

Note

Dispersion and selectivity indices of the halogenated derivatives of cyclohexane, benzene and anisole

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In a recent paper¹ we reported an extension of the Kováts retention index system such that the retention index value may be divided to allow a contribution indicating non-polar dispersion forces, which are largely additive and increase with molecular weight, and a contribution due to polar forces. Such a subdivision highlights the analyte selectively as the polar forces largely determine the effect. Assuming that the apolar forces involved in retention are directly proportional to molecular weight, the retention index may be expressed in the form

$$I = I_m + I^*$$

where I_m is defined as the retention index of a hypothetical n -alkane having the same molecular weight as the analyte, its value being determined by

$$I_m = \frac{M - 2.016}{0.14026}$$

which is an expression that arises from the definition of retention index in terms of the carbon number of a hypothetical n -alkane having the same retention as the analyte, *viz.*, $I = 100i$, where i is the carbon number of a hypothetical n -alkane C_iH_{2i-2} or $(CH_2)_i + 2H$ with molecular weight $M = 14.026i + 2.016$. I_m may be regarded as equivalent to the contribution of London dispersion forces to the overall retention of a solute, assuming that orientation effects are the same as with n -alkanes.

By definition $I_m = I$ for n -alkanes. For all other solutes I need not necessarily be equal to I_m , the difference I^* reflecting the combined effects of molecular shape and functionality. The expressions I^* and I_m have been described as the dispersion and selectivity indices.

It has been shown that, in general, solutes possessing polar functional groups tend to have positive I^* values, whereas substituents with screened electrons yield negative values. Thus the bromo- and iodoalkanes display strongly negative values whereas solutes possessing strong dipoles, such as nitro- and cyanoalkanes, yield

large positive values of I^* . With alkyl- and alkenylbenzenes, extension of the π -electron system increases the selectivity on apolar phases.

Halogen substitution of aliphatic compounds leads to increasingly negative values for I^* , as illustrated by the retentions of chlorinated propionate esters. It has been shown that there is normally a linear relationship between I^* and the number of substituents. The apparent negative selectivity suggests that a proportion of the electrons within the halogen atoms are unable to participate in London dispersion interactions. Similarly, values for I^* are found to become more negative with position in the Periodic Table for Group 6 and Group 7 elements. In each instance the proportion of unavailable or screened electrons would be expected to increase with increasing atomic weight.

In this work we studied the dispersion and selectivity indices for the halogenated derivatives of cyclohexane, benzene and anisole, the results being discussed with reference to earlier work^{1,2}.

EXPERIMENTAL

Gas chromatography was carried out on a Hewlett-Packard 5750 Research gas chromatograph with flame ionization detection. The chromatograph was interfaced with a Vector MZ microcomputer and retention indices were calculated on-line. The dead volume was calculated using the procedure of Grobler and Balizs³.

The columns used were 12 ft. \times $\frac{1}{4}$ in. O.D. packed with 10% of stationary phase coated on Chromosorb G AW DCMS. The hydrocarbon ($C_{87}H_{176}$ and Carbowax 20M columns were operated at 150°C and the tetrakis(2-cyanoethoxy)butane (TCEB) column at 180°C. The carrier gas was helium at a flow-rate of 50 ml/min.

TABLE I
RETENTION INDICES OF CYCLOHALOGENS

<i>Stationary phase</i>	<i>C₈₇H₁₇₆</i> <i>(150°C)</i>	<i>Carbowax 20M</i> <i>(150°C)</i>	<i>Tetrakis(2-cyanoethoxy)butane</i> <i>(180°C)</i>
Benzene	687	971	1336
Fluoro-	680	996	1341
Chloro-	880	1231	1584
Bromo-	974	1351	1737
Iodo-	1088	1504	1917
Cyclohexane	680	740	1143
Fluoro-	735	990	1379
Chloro-	918	1173	1516
Bromo-	1009	1288	1653
Iodo-	1117	1405	1771
Anisole	928	1340	1788
Fluoro-	916	1367	1791
Chloro-	1120	1592	2057
Bromo-	1212	1706	2210
Iodo-	1326	1852	2390

RESULTS AND DISCUSSION

The retention indices of the cyclic compounds on three stationary phases of increasing polar character are shown in Table I, the dispersion (I_m) and selectivity (I^*) indices are shown in Table II and their dependence on position in the Periodic Table is illustrated in Fig. 1.

With several substituted alkanes it has been shown that on a stationary phase of moderate polarity, *i.e.*, OV-17, in general solutes possessing polar functional groups tend towards positive I^* values whereas substituents with screened electrons yield negative results. The bromo- and iodoalkanes show strongly negative values whereas solutes with strong dipoles such as nitro- and cyanoalkanes yield large positive I^* values.

With the cycloalkanes the saturated ring system is free of the influences of π -bonding and is comparable to the corresponding linear alkanes. On the low-polarity base hydrocarbon stationary phase $C_{87}H_{176}$ a decrease in the retention of cyclohexane on addition of a fluorine atom is evident with a reduction in the selectivity index. The chlorine-substituted compound shows a much greater I^* value that is only slightly lower than that of the parent cycloalkane. Bromine and iodine substituents, with greater size and shielding, produce considerable reductions in I^* .

With polar stationary phases the introduction of a fluorine substituent produces an increased I^* value. The increase also occurs with a chlorine substituent with Carbowax 20M and with both chlorine and bromine substituents on the highly polar TCEB phase. After substitution with these halogens decreased I^* values are observed. It is apparent that the influence of the shielding effects are reduced with

TABLE II
DISPERSION (I_m) AND SELECTIVITY INDICES (I^*) OF HALOGENATED CYCLIC COMPOUNDS

The numbers in parentheses indicate the group of data points plotted in Fig. 1.

Compound	I_m	I^*		
		$C_{87}H_{176}$	Carbowax 20M	TCEB
Benzene	542.5	(1) 144.5	(4) 428.5	(7) 793.5
Fluoro-	670.5	9.2	325.2	670.2
Chloro-	780.0	100.0	451.0	804.0
Bromo-	1105.0	-132.0	246.0	632.0
Iodo-	1440.0	-352.0	64.0	477.0
Cyclohexane	585.7	(2) 94.3	(5) 184.3	(8) 557.3
Fluoro-	714.0	21.0	276.0	665.0
Chloro-	831.0	86.8	342.0	685.0
Bromo-	1148.0	-139.0	140.0	505.0
Iodo-	1483.0	-366.4	-78.0	288.0
Anisole	756.6	(3) 171.4	(6) 583.4	(9) 1031.4
Fluoro-	884.9	31.1	482.1	906.1
Chloro-	1002.1	117.8	589.9	1054.9
Bromo-	1319.1	-107.1	386.9	890.9
Iodo-	1654.4	-328.4	197.5	735.5

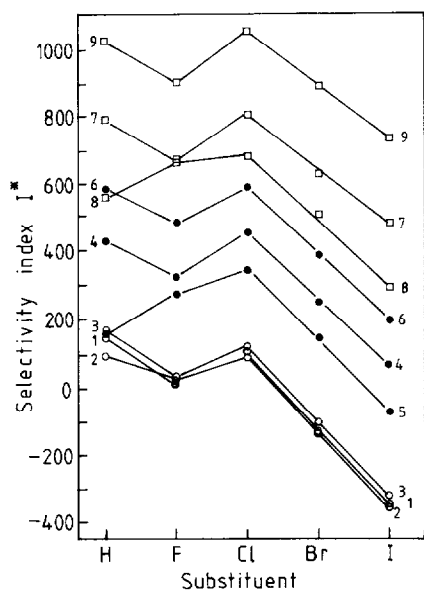


Fig. 1. Relationship between substituent group and selectivity index, I^* . Numbers on plots refer to groups of compounds shown in Table II. (○) $C_{87}H_{176}$; (□) PEG 20M; (●) TCEB.

respect to dipole-dipole interactions with increasing stationary phase polarity, the effects being overcome with the bromine and iodine substituents on the Carbowax 20M and TCEB phases, respectively.

The large increases in the selectivity index of cyclohexane with increasing stationary phase polarity are puzzling, in that they imply that orientation effects can substantially affect the retention of cycloalkanes relative to the corresponding *n*-alkanes. Further studies are now in progress in an attempt to explain these observations and will be reported in a future paper.

With the halogenated benzenes the I^* values are all higher than those of the corresponding cycloalkanes, the effects on the Carbowax 20M and TCEB columns of the aromatic compounds being much greater owing to polar interactions produced by the π bonding system. On the non-polar stationary phases the I^* values follow the same trend as with the cycloalkanes. On the highly polar TCEB column a reduced I^* value is also evident with fluorine substitution, although the maximum value still occurs with chlorobenzene, and I^* is reduced almost linearly with bromo- and iodobenzenes.

The substituted anisole compounds represent an aromatic ring system with a donor substituent group and the I^* values on all three stationary phases are reduced on addition of a fluorine substituent in the *para*-position, increased to a maximum on *para*-chlorine substitution and reduced on the *para*-bromo and iodo substitution. It is particularly evident with the aromatic and anisole compounds that the overall decrease in I^* throughout a series is reduced to a slightly greater extent on the polar stationary phases than with the comparable cycloalkanes.

Preliminary studies have suggested that the selectivity index may be used to compare the efficiencies of derivatization reagents or the selectivity of a particular

TABLE III

COMPARISON OF RETENTION BEHAVIOUR OF CHLORINATED DERIVATIVES AND PARENT HYDROCARBONS

Compound	Stationary phase*					
	$C_{87}H_{176}$		Carbowax 20M		TCEB	
	δI	$\delta I/MW$	δI	$\delta I/MW$	δI	$\delta I/MW$
Benzene						
Fluoro-	135.3	7.12	103.3	5.44	123.3	6.48
Chloro-	44.5	1.25	- 22.5	- 1.18	- 19.5	0.55
Bromo-	276.5	3.46	182.5	2.28	161.5	2.02
Iodo-	396.5	3.12	364.5	2.87	316.5	2.49
Cyclohexane						
Fluoro-	73.3	3.86	- 91.7	- 4.82	- 77.7	- 4.09
Chloro-	7.5	0.21	- 151.7	- 4.45	- 97.7	- 2.76
Bromo-	233.3	2.92	44.3	0.54	82.3	1.03
Iodo-	460.7	3.63	232.2	1.83	299.3	2.36
Anisole						
Fluoro-	140.3	7.38	101.3	5.33	125.3	6.59
Chloro-	53.6	1.53	- 6.5	0.18	- 23.5	- 0.66
Bromo-	288.5	3.61	196.5	2.46	140.5	1.76
Iodo-	499.8	3.94	385.9	3.04	295.9	2.33

* $\delta I = I_{\text{fluorobenzene}} - I_{\text{benzene}}$. MW = Molecular weight of halogen substituent.

substituent with a homologous series. The change in I^* between the parent and the substituted solutes was divided by the molecular weight of the substituent. The results are shown in Table III, where the δI^* values are simply another representation of the effect of I^* as discussed above. The $\delta I^*/MW$ values for the three series of cyclic compounds with the three solvents do not show any particular systematic trend, although the values for the cycloalkanes are each lower than those for the comparable aromatic compounds. The previous indication that the values become more negative and that a nearly linear relationship exists with position in the Periodic Table as shown for several Group 6 and 7 elements is not supported.

Table III provides data additional to those obtained in previous studies in that the first member of the Periodic Group, *i.e.*, fluorine, is considered. An anomaly is expected owing to the difference in orbitals present, *i.e.*, s and p and d, s and p. Similar behaviour is shown with other series in oxygen and sulphur in Group 6. In this work, however, systematic behaviour was not observed with substituents possessing the same electronic configuration.

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