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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XLV*. RETENTION BEHAVIOUR OF C_1–C_{12} *n*-ALKYL ESTERS OF BENZOIC, 4-NITROBENZOIC AND 3,5-DINITROBENZOIC ACIDS ON SE-30 AND OV-351 CAPILLARY COLUMNS

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SUMMARY

The gas chromatographic separation of a mixture of C_1–C_{12} *n*-alkyl esters of benzoic, 4-nitrobenzoic and 3,5-dinitrobenzoic acids was studied on low-polarity (SE-30) and polar (OV-351) capillary columns under isothermal and temperature-programmed operating conditions. The relative retention data, the Kováts retention indices and the retention index increments for the methylene units and the nitro substituents were determined and the separation of the mixture is discussed. The results are compared with those reported earlier for aromatic esters.

INTRODUCTION

In contrast to aliphatic esters, there have been few studies on the gas chromatographic (GC) retention behaviour of aromatic esters[1], and most frequently they have concerned the GC of halogenated esters with substitution in either the acid[1–6] or the alcohol[4,7–12] moiety.

Nitrobenzoic acid isomers have been primarily analysed by using thin-layer[13,14], ion-exchange[15,16] or high-performance liquid chromatography[17]. GC on graphitized thermal carbon black has been used for the isomeric mononitrobenzoic acids[18] and packed columns coated with silicone oil[19] and five other stationary phases, *viz.*, Apiezon L, dodecyl dibenzoate and dodecyl 2-, 3- and 4-nitrobenzoate isomers[20] for the methyl esters. Higher esters, *viz.*, C_1–C_6 4-nitrobenzoates[21] and C_1–C_{10} 3,5-dinitrobenzoates[22], have been separated on low-polarity SE-30 and OV-17 packed columns, the purpose of these studies being to identify lower alkanols in the complex mixture as their nitrobenzoyl derivatives rather than a systematic GC study of the corresponding esters.

This paper describes the isothermal and temperature-programmed capillary GC of C_1–C_{12} *n*-alkyl esters of benzoic, 4-nitrobenzoic and 3,5-dinitrobenzoic acids

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* For Part XLIV, see ref. 6.

on low-polarity (SE-30) and highly polar (OV-351) stationary phases. The relative retentions and the Kováts retention indices of all 36 individual components in the three homologous series were determined and examined, together with the effects of alkyl chain length and acyl nitro substitution, shown by retention index increments. The results are compared with those reported earlier for aromatic esters[1,20–22].

EXPERIMENTAL

Materials

n-Alkyl benzoates (1–12), 4-nitrobenzoates (m1–m12) and 3,5-dinitrobenzoates (d1–d12) were synthesized from the C_1–C_{12} *n*-alkanols (Fluka, Buchs, Switzerland) and acid chlorides (Merck-Schuchart, Darmstadt, F.R.G.) as described earlier[23]. The mixture analysed contained suitable amounts of the individual components for the sensitivity of the flame ionization detector.

Mixtures of *n*-alkanes were obtained from different commercial sources.

Methods

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injection and flame-ionization detection (FID) temperatures, 280°C; nitrogen carrier gas velocities for methane at 180°C, 28.2 (SE-30) and 61.3 cm s^{-1} (OV-351); splitting ratio, 1:30; and chart speed, 10 mm min^{-1}. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.33 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused silica OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The column temperature was programmed from 100 to 310°C (SE-30) and from 100 to 220°C (OV-351) at 6°C min^{-1} and held on OV-351 at 220°C until elution of peaks had ceased. The isothermal data were determined at the temperatures indicated in Tables II and III.

The chromatographic data were recorded with a Hewlett-Packard Model 3390A reporting integrator using standard programs. The retention times were measured from the time of sample injection and the Kováts retention indices were calculated off-line by using two appropriate *n*-alkanes[24]; the dead volume was determined by the injection of methane. Owing to the incomplete resolution of a complex mixture of all compounds, each of the three groups of esters and *n*-alkanes were chromatographed separately in turn.

RESULTS AND DISCUSSION

Chromatograms of a mixture of C_1–C_{12} *n*-alkyl benzoates (1–12), 4-nitrobenzoates (m1–m12) and 3,5-dinitrobenzoates (d1–d12) are illustrated in Figs. 1 and 2, separated on SE-30 and OV-351 with temperature programming, respectively. The corresponding retention data of the compounds are given in Table I.

Fig. 1 shows a relatively good separation of the individual components in the mixture on the low-polarity SE-30 column. The elution order observed is C_{n-6}-alkyl 3,5-dinitrobenzoate < C_n-alkyl benzoate < C_{n-3}-alkyl 4-nitrobenzoate. Methyl 3,5-dinitrobenzoate (d1) is a diverging compound in this respect, eluting later than heptyl benzoate (7) and overlapping partly with butyl 4-nitrobenzoate (m4). Partially

TABLE I

RETENTION DATA FOR C_1–C_{12} *n*-ALKYL ESTERS OF BENZOIC, 4-NITROBENZOIC AND 3,5-DINITROBENZOIC ACIDS, DETERMINED ON SE-30 AND OV-351 CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING

Conditions as in Figs. 1 and 2.

Peak No.	*Compound*	*Column*						
		SE-30			*OV-351*			
		*ART**	*RRT***	*RRT****	*ART**	*RRT***	*RRT****	*RRT§*
1	Methyl benzoate	3.37	0.41	1.00	3.62	1.98	1.00	1.07
2	Ethyl benzoate	4.20	0.51	1.00	4.13	2.26	1.00	0.98
3	Propyl benzoate	5.64	0.69	1.00	5.26	2.87	1.00	0.93
4	Butyl benzoate	7.35	0.90	1.00	6.70	3.66	1.00	0.91
5	Pentyl benzoate	9.21	1.13	1.00	8.22	4.49	1.00	0.89
6	Hexyl benzoate	11.02	1.35	1.00	9.84	5.38	1.00	0.89
7	Heptyl benzoate	12.91	1.58	1.00	11.51	6.29	1.00	0.89
8	Octyl benzoate	14.83	1.81	1.00	13.18	7.20	1.00	0.89
9	Nonyl benzoate	16.62	2.03	1.00	14.80	8.09	1.00	0.89
10	Decyl benzoate	18.40	2.25	1.00	16.32	8.92	1.00	0.89
11	Undecyl benzoate	20.08	2.45	1.00	17.80	9.73	1.00	0.89
12	Dodecyl benzoate	21.70	2.65	1.00	19.28	10.54	1.00	0.89
m1	Methyl 4-nitrobenzoate	8.61	1.05	2.55	13.02	7.11	3.60	1.51
m2	Ethyl 4-nitrobenzoate	9.99	1.22	2.38	13.46	7.36	3.26	1.35
m3	Propyl 4-nitrobenzoate	11.84	1.45	2.10	14.76	8.07	2.81	1.25
m4	Butyl 4-nitrobenzoate	13.76	1.68	1.87	16.30	8.91	2.43	1.18
m5	Pentyl 4-nitrobenzoate	15.65	1.91	1.70	17.78	9.72	2.16	1.14
m6	Hexyl 4-nitrobenzoate	17.49	2.14	1.59	19.23	10.51	1.95	1.10
m7	Heptyl 4-nitrobenzoate	19.23	2.35	1.49	20.73	11.33	1.80	1.08
m8	Octyl 4-nitrobenzoate	20.91	2.56	1.41	22.54	12.32	1.71	1.08
m9	Nonyl 4-nitrobenzoate	22.53	2.75	1.36	24.78	13.54	1.67	1.10
m10	Decyl 4-nitrobenzoate	24.08	2.94	1.31	27.61	15.09	1.69	1.15
m11	Undecyl 4-nitrobenzoate	25.58	3.13	1.27	31.31	17.11	1.76	1.22
m12	Dodecyl 4-nitrobenzoate	27.01	3.30	1.24	36.14	19.75	1.87	1.34
d'	Methyl 3,5-dinitrobenzoate	13.63	1.67	4.04	20.04	10.95	5.54	1.47
d2	Ethyl 3,5-dinitrobenzoate	14.80	1.81	3.52	20.10	10.98	4.87	1.36
d3	Propyl 3,5-dinitrobenzoate	16.51	2.02	2.93	20.77	11.35	3.95	1.26
d4	Butyl 3,5-dinitrobenzoate	18.27	2.23	2.49	22.40	12.24	3.34	1.23
d5	Pentyl 3,5-dinitrobenzoate	19.91	2.43	2.16	24.36	13.31	2.96	1.22
d6	Hexyl 3,5-dinitrobenzoate	21.54	2.63	1.95	26.87	14.68	2.73	1.25
d7	Heptyl 3,5-dinitrobenzoate	23.11	2.83	1.79	30.21	16.51	2.62	1.31
d8	Octyl 3,5-dinitrobenzoate	24.59	3.01	1.66	34.60	18.91	2.63	1.41
d9	Nonyl 3,5-dinitrobenzoate	26.04	3.18	1.57	40.15	21.94	2.71	1.54
d10	Decyl 3,5-dinitrobenzoate	27.41	3.35	1.49	47.50	25.96	2.91	1.73
d11	Undecyl 3,5-dinitrobenzoate	28.74	3.51	1.43	56.90	31.09	3.20	1.98
d12	Dodecyl 3,5-dinitrobenzoate	30.05	3.67	1.38	69.22	37.83	3.59	2.30
C_{14}	*n*-Tetradecane	8.18	1.00	–	1.83	1.00	–	0.22

* Absolute retention times (min) were measured from the time of sample injection (Figs. 1 and 2).

** Relative retention time for *n*-tetradecane (C_{14}) taken as 1.00.

*** Relative retention time for the corresponding *n*-alkyl benzoate (1–12) taken as 1.00.

§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.

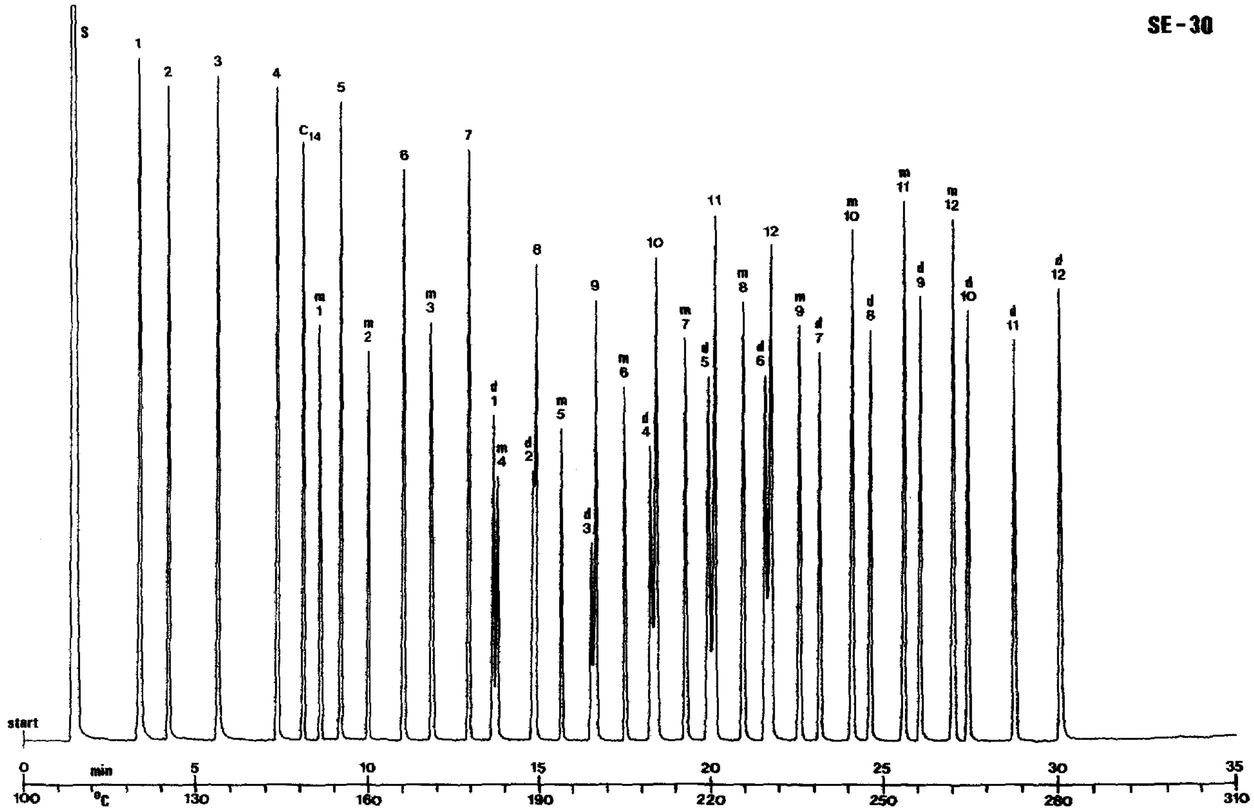

Fig. 1. Chromatogram of a mixture of C_1–C_{12} *n*-alkyl esters of benzoic (1–12), 4-nitrobenzoic (m1–m12) and 3,5-dinitrobenzoic (d1–d12) acids, separated on an SE-30 quartz capillary column with temperature programming from 100 to 310°C at 6°C min^{-1}. S = Solvent; C_{14} = *n*-tetradecane; m = mono-; d = di-; number = alkyl chain length.

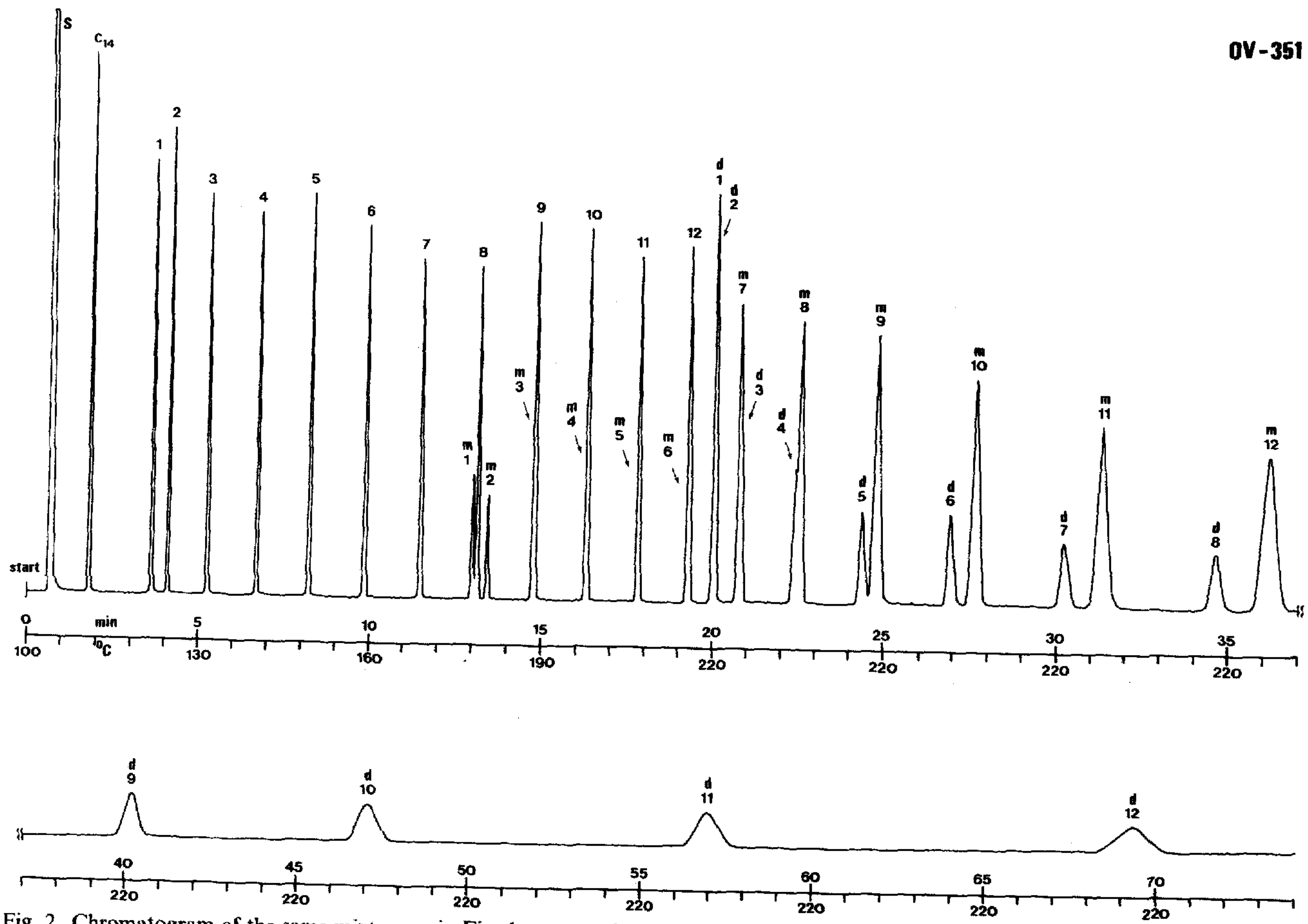

Fig. 2. Chromatogram of the same mixture as in Fig. 1, separated on an OV-351 quartz capillary column with temperature programming from 100 to 220°C at 6°C min^{-1} and held at the final temperature until elution of peaks had ceased. S = Solvent; C_{14} = *n*-tetradecane; m = mono-; d = di-; number = alkyl chain length.

TABLE II

RETENTION INDICES (*I*) FOR C_1–C_{12} *n*-ALKYL ESTERS OF BENZOIC, 4-NITROBENZOIC AND 3,5-DINITROBENZOIC ACIDS, DETERMINED ON SE-30 CAPILLARY COLUMN AT A VARIETY OF TEMPERATURES

n-Alkyl ester	*Chain length*	*Column (SE-30) temperature*						
		Programmed from 100 to 310°C at 6°C min^{-1}		*Isothermal*				
				160°C	*180°C*	*200°C*	*220°C*	*240°C*
		I	*E.T. (°C)**	*I*	*I*	*I*	*I*	*I*
Benzoate	C_1	1071	120.2	1067	1064	1063	–	–
	C_2	1145	125.2	1144	1142	1142	–	–
	C_3	1249	133.8	1249	1248	1248	1262	–
	C_4	1353	144.1	1356	1352	1353	1360	1386
	C_5	1455	155.3	1458	1454	1455	1465	1480
	C_6	1551	166.1	1556	1555	1557	1568	1572
	C_7	1651	177.5	1657	1657	1660	1670	1672
	C_8	1757	189.0	1755	1758	1762	1774	1777
	C_9	1860	199.7	1857	1859	1864	1874	1879
	C_{10}	1965	210.4	1957	1959	1964	1977	1981
	C_{11}	2068	220.5	2058	2059	2065	2076	2080
	C_{12}	2173	230.2	2157	2159	2166	2180	2184
4-Nitrobenzoate	C_1	1423	151.6	1432	1427	1449	1440	1411
	C_2	1497	159.9	1500	1501	1511	1522	1527
	C_3	1594	171.0	1600	1602	1612	1625	1636
	C_4	1697	182.6	1700	1704	1715	1727	1738
	C_5	1803	193.9	1799	1805	1817	1829	1839
	C_6	1911	204.9	1900	1907	1917	1930	1939
	C_7	2016	215.4	1999	2007	2018	2031	2039
	C_8	2121	225.5	2101	2108	2120	2131	2140
	C_9	2227	235.2	2200	2208	2220	2232	2241
	C_{10}	2333	244.5	2299	2308	2321	2333	2342
	C_{11}	2443	253.5	–	2408	2421	2435	2444
	C_{12}	2550	262.1	–	2509	2521	2536	2546
3,5-Dinitrobenzoate	C_1	1690	181.8	1694	1701	1714	1724	1745
	C_2	1755	188.8	1757	1760	1767	1781	1810
	C_3	1853	199.1	1846	1853	1860	1874	1892
	C_4	1957	209.6	1942	1950	1959	1975	1985
	C_5	2058	219.5	2039	2047	2058	2074	2083
	C_6	2162	229.2	2138	2146	2157	2173	2182
	C_7	2266	238.7	2236	2244	2256	2269	2281
	C_8	2370	247.5	–	2343	2355	2368	2380
	C_9	2476	256.2	–	2442	2454	2467	2478
	C_{10}	2581	264.5	–	2541	2552	2564	2578
	C_{11}	2686	272.4	–	–	2651	2663	2677
	C_{12}	2791	280.3	–	–	2750	2764	2777

* E.T. = Elution temperature.

TABLE III

RETENTION INDICES (*I*) FOR C_1–C_{12} *n*-ALKYL ESTERS OF BENZOIC, 4-NITROBENZOIC AND 3,5-DINITROBENZOIC ACIDS, DETERMINED ON OV-351 CAPILLARY COLUMN AT A VARIETY OF TEMPERATURES

n-Alkyl ester	*Chain length*	*Column (OV-351) temperature*					$I_{OV\text{-}351} - I_{SE\text{-}30}$** *(programmed)*
		Programmed from 100 to 220°C at 6°C min⁻¹		*Isothermal*			
				180°C	*200°C*	*220°C*	
		I	*E.T. (°C)**	*I*	*I*	*I*	
Benzoate	C_1	1612	121.7	1661	–	–	541
	C_2	1655	124.8	1706	–	–	510
	C_3	1742	131.6	1791	1812	–	493
	C_4	1841	140.2	1879	1901	–	488
	C_5	1943	149.3	1971	2000	1999	488
	C_6	2046	159.0	2069	2097	2093	495
	C_7	2151	169.1	2169	2198	2199	500
	C_8	2258	179.1	2270	2298	2300	501
	C_9	2366	188.8	2372	2400	2400	512
	C_{10}	2473	197.9	2474	2500	2504	508
	C_{11}	2583	206.8	2578	2601	2606	515
	C_{12}	2694	215.7	2681	2701	2708	521
4-Nitrobenzoate	C_1	2250	178.1	2273	2314	2314	827
	C_2	2280	180.8	2298	2334	2343	783
	C_3	2367	188.6	2376	2414	2426	773
	C_4	2474	197.8	2472	2511	2524	777
	C_5	2582	206.7	2572	2606	2620	779
	C_6	2689	215.4	2671	2704	2719	778
	C_7	2800	220.0	2771	2806	2824	784
	C_8	2911	220.0	2874	2910	2926	790
	C_9	3021	220.0	2979	3014	3029	794
	C_{10}	3130	220.0	3082	3117	3131	797
	C_{11}	3235	220.0	3185	3220	3235	792
	C_{12}	3342	220.0	3288	3326	3341	792
3,5-Dinitrobenzoate	C_1	2749	220.0	2729	2762	2780	1059
	C_2	2753	220.0	2739	2764	2781	998
	C_3	2803	220.0	2784	2809	2826	950
	C_4	2906	220.0	2873	2898	2915	949
	C_5	3007	220.0	2969	2993	3007	949
	C_6	3108	220.0	3067	3089	3103	946
	C_7	3210	220.0	3164	3189	3205	944
	C_8	3313	220.0	3265	3288	3305	943
	C_9	3413	220.0	3367	3390	3406	937
	C_{10}	3515	220.0	3469	3490	3505	934
	C_{11}	3616	220.0	–	3589	3605	930
	C_{12}	3719	220.0	–	3690	3708	928

* E.T. = Elution temperature.

** For the retention indices on SE-30, see Table II.

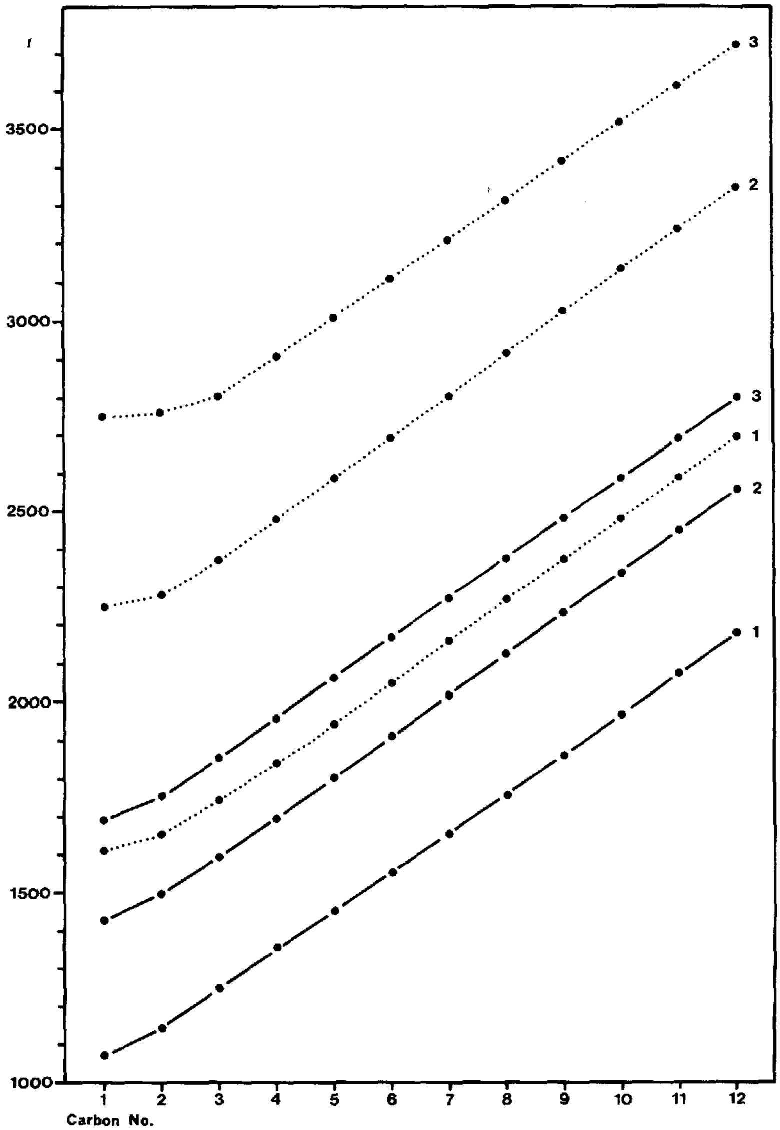

Fig. 3. Plot showing retention of C_1–C_{12} *n*-alkyl esters of benzoic (curve 1), 4-nitrobenzoic (curve 2) and 3,5-dinitrobenzoic (curve 3) acids, obtained on SE-30 (solid lines) and OV-351 (dotted lines) capillary columns with temperature programming (Figs. 1 and 2). *I* = Retention index units.

resolved peaks are also observed for the closely related 3,5-dinitrobenzoates (d2–d6) and benzoates (8–12). As would be expected, the retention order of the compounds is the same as on the packed column[21,22].

The analysis time of the mixture on OV-351 is more than double that on SE-30 in spite of the greatly increased carrier gas velocity used (Fig. 2). This is due to the polar column and the low thermal stability of the stationary phase. The retentions of the nitro isomers are markedly increased, the mixture showing the following elution orders: C_{n-6}-alkyl 4-nitrobenzoate $\leqslant C_n$-alkyl benzoate ($n \geqslant 9$) and C_{n-4}-alkyl 3,5-dinitrobenzoate < C_n-alkyl 4-nitrobenzoate ($n \geqslant 8$). The overlapping that occurred is more pronounced on OV-351 than on SE-30 and the peak shapes are broadened (but symmetrical) particularly with the 3,5-dinitro isomers (Fig. 2).

The retention indices of the compounds are shown in Tables II and III, determined on SE-30 and OV-351 at a variety of temperatures, respectively. Plots of the retention of the three homologous series on both phases are illustrated in Fig. 3. Tables IV and V give the incremental effects for the methylene units and the nitro substitution. A summary and correlation of the increments with the values for the corresponding 4-chloro esters[1] and a comparison between the highly polar and low-polarity columns are shown in Table VI.

The retention behaviour of methyl 4-nitrobenzoate on the SE-30 capillary column is in good agreement with that reported previously on a packed column coated with Apiezon L[20]; values for the higher esters and the 3,5-dinitro isomers, however, are not available.

The increased retention values on OV-351 with respect to SE-30 are shown in Table III, these being markedly higher than observed previously for the corresponding chlorinated esters[1], *viz.*, 773–827 retention index units (i.u.) with *n*-alkyl 4-nitrobenzoates and 928–1059 i.u. with *n*-alkyl 3,5-dinitrobenzoates.

As usual, the retention index increments for the methylene groups on both columns are close to 100 i.u., the temperature-programmed runs showing higher increments than the isothermal runs. The nitro substitution in the acid group seems to have a greater effect on the alkyl chain, as found previously with chlorine substitution[1], *i.e.*, the average increment for the 4-nitro isomers on both columns with isothermal runs is 101 i.u., decreasing to 98 i.u. with the 3,5-dinitro isomers (Tables IV and V). The greatest disparity (6 i.u.) between the nitro derivatives is shown on OV-351 with temperature programming.

The incremental effects of the nitro substitution shown in Tables IV (SE-30), V (OV-351) and VI (summary) are highest with the temperature-programmed runs. On SE-30 the average retention enhancement due to the 4-nitro substitution at 180°C is 351 i.u., which is markedly higher than with the corresponding 4-chloro esters (159 i.u.)[1], but lower than with nitrated polynuclear aromatic hydrocarbons (nitro-PAHs)[25]. On OV-351 the increment is increased to 602 i.u. (187 i.u.), with the value for the 4-chloro isomers[1] given in parentheses.

The retention enhancements due to the 3,5-dinitro substitution are further increased, *viz.*, to 594 i.u. on SE-30 and to 1006 i.u. on OV-351. The increase per nitro substituent, however, is lower than that with the 4-nitro isomers, being in agreement with the chlorine substitution in several aromatic series studied previously[9,10,26,27].

The retention increment ratios between the highly polar and low-polarity columns shown in Table VI indicate that the polar effects are maximal (1.72) with the 4-nitro isomers, although the disparity between the two groups of the esters investigated is negligible. The corresponding ratio with the 4-chloro isomers is markedly lower (1.18), but that of the most polar 2-chloro isomers is of the same magnitude, *viz.*, 1.68[1].

TABLE IV

INCREMENTAL EFFECTS FOR METHYLENE UNITS AND NITRO SUBSTITUTION ON SE-30 AT VARIOUS COLUMN TEMPERATURES

n-Alkyl ester	*Chain length*	*Column (SE-30) temperature*								
		Programmed from 100 to 310°C at 6°C min^{-1}			*Isothermal*					
		ΔI_{CH_2}	$\Sigma\Delta I_{nNO_2}^{*}$	$\Delta I_{1NO_2}^{**}$	*180°C*			*200°C*		
					ΔI_{CH_2}	$\Sigma\Delta I_{nNO_2}^{*}$	$\Delta I_{1NO_2}^{**}$	ΔI_{CH_2}	$\Sigma\Delta I_{nNO_2}^{*}$	$\Delta I_{1NO_2}^{**}$
Benzoate	C_1	—			—			—		
	C_2	74§			78§			79§		
	C_3	104			106			106		
	C_4	104			104			105		
	C_5	102			102			102		
	C_6	96			101			102		
	C_7	100			102			103		
	C_8	106			101			102		
	C_9	103			101			102		
	C_{10}	105			100			100		
	C_{11}	103			100			101		
	C_{12}	105			100			101		
	C_1–C_{12}	103***			102***			102***		

4-Nitrobenzoate	C_1	–	352	352	–	363§	363§	–	386§	386§
	C_2	74§	352	352	74§	359	359	62§	369	369
	C_3	97	345	345	101	354	354	101	364	364
	C_4	103	344	344	102	352	352	103	362	362
	C_5	106	348	348	101	351	351	102	362	362
	C_6	108	360	360	102	352	352	100	360	360
	C_7	105	365	365	100	350	350	101	358	358
	C_8	105	364	364	101	350	350	102	358	358
	C_9	106	367	367	100	349	349	100	356	356
	C_{10}	106	368	368	100	349	349	101	357	357
	C_{11}	110	375	375	100	349	349	100	356	356
	C_{12}	107	377	377	101	350	350	100	355	355
	C_1–C_{12}	105***	360***	360***	101***	351***	351***	101***	360***	360***
3,5-Dinitrobenzoate	C_1	–	619	310	–	637§	319§	–	651§	326§
	C_2	65§	610	305	59§	618	309	53§	625	313
	C_3	98	604	302	93	605	303	93	612	306
	C_4	104	604	302	97	598	299	99	606	303
	C_5	101	603	302	97	593	297	99	603	302
	C_6	104	611	306	99	591	296	99	600	300
	C_7	104	615	308	98	587	294	99	596	298
	C_8	104	613	307	99	585	293	99	593	297
	C_9	106	616	308	99	583	292	99	590	295
	C_{10}	105	616	308	99	582	291	98	588	294
	C_{11}	105	618	309	–	–	–	99	586	293
	C_{12}	105	618	309	–	–	–	99	584	292
	C_1–C_{12}	104***	612***	306***	98***	594***	297***	98***	598***	299***

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* Total retention index increase.

** Retention index increase per nitro group.

*** Average value.

§ Not included in average values.

TABLE V

INCREMENTAL EFFECTS FOR METHYLENE UNITS AND NITRO SUBSTITUTION ON OV-351 AT VARIOUS COLUMN TEMPERATURES

n-Alkyl ester	*Chain length*	*Column (OV-351) temperature*								
		Programmed from 100 to 220°C at 6°C min^{-1}			*Isothermal*					
					180°C			*200°C*		
		ΔI_{CH_2}	$\Sigma\Delta I_{nNO_2}$*	ΔI_{1NO_2}**	ΔI_{CH_2}	$\Sigma\Delta I_{nNO_2}$*	ΔI_{1NO_2}**	ΔI_{CH_2}	$\Sigma\Delta I_{nNO_2}$*	ΔI_{1NO_2}**
Benzoate	C_1	—			—			—		
	C_2	43§			45§			—		
	C_3	87			85			—		
	C_4	99			88			89		
	C_5	102			92			99		
	C_6	103			98			97		
	C_7	105			100			101		
	C_8	107			101			100		
	C_9	108			102			102		
	C_{10}	107			102			100		
	C_{11}	110			104			101		
	C_{12}	111			103			100		
	C_1–C_{12}	104***			98***			99***		

4-Nitrobenzoate	C_1	–	638	638	–	612	612	–	–	–
	C_2	30[§]	625	625	25[§]	592	592	20[§]	–	–
	C_3	87[§]	625	625	78[§]	585	585	80[§]	602	602
	C_4	107	633	633	96	593	593	97	610	610
	C_5	108	639	639	100	601	601	95	606	606
	C_6	107	643	643	99	602	602	98	607	607
	C_7	111	649	649	100	602	602	102	608	608
	C_8	111	653	653	103	604	604	104	612	612
	C_9	110	655	655	105	607	607	104	614	614
	C_{10}	109	657	657	103	608	608	103	617	617
	C_{11}	105	652	652	103	607	607	103	619	619
	C_{12}	107	648	648	103	607	607	106	625	625
	C_1–C_{12}	108***	643***	643***	101***	602***	602***	101***	612***	612***
3,5-Dinitrobenzoate	C_1	–	1137	569	–	1068	534	–	–	–
	C_2	4[§]	1098	549	10[§]	1033	517	2[§]	–	–
	C_3	50[§]	1061	531	45[§]	993	497	45[§]	997	499
	C_4	103	1065	533	89	994	497	89	997	499
	C_5	101	1064	532	96	998	499	95	993	497
	C_6	101	1062	531	98	998	499	96	992	496
	C_7	102	1059	530	97	995	498	100	991	496
	C_8	103	1055	528	101	995	498	99	990	495
	C_9	100	1047	524	102	995	498	102	990	495
	C_{10}	102	1042	521	102	995	498	100	990	495
	C_{11}	101	1033	517	–	–	–	99	988	494
	C_{12}	103	1025	513	–	–	–	101	989	495
	C_1–C_{12}	102***	1062***	531***	98***	1006***	503***	98***	992***	496***

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* Total retention index increase.
** Retention index increase per nitro group.
*** Average value.
[§] Not included in average values.

TABLE VI

SUMMARY AND CORRELATION BETWEEN RETENTION INCREMENTS OF 4-CHLORO-, 4-NITRO- AND 3,5-DINITROBENZOATES ON SE-30 AND OV-351

*Retention increment**	*Temperature*		
	*Programmed****	*Isothermal*	
		180°C	*200°C*
SE-30			
$\Delta I_{4\text{-Chloro}}$**	166	159	162
$\Delta I_{4\text{-Nitro}}$	360	351	360
$\Delta I_{3,5\text{-Dinitro}}$	612	594	598
$\Delta I_{4\text{-Nitro}} - \Delta I_{4\text{-Chloro}}$	194	192	198
$\Delta I_{3,5\text{-Dinitro}} - \Delta I_{4\text{-Nitro}}$	252	243	238
OV-351			
$\Delta I_{4\text{-Chloro}}$**	197	187	189
$\Delta I_{4\text{-Nitro}}$	643	602	612
$\Delta I_{3,5\text{-Dinitro}}$	1062	1006	992
$\Delta I_{4\text{-Nitro}} - \Delta I_{4\text{-Chloro}}$	446	415	423
$\Delta I_{3,5\text{-Dinitro}} - \Delta I_{4\text{-Nitro}}$	419	404	380
OV-351/SE-30			
$\Delta I_{4\text{-Chloro}}$**	1.19	1.18	1.17
$\Delta I_{4\text{-Nitro}}$	1.79	1.72	1.70
$\Delta I_{3,5\text{-Dinitro}}$	1.74	1.69	1.66
$\Delta I_{4\text{-Nitro}} - \Delta I_{4\text{-Chloro}}$	2.30	2.16	2.14
$\Delta I_{3,5\text{-Dinitro}} - \Delta I_{4\text{-Nitro}}$	1.66	1.66	1.60
OV-351 – SE-30			
$\Delta I_{4\text{-Chloro}}$**	31	28	27
$\Delta I_{4\text{-Nitro}}$	283	251	252
$\Delta I_{3,5\text{-Dinitro}}$	450	412	394
$\Delta I_{4\text{-Nitro}} - \Delta I_{4\text{-Chloro}}$	252	223	225
$\Delta I_{3,5\text{-Dinitro}} - \Delta I_{4\text{-Nitro}}$	167	161	142

* From Tables IV and V.
** From ref. 1.
*** Under conditions shown in Figs. 1 and 2 and ref. 1.

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