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SEPARATION OF MONOSUBSTITUTED BENZONITRILES BY GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

The forces influencing the separation order of monosubstituted benzonitriles on 1,2,3-tris-(2-cyanoethoxypropane), poly(propyleneglycol), dinonyl phthalate, tritolyl phosphate, 2,4,7-trinitrofluorenone, silicone oil and silicone gum rubber are discussed. Specific retention volumes, heats of solution, electron polarizabilities and dipole moments were calculated. 1,2,3-Tris-(2-cyanoethoxypropane) was found to be selective for the quantitative separation of the isomers studied, followed by dinonyl phthalate, poly(propylene glycol) and tritolyl phosphate.

INTRODUCTION

Gas-liquid chromatography (GLC) has been used for the identification and separation of aromatic compounds, including benzonitriles¹. Toluonitriles were separated by Habboush and Norman² on six liquid phases, while Ratusky and Baster³ studied the effect of hydrogen bonds on the relative retention using cyanophenols and nitrobenzonitriles as test compounds. Farroha and Emeish⁴ studied mono- and dimethyl-substituted benzonitriles on liquid phases with different polarities.

In this work, the quantitative separation of monosubstituted benzonitriles on liquid phases with various chemical and physical properties was investigated and the factors that influence the elution characteristics and resolution were studied.

EXPERIMENTAL

Apparatus

A Beckman GC-45 gas chromatograph equipped with a thermal conductivity detector was used. An optimal carrier gas (nitrogen) flow-rate of 25 ml/min at N.T.P., a current of 125 mA and an attenuation of 8 gave the best experimental peak shapes and heights. A Beckman Model 10 1-mV recorder was used. The columns (Perkin-Elmer, Norwalk, Conn., U.S.A.) consisted of coils of stainless-steel tubing (2 m long and 3 mm O.D.). The column temperature was controlled to within $\pm 0.08^\circ$. The composition of the liquid phases and the packing specifications of the columns are shown in Table I.

TABLE I
SPECIFICATIONS OF STATIONARY LIQUID PHASES

Liquid phase	Abbreviation	Structure	% (w/w)	Wt. of phase (g)	Mol. wt.	Max. operating temperature
1,2,3-Tris-(2-cyanoethoxypropane), Chromosorb W, AW-DMCS	TCEP	NC-CH ₂ CH ₂ O-CH (NC-CH ₂ CH ₂ O-CH ₂) ₂	8	0.2	251.29	175
Poly(propylene glycol)	PPG	(OCH ₂ CH ₂ CH ₂) _n	15	0.37	550	150
(LB-550-X), Chromosorb W	DNP	(CH ₂) ₄ (OH) ₂	10	0.25	418.6	150
Dinonyl phthalate, Chromosorb W	TTP	C ₈ H ₄ (COOC ₉ H ₁₉) ₂	10	0.25	368.37	125
Triethyl phosphate, Chromosorb W	TNF	(CH ₃ C ₆ H ₄ O) ₃ PO	10	0.25	315.12	
2,4,7-Trinitrofluorenone, Chromosorb W	SO	NO ₂ C ₆ H ₃ COC ₆ H ₃ (NO ₂) ₂	10	0.25	—	
Silicone oil MS 550, Chromosorb W		(CH ₃) ₃ -O-Si-(CH ₃) ₂ -O-Si-(CH ₃) ₃	10	0.25	—	
Silicone gum rubber E ₃ O ₁ , Chromosorb G, AW-DMCS	SGR		2.5	0.107	—	240

TABLE II
PHYSICAL PROPERTIES OF MONOSUBSTITUTED BENZONITRILES

No.	Compound	M.p. (°C)	B.p. (°C)	Calculated dipole moment (D)	Refractive index (95°)*	Electron polarizability** (cm ³ × 10 ⁻²⁶)
1	Benzonitrile		190-192	4.39	1.4915	15.0460
2	<i>o</i> -Toluonitrile		205.2	4.22	1.4925	15.0690
3	<i>m</i> -Toluonitrile		214.0	4.59	1.4930	15.0806
4	<i>p</i> -Toluonitrile	29.5	217.0	4.73	1.4960	15.1486
5	<i>p</i> -Fluorobenzonitrile	34- 36		2.82	1.4725	14.6097
6	<i>o</i> -Chlorobenzonitrile	42- 45	232	5.44	1.5210	15.7056
7	<i>m</i> -Chlorobenzonitrile	40- 41		3.83	1.5170	15.6174
8	<i>p</i> -Chlorobenzonitrile	92- 94	223	2.70	1.5245	15.7823
9	<i>o</i> -Bromobenzonitrile	54- 57	251-253	5.45	1.5475	16.2785
10	<i>m</i> -Bromobenzonitrile	38- 40	225	3.84	1.5460	16.2465
11	<i>p</i> -Bromobenzonitrile	113	235	2.68	70° ***	
12	Phenol	43	181.7		1.5179	11.9988
13	<i>o</i> -Cyanophenol	95- 97		3.98	1.5465	16.2572
14	<i>m</i> -Cyanophenol	80- 82		5.23	1.8315	16.4554
15	<i>p</i> -Cyanophenol	112-115		5.79		
16	<i>o</i> -Aminobenzonitrile	50		3.87	1.5650	16.6471
17	<i>m</i> -Aminobenzonitrile	53		5.29		
18	<i>p</i> -Aminobenzonitrile	85- 86		5.87	1.5960	17.2828
19	<i>o</i> -Nitrobenzonitrile	109-110	320-321	7.45		
20	<i>m</i> -Nitrobenzonitrile	117-118	292	4.31		
21	<i>p</i> -Nitrobenzonitrile	147-148	288-289	0.16		

* Measured in this laboratory.

** Calculated.

*** Only for phenol.

Materials

Table II summarizes some of the physical properties of the materials studied, which were obtained from Hopkin & Williams, Chadwell Heath, Great Britain (benzonitrile and *o*-, *m*- and *p*-toluonitrile), Fluka, Buchs, Switzerland (*o*-, *m*- and *p*-nitrobenzonitrile and *o*-, *m*- and *p*-aminobenzonitrile) and Aldrich, Milwaukee, Wisc., U.S.A. (*o*-, *m*- and *p*-chlorobenzonitrile, *o*-, *m*- and *p*-bromobenzonitrile and *o*-, *m*- and *p*-cyanophenol). No further purification was needed, as each of the compounds gave only one peak with a stable baseline.

Sampling

Equal weights of the isomers were blended in a 3-ml cylindrical Pyrex glass cell. Sample sizes ranged from 0.1 to 0.2 μ l for liquid isomers and from 0.2 to 0.6 μ l of a 10% (w/w) solution in acetone for solid isomers. The injections were made with a 1- μ l Hamilton syringe.

RESULTS

The specific retention volumes, V_g^0 , were calculated following the method of Littlewood *et al.*⁵ and are listed in Table III. No difference was found in the retention

TABLE III

SPECIFIC RETENTION VOLUMES, V_g^0 (ml/g), FOR MONOSUBSTITUTED BENZONITRILES AT DIFFERENT TEMPERATURES

No.	Compound	TCEP					PPG		TTP
		160°	150°	130°	120°	110°	140°	120°	110°
1	Benzonitrile	86	108	159	229	335	67	172	228
2	<i>o</i> -Toluonitrile	95	123	182	268	399	93	243	342
3	<i>m</i> -Toluonitrile	105	147	224	328	492	107	302	425
4	<i>p</i> -Toluonitrile	127	169	259	385	580	116	337	491
5	<i>p</i> -Fluorobenzonitrile	69	85	147	147	213	65	154	222
6	<i>o</i> -Chlorobenzonitrile	216	285	479	730	1126	198	669	1 042
7	<i>m</i> -Chlorobenzonitrile	139	181	294	442	661	147	426	653
8	<i>p</i> -Chlorobenzonitrile	157	204	336	505	770	163	515	803
9	<i>o</i> -Bromobenzonitrile	364	493	905	1393	2184	337	1 272	2 049
10	<i>m</i> -Bromobenzonitrile	229	305	541	821	1274	249	817	1 288
11	<i>p</i> -Bromobenzonitrile	255	340	615	939	1459	279	971	1 558
12	Phenol	178	241	—	—	—	—	—	—
13	<i>o</i> -Cyanophenol	1942	2 712	—	—	—	1366	8 842	10 220
14	<i>m</i> -Cyanophenol	5690	8 224	—	—	—	5536	18 346	Not eluted
15	<i>p</i> -Cyanophenol	9574	14 041	—	—	—	8235	—	Not eluted
16	<i>o</i> -Aminobenzonitrile	1006	2 095	—	—	—	740	2 722	4 697
18	<i>p</i> -Aminobenzonitrile	6525	10 423	—	—	—	3354	—	Not eluted
19	<i>o</i> -Nitrobenzonitrile	4270	5 015	—	—	—	1345	10 073	Not eluted
20	<i>m</i> -Nitrobenzonitrile	1661	1 902	—	—	—	705	4 421	7 416
21	<i>p</i> -Nitrobenzonitrile	1450	1 657	—	—	—	705	4 421	7 416

times when the components were injected individually or in a blend, and the results were reproducible to within $\pm 1\%$. Heats of solution were calculated from the slopes of the linear plots of $\log V_g^0$ versus $1/T$ according to eqn. 1 and are listed in Table IV.

$$\log V_g^0 = -\frac{\Delta H}{2.303 R} + C \quad (1)$$

where ΔH is the heat of solution, T is the absolute temperature and R and C are constants. Electron polarizabilities per unit volume, α_e^v , were calculated using the Clausius-Mosotti equation:

$$\alpha_e^v = 3(n^2 - 1)/4\pi N(n^2 + 2) \quad (2)$$

where n is the refractive index and N is Avogadro's number. Refractive indices of monosubstituted benzonitriles at 30° were measured using an APe refractometer fitted with a Corala KO 930 ultrathermostat.

Dipole moments were calculated as described by Smith⁶ and are listed in Table II.

Monosubstituted benzonitriles were selectively resolved on TCEP and less

100°	DNP				TNF		SO		SGR			
	140°	130°	120°	110°	190°	180°	120°	110°	100°	120°	110°	100°
376	84	104	144	198	32	37	102	138	211	80	104	142
588	121	158	218	302	37	45	147	210	329	136	156	227
746	143	196	272	380	46	55	169	247	391	136	185	273
861	159	212	301	422	46	55	181	267	422	136	185	273
352	87	107	192	205	25	33	91	129	242	74	94	123
1 807	262	382	560	812	71	88	288	435	711	179	259	387
1 122	187	265	381	539	55	67	216	328	523	150	213	313
1 359	215	309	449	650	55	67	237	366	597	150	213	313
3 748	442	679	1 012	—	120	154	491	771	1322	278	399	625
2 347	2341	474	685	—	92	114	377	582	988	233	334	527
2 863	364	549	807	—	92	114	415	651	1102	233	334	527
Not eluted		183	275									
	—	1263	1 876	3390	34	42	160°	150°	140°	160°	150°	140°
	—	5684	9 157	Not eluted	165	224	33	39	49	36	43	50
	—	8481	13 429	Not eluted	479	656	110	152	204	57	76	93
8 090	—	1128	1 678	2731	728	1021	430	626	902	145	199	295
	—	5273	8 684	} Not eluted	293	397	134	177	253	84	107	147
	—	3556	5 527		1313	1860	426	557	939	169	229	333
13 379	—	1822	2 818	382	515	197	285	421	109	138	194	
13 379	—	1822	2 818	340	455	197	285	421	109	138	194	

well on DNP, TTP and PPG in order of decreasing efficiency, as can be seen in Table III.

DISCUSSION

The specific retention volumes and heats of solution (Tables III and IV) showed that the elution order of halobenzonitriles was always *m*-, *p*-, *o*-, of nitrobenzonitriles *p*-, *m*-, *o*-, and of toluonitriles, aminobenzonitriles and cyanophenols *o*-, *m*-, *p*-. These orders were mainly the same as those of the calculated dipole moments and vapour pressures of these isomers, with the exception of the halobenzonitriles in which the *p*-isomers were eluted after the *m*-isomers, in spite of the higher dipole moments of the latter (Table II). This result is attributed to the higher vapour pressures of the *p*-isomers in addition to the mesomeric interaction between halo and cyano groups, which lead to enhanced dipole moments. The values of the electron polarizabilities (Table II) support the above mechanism.

For chloro-, bromo- and nitrobenzonitriles, the *ortho*-derivatives have larger dipole moments, leading to stronger interactions with the solvents (Tables III and IV). In toluonitriles, cyanophenols and aminobenzonitriles, this effect does not occur (the dipole moments of alkyl, hydroxy and amine groups are small) and steric hindrance to solvent interactions with the dipole via the methyl group becomes dominant in *o*-toluonitrile, which, together with intramolecular hydrogen bonding

TABLE IV

HEATS OF SOLUTION ($-\Delta H$) OF MONOSUBSTITUTED BENZONITRILES (cal/mole) IN DIFFERENT LIQUID PHASES

No.	Compound	TCEP	TTP	DNP	SO	SGR
1	Benzonitrile	8 331	10 488	8 732	10 423	7 278
2	<i>o</i> -Toluobenzonitrile	8 851	12 436	9 672	11 960	
3	<i>m</i> -Toluobenzonitrile	9 471	12 377	10 315	12 071	5 700
4	<i>p</i> -Toluobenzonitrile	9 731	12 666	10 410	12 113	
5	<i>p</i> -Fluorobenzonitrile	9 530	11 856		10 032	6 078
6	<i>o</i> -Chlorobenzonitrile	11 054	14 820	12 002	13 028	9 672
7	<i>m</i> -Chlorobenzonitrile	9 771	13 680	11 104	12 666	8 824
8	<i>p</i> -Chlorobenzonitrile	9 889	13 817	11 400	13 127	
9	<i>o</i> -Bromobenzonitrile	11 570	15 200	13 557	14 250	9 973
10	<i>m</i> -Bromobenzonitrile	10 967	14 440	12 668	14 592	
11	<i>p</i> -Bromobenzonitrile	11 146	15 390	12 918	14 316	9 325
12	Phenol				6 514	7 597
13	<i>o</i> -Cyanophenol				11 745	9 120
14	<i>m</i> -Cyanophenol				12 666	12 376
15	<i>p</i> -Cyanophenol				13 412	12 212
16	<i>o</i> -Aminobenzonitrile				11 400	10 132
17	<i>m</i> -Aminobenzonitrile					
18	<i>p</i> -Aminobenzonitrile				12 435	11 769
19	<i>o</i> -Nitrobenzonitrile				14 400	11 400
20	<i>m</i> -Nitrobenzonitrile					
21	<i>p</i> -Nitrobenzonitrile				13 680	9 562

(*o*-hydroxy and -amino), leads to a lower interaction of these *ortho*-isomers with the solvent (Tables III and IV). The intramolecular hydrogen bonding occurs between the π -electrons of the triple bond of the cyano group and the hydrogen atom of the hydroxyl and amino groups⁷⁻⁹.

These results also showed that the most selective liquid phase for separation and quantitative determination in this study is TCEP, followed by DNP, TTP and PPG. TCEP is a polar liquid phase, the polarity being attributed to the presence of a cyano group that is able to polarize the benzonitriles according to their solubilities, and complete resolution of all of the isomers was achieved.

In TTP and DNP, the solute-solvent interaction is due mainly to hydrogen bonding, which can occur in more than one position. Higher specific retention volumes and more negative heats of solution in TTP than DNP are due to the P = O group, in addition to the tolyl groups, which enhance the polarity of this liquid phase.

In TNF, which is a strong acceptor liquid phase¹⁰, nitrobenzonitriles, aminobenzonitriles and cyanophenols were completely resolved via donor-acceptor interactions, while the other isomers were eluted with shorter retention times mainly according to their vapour pressures.

In PPG, the lower specific retention volumes of benzonitriles (except amino-, cyano- and nitrobenzonitriles) than on DNP are due to the nature of this liquid phase, which exerts internal association through intramolecular hydrogen bonding^{11,12}. Aminobenzonitriles, cyanophenols and nitrobenzonitriles reduced the self-association of this liquid phase via intermolecular hydrogen bonding between these isomers and the liquid phase.

TTP, DNP and PPG are considered as selective stationary liquid phases, except for nitrobenzonitriles, the *m*- and *p*-isomers completely overlapping (Table III).

In SO and SGR, the selectivity obtained was lower than in the other liquid phases (Tables III and IV) (although the extent of interaction between the former liquid phase and the compounds under study was relatively higher), because these two liquid phases are non-polar and do not polarize the benzonitrile isomers sufficiently to permit resolution.

Straight lines were obtained by plotting $\log V_g^0$ for some of the studied isomers on DNP against $\log V_g^0$ for TCEP, TTP and PPG, on TTP against TCEP and on SO against SGR (Fig. 1), which indicated that similar factors were involved in solutions of these isomers and the liquid phases¹³. In the graphs for DNP against TCEP, DNP against PPG and TTP against TCEP, the lines lay closer to the TCEP, DNP and TCEP axes. These results are consistent with the greater solubilities and stronger

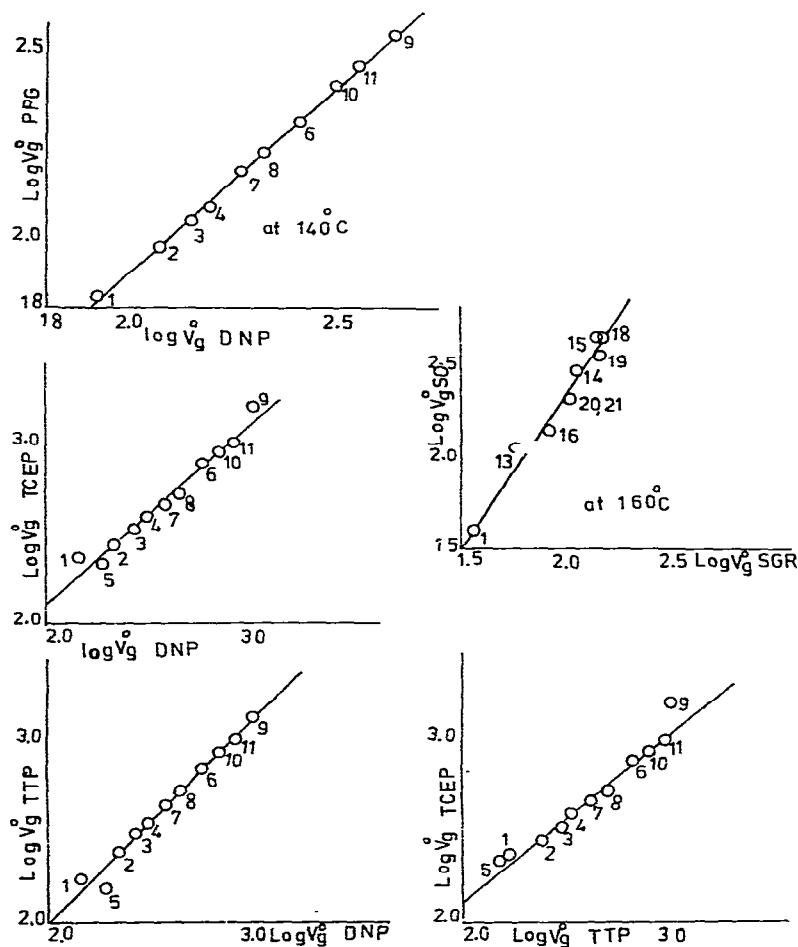


Fig. 1. $\log V_g^0$ plots for benzonitrile isomers at different temperatures. The numbers correspond to the isomers listed in Table II.

interactions of benzonitrile isomers with these liquid phases than with DNP, PPG and TTP.

In the graphs for DNP against TTP and SO against SGR, the lines passed through the origin, which indicate nearly identical solubilities and interactions of the benzonitriles isomers on the two liquid phases in each instance.

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