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Relationship between Liquid and Gas Chromatographic Retention Behavior and Calculated Molecular Surface Area of Selected Polyhalogenated Biphenyls

Frank Höfler, Horst Melzer, Hermann J. Möckel, Larry W. Robertson, and Elke Anklam*

The retention behavior of 57 mono- or polyhalogenated biphenyls was characterized by gas chromatography on a DB-210-CB capillary column and by high-pressure liquid chromatography on ODS phases. A possible relationship between the recorded retention data (Kovats index) and molecular surface area was explored. Generally, the addition of halogen atoms (Cl, Br, I) to biphenyl increased both the retention index and the calculated molecular surface area for the series of polyhalogenated biphenyls investigated. The addition of fluorine however resulted in a decreased retention index although the molecular surface area was slightly increased. The addition of halogen substituents resulted in more dramatic changes in retention as demonstrated by the Kovats index (I_K) for gas chromatography than for liquid chromatography. The homologues with chloro or bromo substituents in ortho positions displayed lower I_K values than those with halogens in meta and para positions. Generally, good correlation was observed between I_K and the calculated molecular surface area values.

Polyhalogenated biphenyls are particularly well-suited for a number of industrial uses, and these chemicals have been widely manufactured (e.g., Aroclor and fireMaster products are commercial mixtures used as fire retardants). Unfortunately their chemical stability and fat solubility contribute to their environmental persistence and biomagnification. Today polyhalogenated biphenyls, particularly polychlorinated biphenyls (PCBs), are routinely detected in environmental samples, in foodstuffs, and in human tissues. These products are complex in nature [209 isomers each of PCBs, polybrominated biphenyls (PBBs), and polyfluorinated biphenyls (PFBs) are possible]. Such a degree of complexity complicates the analysis of these mixtures in environmental samples. Even the use of ca-

pillary gas chromatography and high-resolution mass spectroscopy does not always give satisfactory results.

Often reversed-phase high-pressure liquid chromatography (HPLC) separations are used in sample cleanup procedures. In order to get more information about the influence of structure on the HPLC retention behavior of polyhalogenated biphenyls, 57 selected compounds have been synthesized and their retention characteristics are presented in this paper. The corresponding retention measurements are also presented for capillary (DB-210-CB column) gas chromatography.

The structures of several PCBs and PBBs have been shown to strongly influence retention behavior in both gas and liquid chromatography (Robertson et al., 1984; de Kok et al., 1977). Likewise, for many classes of compounds an excellent correlation between HPLC and GC retention times and the corresponding calculated molecular surface area (SA) has been demonstrated (Dunn et al., 1986; Möckel et al., 1987a-d). In order to explore such a correlation for polyhalogenated biphenyls and to eventually predict the structure of unknown compounds, we present

Hahn-Meitner-Institut GmbH, Glienicke Strasse 100, D-1000 Berlin 39, FRG (F.H., H.M., H.J.M., E.A.), and Graduate Center for Toxicology, University of Kentucky, 204 Funkhouser Building, Lexington, Kentucky 40506-0054 (L.W.R.).

here the calculated molecular surface areas for the investigated polyhalogenated biphenyls.

EXPERIMENTAL SECTION

In this paper the halogenated biphenyls are named by listing the substitution site and the halogen atom; the word biphenyl is omitted (e.g. 2-fluorobiphenyl = 2-F). 2-F, 4-F, 4-Cl, 2-Br, 3-Br, and 4-Br were purchased from Aldrich; deca-Cl, 2,2'-Cl, and 3,3',4,4'-Cl were from Riedel de Haen; 4,4'-Br was from Kodak; 2-Cl was from Ventron; and 3,4-Cl was from Promochem.

Synthesis. 2,2',4,4',5,5'-Cl was prepared as previously described (Mönig et al., 1986). 2,2',4,4'-Cl and 3,3',4,4'-Br were synthesized by a benzidine rearrangement of the related hydrazobenzenes (Schulz, 1881) followed by a Sandmeyer reaction (van Roosmalen, 1934); 3,3',5,5'-Br was obtained by the reductive deamination and 3,3',4,4',5,5'-Br by a Sandmeyer reaction from the 3,3',5,5'-tetrabromobenzidine (van Roosmalen, 1934). 2,2',4,4',6,6'-Cl and 2',3,3',4,5-Cl were synthesized by a Cadogan coupling reaction (Cadogan, 1962) of the respective chlorinated anilines with 1,3,5-trichlorobenzene or 1,2-dichlorobenzene. All other investigated mono- and polyhalogenated biphenyls were obtained by a Cadogan reaction of halogenated anilines in excess benzene.

The crude samples were mixed (1:10) with Florisil (Macherey-Nagel) and purified by alumina chromatography (Aluminiumoxid 90, Merck) and recrystallization from methanol or distillation under reduced pressure. Structural assignments were confirmed by NMR (Bruker WM 400) and mass spectroscopy (Varian MAT, CA 7A, EI, 70-eV spectra).

Gas Chromatography (GC). GC analysis was performed on a Varian 3700 gas chromatograph equipped with a split injector and a flame ionization detector (FID). A 25 m × 0.25 mm DB-210-CB capillary column (ICT) was used with a film thickness of 0.2 μm. The column was operated with hydrogen carrier gas (0.85 bar); the injector split was 1:200. The oven temperature was held at 110 °C for 1 min and then programmed to 240 °C at 4 °C/min; the injector temperature was 250 °C and the detector temperature 310 °C. The polyhalogenated biphenyls were dissolved in a mixture of *n*-alkanes ranging from pentane to tridecane. Samples of 1 μL were injected with a Varian 8020 autosampler. The data were collected on a Trio-Integrator (Trivector).

High-Pressure Liquid Chromatography (HPLC). HPLC separations were carried out on a Varian 5000 liquid chromatograph using a Waters RAD PAK A column. The polyhalogenated biphenyls were dissolved in methanol (p.a.) (Merck) and injected with a Rheodyne Model 7010 injection valve equipped with a 20-μL loop. Methanol (100%) (p.a.) (Merck) was used as eluent at a flow rate of 1 mL/min. The separated compounds were detected with a PC1 4021 multichannel detector, operating in the absorption range from 220 to 300 nm, and a refractive index detector (Melz) in series. Data were evaluated by a SP 4820 computing integrator (Spectra Physics).

Retention Indexes. The experimental results will be discussed mainly in terms of the retention index I_K . In gas chromatography the retention index I_K was introduced by Kovats (1958) and describes the retention time of a compound X relative to that of *n*-alkanes (eq 1) where

$$I_K(X) = \frac{\log t_R(X) - \log t_R(C_1)}{\log t_R(C_2) - \log t_R(C_1)} \times 100(n_{C_2} - n_{C_1}) + 100n_{C_1} \quad (1)$$

$t_R(X)$ = net retention time of the sample X, $t_R(C_1)$ = net retention time of the *n*-alkane eluting before the sample,

$t_R(C_2)$ = net retention time of the *n*-alkane eluting after the sample, n_{C_1} = number of carbon atoms of the *n*-alkane eluting before the sample, and n_{C_2} = number of carbon atoms of the *n*-alkane eluting after the sample. In reversed-phase liquid chromatography the logarithm of the capacity ratio k' of *n*-alkanes is linearly related to the number of carbon atoms, within a limited range (Engelhardt and Ahr, 1981; Möckel, 1984) (eq 2), where *n*-alk =

$$\ln k'(n\text{-alk}) = a(n\text{-alk}) + b(n\text{-alk})n_C \quad (2)$$

n-alkane and n_C = number of carbon atoms. The intercept, $a(n\text{-alk})$, and slope, $b(n\text{-alk})$, of eq 2 depend on the chromatographic system. For the system in use, $a(n\text{-alk}) = -1.4814$ and $b(n\text{-alk}) = 0.2009$ were found. The retention index I_K , although analogous to that in gas chromatography, is now determined by treatment of a component X as a hypothetical *n*-alkane. By substitution of $\ln k'(X)$ into eq 2, the theoretical number of carbon atoms of the component is calculated. Multiplication by 100 yields the retention index. Equation 3 shows the relationship between the retention index I_K and the $\ln k'$ value (Möckel, 1984). In both gas and liquid chromatography I_K is dimensionless.

$$I_K(X) = (100/b(n\text{-alk}))[\ln k'(X) - a(n\text{-alk})] \quad (3)$$

Molecular Surface Area (SA). Molecular surface areas were calculated on a Siemens 7880 computer using the Fortran programs COORD and SAREA from Pearlman (1980). Some structural data were taken from the literature (Dynes et al., 1985; McKinney and Singh, 1981; Field et al., 1985). However, for most of the investigated compounds, no structural data were available. Therefore, data for these compounds were generated by analogy to well-described ones by changing the C-halogen bond distance. Halogen out-of-plane angles and the torsion angle between the phenyl rings were adjusted such that the distance between all nonbonded atoms exceeded the sum of the corresponding van der Waals radii. These results should be viewed only as an estimate of surface area.

RESULTS AND DISCUSSION

HPLC Data. The following effects influence retention data on reversed phases for groups of compounds differing in their degree of substitution: variation of the SA, an increase in solvophobic surface usually corresponding to an increase in retention time; polarity of the substituent, primarily those able to form H bonds; change in dipole moment, especially when this is due to the introduction of the first substituent (e.g., benzene → chlorobenzene) or when it becomes zero due to persubstitution (e.g., pentachlorobenzene → hexachlorobenzene); steric effects that influence sorption surface area.

In the series of halogenated biphenyls, an increase in retention time is to be expected when the solute surface area increases, which in turn may be caused by increasing the degree of substitution or by varying the halogen in the order F → Cl → Br → I. The surface area of biphenyl (191.3 Å²) is only moderately affected by introducing fluorine substituents, adding approximately 4 Å²/F atom. This introduction of fluorine atoms into biphenyl however decreases the retention index as reported for benzene (Möckel et al., 1987b). Only for decafluorobiphenyl is there a slight increase in retention index (Table I). The fact that decafluorobiphenyl (deca-F) shows a much lower retention behavior ($I_K = 278$) than biphenyl itself ($I_K = 451$)—although its surface is 20% greater—indicates that the fluorine substituents interact with the eluent (MeOH), most probably by forming H bonds. Decafluorobiphenyl itself has no dipole moment, and therefore I_K increases

Table I. Calculated Torsion Angles, Molecular Surface Areas, and Measured Retention Times in HPLC and GC for Selected Polyfluorinated Biphenyls

subst	torsion angle,° deg	SA, Å	HPLC		GC	
			ret time, min	I_K	ret time, min	I_K
2	49 [1]	194.3	4.01	367	5.67	1627.1
3	45 [2]	195.8	4.04	382	6.08	1654.2
4	45 [2]	195.8	4.02	370	6.05	1651.0
2,3	49 [2]	198.8	3.98	355	6.42	1672.3
2,4	45 [2]	198.8	3.85	304	5.38	1604.3
2,5	45 [2]	198.8	3.83	295	5.82	1636.1
2,6	65 [2]	197.4	3.68	223	5.62	1622.2
3,4	45 [2]	200.3	3.95	347	5.43	1609.0
3,5	45 [2]	200.3	4.04	382	5.57	1636.1
4,4'	45 [2]	200.3	3.68	227	6.62	1684.3
2,4,6'	55 [2]	201.9	3.69	228	4.75	1557.7
2,3,5,6	55 [2]	210.1	3.66	212	5.88	1639.4
deca	45 [2]	229.9	3.78	278	4.65	1550.5

^aKey: [1] Dynes et al. (1985); [2] authors' evaluation; [3] Field et al. (1985); [4] McKinney and Singh (1981).

Table II. Calculated Torsion Angles, Molecular Surface Areas, and Measured Retention Times in HPLC and GC for Selected Polychlorinated Biphenyls

subst	torsion angle,° deg	SA, Å	HPLC		GC	
			ret time, min	I_K	ret time, min	I_K
2	62 [1]	206.7	4.18	442	7.14	1717.0
3	47 [1]	209.3	4.63	578	9.32	1844.6
4	50 [1]	209.6	4.46	521	9.45	1852.5
2,3	72 [1]	224.6	4.53	540	11.45	1956.8
2,4	68 [1]	225.2	4.78	605	10.28	1897.5
2,5	60 [1]	224.1	4.56	559	10.35	1900.0
2,6	82 [1]	224.8	4.13	415	9.12	1831.7
3,4	49 [1]	225.4	5.17	706	13.78	2082.5
4,4'	50 [1]	227.4	4.69	583	14.32	2113.2
2,3,4	72 [2]	241.1	5.36	732	15.50	2169.6
2,4,5	60 [2]	240.9	5.86	817	14.02	2097.7
2,4,6	78 [1]	239.4	5.21	700	11.37	1951.8
3,4,5	62 [2]	242.3	6.40	891	17.53	2277.8
2,3,4,5	70 [2]	255.4	7.05	978	18.68	2338.7
2,3,4,6	85 [2]	257.2	5.96	832	16.38	2209.4
2,3,5,6	85 [2]	256.5	5.72	794	16.22	2202.9
2,2',4,4'	68 [2]	258.0	5.12	682	16.92	2240.5
3,3',4,4'	47 [3]	259.3	5.94	871	23.52	2632.1
2',3,3',4,5	72 [2]	274.9	7.09	982	24.45	2669.6
2,2',4,4',5,5'	69 [1]	290.2	7.04	977	24.28	2661.6
2,2',4,4',6,6'	87 [4]	292.7	6.36	916	26.35	2784.4
deca	85 [2]	393.3	15.54	1523	34.40	3253.7

^aKey: [1] Dynes et al. (1985); [2] authors' evaluation; [3] Field et al. (1985); [4] McKinney and Singh (1981).

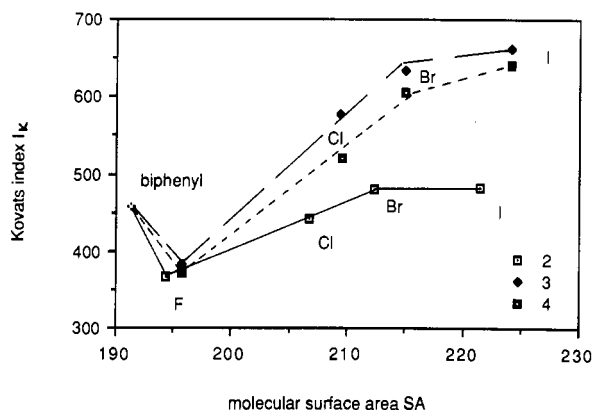


Figure 1. Relationship between molecular surface area and retention index in HPLC of monohalogenated biphenyls.

from 9 to 10 F atoms. Introduction of the heavier halogen atoms leads to larger changes—usually positive—in retention times (Tables II–IV).

Only 2-Cl and 2,6-Cl show lower I_K values than biphenyl itself. Apparently here the increase in surface area is overcompensated for by their high dipole moments. In contrast 3-Cl and 4-Cl exhibit a positive I_K .

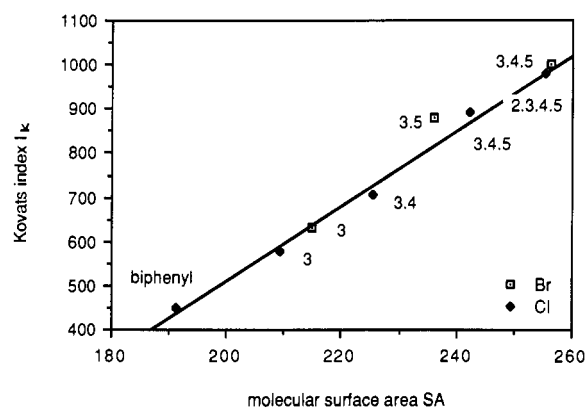


Figure 2. Relationship between molecular surface area and retention index in HPLC of several 3-X-substituted chlorinated and brominated biphenyls ($I_K = -1183 + 8.47SA$, $r = 0.998$).

Generally the highest retention times can be observed for 3-monohalogenated (meta substituted) and the lowest for 2-monohalogenated (ortho substituted) biphenyls (Figure 1).

The relation $I_K(3\text{-X-biphenyl})/I_K(2\text{-X-biphenyl})$ increases from 1.04 for X = F to 1.37 for X = I, although the

Table III. Calculated Torsion Angles, Molecular Surface Areas, and Measured Retention Times in HPLC and GC for Selected Polybrominated Biphenyls

subst	torsion angle, ^a deg	SA, Å	HPLC		GC	
			ret time, min	I_K	ret time, min	I_K
2	68 [2]	212.3	4.38	480	8.37	1791.7
3	47 [2]	214.9	4.95	633	11.25	1946.9
4	52 [2]	214.9	4.84	606	11.47	1959.4
2,3	75 [2]	234.6	4.91	624	14.67	2129.0
2,4	70 [2]	236.1	5.40	728	13.65	2075.7
2,5	60 [2]	234.5	5.06	669	13.65	2072.7
2,6	85 [2]	235.3	4.37	494	11.82	1975.5
3,4	50 [2]	236.1	5.53	761	18.10	2307.3
3,5	60 [2]	239.5	6.30	882	16.30	2210.5
4,4'	50 [2]	239.2	5.28	703	18.68	2340.6
2,4,5	80 [2]	257.7	6.60	923	19.60	2383.1
2,4,6	80 [2]	258.2	5.96	832	16.52	2221.5
3,4,5	62 [2]	256.2	7.25	1000	23.70	2640.3
2,3,4,5	80 [2]	276.2	7.75	1053	26.45	2792.2
2,3,4,6	80 [2]	276.5	6.73	939	23.53	2629.8
3,3',4,4'	47 [3]	280.1	7.21	996	31.28	3124.2
3,3',5,5'	59 [2]	286.5	12.58	1031	28.12	2907.1
3,3',4,4',5,5'	50 [2]	321.8	12.93	1365		

^aKey: [1] Dynes et al. (1985); [2] authors' evaluation; [3] Field et al. (1985); [4] McKinney and Singh (1981).

Table IV. Calculated Torsion Angles, Molecular Surface Areas, and Measured Retention Times in HPLC and GC for Three Monoiodinated Biphenyls

subst	torsion angle, ^a deg	SA, Å	HPLC		GC	
			ret time, min	I_K	ret time, min	I_K
2	80 [2]	221.4	4.35	483	9.54	1857.9
3	45 [2]	224.1	5.03	663	13.50	2062.3
4	45 [2]	224.1	6.40	640	13.72	2081.5

^aKey: [1] Dynes et al. (1985); [2] authors' evaluation; [3] Field et al. (1985); [4] McKinney and Singh (1981).

SA values for these compounds are very similar. Figure 1 shows I_K as a function of SA. It is obvious that monoiodinated biphenyls have smaller I_K values than expected, probably due to the polarization of iodine, which leads to stronger interaction with the eluent. For biphenyl, 3-Cl, 3-Br, 3,4-Cl, 3,5-Br, 3,4,5-Cl, and 3,4,5-Br a linear correlation between I_K and SA values is seen ($I_K = 1254 + 8.8TSA$) with a correlation factor $r = 0.996$ (Figure 2).

The other homologues, especially those with substituents in the C-2 or C-6 positions, have lower I_K values (Figure 3). In the series biphenyl (bp), 3-Br, 3,5-Br, and 3,4,5-Br the addition of each bromine atom leads to a regular increase in I_K of 180. In contrast, additional bromine substituents in the second benzene ring lead to much smaller I_K values: 4-Br \rightarrow 4,4'-Br, $\Delta I_K = 97$; 3,5-Br \rightarrow 3,3',5,5'-Br ($\Delta I_K = 149$) (Table III). This effect is probably not limited to bromine and may also be responsible for the relatively low retention behavior of decachlorobiphenyl.

GC Data. Retention times of fluorinated biphenyls on the semipolar DB-210-CB phase are similar to those of biphenyl itself (Table I). Even perfluorination decreases the Kovats index by only 5% from 1624 to 1550.5. Biphenyls substituted with Cl, Br, and I atoms exhibit much greater increases in retention behavior (Tables II-IV): 3,3',4,4'-Cl, $I_K = 2632.1$; 3,3',4,4'-Br, $I_K = 3124.0$.

Substituents on C-4 and C-4' show the strongest effects. This has been also described for PBBs (Robertson et al., 1984). Excellent correlations between I_K and SA values are observed for mono- as well as polysubstituted biphenyls (Figure 4).

In conclusion, the analytical data reported here provide the necessary basis for an unambiguous analytical determination of the investigated polyhalogenated biphenyls in complex mixtures, e.g. environmental samples. The observed good correlation (except the fluorinated biphenyls) between I_K and SA values allows the prediction

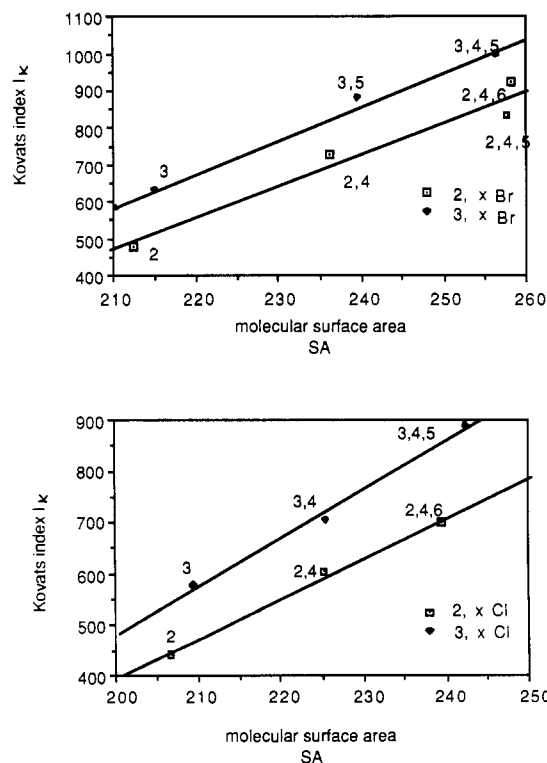


Figure 3. Relationship between molecular surface area and retention index in HPLC: (bottom) 2-X- and 3-X-substituted chlorinated biphenyls ($I_K = -1193 + 7.93SA$, $r = 0.997$; $I_K = -1418 + 9.51x$, $r = 0.996$); (top) 2-X- and 3-X-substituted brominated biphenyls ($I_K = -1328 + 8.62SA$, $r = 0.984$; $I_K = -1289 + 8.98x$, $r = 0.999$).

of the SA value purely on the basis of the retention times. From these values a reasonably good guess can be made

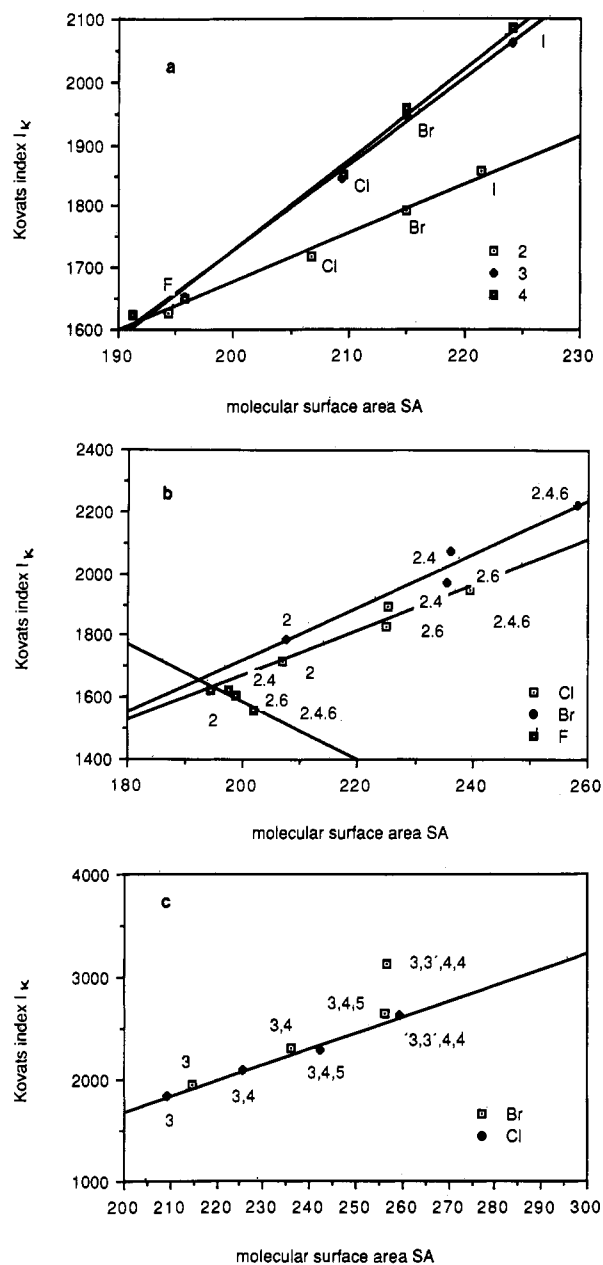


Figure 4. Relationship between molecular surface area and retention index in GC: (a) monohalogenated biphenyls (2, $I_K = 109 + 7.85SA$, $r = 0.993$; 3, $I_K = -1036 + 13.82SA$, $r = 0.998$; 4, $I_K = -1172 + 14.52SA$, $r = 0.998$); (b) 2-X-substituted fluorinated, chlorinated, and brominated biphenyls (F, $I_K = 3438 - 9.32SA$, $r = 0.924$; Cl, $I_K = 219 + 7.32SA$, $r = 0.963$; Br, $I_K = 251 + 8.52SA$, $r = 0.984$); (c) 3-X-substituted chlorinated and brominated biphenyls ($I_K = -1384 + 15.35SA$, $r = 0.993$).

about the structures of unknown compounds.

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Registry No. 2-F-BP, 321-60-8; 3-F-BP, 2367-22-8; 4-F-BP, 324-74-3; 2,3-F-BP, 67277-32-1; 2,4-F-BP, 37847-52-2; 2,5-F-BP, 67277-34-3; 2,6-F-BP, 2285-29-2; 3,4-F-BP, 67277-33-2; 3,5-F-BP, 62351-48-8; 4,4'-F-BP, 398-23-2; 2,4,6'-F-BP, 115245-05-1; 2,3,5,6-F-BP, 834-89-9; 2,2',3,3',4,4',5,5',6,6'-F-BP, 434-90-2; 2-Cl-BP, 2051-60-7; 3-Cl-BP, 2051-61-8; 4-Cl-BP, 2051-62-9; 2,3-Cl-BP, 16605-91-7; 2,4-Cl-BP, 33284-50-3; 2,5-Cl-BP, 34883-39-1; 2,6-Cl-BP, 33146-45-1; 3,4-Cl-BP, 2974-92-7; 4,4'-Cl-BP, 2050-68-2; 2,3,4-Cl-BP, 55702-46-0; 2,4,5-Cl-BP, 15862-07-4; 2,4,6-Cl-BP, 35963-92-6; 3,4,5-Cl-BP, 53555-66-1; 2,3,4,5-Cl-BP, 33284-53-6; 2,3,4,6-Cl-BP, 54230-22-7; 2,3,5,6-Cl-BP, 33284-54-7; 2,2',4,4',

Cl-BP, 2437-79-8; 3,3',4,4'-Cl-BP, 32598-13-3; 2',3,3',4,5-Cl-BP, 76842-07-4; 2,2',4,4',5,5'-Cl-BP, 35065-27-1; 2,2',4,4',6,6'-Cl-BP, 33979-03-2; 2,2',3,3',4,4',5,5',6,6'-Cl-BP, 2051-24-3; 2-Br-BP, 2052-07-5; 3-Br-BP, 2113-57-7; 4-Br-BP, 92-66-0; 2,3-Br-BP, 115245-06-2; 2,4-Br-BP, 53592-10-2; 2,5-Br-BP, 57422-77-2; 2,6-Br-BP, 59080-32-9; 3,4-Br-BP, 60108-72-7; 3,5-Br-BP, 16372-96-6; 4,4'-Br-BP, 92-86-4; 2,4,5-Br-BP, 115245-07-3; 2,4,6-Br-BP, 59080-33-0; 3,4,5-Br-BP, 115245-08-4; 2,3,4,5-Br-BP, 115245-09-5; 2,3,4,6-Br-BP, 115245-10-8; 3,3',4,4'-Br-BP, 77102-82-0; 3,3',5,5'-Br-BP, 16400-50-3; 3,3',4,4',5,5'-Br-BP, 60044-26-0; 2-I-BP, 2113-51-1; 3-I-BP, 20442-79-9; 4-I-BP, 1591-31-7; Cl₂, 7782-50-5; Br₂, 7726-95-6; I₂, 7553-56-2; F₂, 7782-41-4.

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