ directly to produce molecular ions, $[M+H]^+$ (Figure 7).

FIGURE 5. Mass Spectra of compound 3 by using LC-ESI, APCI, APPI and LDTD-APCI MS.

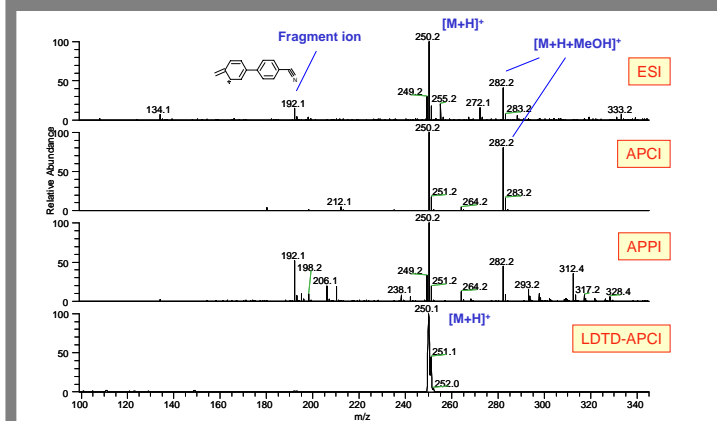


FIGURE 6. Mass Spectra of compound 6 by using LC-ESI, APCI, APPI and LDTD-APCI MS.

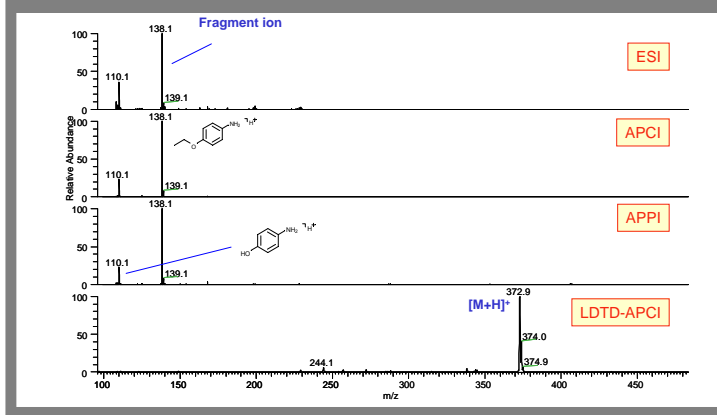
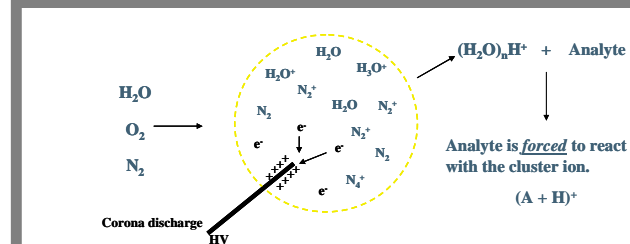
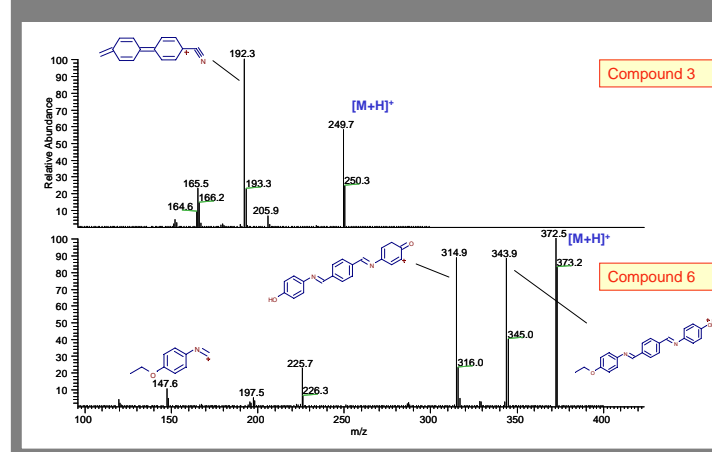


FIGURE 7. Proposed LDTD-APCI mechanism



Producing strong $[M+H]^+$ ions allowed MS/MS spectra to be easily obtained and structures of the product ions could be analyzed by Mass Frontier™ software (HighChem, Ltd.)F. The combination of LDTD-APCI and MS/MS methods allowed detailed structure information of liquid crystals which previously had been unobtainable by LC-MS techniques.

FIGURE 8. LDTD-APCI MS/MS spectra of compound 3 and 6



Conclusions

The LDTD-APCI method allows the ionization of liquid crystals having Schiff bases, which have never been observed using LC-API methods. This method can cover structural and quantitative analysis of known and unknown liquid crystals, and will provide a very useful technique for analysis in the semiconductor market.

References

- 1) S. Sakamoto *et al.* ASMS poster 2005, WP110
- 2) S. Sakamoto *et al.* ASMS poster 2006, TH 027

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