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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The 70 eV electron impact mass spectra of 19 diphenylethyne derivatives are presented and discussed in terms of observed substituent effects.

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 cyclohexylphenylethynylbenzene derivatives are nematic compounds of low viscosity and high optical anisotropy (birefringence).² 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.¹

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.

† For Parts I–III, see Ref. 1.

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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 $(190 + \text{R}^1)$, corresponding to $[\text{R}^1\text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{CH}_2]^+$, account for 30% of the total ion currents. The remaining peaks of importance in these spectra are found at m/z $(190 + \text{R}^2)$, 204, 202 and 189, corresponding to $[\text{H}_2\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^2]^+$, $[\text{H}_2\text{CC}_6\text{H}_4\text{C}\equiv\text{C}_6\text{H}_4\text{CH}_2]^+$, m/z $(204 - \text{H}_2)$ and m/z $(204 - \cdot\text{CH}_3)$, respectively. The peaks at m/z 217 and m/z 102 correspond to $[\text{H}_2\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{CH}=\text{CH}_2]^+$ and $[\text{C}_6\text{H}_5\text{C}\equiv\text{CH}]^+$, respectively. The other peaks have intensities of less than 6%.

The spectra of the alkoxy derivatives 4–12 show base peaks at m/z $(206 + \text{R}^3)$ from $[\text{H}_2\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_3\text{R}^3\text{OH}]^+$ whenever the alkoxy group is larger than methoxy. The methoxy derivatives 4 and 5 give base peaks at m/z 221, corresponding to $[\text{H}_2\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe}]^+$. Apart from peaks at m/z $(192 + \text{R}^3 + \text{R}^1)$, corresponding to $[\text{R}^1\text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_3\text{R}^3\text{OH}]^+$, compounds 6–12 also yield peaks at m/z $(191 + \text{R}^3 + \text{R}^1)$. 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 $[\text{H}_2\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{OEt}]^+$ at m/z 235). The ion at m/z $(205 + \text{R}^3)$ 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 $[\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]^+$ 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 $[\text{C}\equiv\text{CC}_6\text{H}_3(\text{CH}_3)_2\text{OH}]^+$. These compounds, with $\text{R}^3 = \text{Me}$, give more intense peaks at m/z

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

m/z																	
No.	R ¹	R ²	R ³	RMM	M ⁺	175	174	189	189	188	202	191	190	189	178	176	165
						+ R ³ + R ¹ + A ^c	+ R ³ + R ¹ + A ^c		+ R ³ + R ³ + A ^c	+ R ³ + R ³ + A ^c							
1	Et	Pr	H	248	40	100	4 ^d	7	34	6	18	3	2	8	2	2	3
2	Et	Bu	H	262	45	100	5 ^d	5	34	6	16	3	2	7	2	2	3
3	Et	Pe	H	276	39	100	6 ^d	3	36	6	16	3	2	8	2	2	3
4	Bu	OMe	H	264	42	—	—	100	4	16	—	—	—	6	27	9	5
5	Pe	OMe	H	278	36	—	—	100	4	16	2	3	3	6	27	9	5
6	Pr	OEt	H	264	70	20	e	66	100	—	3	—	4	10	41	14	8
7	Bu	OEt	H	278	67	9	13	60	100	—	3	4	5	11	41	14	9
8	Pe	OEt	H	292	62	6	9	67	100	14	3	3	3	11	33	11	8
9	Pr	OPe	H	306	32	49	5	1	100	—	1	2	3	6	17	5	3
10	Pr	OHp	H	334	32	61	7	1	100	—	2	2	3	6	15	5	3
11	Bu	OEt	Me	292	99	14	20	69	100	—	21	39	14	26	28	8	24
12	Pe	OEt	Me	306	99	11	13	86	100	15	17	38	11	20	22	7	18

No.	R ¹	R ²	R ³	RMM	M ⁺	163	152	151	139	115	102	89	77	63	51	43	41	Base peak ^b
1	Et	Pr	H	248	40	3	3	2	4	4	10	5	2	3	2	—	2	219
2	Et	Bu	H	262	45	2	2	2	3	3	6	3	2	1	1	3	6	219
3	Et	Pe	H	276	39	2	2	2	3	3	6	3	2	1	1	3	9	219
4	Bu	OMe	H	264	42	5	11	7	7	3	1	4	3	4	2	9	13	221
5	Pe	OMe	H	278	36	5	10	7	6	3	1	4	3	3	2	3	19	221
6	Pr	OEt	H	264	70	7	19	12	10	5	—	5	4	5	4	2	3	207
7	Bu	OEt	H	278	67	8	18	11	10	6	2	5	3	4	3	11	16	207
8	Pe	OEt	H	292	62	5	14	9	7	4	2	3	2	2	2	4	18	207
9	Pr	OPe	H	306	32	3	6	4	3	2	—	1	1	1	—	30	17	207
10	Pr	OHp	H	334	32	2	5	3	3	1	1	1	1	1	1	17	23	207
11	Bu	OEt	Me	292	99	6	17	8	10	14	4	6	7	5	5	24	35	221
12	Pe	OEt	Me	306	99	4	13	7	7	11	3	5	6	3	3	18	39	221

^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 1–3) or 17 (OH, 4–12).^d At 1 u lower in mass.^e Coincident with *m/z* (189 + R³ + R²).

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 cyclohexylphenyl-ethynylbenzene derivatives 13–19 (class II) are condensed in Table 2. Although these spectra show more abundant fragment ions than those of the diphenylethyne derivatives, the molecular ion is the base peak in all instances. As with all cyclohexylphenyl derivatives,¹ 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)C₆H₄C≡CC₆H₃R³R²]⁺ and the tropylium- or benzyl-type ions [H₂CC₆H₄C≡CC₆H₃R³R²]⁺.

For compounds with R² > Me, the odd-electron ion [H₂CC₆H₄C≡CC₆H₄CH₂]⁺ at *m/z* 204 is also formed. These compounds (14–17) also give peaks at *m/z* (272 + R¹), corresponding with the ions [R¹C₆H₄C≡CC₆H₄CH₂]⁺. Diphenylethyne-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 cyclohexylphenylethynylbenzene derivatives (class II)^a

No.	R ¹	R ²	R ³	RMM	M ⁺⁺	m/z													
						271 + R ³ + R ¹	215 + R ³ + R ²	202 + R ³ + R ²	189 + R ³ + R ²	229	216 + R ³	215 + R ³	215	204	202	191	188 R ³	178	
13	Bu	Me	H	330	100	—	27	38	28	6	35	43	41	—	20	10	14	4	
14	Pr	Et	H	330	100	4	32	42	47	8	74	58	56	24	28	13	14	5	
15	Bu	Et	H	344	100	1	28	34	34	5	46	35	33	16	15	8	8	2	
16	Pr	Pr	H	344	100	34	20	18	27	11	84	28	41	31	27	16	14	3	
17	Pr	Bu	H	358	100	40	16	13	18	12	84	20	35	32	27	16	13	2	
18	Pr	Me	Me	330	100	—	21	25	25	10	10	19	30	—	18	6	13	4	
19	Bu	Me	Me	344	100	—	22	29	29	11	11	19	29	—	17	7	14	4	

No.	R ¹	R ²	R ³	RMM	M ⁺⁺	m/z													
						165	152	138 + R ³	128	114 + R ³	102	89	81	67	57	55	43	41	
13	Bu	Me	H	330	100	6	4	4	5	23	6	4	8	6	6	22	19	50	
14	Pr	Et	H	330	100	6	4	4	5	21	6	3	6	6	2	16	14	29	
15	Bu	Et	H	344	100	4	3	2	5	20	6	2	7	6	7	19	15	40	
16	Pr	Pr	H	344	100	5	4	3	5	21	7	3	6	6	2	18	20	31	
17	Pr	Bu	H	358	100	5	3	2	4	14	3	2	6	5	7	13	15	30	
18	Pr	Me	Me	330	100	5	9 ^b	10	14	30	5	2	6	5	—	16	14	32	
19	Bu	Me	Me	344	100	5	10 ^b	11	14	33	5	2	7	6	7	19	14	42	

^a Me = methyl; Et = ethyl; Pr = *n*-propyl; Bu = *n*-butyl.^b At 1 u higher in mass.

ing ions of m/z ($216 + R^3$), ($215 + R^3$), 215, 202, 191 and ($188 + R^3$) appear abundantly in all spectra. With the exception of peaks at m/z ($114 + R^3$) and those of low-mass alk(en)yl ions, the remaining peaks in these spectra are less intense.

In addition to the R^3 -containing ions already mentioned, derivatives **18** and **19** yield peaks characteristic of $R^3 = \text{Me}$ in their spectra at m/z ($138 + R^3$) and particularly at m/z ($114 + R^3$).

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