Mass spectra of liquid crystals. IV. Diphenylethyne derivatives (nematic tolans)

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Mass Spectra of Liquid Crystals

IV†—Diphenylethyne Derivatives (Nematic Tolans)

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INTRODUCTION

Twisted nematic liquid crystal displays (TN-LCDs) contain carefully balanced mixtures of liquid crystals. Combinations of different dielectric, optical, elastic, viscous and thermal material properties are required to achieve a good overall performance of an LCD for specific applications. Diphenylethyne and cyclohexylphenylethylnylbenzene derivatives are nematic compounds of low viscosity and high optical anisotropy (birefringence). Because of these properties, these compounds are frequently used as components of modern mixtures for quick-response TN-LCDs. To our knowledge, mass spectra of these classes of compounds have not been reported.

EXPERIMENTAL

Gas chromatographic/mass spectrometric analyses were carried out under conditions reported in Part I.

RESULTS AND DISCUSSION

The electron impact (EI) mass spectra of twelve diphenylethyne derivatives 1–12 (class I) are presented in Table 1, and the spectrum of 4-ethoxy-2-methyl-4'-pentyltolan (12) is depicted in Fig. 1.

Prior to discussing these spectra, it should be stressed that the structural formulae of fragment ions presented in this series are not substantiated by high-resolution data. However, the elemental fragment ion compositions are in agreement with the observed shifts of the m/z values of the ions from compounds with various substituents.

All spectra contain abundant molecular ions. In the spectra of the hydrocarbons 1–3, the base peaks at m/z (190 + R'), corresponding to [R'C,H,CECC,H,CH2]+, account for 30% of the total ion currents. The remaining peaks of importance in these spectra are found at m/z (190 + R'), 204, 202 and 189, corresponding to [H2CC6H4C=CCH3R2]+, [H2CC6H4C=C C6H4CH3]+, m/z (204 – H2) and m/z (204 – 'CH3), respectively. The peaks at m/z 217 and m/z 102 correspond to [H2CC6H4C=CCH3CH=CH2]+ and [C6H5 C=C(CH3)]+, respectively. The other peaks have intensities of less than 6%.

The spectra of the alkoxy derivatives 4–12 show base peaks at m/z (206 + R3) from [H2CC6H4C=CCH3R30H]+ whenever the alkoxy group is larger than methoxy. The methoxy derivatives 4 and 5 give base peaks at m/z 221, corresponding to [H2CC6H4C=CCH3OMe] +. Apart from peaks at m/z (192 + R3 + R'), corresponding to [R'1C6H4C=CC6H3R30OH]++, compounds 6–12 also yield peaks at m/z (191 + R3 + R'). The latter peaks are even 50% higher than the former in the spectra of the ethoxy compounds 6–8, 11 and 12, but amount to only a few percent in the spectra of 9 and 10 in the spectrum of compound 6 this peak coincides with that of [H2CC6H4C=CCH3OEt]+ at m/z 235. The ion at m/z (205 + R3) is only found in the spectra of the methoxy derivatives 4 and 5 and of the pentyl compounds 8 and 12. Its genesis is not easily rationalized.

Odd-electron CC,H,C=CC,H, ions appear at m/z 178 in all spectra. In addition to the ions listed in Table 1, a small but characteristic peak is found in the spectra of compounds 11 and 12 at m/z 131 (4%), corresponding to [C=CCH3(CH3)OH]++ These compounds, with R2 = Me, give more intense peaks at m/z

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Table 1. Relative abundances (%) of characteristic ions in the EI mass spectra of diphenylethyne derivatives (class I)*

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<th>m/z 189</th>
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<th>m/z 202</th>
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*a Me = methyl; Et = ethyl; Pr = n-propyl; Bu = n-butyl; Pe = n-pentyl; Hp = n-heptyl.

*b m/z of base peak.

*c A = 14 (CH₂ COMPOUNDS) or 17 (OH & 12).

*d At 1 u lower in mass.

*e Coincident with m/z (189 + R² + R³).

115, 165, 189–191 and 202 than the alkoxy compounds with R³ = H. Generally, the alkoxy derivatives yield more abundant fragment ions than the alkyl derivatives.

The EI mass spectra of seven cyclohexylphenylethynylbenzene derivatives 13–19 (class II) are condensed in Table 2. Although these spectra show more abundant fragment ions than those of the diphenylethylene derivatives, the molecular ion is the base peak in all instances. As with all cyclohexylphenylethynyl derivatives, the major fragment ions are formed by fragmentation of the cyclohexyl ring. The resulting peaks are found at m/z (202 + R³ + R²) and at ±13 u, corresponding to the odd-electron vinyl-type ions [H₂C=CHC₆H₄C≡CC₆H₃R³R₂]⁺, the (iso)propenyl ions [H₂C=C(CH₂)C₆H₄CECC₆H₃R³R₂]⁺, and the tropenylium- or benzyl-type ions [H₂CC₆H₄C≡CC₆H₃R³R₂]⁺.

For compounds with R² > Me, the odd-electron ion [H₂CC₆H₄C≡CC₆H₃R₂]⁺ at m/z 204 is also formed. These compounds (14–17) also give peaks at m/z (272 + R²), corresponding with the ions [R¹C₆H₄C≡CC₆H₃R₂]⁺. Diphenylethylene-contain-

Figure 1. 70 eV EI mass spectrum of 4-ethoxy-2-methyl-1-[(4-pentylphenyl)ethynyl]benzene (12).
Table 2. Relative abundances (%) of characteristic ions in the EI mass spectra of cyclobexylphenylethynylbenzene derivatives (class II)*

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* Me = methyl; Et = ethyl; Pr = n-propyl; Bu = n-butyl.

Additional ions of m/z (216 + R3), (215 + R3), 215, 202, 191 and (188 + R3) appear abundantly in all spectra. With the exception of peaks at m/z (114 + R3) and those of low-mass alk(en)yl ions, the remaining peaks in these spectra are less intense.

In addition to the R3-containing ions already mentioned, derivatives 18 and 19 yield peaks characteristic of R3 = Me in their spectra at m/z (138 + R3) and particularly at m/z (114 + R3).

REFERENCES
