

CIROM. 15,586

THIN-LAYER AND GAS CHROMATOGRAPHY OF SOME FLUOROBIPHENYLS AND FLUORONAPHTHALENES

L. H. KLEMM*, JOHN N. LOURIS and BARBARA BOETTCHER

Department of Chemistry, University of Oregon, Eugene, OR 97403 (U.S.A.)

(First received November 15th, 1982; revised manuscript received December 9th, 1982)

SUMMARY

Relative retention data are reported for biphenyl, naphthalene, seven fluorine-substituted biphenyls (bearing 1, 2, 8, and 10 fluorine atoms per molecule), and mono- and octafluoronaphthalenes in gas chromatography with (a) silicone fluid DC 710, (b) Carbowax 20M, and (c) Bentone 34-silicone fluid DC 710 and in thin-layer chromatography on (d) silica gel and (e) alumina. With a and d retention generally decreases with increasing number of fluoro substituents, n , and, for a given n , is higher for a biphenyl compound than for a naphthalene one. 2,2'-Difluorobiphenyl is an exception in d, since it has the smallest R_F of the various solutes. Some irregularities in these trends are found in cases b, c and e.

INTRODUCTION

There have been extensive chromatographic studies of chlorinated biphenyls and naphthalenes¹⁻³, as well as of brominated biphenyls⁴, in connection with their deleterious effects on the environment. Similarly, methyl derivatives of the biphenyl and naphthalene series have been investigated because of their occurrence in fossil fuels and environmental pollutants⁵. However, no systematic chromatographic investigation of fluorinated biphenyls and naphthalenes has been found in the literature, although comparison of various halobenzenes (including fluorobenzenes) in high-performance liquid chromatography (HPLC) has been reported⁶. The present study was undertaken with ten commercially available fluoroarenes in order to compare the effects of fluoro, chloro, bromo, and methyl substituents on the chromatographic properties of the biphenyl and naphthalene series.

EXPERIMENTAL

All compounds used were commercial samples: naphthalene (reagent grade), biphenyl (reagent grade), octafluorobiphenyl (Aldrich, Milwaukee, WI, U.S.A.), and nine other fluoroarenes (Pierce, Rockford, IL, U.S.A.).

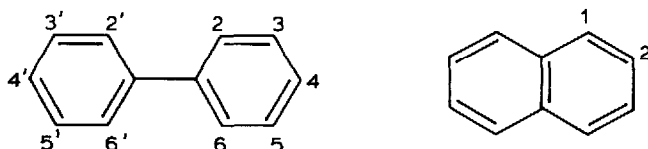
Gas chromatography (GC) was conducted with a Beckman Model GC 4 dual-column analytical instrument with a flame-ionization detecting system and a Leeds

and Northrup Speedomax G 1-mV strip-chart recorder with a paper speed of 2.71 cm/min. The stationary phases, *viz.* 9% silicone fluid DC 710 on 100–120 mesh Chromosorb W HP (designated DC), 10% Carbowax 20M on 80–100 mesh Chromosorb W HP (CW), and 4.5% Bentone 34 plus 4.5% silicone fluid DC 710 on 100–120 mesh Chromosorb W HP (BDC), were packed into aluminum tubing (2 m × 1.65 mm I.D. for phases DC and BDC and 3 m × 1.65 mm I.D. for phase CW). Samples of solutions containing $1.1 \pm 0.3\%$ (w/w) of compound and $1.2 \pm 0.5\%$ (w/w) of 2,2',3,3',5,5',6,6'-octafluorobiphenyl (3) as internal reference, in acetone (plus a small quantity of methane), were injected onto the column, which was maintained at 150°C and with a helium flow-rate of 30 ml/min. Three separate injections were made for each compound and each stationary phase. The adjusted retention times (measured from the methane peak) were 2.3 min for compound 3 on DC; 1.5–1.7 min, on BDC; and 4.6–4.7 min, on CW. Calculated relative retention values (V_R) varied by 0.1–4% for triplicate runs. Average values of V_R are given in Table I.

Thin-layer chromatography (TLC) was conducted by means of 20 × 20 cm commercial plates (E. Merck, Darmstadt, G.F.R.) of type 60 F₂₅₄ silica gel and alumina. Plates were dried at 43°C for 1–7 days, spotted with 2 μ l of 10⁻² M solutions of the compounds in acetone, developed with light petroleum (b.p. 60–110°C) over a period of 30–40 min (solvent front at 16–18 cm), and examined with a UVS-11 254 nm Mineralight for detection of spots. Duplicate runs gave R_F values which varied no more than 0.02 for each compound. Average values of R_F are presented in Table II.

TABLE I

RELATIVE GAS CHROMATOGRAPHIC RETENTION (V_R) OF FLUOROBIPHENYLS AND FLUORONAPHTHALENES AT 150°C



V_R relative to 2,2',3,3',5,5',6,6'-octafluorobiphenyl (3) = 1.00. BP = Biphenyl; N = naphthalene.

No.	Compound	V_R			V_R quotient	
		DC	BDC	CW	BDC/DC	CW/DC
1	F ₁₀ -BP	0.47	0.40	0.19	0.85	0.40
2	F ₈ -N	0.75	1.24	0.47	1.65	0.63
3	F ₈ -BP	1.00	1.00	1.00	1.00	1.00
4	2-F-N	1.50	2.75	2.31	1.83	1.54
5	1-F-N	1.51	2.98	2.13	1.97	1.41
6	N	1.59	3.18	2.29	2.00	1.44
7	2,2'-F ₂ -BP	3.49	6.63	5.27	1.90	1.51
8	3,3'-F ₂ -BP	3.62	7.89	5.95	2.18	1.64
9	2-F-BP	3.78	7.36	5.28	1.95	1.40
10	4,4'-F ₂ -BP	3.80	7.08	6.49	1.86	1.71
11	4-F-BP	3.94	7.37	5.99	1.87	1.52
12	BP	4.17	8.23	5.79	1.97	1.39

TABLE II

COMPARISON OF CHROMATOGRAPHIC ADSORPTION RETENTION OF HALOBIPHENYLS AND HALONAPHTHALENES

BP = Biphenyl; N = naphthalene; X = halogen; LP = light petroleum (b.p. 60–110°C).

No. (for X = F)	Compound	R_F value in TLC			Capacity factor, k' , in HPLC*				
		Silica gel/ LP, X = F**	Alumina/ LP, X = F**	Silica gel/ n-heptane, X = Cl***	Silica gel/ n-hexane		Alumina/n-hexane		
					X = Cl	X = Br	X = Cl	X = Br	
7	2,2'-X ₂ -BP	0.22	0.48	0.38	5.50	6.65	7	12	
12	BP	0.23	0.53		9.25	9.25	35	35	
9	2-X-BP	0.24	0.53	0.35	6.35	6.90	8	10	
11	4-X-BP	0.25	0.52	0.43	5.05	5.20	35	54	
10	4,4'-X ₂ -BP	0.25	0.48	0.41	2.90	3.30	53	large	
8	3,3'-X ₂ -BP	0.27	0.53	0.45	2.65		24		
3	X ₈ -BP [§]	0.28	0.54	0.68					
6	N	0.29	0.59		3.80	3.80	27		
4	2-X-N	0.30	0.57		2.20		28		
5	1-X-N	0.34	0.60		1.80		19		
2	X ₈ -N	0.34	0.56		0.45		4		
1	X ₁₀ -BP	0.40	0.69	0.76	0.45	2.25	1	57	

* See refs. 4, 6, and 23.

** Present study.

*** See ref. 1.

§ See Table I.

Efforts to use iodine vapors or SbCl₅-CCl₄ spray to detect spots on plates devoid of fluorescent indicator were unsuccessful.

Column chromatography of a mixture of 0.2 g of 4,4'-difluorobiphenyl (10) and 0.2 g of decafluorobiphenyl (1) was conducted on a 26-cm column of Baker reagent grade chromatographic silica gel (42 g) with light petroleum and the effluent was monitored by TLC. Compound 1 (0.17 g, m.p. 68–69°C) was recovered from the first 50 ml of effluent and compound 10 (0.17 g, m.p. 87.5–88.5°C) from the next 125 ml.

RESULTS AND DISCUSSION

Examination of Table I shows that for the stationary phase silicone fluid DC 710 (which should effect separation on the basis of volatility) V_R decreases with increasing number of fluorine substituents on the parent arene, naphthalene or biphenyl. There is, however, some overlap in retention of mono- and difluorobiphenyls due to different incremental effects of substituents at the 2-, 3- and 4-positions. The orders 4- > 2- and 4,4'- > 3,3'- > 2,2'- in V_R of fluorobiphenyls are consistent with observations on relative retention times for the chlorobiphenyls on Apiezon L⁷⁻⁹ and SE-30¹⁰ and for the methylbiphenyls on Apiezon M¹¹. In contrast, the marked decrease in V_R with increasing extent of fluorine substitution is somewhat unexpected. As based on the progression in boiling points, the volatility of fluorobenzenes changes irregularly as one increases the number of substituents, n ¹². In contrast, volatility in

chloroarenes¹³, in methylbenzenes¹⁴, and in methylnaphthalenes^{5,15,16} generally decreases with increasing n . More specifically, while the quotient of retention times of decafluorobiphenyl to 4-fluorobiphenyl with phase DC is 0.12 (Table I), the corresponding quotient for decachlorobiphenyl to 4-chlorobiphenyl with phase SE-30 is 48¹⁹. Similarly, the quotient for octafluoronaphthalene to naphthalene with DC is 0.47, while that for hexamethylnaphthalene to naphthalene with silicone fluid DC 550 is 21⁵, and the quotient for octamethylnaphthalene to naphthalene should be even larger. The longer retention time of biphenyl (b.p. 255°C) than that of naphthalene (b.p. 218°C) on all of our phases is consistent with the relative volatilities of the two compounds and with results reported for four other phases¹⁵⁻¹⁷.

It is noteworthy that with stationary phases BDC and CW the V_R quotients are greater than 1 for compounds 4-12, consistent with enhanced retention (*i.e.* attraction) of these molecules by the stationary phase when compared to the effect on the reference compound 3. In contrast, the V_R quotient for compound 1 is less than 1 with both BDC and CW and implies that substituting two more fluorine atoms on compound 3 has significantly decreased the relative attraction of the substrate molecule to these more polar phases. Octafluoronaphthalene (2), in contrast, shows a greater relative attraction ($V_R > 1$) to BDC (where π -electronic interactions may be pertinent¹⁸) and a smaller relative attraction ($V_R < 1$) to CW.

Additionally, one should note that methylnaphthalenes for $n \leq 6$ have been studied in gas chromatography on Bentone 34^{5,19,20} and for $n \leq 2$ on Carbowax 1400²¹. Chloronaphthalenes for $n \leq 4$ in Halowaxes have also been investigated on both Bentone 34 and Carbowax 20M²². In all of these cases retention time increased in general with increasing n , in contradistinction to our findings for the fluoronaphthalenes.

Inspection of Table II shows that the R_F values on silica gel for the fluorinated naphthalenes and biphenyls generally increase as n increases. Compound 7 is an exception to this trend in that it is the most strongly retained solute studied. As in GC, a compound of the biphenyl series is retained more tenaciously than one of the naphthalene series with the same n value. R_F values on alumina also follow the general order found on silica gel, but with some added irregularities. Data for TLC of various chlorobiphenyls with silica gel-heptane¹ and for HPLC capacity factors, k' (*i.e.* relative retention times), of chlorobiphenyls, bromobiphenyls, and chloronaphthalenes with silica gel- n -hexane^{4,6,23} show similar trends. However, the high-retention of compound 7 on silica gel is not found with the chloro or bromo analogs, wherein the larger halo atoms probably hold the parent biphenyl molecule in a more twisted conformation with respect to the 1,1'-bond²⁴. It seems likely that compound 7 will be adsorbed in the *syn* conformation in which it persists even in the gaseous phase²⁴.

Isomers 7 and 10 are not distinguished by TLC on alumina, but their halo analogs show markedly different k' values with this adsorbent, on which the 4,4'-isomer is retained far more strongly than the 2,2' one. The orders in R_F of compound 2 > compound 6 on silica gel while compound 6 > compound 2 on alumina are consistent with the table of group adsorption energies presented by Snyder²⁵. However, the order compound 6 > Cl₈-N in retention on both adsorbents is inconsistent with that table, from which one would expect the opposite order for silica gel. It should be noted that the general trend of decreasing k' with increasing n reported

for HPLC of fluorobenzenes with silica gel-*n*-hexane⁶ is consistent with our TLC results on this adsorbent.

Additionally, comparison of our TLC data for fluoroarenes with those reported for methyl analogs show both similarities and differences. In the methylbiphenyl series there is a general increase in retention on silica gel with increasing *n* for $n \leq 6$, opposite to the trend for the fluoro analogues. On alumina, methylbiphenyls vary widely in retention between those with substitution *ortho* to the 1,1'-bond and those lacking such substitution⁶. This difference is not apparent for our fluorobiphenyls. Also with alumina/cyclohexane, R_F values generally decrease with increasing *n* for $n \leq 6$ in methylnaphthalenes^{2,6} while there is relatively little change in going from $n = 8$ to $n = 0$ in the fluoronaphthalenes on this adsorbent.

As a measure of the significance of the R_F values in Table II on the separability of products from successive fluorinations of biphenyl, we carried out chromatography of a mixture of compounds 1 and 10 ($\Delta R_F = 0.15$) on a column of silica gel on a macroscale. Complete separation was achieved with light petroleum as the eluent.

CONCLUSIONS

GC of fluoronaphthalenes and fluorobiphenyls shows the following trends. (1) Volatility increases with increasing *n*, the number of substituents present on the parent hydrocarbon molecule. This is opposite to the trend reported for chloronaphthalenes and methylnaphthalenes. (2) For a given value of *n*, the fluorobiphenyl has a shorter retention time than the corresponding fluoronaphthalene. (3) Substitution *ortho* to the 1,1'-bond in biphenyl may enhance volatility in the fluoro compounds, as it does in the chloro and methyl analogues.

TLC of the preceding fluoroarenes leads to the following generalizations. (1) In the system silica gel-light petroleum, R_F values increase with increasing *n*. This result is consistent with reported TLC data for chlorobiphenyls and HPLC data for chlorobiphenyls, bromobiphenyls and chloronaphthalenes, but opposite to that for HPLC data on methylbiphenyls. (2) In the system alumina-light petroleum, irregularities from the trend in (1) occur amongst the fluoroarenes. (3) Amongst the fluoroarenes, for a given value of *n* R_F is greater in the naphthalene series than in the biphenyl one with either alumina or silica gel. Except for the *ortho* effect (see below) this trend also occurs for HPLC of chloroarenes. (4) 2,2'-Substitution on biphenyl enhances retention (compared to biphenyl itself) with fluoro substituents but decreases retention with chloro, bromo or methyl substituents.

REFERENCES

- 1 L. Fishbein, *J. Chromatogr.*, 68 (1972) 345.
- 2 O. Hutzinger, S. Safe and V. Zitko, *The Chemistry of PCB's*, CRC Press, Cleveland, O., 1974.
- 3 U. A. Th. Brinkman and H. G. M. Reymer, *J. Chromatogr.*, 127 (1976) 203.
- 4 J. J. de Kok, A. de Kok and U. A. Th. Brinkman, *J. Chromatogr.*, 142 (1977) 367.
- 5 L. H. Klemm, J. Shabtai and K. C. Bodily, *J. Chromatogr.*, 206 (1981) 372.
- 6 U. A. Th. Brinkman and G. de Vries, *J. Chromatogr.*, 169 (1979) 167.
- 7 H. Weingarten, W. D. Ross, J. M. Schlater and G. Wheeler, *Anal. Chim. Acta*, 26 (1962) 391.
- 8 P. W. Albro and L. Fishbein, *J. Chromatogr.*, 69 (1972) 273.
- 9 P. W. Albro, J. K. Haseman, T. A. Clemmer and B. J. Corbett, *J. Chromatogr.*, 136 (1977) 147.
- 10 V. Zitko, O. Hutzinger and S. Safe, *Bull. Environ. Contam. Toxicol.*, 6 (1971) 160.

- 11 G. H. Beaven, A. T. James and E. A. Johnson, *Nature (London)*, 179 (1957) 490.
- 12 A. E. Pavlath and A. J. Leffler, *Aromatic Fluorine Compounds*, Reinhold, New York, 1962, pp. 19-20.
- 13 C. R. Noller, *Chemistry of Organic Compounds*, Saunders, Philadelphia, PA, 1965, pp. 800-801.
- 14 J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, New York, 1965, pp. 771-772.
- 15 F. J. Kabot and L. S. Ettre, *Anal. Chem.*, 36 (1964) 250.
- 16 J. Mostecky, M. Popl and J. Kriz, *Anal. Chem.*, 42 (1970) 1132.
- 17 T.-C. L. Chang and C. Karr, *Anal. Chim. Acta*, 24 (1961) 343.
- 18 L. H. Klemm, J. Shabtai and K. C. Bodily, *J. Chromatogr.*, 198 (1980) 1.
- 19 M. van der Stricht and J. van Rysselberge, *J. Gas Chromatogr.*, 1, August (1963) 29.
- 20 J. Frycka, *Chromatographia*, 8 (1975) 413.
- 21 G. Arich and S. Volpe, *J. Gas Chromatogr.*, 6 (1968) 384.
- 22 F. A. Beland and R. D. Geer, *J. Chromatogr.*, 84 (1973) 59.
- 23 U. A. Th. Brinkman, A. de Kok, H. G. M. Reymer and G. de Vries, *J. Chromatogr.*, 129 (1976) 193.
- 24 O. Bastiansen and L. Smedvik, *Acta Chem. Scand.*, 8 (1954) 1593; O. Bastiansen, K. Kveseth and H. Mollendal, *Topics Current Chem.*, 81 (1979) 99.
- 25 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968, p. 264.
- 26 L. H. Klemm, D. S. W. Chia, C. E. Klopfenstein and K. B. Desai, *J. Chromatogr.*, 30 (1967) 476.