

Mass spectra of liquid crystals. VI.Alkylbicyclohexyl ethers, dioxanylbenzonitrile derivatives and other classes of compounds

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Mass Spectra of Liquid Crystals

VI.[†] — Alkylbicyclohexyl Ethers, Dioxanylbenzonitrile Derivatives and Other Classes of Compounds

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The 70 eV electron impact mass spectra of 17 liquid crystals from various classes are presented and discussed.

INTRODUCTION

Liquid crystal displays contain tailor-made nematic phases. These phases consist of mixtures of 10-25 components, which are blended for specific application areas. The practical value of the compounds dealt with in this part lies in the combination of low melting point and low viscosity.²

The nematic character of the bicyclohexyl system (compounds of class I) is only insignificantly influenced by the type of substitution. Bicyclohexyl ethers are distinguished by particularly low viscosities and low optical anisotropy. Cyanophenyl-1,3-dioxanes (class II) have relatively high dielectric anisotropy, low optical anisotropy and moderate viscosities. These compounds are used to depress melting points in enantiotropic mixtures. The introduction of double bonds into the cyclohexyl ring (class III components), or into alkyl side-chains, leads to expanded band widths of elastic properties. Class IV compounds, in which aromatic and saturated rings are linked via $-CH_2CH_2$ -- bridges, show lower viscosity values than the corresponding esters with --COO- bridges.

EXPERIMENTAL

Gas chromatographic/mass spectrometric analyses were carried out under conditions reported previously.¹ Positive ion chemical ionization mass spectra were acquired as described earlier.³

RESULTS AND DISCUSSION

The electron impact (EI) mass spectra of various classes of liquid crystals are presented in Tables 1-4 and in

† For Parts I and V, see Refs 1 and 3, respectively.

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0030-493X/91/040276-03 \$05.00 © 1991 by John Wiley & Sons, Ltd. Figs 1 and 2. To our knowledge, none of these spectra have been reported before. At this point it should be noted that fragmentation mechanisms will not be discussed, because these are not supported by accurate mass analyses or tandem mass spectrometric data. The proposed structure assignments to fragment ions seem obvious, however, from the intercomparison of spectra of compounds with varying substitution.



The spectra of seven alkylbicyclohexyl ethers and one ester, 1–8 (class I), are condensed in Table 1. Molecular ions are absent in all instances. The heaviest ions measured originate from the loss of the respective alcohols (compound 6: acid) from the molecular ions. Compounds 1–6 thus yield ions $[R^1C_6H_{10}C_6H_9]^{+*}$ at m/z(163 + R¹) and 7 and 8 give $[R^1C_6H_{10}C_7H_{11}]^{+*}$ at m/z(177 + R¹). These odd-electron ions lose a variety of alkyl radicals, as listed Table 1. Ions at m/z 163, corresponding to $[C_6H_{10}C_6H_9]^{+}$, appear in the spectra of 1–6. Cyclohexenyl ions at m/z 81 are abundant in all spectra (38–44% in the spectra of 7 and 8). The spectra of the ethers 7 and 8 display the base peaks at m/z 95, corresponding to the ions $[C_6H_9=CH_2]^+$.

All peaks listed in Table 1 correspond to hydrocarbon ions, except the characteristic peaks at m/z $(40 + R^2)$ and $(27 + R^2)$ in the spectra of 1-5 and at m/z57 (3-5) and 45 (7 and 8). The peaks at m/z (40 + R²) and 57 arise from the ions $[H_2C=CHCH=R^2]^+$ and $[H_2C=CHCH=OH]^+,$ respectively. The latter hydroxy ions are formed only if \mathbb{R}^2 is larger than methoxy, and are even responsible for the base peak in the spectrum of propyl ether 5. The odd-electron ions at m/z (27 + R²) correspond to the ethenyl ether ions $[H_2C=CHR^2]^{+}$. In the spectra of 7 and 8, abundant $[H_2COMe]^+$ ions are found at m/z 45. The spectra of 1 and 6 are very similar. The largest differences are the presence of a peak from protonated butyric acid at m/z89 (30%), the abundant propyl ion at m/z 43 and the

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							m/z												
No.	R1	R ²	RMM	C°	C –Et	C -Pr	C ~Bu	С Ре	163 +A₫	82 +R¹	81 +RI'	80 +R1	79 +R1	66 +R¹	121	97	96	95 +A₫	93
1	Pr	OMe	238	65	19	e	5	10	31	8	28	39	24	30	15	19	13	27	14
2	Pe	OMe	266	43	17	2	5	e	37	2	14	24	7	19	16	34	23	35	15
3	Pr	OEt	252	63	34	e	5	10	31	6	21	29	21	.9	15	13	10	22	12
4	Pe	OEt	280	41	31	2	5	e	40	2	11	21	6	15	16	24	17	28	13
5	Pr	OPr	266	63	41	e	6	10	37	10	20	34	21	29	17	17	10	28	12
6	Pr	OCOPr	294	100	17	e	9	13	51	16	38	57	36	46	26	13	20	37	15
7	Pr	CH ₂ OMe	252	27	27	e	2	5	7	4	7	16	10	19	7	14	22	f	9
8	Ре	CH₂OMe	280	16	19			e	9		3	8	3	12	7	32	26	12	11
							m/z												
No.	R١	R ²	RMM	83	82	81 +A ^d	80 +A₫	40 +R ²	27 +R ²	79	69	67	57	55	53	45	43	41	Base Peak ^b
1	Pr	OMe	238	50	51	100	20	70	24	30	60	54	16	72	16	18	34	93	81
2	Pe	OMe	266	47	38	100	20	69	18	29	39	56	16	66	12	14	43	73	81
3	Pr	OEt	252	34	33	70	12	100	15	22	41	42	52	58	11	3	28	60	85
4	Pe	OEt	280	35	30	77	14	100	16	27	33	50	59	67	9	4	46	61	85
5	Pr	OPr	266	39	32	76	13	57	8	24	51	51	100	69	11	10	64	82	57
6	Pr	OCOPr	294	69	84	99	29			32	86	66	19	73	11	2	99	74	206
7	Pr	CH₂OMe	252	33	20	100	26			19	50	46	9	52	8	52	12	49	95
8	Pe	CH₂OMe	280	33	16	100	29			22	25	54	9	60	10	73	25	56	95
^a Me ^b <i>m/z</i>	= met of ba	hyl, Et = ethy se peak.	∕I, Pr = /i	-propy	l, Pe =	n-penty	/1.												

Table 1. Relative abundances of characteristic ions in the EI mass spectra of alkylbicyclohexyl ethers (class I)^a

 $^{\circ}C = m/z (163 + R^{1} + A^{d}).$

 $^{d}A = 0$ (compounds 1–6) or 14 (CH₂, 7 and 8).

^e See *m/z* (163 + A).

¹ See m/z (166 + R¹).

absence of a peak at m/z 58 in the spectrum of 6. In the spectrum of this ester, there is a peak at m/z 71 (70%), which corresponds to the ions [COPr]⁺ and not to [H₂C=CHCH=R²]⁺, at m/z (40 + R²), as in the spectrum of ether 1.

The mass spectrum of an unsaturated analogue of 4 is given in Fig. 1. Above m/z 90, all peaks appear at 2 u less than in the spectrum of ether 4. Below m/z 90, both spectra are similar in a qualitative sense. Remarkable are the presence of the molecular ions at m/z 278 (10%) and the abundance of the ions at m/z 149 (72%) compared with that of m/z 151 (21%) in the spectrum of 4. The spectrum of another, all-hydrocarbon derivative of cyclohexylcyclohexene is presented in Fig. 2. The molecular ion is present, and losses of propyl and pentyl radicals from M⁺⁺ are easily discernible (m/z 233 and 205, respectively).

The EI spectra of three 1,3-dioxanylbenzonitriles, 9-11 (class II), are condensed in Table 2. The occurrence of two equally high peaks from the molecu-



Figure 1. 70 eV EI mass spectrum of 1-ethoxy-4-(4-pentylcyclohex-3-en-1-yl)cyclohexane.

lar ions and ions of 1 u less sets apart the spectra of this class of compounds. Another distinct feature in the spectra of these compounds is the presence of peak pairs at m/z 130/132 and 102/104. The former pair corresponds to the ions $[O = CC_6H_4CN]^+$ and $[HO=CHC_6H_4CN]^+$. The latter pair possibly originates by loss of CO from the former. Small peaks at m/z148 probably represent ions $[HO=C(OH)C_6H_4CN]^+$. The base peaks are invariably found at m/z 55. Odd-electron alkene ions of m/z $(R^{1} - 1)$ are abundant. Alkyldioxanyl ions $[R^{1}C_{4}H_{6}O_{2}]^{+}$ give peaks at m/z (86 + R¹). Fragmentation of the dioxanyl ring gives rise to series of ions, of which the most abundant ones yield peaks at m/z $(40 + R^{1})$, $(27 + R^{1})$ and $(24 + R^{1})$. These peaks probably correspond to the ions $[O=C=CR^1]^+$, $[H_2C=CHR^1]^+$ and $[C=CR^1]^+$, respectively.

The mass spectra of two cyclohexenylphenyl derivatives, 12 and 13 (class III), are given in Table 3. The molecular ions are present. The spectra are dominated



Figure 2. 70 eV El mass spectrum of 1-pentyl-4-(4-propylcyclohexyl)cyclohexene.

										<i>m/z</i>	7						
No.	R۱	RMM	M+.	M – 1	86 +R1	40 + R1	39 +R'	27 +R'	26 +R¹	25 +R1	24 + R 1	1 +	2 R1	R ¹ – 1			
9	Pr	231	44	43	17	30	20	51	22	5	29		ь	85			
10	Bu	245	34	31	9	28	8	23	11	7	68	3	36	97			
11	Pe	259	11	10	3	5	5	_		20	35	1	0	34			
No.	R1	RMM	M+.	M – 1	148	132	130	104	102	77	76	75	56	55	43	42	41
9	Pr	231	4 4	43	4	68	82	34	34	9	11	8	46	100	25	c	76
10	Bu	245	34	31	3	52	77	33	28	8	9	7	с	100	37	40	82
11	Pe	259	11	10	2	22	30	15	6	8	9	7	45	100	35	40	82
* Pr =	<i>n</i> -pro	pyi, Bu =	n-buty	d, Pe = <i>n</i> -	pentyl.												
^b See	m/z 55	5 .															

Table 2. Relative abundances of characteristic ions in the EI mass spectra of dioxanylbenzonitriles (class II)^a

Table 3. Relative abundances of characteristic ions in the EI mass spectra of cyclohexenylphenyl derivatives (class III)^a

								m/a	2															
					м	м	156	142	129	116	114	104	103	90										Base
No.	R۱	R²	RMM	M+.	Pr	-Bu	+R1	+R1	+R'	+R'	+R1	+R'	+R1	+R'	95	81	7 9	77	69	67	55	53	41	peak ^b
12	NC	Pe	253	23	5	7	39	100	30	27	13	22	51	58	23	37	24	17	13	53	29	18	73	168
13	F	Xc	300	19	2	_	18	35	25	29	9	23	69	100	11	42	25	8	11	43	40	15	38	109
a n	Development Development And Development																							

^a Pr = *n*-propyl, Bu = *n*-butyl, Pe = *n*-pentyl, C₆H₁₀ = 1,4-cyclohexyl. ^b m/z of base peak.

 $^{c}X = C_{6}H_{10}Pr.$

° See R¹ - 1.

Table 4. Relative abundances of characteristic ions in the EI mass spectra of alkoxyphenylethylcyclohexyl derivatives (class IV)^a

							m/z								
No.	R۱	R ²	RMM	M+.	106 +R1	122	120	107	91	77	67	55	43	41	Base peak ^b
14	Et	Pr	274	13	100	4	2	51	3	6	2	6	3	10	135
15	Et	Pe	302	6	100	4	3	62	4	8	4	10	12	16	135

^a Et = ethyl, Pr = *n*-propyl, Pe = *n*-pentyl.

^b m/z of base peak.

$$\begin{array}{c|c} R^{1} & \hline \\ \hline \\ Class III \\ \hline \\ \hline \\ Class IV \\ \hline \\ \end{array}$$

by peaks at m/z (129 + R¹) and (103 + R¹) and their satellites at ± 13 u. These five characteristic peaks correspond to the ions $[R^1C_6H_4C_5H_6]^+$, $[R^1C_6H_4C(=CH_2)CH=CH_2]^{++}$, $[R^1C_6H_4C$ $(=CH_2)CH_2]^+$, $[R^1C_6H_4CH=CH_2]^{++}$ and $[R^1C_6H_4CH_2]^+$. The first two ions are characteristic of class III compounds, and are not found in the spectra of cyclohexylphenyl derivatives.¹

In addition to the peaks at m/z (M - R² = 156 + R¹), the losses of small alkyl radicals from the molecular ion cause small peaks in these spectra. Not included in Table 3 are peaks at m/z 68 (52%) in the spectrum of 12 and 164 (13%) in that of 13. These peaks probably correspond to the ions $[C_5H_8]^{+\cdot}$ and $[R^1C_6H_4C_5H_9]^{+\cdot}$, respectively.

The mass spectra of two alkoxyphenylethylcyclohexane derivatives, 14 and 15 (class IV), are listed in Table 4. These spectra contain the molecular ions, but are dominated by tall peaks at m/z (106 + R¹) and 107, corresponding to the tropylium- or benzyl-like ions $[R^1OC_6H_4CH_2]^+$ and $[HOC_6H_4CH_2]^+$. These ions represent more than 50% of the total ion currents from these crystals. Other fragment ion peaks are small, as tabulated.

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