AccuTOF-GCv Series

The Power of Exact Mass Measurement: An Example of Unknown Compound Identification

Introduction

Recently, JEOL introduced the AccuTOF-GC, an innovative GC/time-of-flight mass spectrometer (TOF MS) that is capable of both high data acquisition rates and easy exact mass measurements. The exact mass measurements can then be used to generate lists of possible elemental compositions, which is a powerful tool for identifying unknown compounds. Additionally, this information can be combined with the fragmentation information to help confirm the identity an unknown compound.

In this work, the AccuTOF-GC system was used to identify an unknown compound in a liquid crystal extract.

Experimental

The system used for this work was the JEOL AccuTOF-GC TOF MS. Liquid crystal from a pocket calculator display was dissolved in hexane. Afterwards, the sample was injected onto a DB-5 GC column (0.18mm x 10m, 0.18µm film thickness). The oven temperature was held at 40°C for 1 min and then increased to 300°C at 50°C/min rate. The TOF MS was tuned to achieve a resolution of 5,000 (FWHM) at *m/z* 293 (Perfluorokerosene). 2,4,6-tris(trifluoromethyl) -1,3,5-triazine was used as an internal standard for the exact mass measurements in both EI and CI modes. The CI reagent gas was isobutane. The NIST mass spectral database (2002) was used for the EI spectrum searches.

Results

Figure 1 shows the total ion chromatograms (TIC) for the liquid crystal extract in both EI and CI modes. All of the peaks in the TIC were identified by the NIST library search using their EI spectra except the last peak (marked with an asterisk). Both the EI and CI spectra for this compound are shown in Figure 2. The base peak at *m/z* 334 ($[M+H]^+$)was observed in the CI spectra which correlated with the small peak at *m/z* 333 ($[M]^{+\bullet}$) in the EI spectra, thus indicating that the molecular weight for this compound is 333. The NIST library search for the EI spectrum yielded a very low matching score and none of the matches had a molecular weight of 333. It is likely that this compound

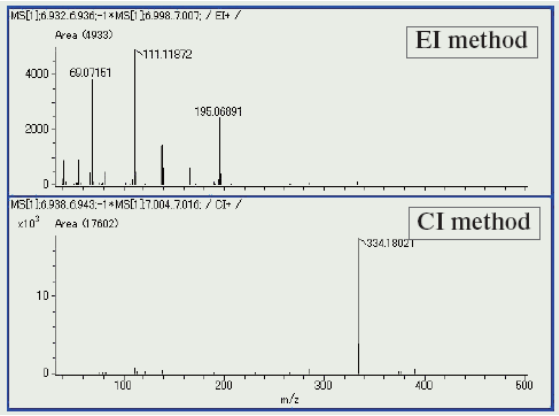

Fig. 1 TIC of liquid crystal extract in both EI and CI modes

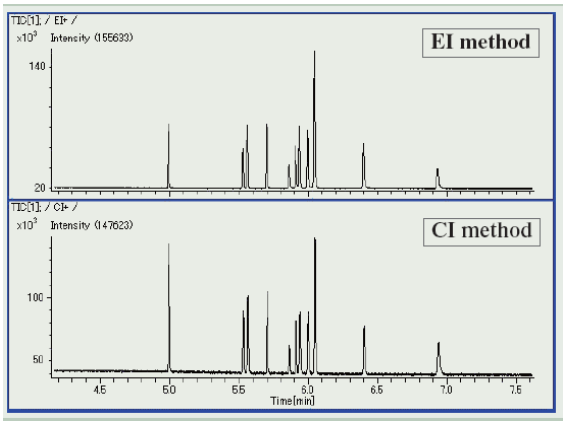

Fig. 2 Mass spectra for the unknown compound marked with an asterisk (*) in Fig. 1

is not in the current version of the NIST library database. To identify this unknown compound, we used the exact mass measurement to generate a list of the possible elemental compositions for each ion. Based on the typical liquid crystal compound structures listed in the book "Liquid Crystal Compound Glossary" (1), only C, H, O, N, and F were included in the elemental composition calculation. The AccuTOF-GC can measure masses with errors smaller than 2 mmu. All possible compositions for each ion within a 2 mmu tolerance are listed in Table 1.

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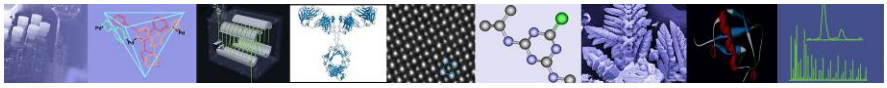

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Candidate	Measured m/z	Theoretical m/z	Error (mmu)	Estimated formula	Unsaturation number
No.1	334.18021	334.18070	−0.49	$C_{22}H_{24}NO_2$	11.5
No.2		334.18185	−1.64	$C_{19}H_{25}FNO_3$	7.5

Ion	Measured m/z	Theoretical m/z	Error (mmu)	Estimated formula	Unsaturation number
m/z 333	333.17432	333.17288	1.44	$C_{22}H_{23}NO_2$	12
m/z 195	195.06891	195.06841	0.5	$C_{13}H_9NO$	10
m/z 111	111.11872	111.11738	1.34	C_8H_{15}	1.5
m/z 69	69.07042	69.07042	1.09	C_6H_9	1.5

Table 1. Results of exact mass measurement and elemental composition determination

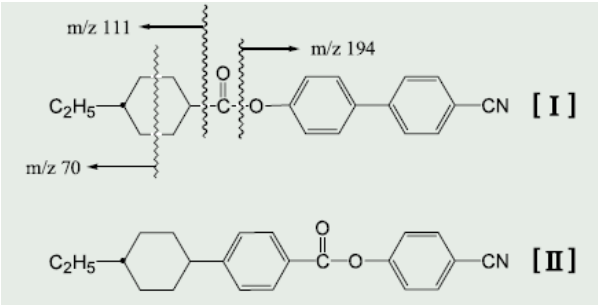

Fig. 3 Possible structures for unknown liquid crystal compound

Let us first consider the No.2 composition $C_{19}H_{25}FNO_3$ as the $[M+H]^+$ ion. Compounds having three oxygen atoms are limited to azoxy compounds and p-cyano-phenyl-ester compounds with *p*-alkyl substitution of a benzoic acid. However, none of these compounds containing a fluorine atom have been previously reported as a possible liquid crystal composition (1). As a result, the elemental composition was assigned as the first composition, $C_{22}H_{24}NO_2$. It is known that there are no liquid crystal compound that contain $–NH_2$ or $–NO_2$ groups (1). Therefore, one nitrogen atom in this composition has to be in the form of –CN. The first composition also has two oxygen atoms, which were assigned as an ester. In addition, the unsaturation number for $[M+H]^+$ is 11.5. There must be at least one or two benzene rings in the structure. Based on all of these estimations and the typical liquid crystal compounds listed in "Liquid Crystal Compound Glossary" (1), two structures for this compound were possible, as shown in Figure 3.

To determine which structure is most probable, the 3 major fragment ions, *m/z* 69, 111, and 195 were considered in the EI spectra. The ion at *m/z* 111 is likely formed by a simple cleavage of an alkyl group and the *m/z* 69 is formed by a cleavage in the cyclohexane ring with a hydrogen transfer. These two fragment ions can be formed from both structures I and II. However, *m/z* 195 can only be formed by a simple cleavage of the alkoxy group with hydrogen transfer in structure I. Thus, the most likely structure for this unknown compound is structure I.

Conclusion

Using a list of possible liquid crystal candidates, the exact mass measurements for the molecular ions and fragment ions were used to determine the structure of an unknown compound that was not identified by the NIST library search.

Reference

(1) Liquid Crystal Compound Glossary, ed. Japan Society for the Promotion of Science, Baifukan Co., Ltd, Tokyo