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Note

Dispersion and selectivity indices of alkyl and alkenyl benzenes

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The retention of any substance in chromatography is the result of both apolar and polar forces, moderated by steric factors. Recently Evans *et al.*¹ introduced a modification of the Kováts' retention index system in an attempt to separate the contributions of these two forces.

Assuming that the non-polar forces involved in retention are proportional to molecular weight, Evans *et al.*¹ expressed Kováts' index as the sum of two factors:

$$I = I_m + I^* \quad (1)$$

where I_m (selectivity index) is defined as the retention index of a hypothetical *n*-alkane having the same molecular weight as the solute and I^* is the dispersion index, which reflects the combined effects of molecular shape and functionality.

Since an *n*-alkane has a molecular formula of C_iH_{2i-2} or $(CH_2)_i + 2H$ its molecular weight is $m = 14.026 i + 2.016$. Therefore I_m can be calculated from;

$$I_m = \frac{m - 2.016}{0.14026} \quad (2)$$

where m is the molecular weight of the solute.

In a further paper Evans and Haken² studied the dispersion and selectivity indices for the halogenated derivatives of cyclohexane, benzene and anisole. Their initial results indicated the potential value of these new parameters for the study of molecular structure-retention relationships, the prediction of retention data and the characterisation of stationary phases.

This paper extends this analysis to alkyl- and alkenylbenzenes.

DATA

The retention data used in this paper are reproduced from work reported by Engewald *et al.*³ who used a Hewlett-Packard Model 5840 gas chromatograph and a Varian Moduline 2740 gas chromatograph with a HP3370B digital integrator. The following columns were used: (a) 50 m × 0.3 mm I.D., soda glass, pretreated by high-temperature silanization with hexamethyldisilazane, dynamically coated with




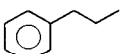
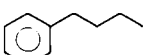
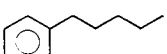
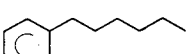
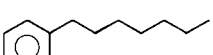
0.5% OV-1; (b) 100 m \times 0.23 mm I.D., soda glass, pretreated by dichloromethane pyrolysis, dynamically coated with 5% Ucon LB 550X.

RESULTS

Table I shows retention data of homologous alkylbenzenes on both a low-polarity (OV-1) phase and one of moderate polarity (LB550X). A consideration of the retention increments (ΔI) show an initial decrease with increasing chain length. However, with butylbenzene an increase occurs and further ΔI values show little variation with alkyl chain length. On both phases the ΔI values level out at approximately 100, giving little insight into the interactions between the homologous series and the stationary phases.

On the other hand, the I^* values show a regular gradual decrease in polar character as the alkyl chain length increases. All the I^* values are positive showing the predominance of the polar interactions produced by the π bonding of the benzene ring. Accepting that most of the I^* contribution is due to the benzene ring, the effect

TABLE I
ANALYSIS OF DATA FROM ENGEWALD *et al.*³, ON ALKYL BENZENES

Compound No.*	Structure	I_m	I_{100}^{OV}	ΔI_{100}^{OV}	I_C	$I_C - I_B$	I_{100}^{LB}	ΔI_{100}^{LB}	I_C	$I_C - I_B$
1		542	664		122		759		217	
2		642	767	103	125	+3	862	103	220	+3
3		742	859	92	117	-5	950	88	208	-9
6		842	950	91	108	-14	1037	87	195	-22
12		942	1047	97	105	-17	1134	97	192	-25
20		1041	1146	99	104	-18	1233	99	191	-26
29		1142	1244	98	102	-20	1332	99	190	-27
32		1242	1342	98	100	-22	-	-	-	-

* Numbers refer to the original numbers used by Engewald *et al.*³.

of the alkyl chain may be gauged by subtraction of I^* for benzene (I^*_B) from the I^* value for the compound (I^*_C). Thus the values shown in Table I as $I^*_C - I^*_B$ confirm the reduction in polar forces with increasing alkyl chain length on both stationary phases. The small negative values show that the effect is small compared to the contributions of the benzene ring.

A comparison of the respective I^* values for LB550X compared to OV-1 clearly indicates the increased polarity of LB550X, as the magnitude of the I^* values are almost double those for OV-1.

Table II shows retention data obtained using homologous series of alkenylbenzenes with terminal unsaturation and 1-phenylalkenes. As with Table I, the ΔI values give little indication of the respective interactions.

Again the positive I^* values indicate the predominance of polar forces in these substances. With the terminal bonded alkenylbenzenes and the *trans*-1-phenylalkenes, there is little variation of I^* values with alkenyl chain length. This indicates that the main influence in both series is the benzene ring and the double bond.

The effect of the double bond can be seen in each series by again calculating $I^*_C - I^*_B$. With the terminally unsaturated alkenylbenzenes, the values are slightly negative (note that ethenylbenzene is not truly a member of the terminal alkenylbenzenes as its double bond is conjugated with the benzene ring). This shows that the double bond has little effect in this position.

The *trans*-1-phenylalkenes on the other hand, show significantly positive values. This can be attributed to the conjugated type bonding existing between the aromatic ring and the alkene double bond.

The *cis*-1-phenylalkenes, however, show significantly different behaviour. The I^* values are again positive, showing the predominance of polar forces. The I^* values, however, decrease with increasing alkenyl chain length. In addition, the $I^*_C - I^*_B$ values decrease from moderately positive values to approximately zero indicating that the polar effect of the conjugated double bond is greatly reduced compared to the *trans*-1-phenylalkenes.

Engewald *et al.*³ postulated that the capability of conjugation between the double bond and aromatic ring is greater for *trans* isomers than for the corresponding *cis* isomers because the steric hindrance between the methylene group in position 3 of the side chain of the *cis* isomers and the α -hydrogen atom of the aromatic ring is stronger than repulsion forces between the hydrogen atoms. This would result in a greater angle between the double bond and the plane of the ring in the case of *cis* isomers and a weaker conjugation effect. Thus the use of I^* values supports the analysis of Engewald *et al.*³.

Comparison of the respective I^* values for LB550X and OV-1 confirm the increased polarity of the LB550X stationary phase.

Recently Evans and Haken⁴ showed that selectivity was constant within several homologous series, within experimental error. Homologous series investigated were aliphatic acetates, alcohols, aldehydes and methyl ketones. The only exception to this constant relationship was the *n*-alkanols on the relatively polar stationary phase PEG400. This deviation was explained as being due to long-range inductive effects.

The *trans*-1-phenylalkenes and the terminally bonded alkenylbenzenes show a similar consistency, although the random variation is larger. With the terminal bonded alkenylbenzenes the variation is most likely a result of the non-planar pre-

ferred conformation of the side chain, where the double bond may interact with the π -electrons of the benzene ring as outlined by Engewald *et al.*³.

The *cis*-1-phenylalkenes, by contrast show a trend from moderately positive I values to values around zero. This can be attributed to steric effects as previously outlined.

Table I shows that the alkylbenzenes also follow a gradual downward trend

TABLE II

ANALYSIS OF DATA FROM ENGEWALD *et al.*³ ON ALKENYLBENZENES AND 1-PHENYLALKENES $f_B = +122$ (OV-1); $f_B = +217$ (LB500X).


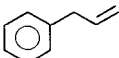
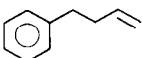
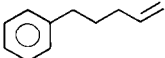
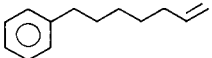

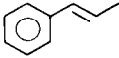
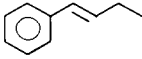
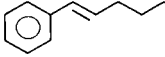
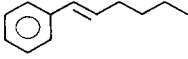
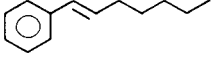




Compound No.	Structure	I_m	I_{100}^{OV}	ΔI_{100}^{OV}	f_C	$f_C - f_B$	I_{100}^B	ΔI_{100}^B	f_C	$f_C - f_B$
<i>(a) Terminal double bonded alkenylbenzenes</i>										
4		728	885		157	+35	1009	—	281	+64
7		828	939	54	111	-11	1044	35	216	-1
16		928	1032	93	104	-18	1137	93	209	-8
25		1028	1140	108	112	-10	1243	106	215	-2
34		1228	1330	≈ 95	102	-19				
<i>(b) trans-1-Phenylalkenes</i>										
4		728	885		157	+35	1009		281	+64
8		828	1019	134	191	+69	1146	137	381	+101
13		928	1112	93	184	+62	1232	86	304	+87
21		1028	1205	93	177	+55	1324	92	296	+79
30		1128	1308	103	180	+58	1425	101	297	+80
32		1228	1400	98	178	+56				

TABLE II (continued)

Compound No.	Structure	I_m	I_{100}^{OV}	ΔI_{100}^{OV}	I_C^*	$I_C - I_B$	I_{100}^{LB}	ΔI_{100}^{LB}	I_C	$I_C - I_B$
(c) <i>cis-1-Phenylalkenes</i>										
4		728	885		157	+35	1009		281	+64
9		828	984	99	156	+34	1095	86	267	+50
22		1028	1155	≈86	127	+5	1258	≈86	230	+13
31		1128	1249	94	121	-1	1353	95	225	+8

in I^* values as the alkyl chain length increases. This can be explained by the moderating effect of the alkyl chain on the π electrons of the benzene ring.

These examples show the significant effect on retention properties of the π electrons in aromatic substituted compounds when compared to aliphatic compounds. It has been shown that the comparison of dispersion indices provides an insight into these structure-retention relationships. In addition the index provides a useful indication of the polarity of the stationary phase.

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