*Journal of Chromatography*, 589 (1992) 231–239
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 719

# Prediction of retention indexes

## IV. Chain branching in alkylbenzene isomers with $C_{10-13}$ alkyl chains identified in a scintillator solvent

C. T. Peng* and R. L. Hua

*Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, CA 94143-0446 (USA)*

D. Maltby

*Mass Spectrometry Research Laboratory and Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, CA 94143 (USA)*

(First received June 18th, 1991; revised manuscript received September 2nd, 1991)

---

ABSTRACT

Twenty solvent components in a commercial scintillator were identified by chromatography on polar and non-polar columns and by gas chromatography–mass spectrometry (GC–MS) as isomeric 1-(alkyl)$_m$(alkyl)$_n$benzenes with formulae $C_{16}H_{26}$, $C_{17}H_{28}$, $C_{18}H_{30}$ and $C_{19}H_{32}$. These isomers occur in four clusters of chromatographic peaks representing *ca.* 6, 44, 34 and 16% of the total solvent mass. The retention indexes of the isomers are influenced by the lengths of the alkyl chains in the molecule, and their polarity and polarizability can affect the column difference, which is the difference between retention indexes on polar and non-polar columns. 1-Methylalkylbenzenes have higher retention indexes and larger column differences than the evenly distributed isomers, such as 1-butylhexyl-, 1-pentylhexyl, 1-pentylheptyl- and 1-pentyloctylbenzene. The results demonstrate the effect of structural symmetry on the retention indexes of the isomers. This study shows that the ability to relate GC data and column differences to structures can facilitate the interpretation of GC–MS data in the structure identification of isomers.

---

INTRODUCTION

The retention index (*I*) of a compound can be predicted from its chemical structure using a quantitative structure–retention index relationship (SRIR) [1,2]. This relationship can also be applied to tentatively identify structures from the retention indexes of unknown chromatographic peaks. According to the SRIR, compounds differing from each other by one carbon atom generally differ in their retention indexes by about 100, but this rule has not been extended to predict the *I* values of isomers containing a constant number of carbon atoms and branched alkyl chains.

Recently, "improved" liquid scintillation cocktails have been introduced by manufacturers to minimize the environmental impact of hydrocarbon solvents. A scan by gas chromatography–mass spectrometry (GC–MS) of the "improved" cocktails was reported to fail to identify the components [3]. Apparently additional analytical data are needed. We found the use of SRIR, *I* and column differences to be useful in facilitating structural identification and this paper reports our findings.

0021-9673/92/$05.00

## EXPERIMENTAL

The liquid scintillator Opti-Fluor was obtained from Packard Instruments (Downers Grove, USA, IL). 1-Phenylalkanes, *n*-alkanes and tributyl phosphate were purchased from Aldrich (Milwaukee, WI, USA).

### *GC analysis*

Dilute solutions of the liquid scintillators in *n*-hexane were analysed on Hewlett-Packard Model 5890 and 5880A gas chromatographs, equipped with thermal conductivity detectors, using non-polar and polar fused-silica capillary columns (30 m × 0.53 mm I.D., film thickness 1.0 μm for DB-Wax and 1.5 μm for DB-1) from J&W Scientific (Folsom, CA, USA). The injector was set at 250°C and the detector at 300°C. The temperature was linearly programmed during the run. The oven temperature was initially at 40°C for 4 min and then increased at 8°C/min to 280°C for the DB-1 and to 200°C for the DB-Wax column. The maximum oven temperature was maintained for 20 min before the run was terminated. A mixture of *n*-alkanes from *n*-hexane to *n*-tricontacosane ($c_6$–$C_{32}$) was used as markers for *I* calculation. *I* was calculated by the equation of Van den Dool and Kratz [4] as reported previously [1,2].

### *GC–MS analysis*

For GC–MS analysis the gas chromatograms were obtained on fused-silica capillary columns (30 m x 0.32 mm I.D.) coated with DB-1 and DB-Wax stationary phases. The temperature program was from 150 to 270°C at 4°C/min for DB-1 from 90 to 230°C at the same rate for DB-wax. Concentration was measured by the total ionization current. These chromatograms are of slightly higher resolution because narrower bore columns were used.

MS was performed on a V670-SE instrument (VG Analytical, Manchester, UK). The instrument was operated in the electron impact (EI) mode. The source temperature was 270°C, the interface temperatures were 280°C, the filament current was 200 μA and the electron energy was 70 eV. The data were acquired by scanning from 30 to 500 dalton at 0.7 s per decade. A V6 Opus Data System was used for data acquisition and processing.

## RESULTS AND DISCUSSION

### *GC analysis*

Sample of Opti-Fluor were chromatographed on DB-1 and DB-Wax fused-silica capillary columns. A single-component analyte can be identified by *I* and column difference ($\Delta I$), the latter being defined as the difference between the *I* values on polar and non-polar columns, and its magnitude reflects the polarity and polarizability of the analyte. Opti-Fluor gave about twenty chromatographic peaks in four clusters, in addition to other peaks. The four peak clusters spanned a region of 368 *I* units from 1526 to 1894 on the non-polar column and a region of 414 *I* units from 1729 to 2143 on the polar column. Their apparent column differences ranged from 200 to 250. On the non-polar column the first cluster contained four closely eluted peaks, and each of the three succeeding clusters contained five closely eluted peaks. These four clusters represent *ca.* 6, 44, 34 and 16% of the total solvent mass. Different fractions of the vacuum distillate of the liquid scintillator showed almost identical peak patterns. The residue in the distillation flask also showed a similar pattern of chromatographic peaks plus a single large peak with an *I* value of 2216 on DB-1 and a column difference of 361, indicating possibly a hydroxylic compound, but no effort was made to identify it further. The toluene extract of the scintillator yielded a peak pattern similar to that of the original liquid scintillator.

Chromatograms of Opti-Fluor on DB-1 and DB-Wax columns obtained by GC—MS analysis are shown in Fig. 1. The presentation of these chromatograms is superior to those from an integrator. All the *I* calculations and column differences were based on chromatograms obtained with the 0.53 mm I.D. column.

A list of aromatic hydrocarbons, their retention indexes on DB-Wax and DB-1 columns and their column differences are given in Table I. The presence of a branched alkyl chain in the aromatic hydrocarbons lowers the column differences. Column differences for the solvent components from Opti-Fluor are estimated to be about 200–250, which is considerably lower than the column differences given for 1-phenylalkanes and other aromatic hydrocarbons. These low column differences, similar to those for isopropylbenzene and *m*-diisopropylbenzene, suggest that the solvent components may be branched-chain alkylbenzenes.

*GC–MS analysis and fragmentation patterns*

The identity of the solvent components was determined by GC–MS. Table II lists the alkylbenzenes and their mass fragments from the GC–MS analysis. The four clusters of alkylbenzenes have the general formulae $C_{16}H_{26}$, $C_{17}H_{28}$, $C_{18}H_{30}$ and $C_{19}H_{32}$. The mass fragmentation data are given in terms of mass peaks ($m/z$) and their relative abundances in Table II.

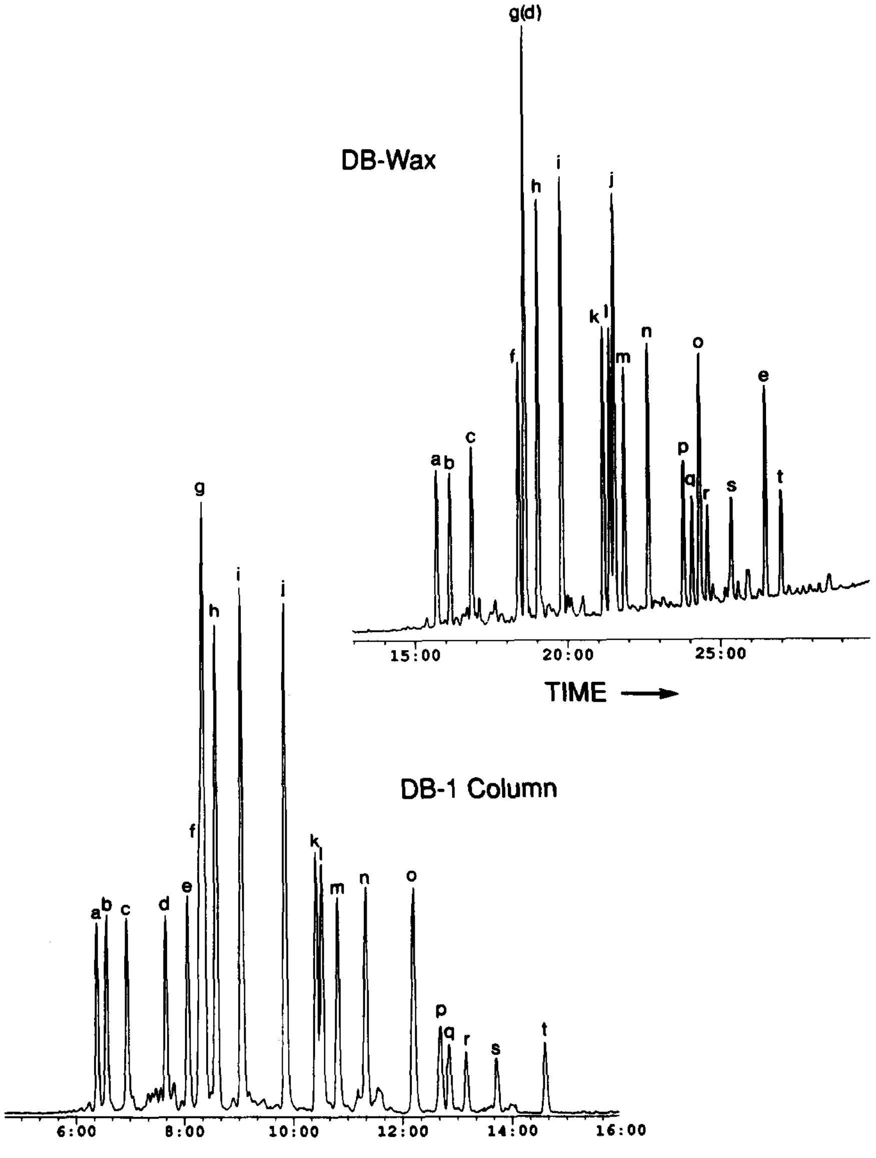

Fig. 1. Chromatograms of solvent components of Opti-Fluor on DB-1 and DB-Wax columns. The peaks on the DB-1 column are identified in Tables II and III. Peaks a–d represent $C_{16}H_{26}$ isomers, f–j $C_{27}H_{28}$ isomers, k–o $C_{18}H_{30}$ isomers and p–t $C_{19}H_{32}$ isomers. On the CB-Wax column, all the peaks follow the same elution pattern as on DB-1, with the exception of peaks d, j, o and t, which have shifted to higher retention indices. Peak d is completely overlapped by peak g on the polar column. Peak e is tributyl phosphate and has a large column difference of 470. Time in min.

TABLE I

RETENTION INDEXES ON POLAR AND NON-POLAR COLUMNS AND COLUMN DIFFERENCES OF SOME ARENES AND 1-PHENYLALKANES

| Compound | Formula | Retention index ($I_{obs}$) | | Column difference ($\Delta I$) |
|---|---|---|---|---|
| | | DB-Wax | DB-1 | |
| *Arenes* | | | | |
| Isopropylbenzene | $C_9H_{12}$ | 1166 | 913 | 253 |
| Cyclopropylbenzene | $C_9H_{10}$ | 1297 | 1010 | 387 |
| *p*-Methylisopropylbenzene | $C_{10}H_{14}$ | 1283 | 1020 | 263 |
| Diethylbenzene | $C_{10}H_{14}$ | 1305 | 1041 | 264 |
| *m*-Diisopropylbenzene | $C_{12}H_{18}$ | 1360 | 1144 | 216 |
| Cyclohexylbenzene | $C_{12}H_{16}$ | 1716 | 1312 | 404 |
| α-Methylnaphthalene | $C_{11}H_1$ | 1896 | 1296 | 600 |
| β-Methylnaphthalene | $C_{11}H_{12}$ | 1932 | 1284 | 648 |
| 1-Phenylbutyronitrile | $C_{11}H_{12}N$ | 2129 | 1304 | 825 |
| Tributyl phosphate | $C_{12}H_{27}O_4P$ | 2075 | 1622 | 453 |
| *n-Alkylbenzenes and 1-phenylalkanes*[a] | | | | |
| Benzene | $C_6H_6$ | 947 | 654 | 293 |
| Toluene | $C_7H_9$ | 1051 | 754 | 287 |
| Ethylbenzene | $C_8H_{10}$ | 1129 | 858 | 271 |
| *n*-Propylbenzene | $C_9H_{12}$ | 1206 | 945 | 261 |
| *n*-Butylbenzene | $C_{10}H_{14}$ | 1306 | 1047 | 259 |
| 1-Phenylhexane | $C_{12}H_{18}$ | 1515 | 1254 | 261 |
| 1-Phenylheptane | $C_{13}H_{20}$ | 1611 | 1348 | 264 |
| 1-Phenyloctane | $C_{14}H_{22}$ | 1715 | 1456 | 259 |
| 1-Phenylnonane | $C_{15}H_{24}$ | 1821 | 1560 | 261 |
| 1-Phenyldecane | $C_{16}H_{26}$ | 1928 | 1664 | 264 |
| 1-Phenyldodecane | $C_{18}H_{30}$ | 2141 | 1870 | 271 |
| 1-Phenyltridecane | $C_{19}H_{32}$ | 2275 | 1978 | 297 |

[a] Linear regression equations for 1-phenylalkanes:
On DB-1: $I = (101.38 \pm 0.57)Z + (41.22 \pm 7.32)$ $(n = 12, R^2 = 0.9997, p = 0.0001)$;
On DB-Wax: $I = (100.74 \pm 1.39)Z + (318.91 \pm 18.00)$ $(n = 12, R^2 = 0.9997, p = 0.0001)$.

The general structure is represented as 1-(alkyl)$_m$(alkyl)$_n$benzene, where $n > m$ and both refer to the number of carbon atoms in the alkyl groups. The value of $m + n$ is 10 for $C_{16}H_{26}$, 11 for $C_{17}H_{28}$, 12 for $C_{18}H_{30}$ and 13 for $C_{19}H_{32}$. In the mass spectra, the mass peaks are those of the molecular ions, phenyl(alkyl)$_{n-1}$, phenyl(alkyl)$_{m+1}$, phenylethyl ($m/z$ 105) and phenylmethyl ($m/z$ 91, 92) ions. In the fragmentation of 1-methyl(alkyl)$_{m+n-1}$ benzenes, the phenylethyl ion is the dominant mass peak but in the fragmentation of all other alkylbenzenes the phenylmethyl ion is dominant. Fragmentation occurs at the marked bonds adjacent to the tertiary carbon atom in the molecule, as shown in Fig. 2.

### *Chain branching and isomers*

The isomers differ in the number of $CH_2$ groups in the two alkyl chains of 1-(alkyl)$_m$(alkyl)$_n$benzenes. The value of $m$ may vary from 1 to $n - 1$ while the value of $m + n$ remains constant. Shifting the $CH_2$ group from the alkyl chain to the short alkyl chain will make the molecule more symmetrical, and the more symmetrical isomer has a lower $I$ value.

Table III lists the $I$ values of 1-(alkyl)$_m$(alkyl)$_n$ benzenes on DB-1 and DB-Wax columns. The chromatographic peaks, shown in Fig. 1, are labeled alphabetically and identified in Table II accordingly to the alphabetical letters listed in the first

TABLE II

MASS FRAGMENTATION DATA FOR 1-(ALKYL)$_m$(ALKYL)$_n$BENZENES

| Peak | Compound | Formula | Mol.wt. | Mass fragments (relative abundance, %)[a] |
|---|---|---|---|---|
| a | 1-Butylhexylbenzene | $C_{16}H_{26}$ | 218 | 91(100), 105(27), 147(50), 161(41), 218(27) |
| b | 1-Propylheptylbenzene | $C_{16}H_{26}$ | 218 | 91(100), 105(18), 133(53), 175(32), 218(26) |
| c | 1-Ethyloctylbenzene | $C_{16}H_{26}$ | 218 | 91(100), 104(23), 119(100), 189(39), 21(32) |
| d | 1-Methylnonylbenzene | $C_{16}H_{26}$ | 218 | 91(38), 105(100), 218(26) |
|  | 1-Decylbenzene[b] | $C_{16}H_{26}$ | 218 | 91(100), 92(98), 105(20), 133(12), 218(66) |
| e | Triethyl phosphate | $C_{12}H_{27}O_4P$ | 266 | 99(100), 155(44), 211(32) |
| f | 1-Pentylhexylbenzene | $C_{17}H_{28}$ | 232 | 91(100), 105(23), 119(10), 161(66), 232(18) |
| g | 1-Butylheptylbenzene | $C_{17}H_{28}$ | 232 | 91(100), 105(82), 147(30), 175(26), 218(12), 232(20) |
| h | 1-Propyloctylbenzene | $C_{17}H_{28}$ | 232 | 91(100), 105(14), 133(76), 189(43), 232(35) |
| i | 1-Ethylnonylbenzene | $C_{17}H_{28}$ | 232 | 91(88), 105(20), 119(100), 203(55), 232(35) |
| j | 1-Methyldecylbenzene | $C_{17}H_{28}$ | 232 | 91(28), 105(100), 106(30), 232(40) |
| k | 1-Pentylheptylbenzene | $C_{18}H_{30}$ | 246 | 91(100), 105(19), 161(32), 175(27), 246(20) |
| l | 1-Butyloctylbenzene | $C_{18}H_{30}$ | 246 | 91(100), 105(16), 147(30), 189(16), 246(10) |
| m | 1-Propylnonylbenzene | $C_{18}H_{30}$ | 246 | 91(100), 105(26), 133(100), 203(53), 246(37) |
| n | 1-Ethyldecylbenzene | $C_{19}H_{30}$ | 246 | 91(100), 119(67), 217(30), 246(22) |
| o | 1-Methylundecylbenzene | $C_{18}H_{30}$ | 246 | 91(29), 105(100), 106(33), 246(37) |
|  | 1-Phenyldodecane[b] | $C_{18}H_{30}$ | 246 | 91(92), 92(100), 105(13), 133(11), 246(45) |
| p | 1-Pentyloctylbenzene | $C_{19}H_{32}$ | 260 | 91(100), 105(16), 161)26), 189(21), 260(16) |
| q | 1-Butylnonylbenzene | $C_{19}H_{32}$ | 260 | 91(100), 147(36), 203(22), 260(15) |
| r | 1-Propyldecylbenzene | $C_{19}H_{32}$ | 260 | 91(100), 105(15), 133(41), 217(23), 260(16) |
| s | 1-Ethylundecylbenzene | $C_{19}H_{32}$ | 260 | 91(100), 105(12), 119(61), 231(21), 260(12) |
| t | 1-Methyldodecylbenzene | $C_{19}H_{32}$ | 260 | 105(100), 106(15), 260(15) |
|  | 1-Phenyltridecane | $C_{19}H_{32}$ | 260 | 91(78), 92(100), 105(11), 133(8), 260(41) |

[a] Mass fragments of alkyl groups that are split off are listed as follows: ethyl = 29; propyl = 43; butyl = 57; pentyl = 71; hexyl = 85, heptyl = 99; octyl = 113; nonyl = 127; decyl = 141; undecyl = 165.

[b] 1-Phenylalkanes were not present in the solvent components of the liquid scintillator but were introduced for comparison.

column. On the DB-1 column the chromatograph peaks a–d belong to $C_{16}H_{26}$ isomers, f–j to $C_{17}H_{28}$ isomers, k–o to $C_{18}H_{30}$ isomers and p–t to $C_{19}H_{32}$ isomers. On the DB-Wax column, all the peaks follow the same elution pattern as shown on DB-1, with the exception of 1-methyl(nonyl, decyl, undecyl and dodecyl)benzenes which are represented by peaks d, j, o and t, respectively. These 1-methyl isomers are more polarizable and show larger column differences than the evenly branched or more symmetrical isomers. Plotting the $I$ values of these isomers against the number of carbon atoms in the short alkyl group yields a family of curves, as shown in Fig. 3. The straight-chain 1-phenylalkanes are not found in the scintillator but were added during analysis for comparison. These graphs show that 1-phenylalkanes and 1-methylalkylbenzenes have considerably higher $I$ values than the branched-chain isomers. The large differences between the $I$ values of these isomers were not expected.

### *Chain branching and the A and GRF values*

The $I$ values of a homologous series, such as 1-phenylalkanes, may be calculated by the following linear regression equation:

$$I = AZ + (\mathrm{GRF})_z \qquad (1)$$

where $A$ is the regression coefficient representing the $I$ increment for atom addition, $(\mathrm{GRF})_z$ the intercept representing the group retention factors of substituents and functional groups and $Z$ the number of atoms in the molecule. Both $A$ and GRF can be predetermined. The basis for using this equation for $I$ calculation is given in ref. 2.

Table IV shows that the isomers of $C_{16}H_{26}$,

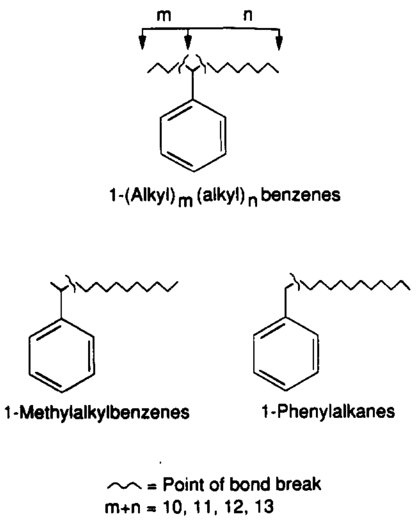

Fig. 2. Structures of the alkylbenzenes and the points of bond breakage. The $m$ and $n$ in 1-(alkyl)$_m$(alkyl)$_n$benzenes represent the carbon numbers in the alkyl chain with $n > m$ and $m + n$ = 10 for $C_{16}H_{26}$ isomers, 11 for $C_{17}H_{28}$ isomers, 12 for $C_{18}H_{30}$ isomers and 13 for $C_{19}H_{32}$ isomers. The isomers are formed by shifting the methylene groups from the long to the short chain. Bond breakage occurs at the tertiary carbon atom for all isomers, including 1-phenylalkanes and 1-methylalkylbenzenes.

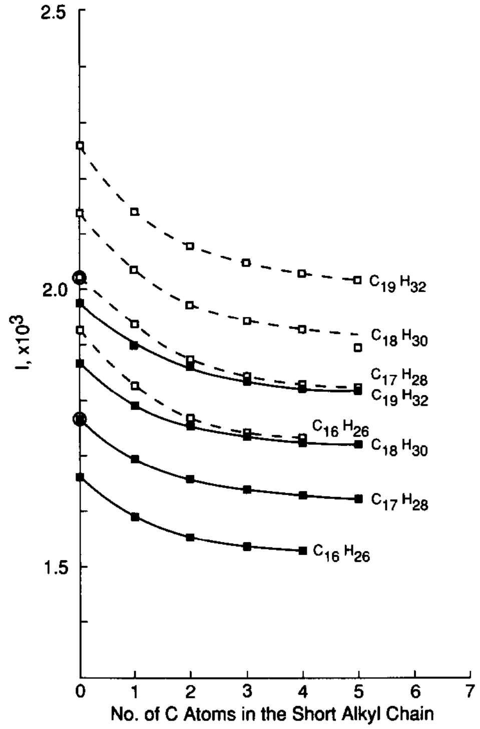

Fig. 3. Plots of retention indices of the solvent components on (solid lines) DB-1 and (dashed lines) DB-Wax columns against the number of carbon atoms in the short chain in the molecule. 1-Phenylalkanes are included for comparison. The $I$ values of 1-phenylundecane ($C_{17}H_{28}$) on polar and non-polar columns are extrapolated from the regression equation in Table I.

$C_{17}H_{28}$, $C_{18}H_{30}$ and $C_{19}H_{32}$ can be selected to form seven homologous series. Plotting the $I$ values against increasing number of carbon atoms in the second alkyl chain in the molecule yields straight lines, as shown in Fig. 4. Four series are formed with methyl, ethyl, propyl and butyl as the short alkyl chain. The $A$ values for these series on DB-1 were found to be 102, 101, 100 and 98 and the GRF values were $-39$, $-59$, $-59$ and $-45$, respectively. The remaining three series are formed with decyl, nonyl and octyl as the long alkyl chain. The $A$ values for these three series are 71, 78 and 87 and their GRF values are $+491$, $+339$ and $+159$, respectively. The observed $A$ values ($A_{obs}$), listed in Table IV, are in agreement with the $A$ values from linear regression equations. According to eqn. 1, the GRF and $A$ values are mutually compensatory. It is therefore difficult to relate the unusually high GRF values to some apparent structure characteristics in the alkylbenzene molecule. However, these changes may be interpreted as disturbances that the addition of a methylene group to the short alkyl chain may have on the chromatographic properties of the molecule, such as electron density distribution. The $A$ and GRF values will regress to normal values when a sufficient number of $CH_2$ groups are added to the short alkyl chain to yield a more symmetrical molecule. It should be pointed out that the number of data values for these homologous series is small, and a single incorrect data value can seriously distort the regression analysis. The regression analysis was performed with SAS/STAT statistical analysis procedures on a Model 486 personal computer. Data given for each homologous series include (i) the number of data point ($n$), (ii) standard errors of the regression coefficient and the intercept ($SE$), (iii) the coefficient of determination ($R^2$) and (iv) the probability of obtaining a greater $F$ statistic than that observed if the hypothesis is true, i.e., the significance probability ($p$). The meaning of these terms is given in ref. 5.

TABLE III

RETENTION INDEXES OF 1-(ALKYL)$_m$(ALKYL)$_n$BENZENES ON NON-POLAR AND POLAR CAPILLARY COLUMNS

| Peak | Compound | Formula | Retention index |  |  |  | Column difference ($\Delta I$) |
|---|---|---|---|---|---|---|---|
|  |  |  | DB-1 |  | DB-Wax |  |  |
|  |  |  | $I_{obs}$ | $I_p$ | $I_{obs}$ | $I_p$ |  |
| a | 1-Butylhexylbenzene | $C_{16}H_{26}$ | 1526 | 1519 | 1729 | 1720 | 203 |
| b | 1-Propylheptylbenzene | $C_{16}H_{26}$ | 1534 | 1529 | 1743 | 1740 | 209 |
| c | 1-Ethyloctylbenzene | $C_{16}H_{26}$ | 1553 | 1549 | 1767 | 1770 | 214 |
| d | 1-Methylnonylbenzene | $C_{16}H_{26}$ | 1588 | 1584 | 1833 | 1830 | 245 |
|  | 1-Phenyldecane | $C_{16}H_{26}$ | 1664 | 1654 | 1928 | 1950 | 264 |
| e | Tributyl phosphate | $C_{12}H_{27}O_4P$ | 1622 |  | 2092 |  | 470 |
| f | 1-Pentylhexylbenzene | $C_{17}H_{28}$ | 1620 | 1614 | 1820 | 1810 | 200 |
| g | 1-Butylheptylbenzene | $C_{17}H_{28}$ | 1626 | 1619 | 1828 | 1820 | 202 |
| h | 1-Propyloctylbenzene | $C_{17}H_{28}$ | 1636 | 1629 | 1843 | 1840 | 207 |
| i | 1-Ethylnonylbenzene | $C_{17}H_{28}$ | 1656 | 1649 | 1873 | 1870 | 217 |
| j | 1-Methyldecylbenzene | $C_{17}H_{28}$ | 1692 | 1684 | 1933 | 1930 | 241 |
| k | 1-Pentylheptylbenzene | $C_{18}H_{30}$ | 1719 | 1714 | 1918 | 1910 | 199 |
| l | 1-Butyloctylbenzene | $C_{18}H_{30}$ | 1723 | 1719 | 1928 | 1920 | 205 |
| m | 1-Propylnonylbenzene | $C_{18}H_{30}$ | 1735 | 1729 | 1943 | 1940 | 208 |
| n | 1-Ethyldecylbenzene | $C_{18}H_{30}$ | 1755 | 1749 | 1972 | 1970 | 217 |
| o | 1-Methylundecylbenzene | $C_{18}H_{30}$ | 1791 | 1784 | 2036 | 2030 | 245 |
|  | 1-Phenyldodecane | $C_{18}H_{30}$ | 1870 | 1854 | 2140 | 2150 | 270 |
| p | 1-Pentyloctylbenzene | $C_{19}H_{32}$ | 1814 | 1814 | 2015 | 2010 | 201 |
| q | 1-Butylnonylbenzene | $C_{19}H_{32}$ | 1821 | 1819 | 2026 | 2020 | 205 |
| r | 1-Propyldecylbenzene | $C_{19}H_{32}$ | 1833 | 1829 | 2046 | 2040 | 213 |
| s | 1-Ethylundecylbenzene | $C_{19}H_{32}$ | 1856 | 1849 | 2079 | 2070 | 223 |
| t | 1-Methyldodecylbenzene | $C_{19}H_{32}$ | 1894 | 1884 | 2143 | 2130 | 249 |
|  | 1-Phenyltridecane | $C_{19}H_{32}$ | 1978 | 1954 | 2275 | 2250 | 297 |

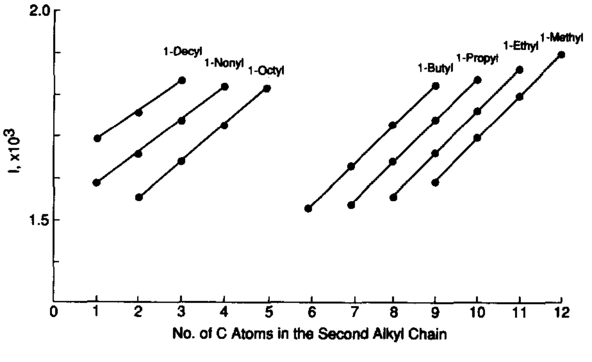

Fig. 4. Linear plots of the retention indices of homologues *vs*. the number of carbon atoms in the alkyl chain in 1-(alkyl)$_m$ (alkyl)$_n$ benzenes. The homologues are formed by allowing one alkyl chain in the molecule to be fixed in length while increasing the number of carbon atoms in the other alkyl chain. Linear plots for homologues with fixed long alkyl chains and fixed short alkyl chains have different slopes.

### *Chain branching and predicted retention indexes*

The $I$ values of the phenylalkanes can also be predicted on the assumption that $A = 100$, by the following equation [1,2]:

$$I_p = 100Z + \sum m_i - \sum n_i \qquad (2)$$

where $I_p$ is the predicted $I$, $Z$ is the number of carbon atoms in the phenylalkane, $m_i$ is the group retention factor (GRF) for the phenyl ring and $n_i$ is the GRF for the tertiary carbon or methyl branching; the subscript "$i$" refers to the $i$th functional group or substitution. The term $100Z$ is known as the base value. The GRF for the phenyl ring is +54 on DB-1 and +350 on DB-Wax. The GRF for the tertiary carbon connected to a methyl group and a phenyl ring is about −70 on DB-1 and about −120 on DB-Wax columns. Addition of a $CH_2$ unit to the

TABLE IV

RETENTION INDICES OF BRANCH-CHAIN 1-(ALKYL)$_m$(ALKYL)$_n$BENZENES

| Compound | Formula | Retention index[a] | | | | Linear regression equation[b] | |
|---|---|---|---|---|---|---|---|
| | | DB-1 | | DB-wax | | On DB-1 | On DB-Wax |
| | | $I_p$ | $A_{obs}$ | $I_p$ | $A_{obs}$ | | |
| *Homologues with fixed short chain* | | | | | | | |
| 1-Methylnonylbenzene | $C_{16}H_{26}$ | 1588 | 104 | 1833 | 100 | $(101.70 \pm 0.66)Z - (38.5 \pm 11.50)$ | $(103.30 \pm 1.11)Z + (178.50 \pm 19.45)$ |
| 1-Methyldecylbenzene | $C_{17}H_{28}$ | 1692 | 99 | 1933 | 103 | $(n=4,\ R^2=0.9999,\ p=0.0001)$ | $(n=4,\ R^2=0.9998,\ p=0.0001)$ |
| 1-Methylundecylbenzene | $C_{18}H_{30}$ | 1791 | 103 | 2036 | 107 | | |
| 1-Methyldodecylbenzene | $C_{19}H_{32}$ | 1894 | | 2143 | | | |
| 1-Ethyloctylbenzene | $C_{16}H_{26}$ | 1553 | 103 | 1767 | 106 | $(1000.80 \pm 0.53)Z - (59.00 \pm 9.28)$ | $(103.50 \pm 1.07)Z + (111.50 \pm 18.80)$ |
| 1-Ethylnonylbenzene | $C_{17}H_{28}$ | 1656 | 99 | 1873 | 99 | $(n=4,\ R^2=0.9999,\ p=0.0001)$ | $(n=4,\ R^2=0.9998,\ p=0.0001)$ |
| 1-Ethyldecylbenzene | $C_{18}H_{30}$ | 1755 | 101 | 1972 | 107 | | |
| 1-Ethylundecylbenzene | $C_{19}H_{32}$ | 1856 | | 2079 | | | |
| 1-Propylheptylbenzene | $C_{16}H_{26}$ | 1534 | 102 | 1743 | 100 | $(99.6 \pm 0.65)Z - (58.50 \pm 1.36)$ | $(100.90 \pm 0.52)Z + (128.00 \pm 9.11)$ |
| 1-Propyloctylbenzene | $C_{17}H_{28}$ | 1636 | 99 | 1843 | 100 | $(n=4,\ R^2=0.9999,\ p=0.0001)$ | $(n=4,\ R^2=1.0000,\ p=0.0001)$ |
| 1-Propylnonylbenzene | $C_{18}H_{30}$ | 1735 | 98 | 1943 | 103 | | |
| 1-Propyldecylbenzene | $C_{19}H_{32}$ | 1833 | | 2046 | | | |
| 1-Butylhexylbenzene | $C_{16}H_{26}$ | 1526 | 100 | 1729 | 99 | $(98.20 \pm 0.42)Z - (44.50 \pm 7.44)$ | $(99.10 \pm 0.26)Z + (143.50 \pm 4.64)$ |
| 1-Butylheptylbenzene | $C_{17}H_{28}$ | 1626 | 97 | 1828 | 100 | $(n=4,\ R^2=1.0000,\ p=0.0001)$ | $(n=4,\ R^2=1.0000,\ p=0.0001)$ |
| 1-Butyloctylbenzene | $C_{18}H_{30}$ | 1723 | 98 | 1928 | 98 | | |
| 1-Butylnonylbenzene | $C_{19}H_{32}$ | 1821 | | 2026 | | | |
| *Homologues with fixed long chain* | | | | | | | |
| 1-Ethyloctylbenzene | $C_{26}H_{26}$ | 1553 | 83 | 1767 | 76 | $(87.00 \pm 1.26)Z - (159.00 \pm 22.18)$ | $(82.90 \pm 1.81)Z + (437.50 \pm 31.71)$ |
| 1-Propyloctylbenzene | $C_{17}H_{28}$ | 1636 | 87 | 1843 | 85 | $(n=4,\ R^2=0.9996,\ p=0.0001)$ | $(n=4,\ R^2=0.9990,\ p=0.0005)$ |
| 1-Butyloctylbenzene | $C_{18}H_{30}$ | 1723 | 91 | 1928 | 87 | | |
| 1-Pentyloctylbenzene | $C_{19}H_{32}$ | 1814 | | 2015 | | | |
| 1-Methylnonylbenzene | $C_{16}H_{26}$ | 1588 | 68 | 1833 | 40 | $(77.80 \pm 2.86)Z - (338.50 \pm 50.15)$ | $(64.90 \pm 6.90)Z + (783.00 \pm 121.07)$ |
| 1-Ethylnonylbenzene | $C_{17}H_{28}$ | 1656 | 79 | 1873 | 70 | $(n=4,\ R^2=0.9973,\ p=0.0013)$ | $(n=4,\ R^2=0.9779,\ p=0.0111)$ |
| 1-Propylnonylbenzene | $C_{18}H_{30}$ | 1735 | 86 | 1943 | 83 | | |
| 1-Butylnonylbenzene | $C_{19}H_{32}$ | 1821 | | 2026 | | | |
| 1-Decylbenzene | $C_{16}H_{26}$ | 1665 | | | | | |
| 1-Methyldecylbenzene | $C_{17}H_{28}$ | 1692 | 63 | 1933 | 39 | $(70.50 \pm 4.33)Z - (491.00 \pm 78.02)$ | $(56.50 \pm 10.10)Z + (966.67 \pm 182.05)$ |
| 1-Ethyldecylbenzene | $C_{18}H_{30}$ | 1755 | 78 | 1972 | 74 | $(n=3,\ R^2=0.9962,\ p=0.0391)$ | $(n=3,\ R^2=0.9690,\ p=0.1127)$ |
| 1-Propyldecylbenzene | $C_{19}H_{32}$ | 1833 | | 2046 | | | |

[a] $I_p$ = observed retention index; $A_{obs}$ = observed $A$ value, obtained from the difference between $I$ values of two homologues differing by one methylene group.

[b] The linear regression equations are given in the form $(A \pm \text{S.E.})Z + (GRF + \text{S.E.})$, where $A$ is the regression coefficient, $GRF$ the intercept, and S.E. the standard error. For the meaning of other terms, see text.

methyl to form an ethyl group further lowers *I* by −35 on DB-1 and by −60 on DB-Wax. Shifting the $CH_2$ group from the long to the short alkyl group will also lower *I*. The predicted *I* values ($I_p$) of the isomers of 1-(alkyl)$_m$(alkyl)$_n$benzenes are listed in Table III. Their calculation is based on the use of the following GRF values: for the DB-1 column, base value 100*Z*, phenyl ring +54, methyl −70, ethyl −35, propyl −20, butyl −10 and pentyl −5, and for the DB-Wax column, base value 100*Z*, phenyl ring +350, methyl −120, ethyl −60, propyl −30, butyl −20 and pentyl −10. The negative GRF values for the higher alkyl groups are cumulative from the methyl group onwards and only increments are given above. The error between the predicted and the observed *I* values is less than 3%.

## CONCLUSIONS

In a homologous series, the *I* value of the molecule increases by *ca.* 100 units for each increase in the number of carbon atoms [1,2]. In an isomeric series the number of carbon atoms remains constant but the *I* values vary according to structural symmetry. For example, in the isomeric series represented by $C_{19}H_{32}$, the straight-chain 1-phenyltridecane has the highest *I*. Shifting a methylene group to position 1 in the alkane chain to create 1-methyldodecylbenzene lowers the *I* by 70. The abrupt decrease in *I* is attributed to the presence of a tertiary carbon atom resulting from chain branching. In 1-ethylundecylbenzene, *I* is further lowered by 35. A small decrease in *I* appears to accompany each shift of the methylene group until the two chains are approximately equal in length, and the molecule appears to be more symmetrical. The bonds at the tertiary carbon are weakened and can break to yield the observed mass fragments in GC–MS analysis.

The column difference ($\Delta I$) reflects the polarity and polarization of the molecule [2]. 1-Phenyltridecane has the largest column difference, 1-methyldodecylbenzene the next largest and 1-hexylheptylbenzene the least. A small column difference implies that the molecule appraoches aliphatic hydrocarbons in chromatographic behavior.

The ability to predict *I* values and to derive information on structure from the *I* values and the column differences has facilitated our interpretation of the data from GC–MS in the effort to identify the isomers of 1-(alkyl)$_m$(alkyl)$_n$(benzenes).

## ACKNOWLEDGEMENTS

This publication was made possible by grant number CA33537 from the National Cancer Institute. We acknowledge the Mass Spectrometry Facility, University of California San Francisco, supported by NIH Division of Research Resources grants RR01614 and RR04112. We thank Z. C. Yang and S. Q. Liu for assistance with the analyses.

## REFERENCES

1 C. T. Peng, S. F. Ding, R. L. Hua and Z. C. Yang, *J. Chromatogr.*, 436 (1988) 137.
2 C. T. Peng, Z. C. Yang and S. F. Ding, *J. Chromatogr.*, 586 (1991) 85.
3 J. McCormick, *Trans. Am. Nucl. Soc.*, 61 (1990) 10.
4 H. van den Dool and P. D. Kratz, *J. Chromatogr.*, 11 (1963) 463.
5 *SAS/STAT User's Guide, Release 6.03 Edition*, SAS Institute, Cary, NC, 1988, pp. 854–857.