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RETENTION INDICES OF BIPHENYLS AND DIPHENYLALKANES

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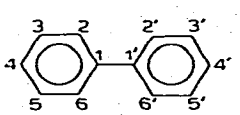
SUMMARY

The retention indices of biphenyl and all isomeric methyl-, ethyl-, isopropyl- and dimethylbiphenyls and those of several diisopropylbiphenyls, diphenylalkanes and stilbenes were measured on three capillary columns with Apiezon L, polyphenyl ether and SP 1000 at temperatures of 170, 185 and 200°.

The position of substitution has the greatest influence, while the influence of the size of the substituents is secondary. An equation that enables the retention indices (I) of polysubstituted homologues to be estimated is proposed. The relationship between the position of a substituent and the H'-factor, compound structure and I value is discussed. A plot of the dependence of I on a non-polar phase showed the consistency of the chromatographic data and served for the estimation of the I values of several biphenyl homologues.

INTRODUCTION

Studies of the chromatographic behaviour of biphenyl-type hydrocarbons are concerned with theoretical, analytical and applicational aspects. Biphenyl can also be considered as a substituted benzene compound, and there are certain analogies in the behaviour of the two substances. On the other hand, only the biphenyl system involves the free rotation of two phenyl rings around a connecting bond, and the substitution of an alkyl group on the biphenyl molecule affects the mutual positions of the two rings. The sterically sensitive positions 2-, 6-, 2'- and 6'- are especially interesting in this respect. In gas–liquid chromatography (GLC), the substitution of a methyl group on these positions causes only a minor change in the retention time[1,2]. The increment per methyl group in a *meta*-position is comparable with the increment per carbon atom in the case of *n*-paraffins. For *para*-substitution, the figure is higher.



The analysis of biphenyls is of particular interest when they are identified in various hydrocarbon mixtures such as petroleum fractions, tars and petrochemical residues and intermediates[3–10]. In such materials they are usually accompanied by hydrocarbons of other types, which must be removed to some extent before GLC.

In this paper, the relationship between the structures and elution data of biphenyl, three isomeric methylbiphenyls, three ethylbiphenyls, three isopropylbiphenyls, all twelve dimethylbiphenyls, diphenylmethane, three methyldiphenylmethanes, two diphenylethanes and some stilbenes are considered.

EXPERIMENTAL

Chromatographic data were measured on three capillary columns with different polarities for aromatic hydrocarbons, expressed by means of McReynolds constants[11]. The stationary phase had to be resistant to operating temperatures of 170–200°, and possibly even higher. As the phase of lowest polarity, Apiezon L was chosen (McReynolds constant measured for benzene, $X' = 32$; maximum temperature, 250°), the phase of medium polarity was polyphenyl ether (5 rings) ($X' = 176$; maximum temperature, 200°) and the most polar phase was SP 1000 ($X' = 332$; maximum temperature, 275°)[12].

Apparatus

The standard Chrom 2 apparatus (Laboratorní Přístroje, Prague, Czechoslovakia) with flame-ionization detection was used, with nitrogen as the carrier gas. All analyses were carried out isothermally on stainless-steel capillary columns, length 50 m, I.D. 0.25 mm. A 1-μl Hamilton syringe was used for injection.

The operating conditions for the column with Apiezon L (Metropolitan-Vickers, Great Britain) were as follows: temperature, 170° and nitrogen flow-rate 0.42 ml/min; 185° and nitrogen flow-rate 0.33 ml/min; and 200° and nitrogen flow-rate 0.25 ml/min; the column efficiency was 55 000 theoretical plates. The operating conditions for the column with polyphenyl ether (5 ring) (Consol. Vac. Co.) were as follows: temperature 170° and nitrogen flow-rate 0.38 ml/min; 185° and nitrogen flow-rate 0.33 ml/min; and 200° and nitrogen flow-rate 0.25 ml/min; the column efficiency was 75 000 theoretical plates. The operating conditions for the column with SP 1000 (Supelco, Bellefonte, Pa., U.S.A.) were as follows: temperature 170° and nitrogen flow-rate 0.51 ml/min; and 185° and nitrogen flow-rate 0.34 ml/min; the column efficiency was 70 000 theoretical plates.

Most of the hydrocarbons of the biphenyl and diphenylmethane series were prepared in our laboratory[13,14]. 1,2-Diphenylethane was prepared by the hydrogenation of *trans*-stilbene. The stilbenes were of commercial origin, *viz.*, *trans*-stilbene (Lachema, Brno, Czechoslovakia), *cis*-stilbene (K & K Labs., Plainview, N.Y., U.S.A.) and α-methylstilbene (Koch-Light, Colnbrook, Great Britain).

Procedure

In order to measure the retention indices, seven mixtures of standards were prepared so as to have the individual components well separated chromatographically on all phases and at all temperatures. *n*-Paraffins with retention times corresponding to the given mixture and column used were added to the mixtures. The Kováts reten-

tion indices were calculated from the results of three measurements corrected for the column dead volume determined from the retention time of methane. The calculations were carried out using a Hewlett-Packard 9100 A electronic calculator. The reproducibility of the retention indices varied within a range of one unit for the Apiezon L and polyphenyl ether columns and within a range of three units for the SP 1000 column.

RESULTS AND DISCUSSION

The retention indices measured are shown in Table I. It is clear that the retention indices of biphenyls are predominantly influenced by the position of substitution, while the influence of the size of the substituents is secondary. The first compounds

TABLE I

RETENTION INDICES

Compound	*Symbol*	*Apiezon L*			*Polyphenyl ether*			*SP 1000*	
		200	*185*	*170*	*200*	*185*	*170*	*185*	*170*
Biphenyl	BP	1475	1459	1446	1737	1719	1705	2078	2029
2-Methylbiphenyl	2-MBP	1464	1449	1438	1709	1694	1683	2000	1960
3-Methylbiphenyl	3-MBP	1571	1556	1545	1833	1812	1801	2167	2120
4-Methylbiphenyl	4-MBP	1587	1570	1558	1845	1824	1811	2182	2134
2,3-Dimethylbiphenyl	2,3-DMBP	1588	1574	1562	1842	1827	1811	2137	2100
2,4-Dimethylbiphenyl	2,4-DMBP	1569	1556	1545	1813	1800	1784	2100	2063
2,5-Dimethylbiphenyl	2,5-DMBP	1557	1544	1535	1800	1788	1774	2086	2050
2,6-Dimethylbiphenyl	2,6-DMBP	1489	1477	1465	1721	1705	1693	1983	1948
3,4-Dimethylbiphenyl	3,4-DMBP	1713	1697	1683	1981	1962	1946	2324	2279
3,5-Dimethylbiphenyl	3,5-DMBP	1667	1652	1641	1928	1912	1898	2252	2211
2,2′-Dimethylbiphenyl	2,2′-DMBP	1471	1458	1446	1700	1685	1671	1950	1916
2,3′-Dimethylbiphenyl	2,3′-DMBP	1548	1536	1526	1797	1780	1768	2074	2037
2,4′-Dimethylbiphenyl	2,4′-DMBP	1570	1556	1546	1818	1800	1787	2100	2061
3,3′-Dimethylbiphenyl	3,3′-DMBP	1669	1655	1642	1928	1910	1895	2254	2212
3,4′-Dimethylbiphenyl	3,4′-DMBP	1683	1668	1656	1941	1922	1906	2267	2224
4,4′-Dimethylbiphenyl	4,4′-DMBP	1697	1681	1669	1952	1933	1916	2281	2236
2-Ethylbiphenyl	2-EBP	1513	1500	1488	1757	1743	1729	2033	1994
3-Ethylbiphenyl	3-EBP	1647	1633	1621	1909	1892	1877	2234	2190
4-Ethylbiphenyl	4-EBP	1678	1661	1647	1938	1920	1903	2268	2220
2-Isopropylbiphenyl	2-IPBP	1524	1512	1500	1763	1750	1738	2015	1980
3-Isopropylbiphenyl	3-IPBP	1687	1671	1660	1939	1923	1909	2244	2204
4-Isopropylbiphenyl	4-IPBP	1730	1713	1700	1986	1968	1953	2300	2255
3,5-Diisopropylbiphenyl	3,5-DIPBP				2077	2066			
3,3′-Diisopropylbiphenyl	3,3′-DIPBP				2132	2119			
3,4′-Diisopropylbiphenyl	3,4′-DIPBP				2191	2175			
4,4′-Diisopropylbiphenyl	4,4′-DIPBP				2239	2223			
Diphenylmethane	DPM	1503	1488	1477	1774	1756	1745	2092	2047
2-Methyldiphenylmethane	2-MDPM	1601	1583	1570	1868	1850	1835	2179	2135
3-Methyldiphenylmethane	3-MDPM	1591	1576	1565	1862	1847	1834	2168	2128
4-Methyldiphenylmethane	4-MDPM	1611	1594	1582	1876	1859	1844	2185	2144
1,1-Diphenylethane	1,1-DPE	1548	1532	1522	1818	1800	1790	2116	2074
1,2-Diphenylethane	1,2-DPE	1593	1576	1563	1862	1841	1827	2171	2126
1,4-Diphenylbutane	1,4-DPBu	1810	1793	1780	2085	2066	2052	2398	2355
trans-Stilbene	*t*-ST	1803	1784		2109	2088	2071	2547	
cis-Stilbene	*c*-ST	1585	1570		1866	1847	1832	2205	
α-Methylstilbene	α-MST	1776	1760		2071	2053	2038	2446	

to be eluted are the *ortho*-substituted biphenyls, followed by the *meta*-substituted and finally the *para*-substituted derivatives. As with benzenes substituted in adjacent positions[15], the elution time of analogous biphenyls is prolonged: in the dimethylbiphenyl series in which one substituent is in the *ortho*-position, the longest elution time is that of 2,3-dimethylbiphenyl. Of the *meta*- and *para*-substituted derivatives, 3,4-dimethylbiphenyl is eluted last. The number of biphenyl homologues eluted before biphenyl itself increases with increase in phase selectivity. On the Apiezon L column, only 2-methylbiphenyl has a shorter elution time than biphenyl on polyphenyl ether. 2,2'-dimethylbiphenyl and 2,6-dimethylbiphenyl are also eluted before biphenyl, and on SP 1000, 2-ethylbiphenyl, 2-isopropylbiphenyl and 2,3'-dimethylbiphenyl are further eluted before biphenyl.

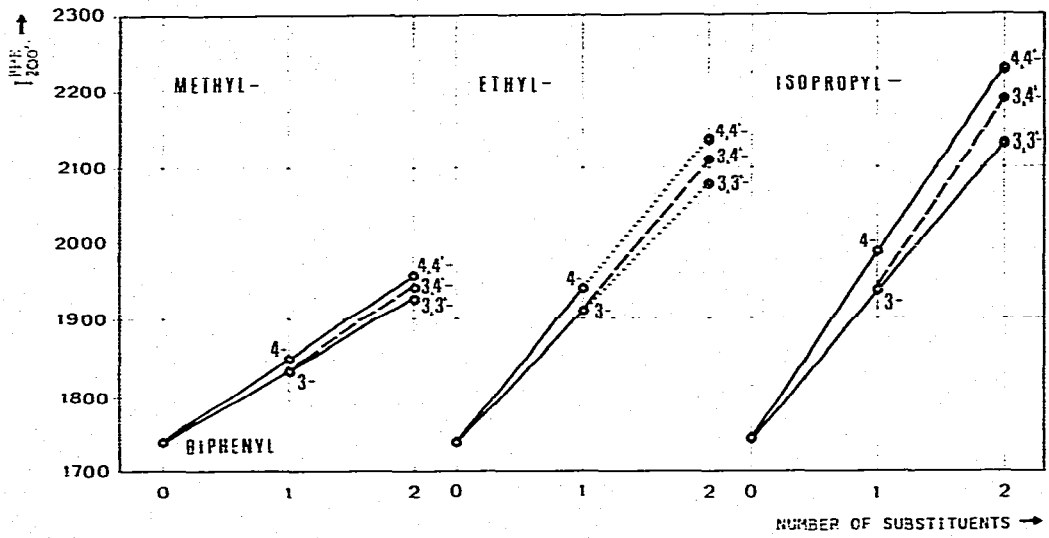


Fig. 1. Plot of retention indices *versus* number of substituents.

An interesting relationship follows from the plot of retention indices as a function of the number of carbon atoms in the substituent alkyl groups, in the modified form of a plot of the dependence of retention indices on the number and size of the substituents (Fig. 1). This plot shows a linear dependence of retention times on the number of substituents for *meta*- and *para*-substituted biphenyls, which can be expressed in general terms by the following equation:

$$I_{X_i} = k \cdot p + I_{BP} \qquad (1)$$

where

I_{X_i} = retention index of mono-substituted biphenyls in position 3 or 4 and of biphenyls substituted on both rings in positions 3,3' or 4,4';
I_{BP} = retention index of biphenyl;
k = slope of the straight line;
p = number of substituents.

The equation can be used, for example, to calculate the retention indices of *meta*- and *para*-substituted biphenyls if the retention index of biphenyl and of its mono-substituted derivative is known. In this case the equation is transformed into:

$$I_{X_1} = 2\,(I_{X_2} - I_{BP}) + I_{BP} = 2\,I_{X_1} - I_{BP} \qquad (2)$$

where I_{X_1} and I_{X_2} are the retention indices of mono- or disubstituted biphenyls, respectively. The mean deviation of the retention index measured from the value calculated is 2 for dimethylbiphenyls and 6 for diisopropylbiphenyls, for all columns and temperatures.

3,4'-Disubstituted biphenyls are eluted approximately mid-way between the homologues substituted in positions 3,3'- and 4,4'- and for a given column, this position is a function of the temperature. When a column with polyphenyl ether was operated at 200°, the difference between the retention indices for the pairs 4-methylbiphenyl–3-methylbiphenyl and 4,4'-dimethylbiphenyl–3,4'-dimethylbiphenyl was the same, and the straight line passing through points 3-MBP and 3,4'-DMBP is thus parallel to the line connecting 4-MNP and 4,4'-DMBP (Fig. 1). The retention index of the 3,4'-disubstituted derivative can then be expressed analytically by the equation

$$I_{3,4'} = I_{4,4'} - (I_4 - I_3) \qquad (3)$$

and applying eqn. 2 adjusted for calculating $I_{4,4'}$ disubstituted:

$$I_{4,4'} = 2\,I_4 - I_{BP} \qquad (2a)$$

eqn. 3 is transformed into

$$I_{3,4'} = I_4 + I_3 - I_{BP} \qquad (4)$$

Eqn. 4 also contains eqn. 2 and can be used to estimate the retention indices of 3,4'-disubstituted biphenyls. The average deviation of the actually measured retention index from the calculated value over all columns and temperatures for 3,4'-dimethylbiphenyl is 2. The average deviation of the calculation of the retention index of 3,4'-diisopropylbiphenyl at two temperatures on a column of polyphenyl ether is 3.5. Eqn. 4 can also be used for the estimation of the retention indices of multi-substituted biphenyls or of biphenyls with different substituents according to the expression

$$I_{RS} = I_R + I_S - I_{BP}$$

where I_R, I_S and I_{RS} are retention indices of biphenyls with a substituent R in one ring only, a substituent S in one ring only and a substituent R in one ring and S in the other ring, respectively.

Variation of the retention index with temperature

The changes in retention indices with temperature are shown in Table II for the hydrocarbons studied on all three stationary phases. The values denoted by $\delta I/10°$ characterize the increase in the retention index with a 10° increase in temperature. The $\delta I/10°$ values increase with increasing selectivity of the stationary phase: the increment I for biphenyl on Apiezon L is 9.7 and on polyphenyl ether 10.8; the

TABLE II

VARIATION OF RETENTION INDEX WITH TEMPERATURE

Compound	$\delta I^{API}/10^{-}$	$\delta I^{PPE}/10^{-}$	$\delta I^{SP\ 1000}/10^{-}$
Biphenyl	9.7	10.7	32.7
2-Methylbiphenyl	8.7	8.7	26.7
3-Methylbiphenyl	8.7	10.7	31.3
4-Methylbiphenyl	9.7	11.3	32.0
2,3-Dimethylbiphenyl	8.7	10.3	24.7
2,4-Dimethylbiphenyl	8.0	9.7	24.7
2,5-Dimethylbiphenyl	7.3	8.7	24.0
2,6-Dimethylbiphenyl	8.0	9.3	23.3
3,4-Dimethylbiphenyl	10.0	11.7	30.0
3,5-Dimethylbiphenyl	8.7	10.0	27.3
2,2'-Dimethylbiphenyl	8.3	9.7	22.7
2,3'-Dimethylbiphenyl	7.3	9.7	24.7
2,4'-Dimethylbiphenyl	8.0	10.3	26.0
3,3'-Dimethylbiphenyl	9.0	11.0	28.0
3,4'-Dimethylbiphenyl	9.0	11.7	28.7
4,4'-Dimethylbiphenyl	9.3	12.0	30.0
2-Ethylbiphenyl	8.3	9.3	26.0
3-Ethylbiphenyl	8.7	10.7	29.3
4-Ethylbiphenyl	10.3	11.7	32.0
2-Isopropylbiphenyl	8.0	8.3	23.3
3-Isopropylbiphenyl	9.0	10.0	26.7
4-Isopropylbiphenyl	10.0	11.0	30.0
3,5-Diisopropylbiphenyl	-	7.3	-
3,3'-Diisopropylbiphenyl	-	8.7	-
3,4'-Diisopropylbiphenyl	-	10.7	-
4,4'-Diisopropylbiphenyl	-	10.7	-
Diphenylmethane	8.7	9.7	30.0
2-Methyldiphenylmethane	10.3	11.0	29.3
3-Methyldiphenylmethane	8.7	9.3	26.7
4-Methyldiphenylmethane	9.7	10.7	27.3
1,1-Diphenylethane	8.7	9.3	28.0
1,2-Diphenylethane	10.0	11.7	30.0
1,4-Diphenylbutane	10.0	11.0	28.7
trans-Stilbene	12.7	12.7	-
cis-Stilbene	10.0	11.3	-
α-Methylstilbene	10.7	11.0	-

highest increment of 32.7 occurs on the SP 1000 column. The variation in *I* with temperature is influenced primarily by the type and position of substitution, the influence of the number of substituents being secondary. For sterically hindered biphenyls substituted on positions 2 and 6, the increment is lower although the order of minimum increments on each of the three phases is not the same. This is valid for the columns of Apiezon L and SP 1000. The largest increment in *I* on SP 1000 is shown by biphenyl, on polyphenyl ether by 4,4'-dimethylbiphenyl and on Apiezon L by 2-methyldiphenylmethane. The highest increments are in general shown by *para*-substituted biphenyls and stilbenes. In individual cases, operation at different temperatures can be used in order to separate certain pairs in small groups. For example, two pairs eluted together at 185°, *i.e.* 3,4'-dimethylbiphenyl–4-ethylbiphenyl and 3-methylbiphenyl–3-methyldiphenylmethane, on a column of SP 1000, show a differ-

ence of 4 and 8 I units, respectively, at 170°. The three methyldiphenylmethanes are well separated on a polyphenyl ether column at 200°. By reducing the temperature, the difference in I between 2-methyldiphenylmethane and 3-methyldiphenylmethane is decreased to such an extent that at 170° the two compounds are eluted together. In general, however, the variations in the retention index increments with temperature are not sufficiently great for the individual hydrocarbons of the biphenyl and diphenylmethane series to be of help in their resolution. For hydrocarbons with condensed rings, higher $\delta I/10°$ variations were found than in the case of aromatic compounds with isolated rings, *i.e.*, biphenyls and diphenylalkanes. This result, which becomes more marked on a column with higher polarity, could be of more substantial use in the analysis of both types of compounds.

Relationship between the substituent position and the H'-factor

The H-factor is defined as the difference between the retention index of the biphenyl and the I value of an n-paraffin with the same number of carbon atoms. If we relate the H-factor to biphenyl, we can write $H'_{BP} = 0$ and obtain the expression

$$H' = H - H_{BP} = I_{BP(z)} - 100\,z - H_{BP}$$
$$= I_{BP(z)} - I_{BP} - 100\,(z - 12) \qquad (5)$$

where z is the number of carbon atoms in the molecule. The H'-factor expresses the change in the retention index of the investigated hydrocarbons brought about by the introduction of an alkyl group into the biphenyl configuration.

The values calculated from eqn. 5 range from +43 to −270 and are listed in Table III in descending order. The H'-factor decreases to such an extent that the biphenyl–stationary phase interaction is weakened in the case of sterically hindered *ortho*-substituted biphenyls. Homologues with most limited rotation of the rings around their connecting bond, resulting from the introduction of either two small alkyl groups or one large alkyl group, have the lowest values. Relatively smaller changes in the H'-factor in the negative sense are caused by the transition from a purely aromatic system to an aliphatic–aromatic system by an increase in the number of alkyl groups or their size. We can assume that the alkyl groups located in *meta*-positions in particular help to reduce the H'-factor in this manner. Only methylbiphenyls and dimethylbiphenyls substituted in *para*-position have positive values. The highest H'-factor occurs with the *ortho*-substituted 3,4-derivative. An increase in the size of the alkyl group has a negative influence on the H'-factor in the case of *para*-substituted derivatives also. In the series 4-methyl-, 4-ethyl- and 4-isopropyl-, its values move from positive through zero to negative. For the hydrocarbons studied, a linear dependence of the H'-factor on the number of substituents occurs, as shown in Fig. 2. The H'-values for diethylbiphenyls were calculated on the basis of retention indices assessed with the help of eqn. 2.

Dependence of ΔI on compound structure

The quantity ΔI is defined as the difference between the retention indices of a substance on a polar and a non-polar phase, or on phases with different selectivities with respect to the eluted substance.

When three columns are used, three combinations of the difference in retention

TABLE III

DEPENDENCE OF H'-FACTOR ON SUBSTITUTION

Results obtained on polyphenyl ether at 185°.

Compound	H'	*Number of aliphatic carbon atoms*	*Position*
3,4-Dimethylbiphenyl	43	2	*m,p*"
4,4'-Dimethylbiphenyl	14	2	*p,p'*
4-Methylbiphenyl	5	1	*p*
3,4'-Dimethylbiphenyl	3	2	*m,p'*
4-Ethylbiphenyl	0	2	*p*
Biphenyl	0	0	—
3-Methylbiphenyl	−7	1	*m*
3,5-Dimethylbiphenyl	−7	2	*m,m*
3,3'-Dimethylbiphenyl	−9	2	*m,m'*
3-Ethylbiphenyl	−27	2	*m*
4-Isopropylbiphenyl	−51	3	*p*
2,3-Dimethylbiphenyl	−92	2	*o,m*"
4,4'-Diisopropylbiphenyl	−96	6	*p,p'*
3-Isopropylbiphenyl	−96	3	*m*
2,4'-Dimethylbiphenyl	−119	2	*o,p'*
2,4-Dimethylbiphenyl	−119	2	*o,p*
2-Methylbiphenyl	−125	1	*o*
2,5-Dimethylbiphenyl	−131	2	*o,m*
2,3'-Dimethylbiphenyl	−139	2	*o,m'*
2-Ethylbiphenyl	−176	2	*o*
2,3'-Diisopropylbiphenyl	−200	6	*m,m'*
2,6-Dimethylbiphenyl	−214	2	*o,o*
2,2'-Dimethylbiphenyl	−234	2	*o o'*
2-Isopropylbiphenyl	−269	3	*o*

" *Vicinal*-substitution.

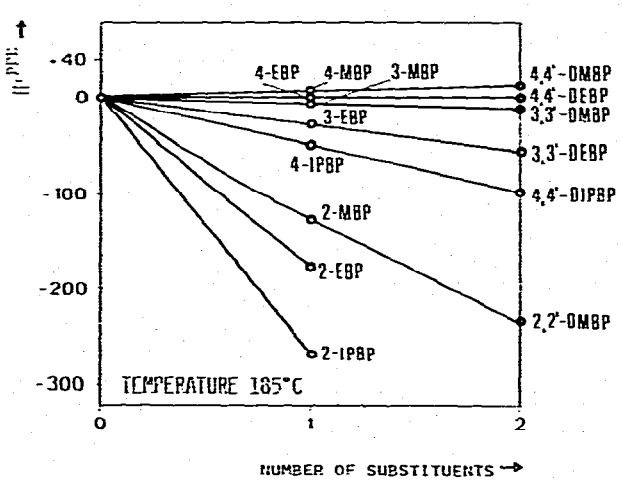


Fig. 2. Dependence of H'-factor on number of substituents for polyphenyl ether columns.

indices are possible at each temperature. At the same time, the values obtained by measuring ΔI for biphenyl at 185° are approximately double the difference in the McReynolds constants (X') for benzene on the individual phases[11]. Thus, for the pair SP 1000–polyphenyl ether, the values are $X' = 156$ and $\Delta I_{\text{biphenyl}} = 359$. For the pair polyphenyl ether–Apiezon L, $X' = 144$ and $\Delta I_{\text{biphenyl}} = 260$. The largest difference in retention indices is encountered on columns with the largest difference in polarity, *i.e.*, SP 1000–Apiezon, where $X' = 300$ and $\Delta I_{\text{biphenyl}} = 619$.

Table IV lists the ΔI values calculated for all three cases at 185°. The order of the individual components according to the decreasing values $\Delta I^{\text{SP 1000–API}}$ and $\Delta I^{\text{SP 1000–PPE}}$ is similar to the order for H'-factors. The *ortho*-substituted derivatives are the lowest, followed by the *meta*-substituted and finally the *para*-substituted derivatives. The ΔI value is also reduced with increasing size of the alkyl group. In the case of the $\Delta I^{\text{PPE–API}}$ values, a relative increase in the ΔI values for *meta*-substituted hydrocarbons was found. The usual order *ortho* < *meta* < *para* alters for methyl derivatives into *ortho* < *para* < *meta*, which is also illustrated in reverse order for

TABLE IV

ΔI VALUES

SP 1000–API L		*SP 1000–PPE*		*PPE–API L*	
Compound	ΔI	*Compound*	ΔI	*Compound*	ΔI
2,2'-DMBP	492	2,2'-DMBP	265	2,2'-DMBP	227
2-IPBP	503	2-IPBP	265	2-IPBP	228
2,6-DMBP	506	2,6-DMBP	278	2,6-DMBP	238
2-EBP	533	2-EBP	290	2-EBP	243
2,3'-DMBP	538	2,3-DMBP	294	2,5-DMBP	244
2,5-DMBP	542	2,5-DMBP	298	2,4-DMBP	244
2,4-DMBP	544	2,4-DMBP	300	2,3'-DMBP	244
2,4'-DMBP	544	2,4'-DMBP	300	2,4'-DMBP	244
2-MBP	551	2-MBP	306	2-MBP	245
2,3-DMBP	563	2,3-DMBP	310	3-IPBP	252
3-IPBP	573	1,1-DPE	316	4,4'-DMBP	252
1,1-DPE	584	3-IPBP	321	2,3-DMBP	253
4-IPBP	587	3-MDPM	321	3,4'-DMBP	254
4-MDPM	591	4-MDPM	326	4-MBP	254
3-MDPM	592	2-MDPM	329	3,3'-DMBP	255
1,2-DPE	595	1,2-DPE	330	4-IPBP	255
2-MDPM	596	4-IPBP	332	3-MBP	256
3,4'-DMBP	599	DPM	336	3-EBP	259
3,3'-DMBP	599	3,5-DMBP	340	4-EBP	259
4,4'-DMBP	600	3-EBP	342	BP	260
3,5-DMBP	600	3,3'-DMBP	344	3,5-DMBP	260
3-EBP	601	3,4'-DMBP	345	4-MDPM	265
DPM	604	4,4'-DMBP	348	1,2-DPE	265
4-EBP	607	4-EBP	348	3,4-DMBP	265
3-MBP	611	3-MBP	355	2-MDPM	267
4-MBP	612	4-MBP	358	DPM	268
BP	619	*c*-ST	358	1,1-DPE	268
3,4-DMBP	627	BP	359	3-MDPM	271
c-ST	635	3,4'-DMBP	362	*c*-ST	277
a-MST	686	*a*-MST	393	*a*-MST	293
t-ST	763	*t*-ST	459	*t*-ST	304

the dimethyl-substituted compounds 4,4'-DMBP < 3,4'-DMBP < 3,3'-DMBP. In this series, diphenylalkanes have the highest $I^{PPE-API}$ values, whereas in the remaining two cases they ranged approximately in the centre of the alkylbiphenyl series. Of the whole series of investigated substances, stilbenes have the highest difference in retention indices on two phases.

Plot of retention indices on two phases

By plotting the retention indices on two different phases, a diagram is obtained that enables, in some instances, minute details in the configuration of the investigated substances to be established[16]. In another case it may serve as an estimate of the retention indices of further members of homologous series[17] or to characterize individual positions of substitution[18].

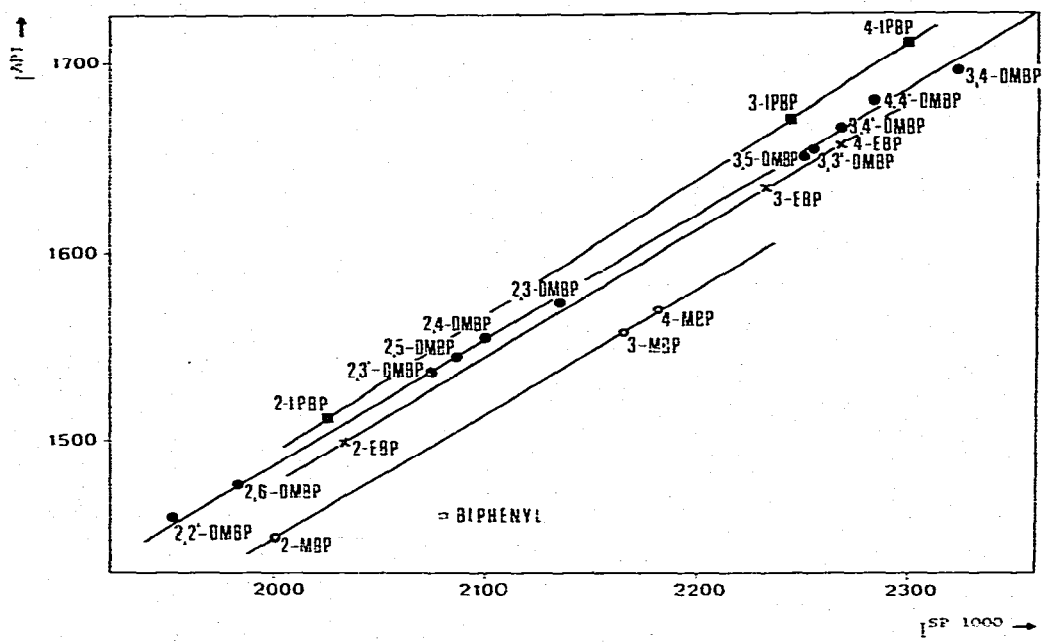


Fig. 3. Plot of retention indices for substituted biphenyls on Apiezon L column *versus* SP 1000 column at 185 °. ○, Methylbiphenyls; ●, dimethylbiphenyls; ×, ethylbiphenyls; ■, isopropylbiphenyls.

A most interesting relationship appears when plotting the retention indices for the Apiezon L column against the I values on the SP 1000 column (Fig. 3). The plot shows a straight-line dependence for biphenyls substituted with the same alkyl group, *i.e.* methyl, ethyl and isopropyl, and of biphenyls substituted with two of the same alkyl group, as in the case of dimethylbiphenyls. Biphenyl, located below the group of straight lines, has a unique position.

The straight lines can be expressed analytically by the following general equation:

$$I^{API} = k \cdot I^{SP\ 1000} - q \qquad (6)$$

where k is the slope of the straight line and q is the intercept on the I^{API} axis.

Both constants were calculated for all straight lines with the help of the method of least squares together with the correlation factor (r), indicating the extent to which the points measured comply with the equation calculated. The values are given in Table V.

TABLE V

PARAMETERS OF RELATIONSHIP I^{API} *versus* $I^{SP\,1000}$ (ACCORDING TO EQN. 6)

Biphenyls	*Slope of the straight line*	*Intercept on the* I^{API} *axis*	*Correlation factor*
Methyl-	0.6544	140.0	0.99961
Dimethyl-	0.6572	174.5	0.99892
Ethyl-	0.6761	125.2	0.99965
Isopropyl-	0.7002	101.0	0.99991

The calculated values listed in Table V show that the angles formed by the straight lines and the axis do not differ by more than 2°. Their distance from the point indicating biphenyl increases with increasing substitution. The plot clearly indicates that for better separation of the individual components, it is advantageous to use a polar column or a column with a high Rohrschneider or McReynolds constant for benzene.

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