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# Prediction of retention indexes

## II. Structure–retention index relationship on polar columns

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ABSTRACT

A method is described for the prediction of the retention index ($I$) from chemical structure, using the number of atoms in the molecule ($Z$), the $I$ increment for atom addition ($A$) and the group retention factors (*GRF*s) of the functional groups and substituents. This method can predict the retention indexes of a wide range of compounds, such as acids, alcohols, amines, acid esters, aldehydes, ketones, ethers, aromatic hydrocarbons, alicyclics, heterocyclics, etc. on polar as well as non-polar columns to within 3% error. Accurate $A$ and *GRF* values are essential to the prediction. These values can be obtained from homologous series, but a system of arbitrarily assigned $A$ value and adjusted *GRF*s are also used. The *GRF*s of the substituents and functional groups depend on the polarity and polarizability of the analyte and the stationary phase and also on the molecular connectivity of the atoms, namely, primary, secondary and tertiary carbon atoms or hydrogen atoms, to which these groups are attached. Highly polar and polarizable groups can alter the $A$ value. When the functionality of a group is masked by substitution, the analyte molecule will tend to behave chromatographically like hydrocarbons. The difficulty in predicting the $I$ values of compounds of multi-functionality by the rule of additivity is the unknown intramolecular interaction that can alter both $A$ and *GRF* values.

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## INTRODUCTION

In tritium labeling by radiation–induced reactions, the desired product is often formed together with some labeled by-products. To understand the mechanism of labeling, these by-products must be identified. The by-products are formed in no-carrier-added state and have negligible mass; even if all the material formed in a single run is collected, the amount will still be insufficient to establish their identity by conventional analytical techniques. The volatile by-products can be separated by gas chromatography and detected by radioactivity. On non-polar and polar columns, the radioactive peaks have characteristic retention indexes ($I$), from which one may gain preliminary structural information.

We reported earlier [1] a structure–retention index relationship for predicting the retention index of a compound on non-polar columns (SE-30, DB-1), based on (i) the number of carbon and carbon equivalent atoms ($Z$) in the molecule, (ii) the retention index increment ($A$) for atom addition and (iii) the group retention factors (*GRF*s) for substituents and functional groups. This report shows that this same approach can be applied to predict $I$ on polar columns using *GRF* constants derived for substituents and functional groups on polar columns.

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## EXPERIMENTAL

The materials and methods are essentially those described in the previous paper [1]. A stainless-steel column, 3.05 m × 3.175 mm I.D., packed with 10% Carbowax 20M (CW-20M) on 80–100 mesh Supelcoport (Supelco, Bellefonte, PA, USA) and a fused-silica capillary column DB-Wax (15 m × 0.53 mm I.D., film thickness 1.0 $\mu$m) (J & W Scientific, Folsom, CA, USA) were used. A linear temperature program was adopted, beginning at 40°C isothermally for 4 min, after which the temperature was increased to 200°C at the rate of 8°C/min and maintained for 60 min or longer as required. The injection port was kept at 250°C and the detector at 300°C. A mixture of *n*-alkanes, from pentane ($C_5$) to hexacosane ($C_{26}$) or to dotriacontane ($C_{32}$), was used as markers; when necessary the standard were injected together with the analyte. Retention index measurements were preferably made on small mass peaks. For large mass peaks that are truncated at the full-scale height, the truncated width, expressed in time, is subtracted from the retention time reported by the electronic integrator for *I* calculation. *I* was computed using the equation of Van den Dool and Kratz [2], thus:

$$I = 100i \cdot \frac{X - M_{(n)}}{M_{(n+i)} - M_{(n)}} + 100n \qquad (1)$$

where *n* is the number of carbon atoms in *n*-alkanes used as markers; $X$, $M_{(n)}$, and $M_{(n+i)}$ are the adjusted retention times of the analyte, the normal alkane marker with *n* carbon atoms eluting before and that with $(n+i)$ carbon atoms eluting after the analyte, respectively; *i* is the interval and usually has the value of 1 or 2.

Linear regression analysis of *I vs.* the number of atoms in homologous series was performed on a 486 personal computer, using SAS statistical program for the PC, from the SAS Institute (Cary, NC, USA). Statistical data listed for the regression equations include (i) the number of data values in the set (*n*), (ii) the standard errors (S.E.) for the regression coefficient and the intercept, (iii) the coefficient of determination ($R^2$) and (iv) significance probability (*p*), *i.e.*, the probability of getting a greater *F* statistic than that obtained if the hypothesis is true. The meaning of these terms is given in ref. 3.

## RESULTS AND DISCUSSION

The prediction of *I* is based on the fact that the *I* value of a monofunctional molecule is invariably higher than that of a *n*-alkane molecule of equal atom number. This leads to the use of *GRF*s for *I* contributions from substituents and functional groups. The Kováts convention for calculating *I* is adopted [4]. According to this convention, *n*-hexane will be assigned a *I* of 600 on both non-polar and polar columns, irrespective of their different retention times.

The *I* values of *n*-alkanes increase with the number of carbon atoms (*n*) in the molecule and can be expressed as:

$$I = 100n \qquad (2)$$

This value is also known as the base value [1] when *n* is replaced with *Z*, the total number of atoms in the molecule. *Z* includes carbon atoms and carbon equivalent atoms, such as oxygen, nitrogen, sulfur, chlorine, bromine and iodine, which may be found in the molecule. Compounds containing substituents, functional groups and other structural features will have higher *I* values than the base values. The *I* values of a homologous series will increase smoothly with increasing numbers of the carbon atoms or methylene groups in the homologues. A plot of the observed *I* values against *n* or *Z* values will yield a straight line which may be represented by the following linear regression equations:

$$I = An + (GRF)_n \qquad (3)$$

$$= AZ + (GRF)_Z \qquad (4)$$

where *A* is the regression coefficient, representing the *I* increment for atom addition, and *GRF* the intercept, representing the group retention factor or functionality constant. The subscript differentiates between the *GRF*s based on *n* or *Z*. In eqns. 3 and 4 shown above, *Z* is greater than *n* but $(GRF)_z$ is smaller than $(GRF)_n$. The term $(GRF)_n$ may also contain the atom contribution of the substituent. Table I lists the *GRF* and A values for a number of homologues of monofunctionality on DB-Wax and CW-20M columns.

The magnitude of the *GRF* is dependent not only upon the polarity and polarizability of the substituent and functional group but also on the stationary

TABLE I

GROUP RETENTION FACTORS (GRFs) AND THE ATOM INCREMENTS (*A* VALUES)

| Substituent and functional group | Formula | *GRF* | |
|---|---|---|---|
| | | Calculated by eqn. 7 ($A = 100$) | By linear regression equation |
| *(A) Aliphatic series* | | | |
| (1) Alkanoic acids | R–COOH | | |
| Analabs data[a] | | | $997.15 \pm 2.61$ ($107.69 \pm 0.27$)[b]<br>($n = 6$, $R^2 = 1.0000$, $p = 0.0001$) |
| Our data | | 1029 | $994.09 \pm 9.85$ ($103.72 \pm 0.99$)<br>($n = 11$, $R^2 = 0.9992$, $p = 0.0001$) |
| (2) Primary alcohols | $R–CH_2–OH$ | | |
| Analabs data[a] | | | $648.79 \pm 0.65$ ($102.65 \pm 0.066$)<br>($n = 5$, $R^2 = 1.000$, $p = 0.0001$) |
| Our data | | 647 | $632.86 \pm 5.97$ ($100.92 \pm 0.49$)<br>($n = 11$, $R^2 = 0.9998$, $p = 0.0001$) |
| (3) Secondary alcohols | >CH–OH | 530 | |
| (4) Tertiary alcohols (2-methyl-2-alkanols) | $-\overset{\vert}{\underset{\vert}{C}}-OH$ | 410 | $394.90 \pm 2.73$ ($98.53 \pm 0.73$)<br>($n = 5$, $R^2 = 1.0000$, $p = 0.0001$) |
| (5) Primary amines, 1° | $R–CH_2–NH_2$ | 417 | $407.29 \pm 3.35$ ($101.06 \pm 0.35$)<br>($n = 8$, $R^2 = 0.9999$, $p = 0.0001$) |
| 2° | $R–CH–NH_2$ | 350 | |
| 3° | $R–C–NH_2$ | 229 | |
| (6) Secondary amines | $R–CH_2–NH–R'$ | 180 | |
| (7) Tertiary amines | R'R''NR''' | (See text) | (See text) |
| (8) Aldehydes | $R–CH_2–CHO$ | 388 | $375.50 \pm 3.11$ ($102.50 \pm 0.34$)<br>($n = 5$, $R^2 = 1.0000$, $p = 0.0001$) |
| (9) Ketones, "peripheral" | $R–CH_2–CO–CH_3$ | 388 | |
| "inner" | $R–CH_2–CO–CH_2–R'$ | 355 | |
| (10) Fatty acid esters (our data) | | | |
| methyl esters | $R–CH_2–COOCH_3$ | 294 | $302.88 \pm 4.71$ ($99.91 \pm 0.45$)<br>($n = 9$, $R^2 = 0.9999$, $p = 0.0001$) |
| ethyl esters | $R–CH_2–COOC_2H_5$ | 270 | $288.85 \pm 16.55$ ($96.79 \pm 1.50$)<br>($n = 10$, $R^2 = 0.9981$, $p = 0.0001$) |
| propyl esters | $R–CH_2–COOC_3H_7$ | 259 | $288.70 \pm 16.09$ ($95.93 \pm 1.34$)<br>($n = 10$, $R^2 = 0.9984$, $p = 0.0001$) |
| butyl esters | $R–CH_2–COOC_4H_7$ | 256 | $276.50 \pm 25.48$ ($96.34 \pm 2.15$)<br>($n = 6$, $R^2 = 0.9980$, $p = 0.0001$) |
| (11) Ether linkage | $C–CH_2–O–CH_2–C$ | 70 | |
| (12) Alkyl thiol | R–SH | 370 | |
| (13) Sulfide linkage | R–S–R' | 256 | |
| (14) Disulfide linkage | R–S–S–R' | 377 | |
| (15) Terminal carbon-carbon double bond | $R–CH_2–CH{=}CH_2$ | 40 | |
| (16) Terminal carbon-carbon triple bond | $R–CH_2–C{\equiv}CH$ | 300 | |
| (17) Non-terminal carbon-carbon double bond | $R–CH{=}CH–R'$ | 60 | |
| (18) Quaternary carbon atom | $C–\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}–C$ | (−)100 | |

(*Continued on p. 88*)

TABLE I (*continued*)

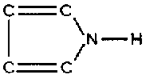
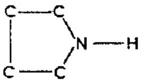
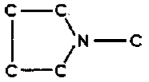
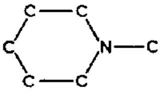
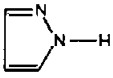
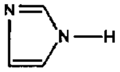
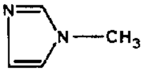
| Substituent and functional group | Formula | *GRF* | |
|---|---|---|---|
| | | Calculated by eqn. 7 ($A = 100$) | By linear regression equation |
| (19) Tertiary carbon atom |  $\begin{matrix} & \mathrm{C} & \\ & | & \\ \mathrm{C}- & \mathrm{C} & -\mathrm{X} \\ & | & \\ & \mathrm{C} & \end{matrix}$ | (−) 75 | |
| (20) Iso carbon/chain branching | R–CH(CH$_3$)$_2$ or<br>R–CHR$_1$R$_2$ | (−) 50 | |
| (21) Adjacent carbon-carbon double bond and carbonyl bond | R–C=C–C=O | 53 | |
| (22) N-Ethylamine group | R–NH–C$_2$H$_5$ | (−) 50 | |
| (23) Acid amide group | R–CO–NH$_2$ | 1600 ($A = 45$) | |
| (24) Monosubstituted acid amido group | R–CO–NHR′ | 1430 ($A = 45$) | |
| (25) Disubstituted acid amido group | R–CO–NR$'_2$ | 1016 ($A = 64$) | |
| (26) Chlorine atom connected to methylene group | R–CH$_2$–Cl | 464 | 426.91 ± 2.42 (104.11 ± 0.24)<br>($n = 11, R^2 = 1.0000, p = 0.0001$) |
| (27) Bromine atom connected to methylene carbon | R–CH$_2$–Br | 592 | 515.33 ± 8.75 (107.89 ± 0.81)<br>($n = 12, R^2 = 0.9994, p = 0.0001$) |
| (28) Bromine atom connected to tertiary carbon | R–CH–Br | 492 | 486.05 ± 18.18 (100.72 ± 2.22)<br>($n = 5, R^2 = 0.9985, p = 0.0001$) |
| (29) Bromine atom in 2-bromoalkanoic acids, ethyl ester | R–CHBr–COOC$_2$H$_5$ | 386 | |
| (30) Iodine atom connected to methylene atom | R–CH$_2$–I | 710 | 633.85 ± 5.71 (109.88 ± 0.66)<br>($n = 12, R^2 = 0.9996, p = 0.0001$) |
| (31) Difference between *cis* and *trans* isomers | | 60 | |
| *(B) Alicyclic series* | | | |
| (1) Cyclopropane ring | C$_3$H$_6$ | 105 | |
| (2) Cyclobutane ring | C$_4$H$_8$ | 110 | |
| (3) Cyclopentane ring | C$_5$H$_{10}$ | 122 | |
| (4) Cyclopentene ring | C$_5$H$_8$ | 163 | |
| (5) Cyclopentadiene ring | C$_5$H$_6$ | 210 | |
| (6) Cyclohexane ring | C$_6$H$_{12}$ | 123 | |
| (7) Cyclohexene ring | C$_6$H$_{10}$ | 208 | |
| (8) Cycloheptane ring | C$_7$H$_{14}$ | 183 | |
| (9) Cycloheptene ring | C$_7$H$_{12}$ | 217 | |
| (10) Difference between *cis* and *trans* isomers | | 30 | |
| (11) Alicyclic –OH group | >CH–OH | 580 | |
| (12) Alicyclic C=O group | >C=O | 465 | |
| (13) C=C–C=O group in cyclopentene ring | C=C–C=O | 106 | |
| (14) C=C–C=O group in cyclohexene ring | C=C–C=O | 40 | |
| (15) Oxygen atom in the 5-membered ring | –O– | 80 | |
| (16) Oxygen atom in the 6-membered ring | –O– | 160 | |
| (17) Alicyclic amino group | >CH–NH$_2$ | 350 | |
| (18) Sulfur atom in 5-membered ring | >S | 200 | |
| (19) Imino group in cyclopentadiene ring |  | 800 | |
| (20) Imino group in cyclopentane ring |  | 380 | |

TABLE I (*continued*)

| Substituent and functional group | Formula | *GRF* | |
|---|---|---|---|
| | | Calculated by eqn. 7 ($A = 100$) | By linear regression equation |
| (21) Tertiary nitrogen atom in azole ring |  | 140 | |
| (22) Tertiary nitrogen atom in azine ring |  | 200 | |
| (23) 1,2-Diaza group in azole ring |  | 300 | |
| (24) 1,3-Diaza group in azole ring |  | 800 | |
| (25) 1,3-Diaza group in N-methylated azole ring |  | 550 | |
| (26) One C=C bond in azole ring, additional contribution | | 40 | |
| (27) Two C=C bonds in azole ring, additional contribution | | 190 | |
| (28) Imino –NH– group connected to 2 double bonds in 5-membered ring | C=C–NH–C=C | 800 | |
| (29) Methyl group ortho to ring N | | (–) 70 | |
| (30) Imino –NH– group in azine ring | | 325 | |
| (31) 1,4-Diaza group in azine ring | | 30 | |
| (32) 1,3-Diaza group in azine ring | | 80 | |
| (33) 1,2-Diaza group in azine ring | | 520 | |
| (34) Cl atom attached to cyclohexane ring | R′–Cl | 440 | |
| (35) Cl atom attached to 1-cyclohexene ring | | 369 | |
| (36) Br atom attached to cyclohexane ring | R′–Br | 580 | |
| (37) Br atom attached to 1-cyclohexene ring | | 516 | |
| (38) I atom attached to cyclohexane ring | R′–I | 726 | |
| (39) I atom connected to 1-cyclohexene ring | | 676 | |
| *(C) Aromatic series* | | | |
| (1) Benzene ring | | 350 | |
| (2) 1,3-Cyclohexadiene ring | | 264 | |
| (3) 1,4-Cyclohexadiene ring | | 314 | |
| (4) Ethynyl group connected to phenyl ring | Ar–C≡CH | 210 | |
| (5) Carbon-carbon double bond connected to phenyl ring | $Ar–CH=CH_2$ | 80 | |
| (6) Fusion between two phenyl rings | | 60 | |
| (7) Link between two phenyl rings | | 80 | |
| (4) Phenolic -OH | Ar–OH | 900 | |
| (5) Aryl ether –O– linkage | Ar–O–R | 190 | |
| (6) Aryl aldehyde/ketone | Ar–CHO or<br>Ar–CO–R(Ar′) | 388 | |
| (7) Aryl thiol | Ar–SH | 340 | |
| (8) Aryl $-NH_2$ group | $Ar–NH_2$ | 667 | |

(*Continued on p. 90*)

TABLE I (*continued*)

| Substituent and functional group | Formula | *GRF* | |
|---|---|---|---|
| | | Calculated by eqn. 7 ($A = 100$) | By linear regression equation |
| (9) Aryl aryl imino –NH– group | Ar–NH–Ar′ | 586 | |
| (10) Aryl alkyl imino –NH– group | Ar–NH–R | 523 | |
| (11) Additional –NH– group to N-methyl piperidine ring | | 240 | |
| (12) Phenyldimethylamino group | $Ar-N(CH_3)_2$ | 260 | |
| (13) Tertiary nitrogen in 6-membered ring | C–N=C | 240 | |
| (14) Additional nitrogen to form 1,4-diaza ring | C–N=C–C=N | 30 | |
| (15) Additional nitrogen to form 1,3-diaza ring | C–N=C–N=C | 80 | |
| (16) Additional nitrogen to form 1,2-diaza ring | C–N=N–C or C=N–N=C | 520 | |
| (17) Nitrogen in the iso position of the quinoline ring | | 40 | |
| (18) Methyl group in the *ortho* position to ring N | | (−) 70 | |
| (19) Methyl group in the *para* position to ring N | | 70 | |
| (20) Methyl group in the *peri* position to ring N | | (−)100 | |
| (21) Aryl chlorine atom | Ar–Cl | 276 | |
| (22) Aryl bromine atom | Ar–Br | 426 | |
| (23) Aryl iodine atom | Ar–I | 604 | |
| (24) Size factor | | 120 | |
| (*D*) *Ortho effects* | | | |
| (1) Adjacent groups in benzene ring | | *Ortho* effect *a*/*b* | |
| $CH_3 + CH_3$ | | (+) 50 | |
| $CH_3 + COOH$ | | (−) 40 | |
| $CH_3 + N(C_2H_5)_2$ | | (−)300 | |
| $C_6H_5 + C_6H_5$ | | (−)400 | |
| $NH_2 + C_2H_5$ | | (−) 70 | |
| $NH_2 + Cl$ | | (−) 70 | |
| $NH_2 + OCH_3$ | | (−)160 | |
| $NH_2 + OC_2H_5$ | | (−)227 | |
| $NH_2 + COOCH_3$ | | (−)200 | |
| $NH_2 + CHO$ | | (−)220 | |
| $OH + CH_3$ | | (−)100 | |
| $OH + C_2H_5$ | | (−)100 | |
| $OH + CH_2CH{=}CH_2$ | | (−)150 | |
| OH + *tert.*-butyl | | (−) 90 | |
| $OH + OCH_3$ | | (−)500 | |
| $OH + OC_2H_5$ | | (−)610 | |
| $OH + CHO$ | | (−)870 | |
| $OH + CO{-}CH_3$ | | (−)870 | |
| $OH + CO{-}OC_2H_5$ | | (−)925 | |
| $Cl + OH$ | | (−)390 | |
| $Br + OH$ | | (−)242 | |
| $Br + CHO$ | | (−)126 | |
| $CO{-}OC_2H_5 + CO{-}OC_2H_5$ | | (−) 90 | |
| (2) Conjugate substituents in 1,4 positions of phenyl ring | | *Para* effect | |
| $CHO + OCH_3$ | | (+) 60 | |
| $CHO + N(CH_3)_2$ | | (+)360 | |

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[a] Data from ref. 15.

[b] The *GRF* values calculated by linear regression equations are given in the form of *GRF* ± S.E. ($A$ ± S.E.) where $A$ is the regression coefficient and S.E. the standard errors. The statistics given are the number of data points ($n$), standard errors for the regression coefficient and the intercept (S.E.), the coefficient of determination ($R^2$) and the significance probability ($p$), *i.e.*, the probability of getting a greater $F$ statistic than that obtained if the hypothesis is true. It should be pointed out that all regression analysis can be seriously distorted by a single incorrect data value (see ref. 3).

phase. The highly polar carboxyl, hydroxyl and amino groups interact strongly with the polar stationary phase and are retained longer than the less polar substituents. The difference between the $I$ values of the analyte on polar and non-polar columns is known as the column difference ($\Delta I$), expressed as follows:

$$\Delta I = (I)_{\text{CB-20M}} - (I)_{\text{SE-30}} \quad (5)$$

or

$$\Delta I = (GRF)_{\text{polar}} - (GRF)_{\text{non-polar}} \quad (6)$$

Eqn. 6 is based on the assumption that the analyte has similar $A$ values on both polar and non-polar columns. The column difference is characteristic of the analyte molecule and is determined by aromaticity, unsaturation, conjugation, electron density and polarizability of the molecule [5].

It may be pointed out that the use of $n$-alkanes as markers for $I$ calculation is preferred. Other markers such as methyl esters of fatty acids [6,7], 1-nitroalkanes [8], $n$-alkyl trichloroacetates [9], etc. [10,11] containing polar and polarizable groups that are not inert, may render the calculation of *GRF*s difficult. The *GRF* can be a good index for ranking the polarity and polarizability of the stationary phases; this ability will be lost when polar and polarizable substances are used as markers. Research activities in the field of retention index, especially regarding the use of $n$-alkanes, have been comprehensively reviewed [12,13]. Contributions to $I$ by primary, secondary, and tertiary alcohol functionalities were first discussed by Kováts in 1965 [14].

In the absence of known $A$ and *GRF* values, the $I$ value ($I_p$) may be predicted using the following expression [1]:

$$I_p = 100Z + \Sigma m_i - \Sigma n_i \quad (7)$$

where $Z$ is the total number of carbon atoms and carbon equivalent atoms. The terms $m_i$ and $n_i$ represent the *GRF*s of $i$th functional group and substituent. Acid, alcohol, aldehyde, amine, ether, ketone, phenol, single and fused phenyl rings, isolated and conjugated double bonds, *ortho* effect *a*, *para* effect, etc. give positive *GRF*s, and chain branching, quaternary carbon, *ortho* effect *b*, etc. give negative *GRF*s.

The $A$ in eqn. 7 is arbitrarily assigned a value of 100 with the $m_i$ and $n_i$ adjusted accordingly to match the $I_p$ with the observed value ($I_{obs}$). The $I_p$ from eqn. 7 and the $I$ from eqns. 3 and 4 should be within 3% error of the $I_{obs}$. On polar columns the $I$ values for small molecules may show large fluctuations, and many polar compounds do not emerge from the column. Linear regression equations for all the homologous series studied have regression coefficients near 100, with only a few exceptions. This justifies the use of eqn. 7 as a predictor of $I$. *GRF*s of substituents and functional groups for CW-20M and DB-Wax columns are given in Table I. Groups of the compounds studied are given below. $I$ data from other sources are also included for comparison [15,16].

### *Cycloalkanes, cycloalkenes and aromatic hydrocarbons*

Ring formation and the presence of double bonds increase $I$. For 6-membered carbocyclic ring compounds, the increase in $I$ progresses from cyclohexane to cyclohexene to benzene. Cyclohexane, cyclohexene and benzene show *GRF* values of 123, 208 and 350 on polar column, and 62, 64 and 58 on non-polar column [1], respectively. The column difference ($\Delta I$) is small for cyclohexane, moderate for cyclohexene and large for benzene. The *GRF* value for ring formation increases with increasing ring size from cyclopropane to cyclodecane. Other structural features, such as ring fusion, ring linkage, chain branching, etc. alter bond connectivity [17,18] and show only small column differences.

Table II lists the *GRF* and the functionality constants ($\Delta m_f$) of different hydrocarbon rings. Derivation of *GRF* and $\Delta m_f$ is given by eqns. 4 and 5 in ref. 1. These terms are used interchangeably here. The $I$ of cyclopentadiene is unavailable but can be extrapolated from those of cyclopentane and cyclopentene; the extrapolated value is used for predicting the $I$ values of polynuclear aromatics and heterocyclics containing the cyclopentadiene ring.

The terminal double bonds in aliphatic hydrocarbons contribute less to $I$ than the non-terminal double bonds; chain branching and the presence of tertiary and quaternary carbon atoms in the molecule reduce the $I$ by 50, 75 and 100 on polar column, respectively. Substitution of a H atom in alicyclic hydrocarbons by a methyl or an alkyl group decreases the $I$ by 50, due to chain branching. Chain

TABLE II

*GRF*s ($\Delta m_f$ VALUES) FOR THE FORMATION OF ALICYCLIC HYDROCARBONS FROM THEIR LINEAR ANALOGUES

| Compound | Formula | $I_{obs}$[a] | 100$Z$ | $\Delta m_f$[a] |
|---|---|---|---|---|
| Cyclopropane | $C_3H_6$ | 405 | 300 | 105 |
| Cyclopentane | $C_5H_{10}$ | 622 | 500 | 122 |
| Cyclopentene | $C_5H_8$ | 663 | 500 | 163 |
| Cyclohexane | $C_6H_{12}$ | 723 | 600 | 123 |
| Cyclohexene | $C_6H_{10}$ | 808 | 600 | 208 |
| 1,3-Cyclohexadiene | $C_6H_8$ | 864 | 600 | 264 |
| 1,4-Cyclohexadiene | $C_6H_8$ | 914 | 600 | 314 |
| Benzene | $C_6H_6$ | 950 | 600 | 350 |
| Cycloheptane | $C_7H_{14}$ | 883 | 700 | 183 |
| Cycloheptene | $C_7H_{12}$ | 917 | 700 | 217 |
| 1,3-Cycloheptadiene | $C_7H_{10}$ | 1060 | 700 | 360 |
| 1,3,5-Cycloheptatriene | $C_7H_8$ | 1089 | 700 | 389 |
| Cyclooctane | $C_8H_{16}$ | 1014 | 800 | 214 |
| Cyclooctene | $C_8H_{14}$ | 1035 | 800 | 235 |
| 1,3-Cyclooctadiene | $C_8H_{12}$ | 1100[b] | 800 | 300 |
| 1,5-Cyclooctadiene | $C_8H_{12}$ | 1164 | 800 | 364 |
| 1,3,5,7-Cyclooctatetraene | $C_8H_8$ | 1199 | 800 | 399 |
| Cyclodecane | $C_{10}H_{20}$ | 1361 | 1000 | 361 |

[a] $I_{obs}$ is the observed $I$; $\Delta m_f$ is the functionality constant.

[b] Value taken from ref. 16.

branching alters the molecular connectivity. The fusion and bond linking of two alicyclic rings in decahydrodronaphthalene and bicyclohexyl exert no influence on their $I$ values. A comparison of the observed and predicted $I$ values of some aliphatic and aromatic hydrocarbons is given in Tables III and IV.

The $I$ values of polynuclear aromatic hydrocarbons may require the inclusion of a size factor. The co-planarity resulting from two or more phenyl rings fusing together may increase the $I$ of the molecule beyond the usually predicted value. Extended conjugated systems may also cause an increase in $I$.

### *Aliphatic carboxylic acids*

The carboxylic acid group is highly polar; the lower homologues of the aliphatic acids can be chromatographed underivatized on polar and non-polar columns. The *GRF* for the aliphatic carboxyl group is 1029 for the $A$ value equal to 100. In comparison, the *GRF* for the carboxyl group on non-polar DB-1 column is 257.09 with an associated $A$ value of 93.38 [1]. The column difference ($\Delta I$) for the carboxyl group is about 770 units. Plotting the $I_{obs}$ of a series of aliphatic carboxylic acid homologues against $Z$ yields a straight line, as shown in Fig. 1. The regression coefficient ($A$) and the intercept (*GRF*) of the linear regression equation are given in Table I. The $\Delta m_f$ for the aliphatic carboxyl group and the comparison of observed and predicted $I$ of aliphatic carboxylic acids are given in Table V.

### *Carboxylic acid esters*

On non-polar SE-30 column the esters of the fatty acids were found to behave chromatographically in the same way as aliphatic hydrocarbons [1]. The residual polarity and polarizability of the acid ester group may cause additional retention on CW-20M column. The *GRF* on polar column for this molecular moiety is equal to the column difference ($\Delta I$). The methyl, ethyl, propyl and butyl acid esters have column differences of +294, +270, +259 and +256 units, respectively. This value must be added to the base value to yield the predicted $I$ of the ester

TABLE III

COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF ALKANES[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) quaternary carbon atom = −100, (2) non-terminal C=C double bond = +60, (3) chain branching = −50, (4) cyclohexane ring = +123, (5) cyclohexene ring = +208, (6) phenyl ring = +350, (7) ethynyl group connected to phenyl ring = +210, (8) cycloheptane ring = +183, (9) cycloheptene ring = +217, (10) terminal C=C bond = +40, (11) aryl ether –O– linkage = +190, (12) 1,3-cyclohexadiene = +264, (13) 1,4-cyclohexadiene ring = +314.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Neohexane | $C_6H_{14}$ | 500 | | 600 − 100 | 500 | 0 |
| *n*-Hexane | $C_6H_{14}$ | 619 | | 600 | 600 | 3.07 |
| 2,2,4-Trimethylpentane | $C_8H_{18}$ | 711 | | 800 − 50 − 100 | 650 | 8.58 |
| *n*-Heptane | $C_7H_{16}$ | 712 | | 700 | 700 | 1.69 |
| 2,4,4-Trimethyl-1-pentene | $C_8H_{16}$ | 750 | | 800 + 50 − 100 − 50 | 700 | 6.67 |
| 2-Heptene | $C_7H_{14}$ | 753 | | 700 + 60 | 760 | 0.92 |
| Methylcyclohexane | $C_7H_{14}$ | 784 | | 700 + 123 − 50 | 773 | 1.4 |
| 1-Octene | $C_8H_{16}$ | 831 | | 800 + 50 | 850 | 2.23 |
| 3-Methyl-1-cyclohexene | $C_7H_{12}$ | 852 | | 700 + 208 − 50 | 858 | 0.7 |
| 4-Methyl-1-cyclohexene | $C_7H_{12}$ | 859 | | 700 + 208 − 50 | 858 | 1.16 |
| 1,3-Dimethylcyclohexane | $C_8H_{16}$ | 860 | | 800 + 123 − 2 × 50 | 823 | 4.3 |
| 2-Octene | $C_8H_{16}$ | 875 | | 800 + 60 | 860 | 1.71 |
| 1-Methyl-1-cyclohexene | $C_7H_{12}$ | 900 | | 700 + 208 | 908 | 0.88 |
| Methylcycloheptane | $C_8H_{16}$ | 935 | | 800 + 183 − 50 | 933 | 0.21 |
| Methylcycloheptene | $C_8H_{14}$ | 1000 | | 800 + 217 − 50 | 967 | 3.3 |
| 4-Vinyl-1-cyclohexene | $C_8H_{12}$ | 1039 | | 800 + 208 − 50 + 50 | 1008 | 2.98 |
| 1-Decene | $C_{10}H_{20}$ | | 1039 | 1000 + 40 | 1040 | 0.1 |
| Dipentene (*p*-Mentha-1,8-diene) | $C_{10}H_{16}$ | 1204 | | 1000 + 203 + 50 − 50 | 1203 | 0.08 |
| 1-Methoxy-1,3-cyclohexadiene | $C_7H_{10}O$ | 1250 | | 800 + 264 + 190 | 1254 | 0.32 |
| 1-Methoxy-1,4-cyclohexadiene | $C_7H_{10}O$ | 1268 | | 800 + 314 + 190 | 1304 | 2.76 |
| 1-Dodecene | $C_{12}H_{24}$ | | 1241 | 1200 + 50 | 1250 | 0.72 |
| Phenylacetylene | $C_8H_6$ | | 1361 | 800 + 350 + 210 | 1360 | 0.07 |
| Tricyclo[6,4,0,0(2,7)]dodecane | $C_{12}H_{20}$ | 1502 | | 1200 + 2 × 123 + 80 | 1526 | 1.57 |
| 1-Hexadecene | $C_{16}H_{32}$ | | 1654 | 1600 + 50 | 1650 | 0.06 |
| 2,6,10,14-Tetramethylpentadecane | $C_{19}H_{40}$ | | 1668 | 1900 − 4 × 50 | 1700 | 1.88 |

[a] The *GRF*s are listed in the order of their appearance in the table. $I_{obs}$ = observed $I$; $I_p$ = predicted $I$; Difference % = (Difference between $I_{obs}$ and $I_p$) × 100/($I_{obs}$ or $I_p$).

on polar column. Tables VI and VII show a comparison of the observed and predicted $I$ values of some fatty acid esters and aromatic acid esters. Substituents and functional groups in the *ortho* positions of the aromatic ring tend to interact and form hydrogen bonding to decrease $I$ substantially. These are known as *ortho* effects $b$ with negative *GRF* values.

### *Acid amides*

The acid amide group contains both N and O atoms and is probably the most polar and polarizable substituent encountered in our study. The acid amido group can drastically alter the $A$ value of the molecule. Since only a small number of the lower members of the acid amide series were studied, the $A$ and the *GRF* values obtained for the lower members may deviate somewhat from the linear relationship for the series. Our study shows that the free, the N-substituted and the N,N-disubstituted acid amides have $A$ values of 45, 45 and 64, and *GRF* values of 1600, 1430 and 1016, respectively. The

TABLE IV

COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF AROMATIC HYDROCARBONS[a]

The *GRFs* ($m_i$ and $n_i$) have the following values: (1) phenyl ring = +350, (2) chain branching = −50, (3) cyclohexane ring = +123, (4) *trans* isomer–*cis* isomer = −60, (5) *ortho* effect *a* between two *ortho* methyl groups in the phenyl ring = +“50”, (6) aryl Cl atom = +276, (7) cyclopentene ring = +163, (8) cyclopropyl ring = +105, (9) cyclohexene ring = +208, (10) cyclopentadiene ring = +210, (11) fusion of two phenyl rings = +60, (12) aryl ether –O– linkage = +190, (13) link between two phenyl rings = +80, (14) double bond conjugated with phenyl ring = +80, (15) aryl Br atom = +426, (16) *ortho* effect *b* between two phenyl rings = −“400”, (17) size factor = +120. The quatation marks indicate that these values were arbitrarily selected.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Benzene | $C_6H_6$ | 947 | | 600 + 350 | 950 | 0.32 |
| Toluene | $C_7H_8$ | 1051 | 1043 | 700 + 350 | 1050 | 0.1 |
| Ethyl benzene | $C_8H_{10}$ | 1129 | | 800 + 350 | 1150 | 1.93 |
| *p*-Xylene | *p*-$C_8H_{10}$ | 1155 | 1138 | 800 + 350 | 1150 | 0.43 |
| *m*-Xylene | *m*-$C_8H_{10}$ | 1164 | | 800 + 350 | 1150 | 1.2 |
| Cumene (isopropyl benzene) | $C_9H_{12}$ | 1182 | | 900 + 350 − 50 | 1200 | 1.5 |
| Decahydronaphthalene, | | | | | | |
| *trans* | $C_{10}H_{18}$ | 1156 | 1163 | 1000 + 2 × 123 − 60 | 1186 | 2.53 |
| *cis* | | 1216 | | 1000 + 2 × 123 | 1246 | 2.41 |
| Decahydronaphthalene, *cis* | $C_{10}H_{18}$ | 1227 | 1232 | 1000 + 2 × 123 | 1246 | 1.52 |
| *n*-Propylbenzene | $C_9H_{12}$ | 1228 | | 900 + 350 | 1250 | 1.76 |
| *o*-Xylene | o-$C_8H_{10}$ | 1232 | | 800 + 350 + “50” | 1200 | 2.6 |
| 1,3,5-Trimethyl benzene | $C_9H_{12}$ | 1271 | | 900 + 350 | 1250 | 1.65 |
| *p*-Cymene (4-isopropyltoluene) | $C_{10}H_{14}$ | 1272 | | 1000 + 350 − 50 | 1300 | 2.15 |
| 1,2,4-Trimethyl benzene | $C_9H_{12}$ | 1311 | | 900 + 350 + 50 | 1300 | 0.84 |
| *n*-Butylbenzene | $C_{10}H_{14}$ | 1312 | 1316 | 1000 + 350 | 1350 | 2.81 |
| *m*-Chlorotoluene | $C_7H_7Cl$ | | 1313 | 700 + 350 + 276 | 1326 | 0.98 |
| Indan | $C_9H_{10}$ | 1377 | 1365 | 900 + 350 + 163 | 1413 | 2.55 |
| Cyclopropyl benzene | $C_9H_{12}$ | 1414 | | 900 + 350 + 105 | 1355 | 4.17 |
| Bicyclohexyl | $C_{12}H_{22}$ | 1420 | 1431 | 1200 + 2 × 123 | 1446 | 1.79 |
| 1,2,4,5-Tetramethylbenzene | $C_{10}H_{14}$ | 1459 | | 1000 + 350 + 2 × 50 | 1450 | 0.62 |
| Tetralin | $C_{10}H_{12}$ | 1525 | 1525 | 1000 + 350 + 208 | 1558 | 2.31 |
| Indene | $C_9H_8$ | 1526 | 1479 | 900 + 350 + 208 + 60 | 1518 | 0.52 |
| Perhydrofluorene | $C_{13}H_{22}$ | | 1632 | 1300 + 2 × 123 + 122 | 1668 | 2.16 |
| Cyclohexyl benzene | $C_{12}H_{16}$ | 1660 | 1662 | 1200 + 350 + 123 | 1673 | 0.66 |
| 1-Fluoronaphthalene | $C_{10}H_7F$ | | 1715 | 1000 + 2 × 350 + 60 | 1760 | 2.56 |
| Naphthalene | $C_{10}H_8$ | 1739 | 1722 | 1000 + 2 × 350 + 60 | 1760 | 1.19 |
| *o*-Dimethoxybenzene | $C_8H_{10}O_2$ | | 1715 | 1000 + 350 + 2 × 190 | 1730 | 0.87 |
| 2-Methyl naphthalene | $C_{11}H_{10}$ | 1852 | | 1100 + 2 × 350 + 60 | 1860 | 0.43 |
| 1-Methyl naphthalene | $C_{11}H_{10}$ | 1855 | | 1100 + 2 × 350 + 60 | 1860 | 0.27 |
| 1-Ethylnaphthalene | $C_{12}H_{12}$ | | 1943 | 1200 + 2 × 350 + 60 | 1960 | 0.87 |
| Biphenyl | $C_{12}H_{10}$ | 1974 | | 1200 + 2 × 350 + 80 | 1980 | 0.3 |
| Diphenylmethane | $C_{13}H_{12}$ | | 1994 | 1300 + 2 × 350 | 2000 | 0.3 |
| 2-Chloronaphthalene | $C_{10}H_7Cl$ | | 2006 | 1000 + 2 × 350 + 276 | 2036 | 1.47 |
| 3,4-Dimethoxystyrene | $C_{10}H_{12}O_2$ | 2039 | | 1200 + 350 + 2 × 190 + 80 | 2010 | 1.42 |
| Bibenzyl | $C_{14}H_{14}$ | 2061 | | 1400 + 2 × 350 | 2100 | 0.8 |
| Acenaphthene | $C_{12}H_{10}$ | 2133 | 2108 | 1200 + 2 × 350 + 163 + 60 | 2123 | 0.47 |
| 1-Methoxynaphthalene | $C_{11}H_{10}O$ | | 2143 | 1200 + 2 × 350 + 60 + 190 | 2150 | 0.32 |
| 1-Phenyldodecane | $C_{18}H_{30}$ | | 2155 | 1800 + 350 | 2150 | 0.23 |
| 1-Bromonaphthalene | $C_{10}H_7Br$ | | 2157 | 1000 + 2 × 350 + 60 + 426 | 2186 | 1.33 |
| 1,2,3,4,5,6,7,8-Octahydroanthracene | $C_{14}H_{18}$ | 2153 | | 1400 + 350 + 2 × 208 | 2166 | 0.6 |

TABLE IV (*continued*)

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Fluorene | $C_{13}H_{10}$ | 2264 | 2311 | 1300 + 2 × 350 + 208 + 2 × 60 | 2328 | 2.75 |
| *o*-Terphenyl | $C_{18}H_{14}$ | 2649 | | 1800 + 3 × 350 + 2 × 80 − "400" | 2610 | 1.47 |
| Anthracene | $C_{14}H_{10}$ | 2630 | | 1400 + 3 × 350 + 2 × 60 + 120 | 2690 | 0.81 |
| Phenanthrene | $C_{14}H_{10}$ | 2712 | | 1400 + 3 × 350 + 2 × 60 + 120 | 2690 | 0.03 |
| *p*-Terphenyl | $C_{18}H_{14}$ | 3129 | | 1800 + 3 × 350 + 2 × 80 + 120 | 3130 | 0.03 |
| Pyrene | $C_{16}H_{10}$ | 3135 | | 1600 + 4 × 350 + 120 | 3120 | 0.48 |
| 2,3-Benzanthracene | $C_{18}H_{12}$ | 9999 | | | | |
| Triphenylene | $C_{18}H_{12}$ | 9999 | | | | |

[a] See footnote in Table III.

magnitude and trend of these *A* and *GRF* values suggest that substitution in highly polar and polarizable functional groups not only reduces the *GRF* but also alters the *A* value. Table VIII shows the comparison of observed and predicted *I* values of some free and substituted acid amides.

In Table VIII, formamide appears to have a higher *I* than acetamide, even though the latter has one more carbon atom than the former. In formamide the acid amido group is connected to a H atom but not to a C atom. The atom to which the functional group is connected can strongly influence the *GRF* value. Other examples are amino $-NH_2$ and alcoholic –OH groups which give different *GRF*s when connected to secondary and tertiary C atoms.

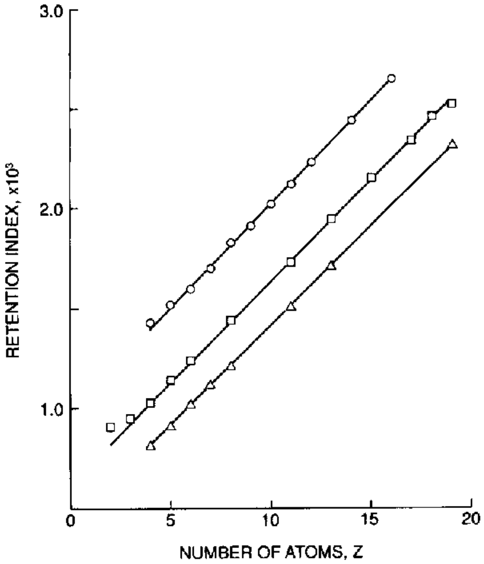

Fig. 1. Linear plots of *I* *vs.* the number of atoms (*Z*) of the homologous series of alkanoic acids (○), alkanols (□) and aminoalkanes (△) on polar column.

*Aliphatic alcohols*

The primary alcohol ($-CH_2-OH$) group has a *GRF* value of +162 on non-polar column [1] and +641 on polar column, with a column difference of approximately 480. The hydroxyl group is one of the most polar functional groups. The linear plot of *Z* *vs.* *I* for the alkanols is given in Fig. 1 and the corresponding coefficient and intercept for the linear regression equation are listed in Table I.

Hydroxyl groups connected to secondary and tertiary carbon atoms form secondary and tertiary aliphatic alcohols and have *GRF* values of +530 and +410, respectively, on polar column. On non-polar column, the secondary and tertiary alcoholic –OH groups have *GRF* values of +85 and +15, respectively [1], yielding a column difference slightly smaller than the primary alcoholic –OH group. Table IX shows the $Am_f$ for the hydroxyl group in *n*-alkanols, and Table X compares the observed and predicted *I* values of other alcohols.

*Phenols*

The phenolic –OH group can undergo conjugation with the ring to yield a co-planar structure which gives a higher *GRF* than the alcoholic –OH group. The *I* values of the phenols listed in Table XI are taken from ref. 14. Substituents at the *ortho*

TABLE V

THE $\Delta m_f$ OF THE ALIPHATIC CARBOXYL GROUP AND COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF $n$-ALKANOIC ACIDS (ON CW-20M)[a]

The *GRF*s have the following values: (1) aliphatic carboxylic acid group, R–COOH = +1029, (2) chain branching = −50, (3) cyclobutane ring = +110, (4) cyclopentane ring = +122.

| Compound | Formula | $I_{obs}$ | Lit. | 100Z | $\Delta m_f$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|---|
| Acetic acid | $C_2H_4O_2$ | 1430 | 1430 [16] | 400 | 1030 | 1429 | 0.07 |
| *n*-Propionic acid | $C_3H_6O_2$ | 1518 | 1523 [16] | 500 | 1018 | 1529 | 0.72 |
| *n*-Butanoic acid | $C_4H_8O_2$ | 1600 | 1614 [16] | 600 | 1000 | 1629 | 1.78 |
| *n*-Pentanoic acid | $C_5H_{10}O_2$ | 1706 | | 700 | 1006 | 1729 | 1.33 |
| 2-Methylpentanoic acid | $C_6H_{12}O_2$ | | 1746 [16] | | | 1779 | 1.86 |
| *n*-Hexanoic acid | $C_6H_{12}O_2$ | 1834 | 1822 [16] | 800 | 1034 | 1829 | 0.27 |
| *n*-Heptanoic acid | $C_7H_{14}O_2$ | 1916 | 1962 [15]<br>1935 [16] | 900 | 1016 | 1929 | 0.67 |
| *n*-Octanoic acid | $C_8H_{16}O_2$ | 2029 | 2072 [15] | 1000 | 1029 | 2029 | 0 |
| *n*-Nonanoic acid | $C_9H_{18}O_2$ | 2132 | 2182 [15] | 1100 | 1032 | 2129 | 0.14 |
| *n*-Decanoic acid | $C_{10}H_{20}O_2$ | 2238 | 2290 [15] | 1200 | 1038 | 2229 | 0.4 |
| Lauric acid | $C_{12}H_{24}O_2$ | 2451 | | 1400 | 1051 | 2429 | 0.9 |
| Myristic acid | $C_{14}H_{28}O_2$ | 2660 | | 1600 | 1060 | 2629 | 1.17 |
| | | | | Average | 1028.55 ± 17.94 | | |
| | | | | $(100Z + \Sigma m_i - \Sigma n_i)$ | | | |
| Cyclobutane carboxylic acid | $C_5H_8O_2$ | | 1831 [16] | 700 + 110 + 1029 | | 1839 | 0.44 |
| Cyclopentane propionic acid | $C_8H_{14}O_2$ | | 2169 [16] | 1000 + 122 + 1029 | | 2151 | 0.83 |
| Cyclopentane carboxylic acid | $C_6H_{10}O_2$ | | 1932 [16] | 800 + 122 + 1029 | | 1951 | 0.97 |

[a] See footnote in Table III.

TABLE VI

COLUMN DIFFERENCES AND $I$ VALUES OF METHYL ESTERS OF ALIPHATIC ACIDS ON NON-POLAR AND POLAR COLUMNS[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) ethyl ester group = +270, (2) ether –O– linkage = +70.

| Compound | Formula | $I_{obs}$ | | Column difference ($\Delta I$) |
|---|---|---|---|---|
| | | On SE-30 | On CW-20M | |
| *Methyl esters* | | | | |
| Methyl propionate | $C_4H_8O_2$ | 613 | 900 | 287 |
| Methyl butyrate | $C_5H_{10}O_2$ | 711 | 1000 | 289 |
| Methyl pentanoate | $C_6H_{12}O_2$ | 808 | 1109 | 301 |
| Methyl hexanoate | $C_7H_{14}O_2$ | 908 | 1200 | 292 |
| Methyl heptanoate | $C_8H_{16}O_2$ | 1007 | 1302 | 295 |
| Methyl octanoate | $C_9H_{18}O_2$ | 1110 | 1400 | 290 |
| Methyl nonanoate | $C_{10}H_{20}O_2$ | 1200 | 1507 | 307 |
| Methyl decanoate | $C_{11}H_{22}O_2$ | 1309 | 1600 | 291 |
| Methyl laurate | $C_{13}H_{26}O_2$ | 1503 | 1800 | 297 |
| | | | Average | 294.33 ± 6.42 |

TABLE VI (*continued*)

| Compound | Formula | $I_{obs}$ | | Column difference ($\Delta I$) |
|---|---|---|---|---|
| | | On SE-30 | On CW-20M | |
| *Ethyl esters* | | | | |
| Ethyl acetate | $C_4H_8O_2$ | 600 | 900 | 300 |
| Ethyl propionate | $C_5H_{10}O_2$ | | 966 | |
| Ethyl butyrate | $C_6H_{12}O_2$ | 787 | 1046 | 262 |
| Ethyl pentanoate | $C_7H_{14}O_2$ | 885 | 1149 | 264 |
| Ethyl hexanoate | $C_8H_{16}O_2$ | 982 | 1246 | 264 |
| Ethyl heptanoate | $C_9H_{18}O_2$ | 1084 | 1345 | 261 |
| Ethyl octanoate | $C_{10}H_{20}O_2$ | 1180 | 1451 | 271 |
| Ethyl nonanoate | $C_{11}H_{22}O_2$ | 1282 | 1552 | 270 |
| Ethyl decanoate | $C_{12}H_{24}O_2$ | 1378 | 1645 | 267 |
| Ethyl laurate | $C_{14}H_{28}O_2$ | 1537 | 1848 | 275 |
| | | | Average | 274.44 ± 11.99 |
| *Propyl esters* | | | | |
| Propyl acetate | $C_5H_{10}O_2$ | | 986 | |
| Propyl propionate | $C_6H_{12}O_2$ | 794 | 1059 | 265 |
| Propyl butyrate | $C_7H_{14}O_2$ | 882 | 1137 | 255 |
| Propyl pentanoate | $C_8H_{16}O_2$ | 980 | 1233 | 253 |
| Propyl hexanoate | $C_9H_{18}O_2$ | 1080 | 1337 | 257 |
| Propyl heptanoate | $C_{10}H_{20}O_2$ | 1177 | 1434 | 257 |
| Propyl octanoate | $C_{11}H_{22}O_2$ | 1277 | 1539 | 262 |
| Propyl nonanoate | $C_{12}H_{24}O_2$ | 1376 | 1631 | 255 |
| Propyl decanoate | $C_{13}H_{26}O_2$ | 1471 | 1729 | 258 |
| Propyl laurate | $C_{15}H_{30}O_2$ | 1661 | 1930 | 269 |
| | | | Average | 259.00 ± 5.27 |
| *Butyl esters* | | | | |
| Butyl formate | $C_5H_{10}O_2$ | 712 | 1033 | 321 |
| Butyl propionate | $C_7H_{14}O_2$ | 891 | 1157 | 266 |
| Butyl butyrate | $C_8H_{16}O_2$ | 979 | 1227 | 248 |
| Butyl valerate | $C_9H_{18}O_2$ | 1078 | 1336 | 258 |
| Butyl hexanoate | $C_{10}H_{20}O_2$ | 1175 | 1427 | 252 |
| Butyl heptanoate | $C_{11}H_{22}O_2$ | 1278 | 1533 | 255 |
| Butyl nonanoate | $C_{13}H_{26}O_2$ | 1470 | 1725 | 255 |
| | | | Average | 255.67 ± 6.09 |

| Compound | Formula | Lit. [16] | ($100Z + \Sigma m_i$ and $\Sigma n_i$) | $I_p$ | Difference (%) |
|---|---|---|---|---|---|
| 2-Ethoxyethanol, acetate | $C_6H_{12}O_3$ | 1290 | $900 + 270 + 70$ | 1240 | 3.88 |
| Ethylene glycol diacetate | $C_6H_{11}O_4$ | 1539 | $1000 + 2 \times 270$ | 1540 | 0.06 |
| 2-(2-Butoxyethoxy)ethanol, acetate | $C_{10}H_{20}O_4$ | 1838 | $1400 + 270 + 2 \times 70$ | 1810 | 1.52 |
| Triethylene glycol, diacetate | $C_{10}H_{18}O_6$ | 2337 | $1600 + 2 \times 270 + 2 \times 70$ | 2337 | 2.44 |

[a] See footnote in Table III.

position of the phenol can interact and hydrogen bond with the adjacent phenolic –OH group to mask its functionality and reduce *I*. The decrease in *I* of the *o*-isomers is attributed to *ortho* effect *b* and is obtained as the difference between the *I* values of the *o*-isomer and the *m*-isomer. In the absence of *para* effect, the *I* values of the *p*-isomer may be used for that of the *m*-isomer.

TABLE VII

COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF SOME MIXED ACID ESTERS[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) non-terminal C=C double bond = +60, (2) methyl ester group = +295, (3) conjugation of the –C=C–C=O group in alkane chain = +53, (4) cyclohexane ring = +123, (5) cyclopentadiene ring = +210, (6) O atom in 5-membered ring = +80, (7) conjugation of –C=C–C=O group in 5-membered ring = +106, (8) phenyl ring = +350, (9) cyclopentane ring = +122, (10) *ortho* effect *b* between methyl and carboxy group = –"40", (11) carbethoxy group = +270, (12) butyl ester group = +256, (13) propyl ester group = +259, (14) *ortho* effect *b* between two carbethoxy groups = –"90".

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i$ and $\Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Crotonic acid, methyl ester | $C_5H_8O_2$ | | 1108 | 700 + 60 + 295 + 53 | 1108 | 0 |
| Methyl cyclohexane carboxylate | $C_8H_{13}O_2$ | 1384 | | 1000 + 123 + 295 | 1418 | 2.39 |
| 2-Furoic acid, methyl ester | $C_6H_6O_3$ | | 1570 | 900 + 210 + 80 + 295 + 106 | 1591 | 1.32 |
| Methyl benzoate | $C_8H_8O_2$ | 1678 | 1614 | 1000 + 350 + 295 | 1645 | 1.97 |
| Tetrahydrofurfuryl alcohol propionate | $C_8H_{14}O_3$ | 1635 | | 1100 + 122 + 80 + 295 | 1597 | 2.32 |
| Phenyl acetate | $C_8H_8O_2$ | 1660 | | 1000 + 350 + 295 | 1645 | 0.9 |
| *o*-Tolyl acetate | $C_9H_{10}O_2$ | 1716 | | 1100 + 350 + 295 – "40" | 1705 | 0.64 |
| Ethyl benzoate | $C_9H_{10}O_2$ | 1718 | 1659 | 1100 + 350 + 270 | 1720 | 0.12 |
| *m*-Tolyl acetate | $C_9H_{10}O_2$ | 1756 | | 1100 + 350 + 295 | 1745 | 0.63 |
| *p*-Tolyl acetate | $C_9H_{10}O_2$ | 1769 | | 1100 + 350 + 295 | 1745 | 1.36 |
| Benzyl acetate | $C_9H_{10}O_2$ | 1779 | | 1100 + 350 + 295 | 1745 | 1.91 |
| Ethyl phenylacetate | $C_{10}H_{12}O_2$ | 1821 | | 1200 + 350 + 270 | 1820 | 0.05 |
| 2-Phenylethyl acetate | $C_{10}H_{12}O_2$ | 1854 | | 1200 + 350 + 295 | 1845 | 0.49 |
| *n*-Butyl benzoate | $C_{11}H_{14}O_2$ | 1903 | | 1300 + 350 + 256 | 1906 | 0.16 |
| 2-Furoic acid, propyl ester | $C_8H_{10}O_3$ | | 1696 | 1100 + 210 + 80 + 259 | 1649 | 2.77 |
| 2-Furoic acid, hexyl ester | $C_{11}H_{16}O_3$ | | 2000 | 1400 + 210 + 80 + 256 | 1946 | 2.7 |
| *n*-Amyl benzoate | $C_{12}H_{16}O_2$ | 2017 | | 1400 + 350 + 256 | 2006 | 0.55 |
| Methyl *p*-anisate | $C_9H_{10}O_3$ | 2084 | | 1200 + 350 + 295 + 190 | 2035 | 1.31 |
| Ethyl cinnamate | $C_{11}H_{12}O_2$ | 2173 | | 1400 + 350 + 60 + 270 + 53 | 2133 | 1.84 |
| *n*-Heptyl benzoate | $C_{14}H_{20}O_2$ | 2217 | | 1600 + 350 + 256 | 2206 | 0.5 |
| *m*-Phenylene diacetate | $C_{10}H_{10}O_4$ | 2301 | | 1400 + 350 + 2 × 295 | 2340 | 1.67 |
| Dimethyl phthalate | $C_{10}H_{10}O_4$ | 2325 | | 1400 + 350 + 2 × 295 | 2340 | 0.64 |
| Diethyl phthalate | $C_{12}H_{14}O_4$ | 2400 | | 1600 + 350 + 2 × 270 – "90" | 2400 | 0 |
| *n*-Decyl benzoate | $C_{17}H_{26}O_2$ | 2519 | | 1900 + 350 + 256 | 2506 | 0.52 |
| Benzyl benzoate | $C_{14}H_{12}O_2$ | 2638 | | 1600 + 2 × 350 + 295 | 2595 | 1.66 |

[a] See footnote in Table III.

*Ethers and sulfides*

On non-polar columns the ethers behave chromatographically as hydrocarbons, but on polar columns the ethers are retained longer. The free electron pairs on the ether oxygen atom can interact with the polar stationary phase to prolong the retention of the ether. The straight chain aliphatic ether oxygen has a *GRF* value of +70.

Oxygen attached to the phenyl ring can assume a co-planar configuration with the ring and enhance retention. Aromatic ether –O– linkage has a *GRF* of +190 in anisole. In diphenyl ether the bulky substituents can sterically hinder the interaction of the ether oxygen with the stationary phase to reduce the *GRF* value. A comparison of the observed and predicted $I$ values of ethers is given in Table XII.

The *GRF* for the sulfide group is +256 and that for the disulfide group is +377. The sulfide group is similar to an ether in structure except that the ether oxygen is replaced with a sulfur atom. The sulfur atom is assigned an equivalency of two carbon atoms and contributes 200 units in $I$.

TABLE VIII

COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF ACID AMIDES[a]

The *GRF*s have the following values: (1) amido $-CO-NH_2$ group = +1600, (2) amido $-CO-NHR$ group = +1430, (3) amido $-CO-NR_2$ group = +1016, (4) for the value of $A$, the $I$ increment for atom addition, see text, (5) $-NH-C_2H_5$ group = −50, (6) phenyl ring = +350, (7) tertiary N atom in aryl ring = +240.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $AZ + \Sigma m_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Formamide | $CH_3NO$ | 1791 | | $3 \times 45 + 1600$ | 1735 | 3.13 |
| Acetamide | $C_2H_4NO$ | 1775 | 1725 | $4 \times 45 + 1600$ | 1780 | 2.81 |
| Propionamide | $C_3H_6NO$ | 1821 | 1801 | $5 \times 45 + 1600$ | 1825 | 0.22 |
| N-Methylformamide | $C_2H_5NO$ | | 1615 | $4 \times 45 + 1430$ | 1610 | 0.31 |
| N-Methylacetamide | $C_3H_6NO$ | 1648 | 1609 | $5 \times 45 + 1430$ | 1655 | 0.42 |
| N-Ethylacetamide | $C_4H_9NO$ | | 1608 | $6 \times 45 + 1430 - 50$ | 1650 | 2.55 |
| N-Methylpropionamide | $C_4H_8NO$ | 1690 | 1645 | $6 \times 45 + 1430$ | 1700 | 0.59 |
| N-Butylacetamide | $C_6H_{13}NO$ | | 1793 | $8 \times 45 + 1430$ | 1790 | 0.17 |
| N-Allylacrylamide | $C_6H_9NO$ | | 1871 | $8 \times 45 + 1430 + 2 \times 40$ | 1870 | 0.05 |
| N,N-Dimethylformamide | $C_3H_6NO$ | 1327 | 1312 | $5 \times 64 + 1016^b$ | 1336 | 0.67 |
| N,N-Dimethylacetamide | $C_4H_8NO$ | 1409 | 1384 | $6 \times 64 + 1016$ | 1400 | 0.64 |
| N,N-Diethylformamide | $C_5H_{11}NO$ | | 1413 | $7 \times 64 + 1016 - 50$ | 1414 | 0.07 |
| N,N-Dimethylpropionamide | $C_5H_{10}NO$ | 1454 | | $7 \times 64 + 1016$ | 1464 | 0.68 |
| N,N-Dibutylformamide | $C_9H_{19}NO$ | | 1744 | $11 \times 64 + 1016$ | 1720 | 1.38 |
| N-Methylformanilide | $C_8H_9NO$ | | 2027 | $10 \times 64 + 1016 + 350$ | 2006 | 1.04 |
| N,N-Diethylnicotinamide | $C_{10}H_{14}N_2O$ | | 2353 | $13 \times 64 + 1016 + 350 + 240 - 2 \times 50$ | 2338 | 0.64 |

[a] See footnote in Table III.

[b] Regression equation for N,N-disubstituted acid amides: $I = 63.50\ Z \pm 1015.67$.

TABLE IX

GRF ($\Delta m_f$) OF ALCOHOL HYDROXYL GROUP AND COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES HOMOLOGOUS PRIMARY ALIPHATIC ALCOHOLS[a]

| Compound | Formula | $I_{obs}$ | Lit. | 100$Z$ | $\Delta m_f$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|---|
| Methanol | $CH_4O$ | 909 | | 200 | 709 | 847 | 6.82 |
| Ethanol | $C_2H_6O$ | 944 | | 300 | 644 | 947 | 0.32 |
| 1-Propanol | $C_3H_8O$ | 1025 | 1027 [16] | 400 | 625 | 1047 | 2.1 |
| 1-Butanol | $C_4H_{10}O$ | 1141 | 1135 [16] | 500 | 641 | 1147 | 0.52 |
| 1-Pentanol | $C_5H_{12}O$ | 1236 | 1200 [16] | 600 | 636 | 1247 | 0.88 |
| 1-Hexanol | $C_6H_{14}O$ | | 1367 [15] | 700 | 667 | 1347 | 1.46 |
| 1-Heptanol | $C_7H_{16}O$ | 1440 | 1470 [15] | 800 | 640 | 1447 | 0.48 |
| 1-Octanol | $C_8H_{18}O$ | | 1573 [15] | 900 | 673 | 1547 | 1.65 |
| 1-Decanol | $C_{10}H_{22}O$ | 1735 | 1778 [15]<br>1752 [16] | 1100 | 635 | 1747 | 0.69 |
| 1-Dodecanol | $C_{12}H_{26}O$ | 1950 | 1983 [15] | 1300 | 650 | 1947 | 0.15 |
| 1-Tetradecanol | $C_{14}H_{30}O$ | 2157 | | 1500 | 657 | 2147 | 0.46 |
| 1-Hexadecanol | $C_{16}H_{34}O$ | 2352 | | 1700 | 652 | 2347 | 0.21 |
| 1-Heptadecanol | $C_{17}H_{36}O$ | 2475 | | 1800 | 657 | 2447 | 0.41 |
| 1-Octadecanol | $C_{18}H_{38}O$ | 2534 | | 1900 | 634 | 2547 | 0.51 |
| | | | | Average | 647.00 ± 13.91 | | |

[a] See footnote in Table III. Regression equation for homologues of $n$-alkanols: $I = 100.54\ Z + 641.34$.

TABLE X

COMPARISON OF OBSERVED AND PREDICTED *I* VALUES OF SOME ALCOHOLS (ON DB-WAX)[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) aliphatic secondary alcohol –OH = +530, (2) aliphatic tertiary alcohol –OH = +410, (3) terminal C=C double bond = +40, (4) chain branching = −50, (5) aliphatic primary alcohol –OH = +647, (6) terminal C–C triple bond = +300, (7) quaternary C atom = −100, (8) 5-membered alicyclic ring = +122, (9) alicyclic –OH = +580, (10) alkyl ether O– link = −70, (11) alkyl –Cl atom = +464, (12) 6-membered alicyclic ring = +123, (13) difference between *cis* and *trans* isomer = +50, (14) cyclohexene ring = +208, (15) alkyl –Br atom = +592, (16) cycloheptane ring = +183, (17) aryl ether –O– linkage = +190.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| 2-Propanol | $C_3H_8O$ | 942 | | 400 + 530 | 930 | 0.96 |
| *tert.*-Butyl alcohol | $C_4H_{10}O$ | 916 | | 500 + 410 | 910 | 0.66 |
| *tert.*-Amyl alcohol | $C_5H_{12}O$ | 1015 | | 600 + 410 | 1010 | 0.49 |
| 2-Methyl-3-buten-2-ol | $C_5H_{10}O$ | | 1023 | 600 + 410 + 40 | 1050 | 2.57 |
| 2-Butanol | $C_4H_{10}O$ | 1031 | 1082 | 500 + 530 | 1030 | 0.1 |
| 2,3-Dimethyl-2-butanol | $C_6H_{14}O$ | | 1082 | 700 + 410 − 50 | 1060 | 2.03 |
| 2-Methyl-1-propanol | $C_4H_{10}O$ | 1092 | | 500 + 647 − 50 | 1097 | 0.46 |
| 2-Pentanol | $C_5H_{12}O$ | | 1110 | 600 + 530 | 1130 | 1.77 |
| 3-Pentanol | $C_5H_{12}O$ | | 1110 | 600 + 530 | 1130 | 1.77 |
| Allyl alcohol | $C_3H_6O$ | 1122 | 1110 | 400 + 647 + 40 | 1087 | 3.12 |
| 1-Methoxy-2-propanol | $C_4H_{10}O_2$ | 1135 | | 600 + 530 | 1130 | 0.44 |
| 4-Methyl-2-pentanol | $C_6H_{14}O$ | 1181 | | 700 + 530 − 50 | 1180 | 0.08 |
| 3-Ethyl-3-pentane | $C_7H_{16}O$ | | 1196 | 800 + 410 | 1210 | 1.16 |
| 2-Methyl-3-butyn-2-ol | $C_5H_8O$ | 1230 | | 600 + 410 + 300 − 100 | 1210 | 1.63 |
| 3-Methyl-1-butanol | $C_5H_{12}O$ | 1231 | | 600 + 647 − 50 | 1197 | 3.09 |
| 3,3-Dimethyl-1-butanol | $C_6H_{14}O$ | | 1249 | 700 + 647 − 100 | 1247 | 0.16 |
| 2-Methyl-2-heptanol | $C_8H_{18}O$ | | 1280 | 900 + 410 | 1310 | 2.29 |
| 2-Ethyl-1-butanol | $C_6H_{14}O$ | 1312 | | 700 + 647 − 50 | 1297 | 1.14 |
| Cyclopentanol | $C_5H_{10}O$ | 1327 | 1297 | 600 + 122 + 580 | 1302 | 1.88 |
| 2-Propyn-1-ol | $C_3H_4O$ | 1357 | | 400 + 647 + 300 | 1347 | 0.74 |
| 2-Methoxy-1-butanol | $C_5H_{12}O_2$ | | 1359 | 700 + 647 + 70 − 50 | 1367 | 0.59 |
| 6-Methyl-2-heptanol | $C_8H_{18}O$ | | 1365 | 900 + 530 − 50 | 1380 | 1.09 |
| 2-Chloroethanol | $C_2H_5OCl$ | 1379 | | 300 + 647 + 464 | 1411 | 2.27 |
| Cyclohexanol | $C_6H_{12}O$ | 1400 | 1392 | 700 + 123 + 580 | 1403 | 0.21 |
| 2-Methyl cyclohexanol | $C_7H_{14}O$ | 1438 | | 800 + 123 + 580 − 50 | 1453 | 1.03 |
| *trans* | | | 1409 | | | |
| 3-Methyl cyclohexanol | $C_7H_{14}O$ | | | | | |
| *trans* (32%) | | 1459 | | | | |
| *cis* (68%) | | 1482 | | 800 + 123 + 580 − 50 | 1453 | 1.96 |
| 4-Methyl cyclohexanol | $C_7H_{14}O$ | | | | | |
| *trans* (18%) | | 1456 | 1447 | | | |
| *cis* (82%) | | 1476 | 1430 | 800 + 123 + 580 − 50 | 1453 | 1.56 |
| 2-Cyclohexen-1-ol | $C_6H_8O$ | 1479 | | 700 + 208 + 580 | 1488 | 0.6 |
| 2-Bromoethanol | $C_2H_5BrO$ | | 1492 | 300 + 647 + 592 | 1539 | 3.05 |
| Tetrahydrofurfuryl alcohol | $C_5H_{10}O_2$ | 1496 | | 700 + 122 + 647 | 1469 | 1.8 |
| Cycloheptanol | $C_7H_{14}O$ | | 1547 | 800 + 183 + 530 | 1513 | 2.2 |
| 1,3-Propanediol | $C_3H_8O_2$ | 1789 | | 500 + 2 × 647 | 1794 | 0.28 |
| Benzyl alcohol | $C_7H_8O$ | | 1857 | 800 + 350 + 647 | 1797 | 3.23 |
| Diethylene glycol | $C_4H_{10}O_3$ | | 1953 | 700 + 2 × 647 | 1994 | 2.06 |
| 2[2-(2-Methoxyethoxy)-ethoxy]-ethanol | $C_7H_{16}O_4$ | | 1963 | 1100 + 647 + 3 × 70 | 1957 | 0.31 |
| α-Butyl benzyl alcohol | $C_{11}H_{16}O$ | | 2050 | 1200 + 530 + 350 | 2080 | 1.44 |
| 2-(Benzyloxy)ethanol | $C_9H_{12}O_2$ | 2129 | | 1100 + 350 + 70 + 647 | 2167 | 1.75 |
| 2-Phenoxyethanol | $C_8H_{10}O_2$ | | 2139 | 1000 + 350 + 190 + 647 | 2187 | 2.19 |

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[a] See footnote in Table III.

TABLE XI

COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF PHENOLS AND THIOLS[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) phenyl ring = +350, (2) aryl thiol -SH group = +340, (3) alkyl thiol -SH group = +370, (4) phenolic -OH group = +900, (5) aryl Cl atom = +276, (6) ortho effect b between -OH and -Cl = −"390", (7) aryl ether -O- linkage = +190, (8) ortho effect b between -OH and $-OC_2H_5$ groups = −"610", (9) ortho effect b between -OH and $-OCH_3$ groups = −"500", (10) ortho effect b between -OH and $-CH_3$ groups = −"100", (11) ortho effect b between -OH and $-C_2H_5$ groups = −"100", (12) ortho effect a between two adjacent methyl groups = +"50", (13) terminal C=C double bond = +40, (14) ortho effect b between -OH and allyl group = −"150", (15) aryl Br atom = +426, (16) ortho effect b between -OH and -Br atom = −"242", (17) quaternary C atom = −100, (18) ortho effect b between -OH and *tert.* butyl group = −"90".

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Benzene thiol | $C_6H_6S$ | | 1491 | 800 + 350 + 340 | 1490 | 0.07 |
| Benzyl mercaptan | $C_7H_8S$ | | 1618 | 900 + 350 + 370 | 1620 | 0.12 |
| *o*-Chlorophenol | $C_6H_5ClO$ | | 1830 | 700 + 350 + 900 + 276 − "390" | 1836 | 0.33 |
| *o*-Ethoxyphenol | $C_8H_{10}O_2$ | | 1831 | 1000 + 350 +900 + 190 − "610" | 1830 | 0.05 |
| Guaiacol | $C_7H_8O_2$ | | 1840 | 900 + 350 + 900 + 190 − "500" | 1840 | 0 |
| 2,6-Dimethylphenol | $C_8H_{10}O$ | | 1889 | 900 + 350 + 900 − 2 × "100" | 1950 | 3.13 |
| *o*-Cresol | $C_7H_8O$ | | 1979 | 800 + 350 + 900 − "100" | 1950 | 1.47 |
| Phenol | $C_6H_6O$ | 1954 | | 700 + 350 + 900 | 1950 | 0.2 |
| 2-Ethylphenol | $C_8H_{10}O$ | | 2044 | 900 + 350 + 900 − "100" | 2050 | 0.29 |
| *p*-Cresol | $C_7H_8O$ | | 2055 | 800 + 350 + 900 | 2050 | 0.24 |
| *m*-Cresol | $C_7H_8O$ | | 2059 | 800 + 350 + 900 | 2050 | 0.44 |
| 2,3-Dimethylphenol | $C_8H_{10}O$ | | 2120 | 900 + 350 + 900 + "50" − "100" | 2100 | 0.94 |
| 2-Allylphenol | $C_9H_{10}O$ | | 2132 | 1000 + 350 + 900 + 40 − "150" | 2140 | 0.37 |
| *o*-Bromophenol | $C_6H_5BrO$ | | 2134 | 700 + 350 + 900 + 426 − "242" | 2134 | 0 |
| 3,5-Dimethylphenol | $C_8H_{10}O$ | | 2146 | 900 + 350 + 900 | 2150 | 0.19 |
| 3-Ethylphenol | $C_8H_{10}O$ | | 2151 | 900 + 350 + 900 | 2150 | 0.05 |
| *o*-*tert.*-Butyl phenol | $C_{10}H_{14}O$ | | 2161 | 1100 + 350 + 900 − 100 − "90" | 2160 | 0.05 |
| 3,4-Dimethylphenol | $C_8H_{10}O$ | | 2189 | 900 + 350 + 900 + "50" | 2200 | 0.5 |
| *m*-Ethoxyphenol | $C_8H_{10}O_2$ | | 2427 | 1000 + 350 + 900 + 190 | 2440 | 0.53 |

[a] See footnote in Table III.

### *Aldehydes and ketones*

Aliphatic aldehyde and ketone groups are different in their attachment to C and H atoms but share the same *GRF* value. A similar situation also prevails for these groups on non-polar column. The keto group attached to a phenyl ring has the same *GRF* of +388 as for aliphatic ketones, but the keto group attached to an alicyclic ring has a higher *GRF* value of +465. Tables XIII and XIV show the comparison of observed and predicted $I$ values of aliphatic, alicyclic and aromatic aldehydes and ketones.

In aromatic aldehydes and ketones, the 1,4 or *para* substituents can extend their conjugation through the phenyl ring to increase $I$; in contrast, the *ortho* substituents can mutually interact and hydrogen bond to decrease $I$. *p*-Hydroxybenzaldehyde, *p*-dimethylaminobenzaldehyde and *p*-anisaldehyde belong to the first category and salicylaldehyde, 2′-hydroxyacetophenone and *o*-anisaldehyde to the second category. The effects of extended conjugation and hydrogen bonding are given, respectively, in terms of *GRF* values under the name of *para* effect and *ortho* effect *b* in Table I.

### *Aliphatic amines*

The N and O atoms have electronegativity values of 3.0 and 3.5, respectively, as compared to 2.5 for the C atom [19]. This difference is reflected in the *GRF*s of the amino and hydroxyl groups. The aliphatic amino $-NH_2$ group is less polar than the

TABLE XII

COMPARISON OF OBSERVED AND PREDICTED *I* VALUES OF ETHERS AND SULFIDES[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) aliphatic ether –O– linkage = +70, (2) sulfide –S– linkage = +256, (3) terminal C=C double bond = +40, (4) chain branching = −50, (5) aliphatic sulfide –S–S– linkage = +377, (6) tertiary C atom = −75, (7) phenyl ring = +350, (8) aryl ether –O– linkage = +190, (9) link between two phenyl rings = +80.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Ethyl ether | $C_4H_{10}O$ | 616 | 1842 | 500 + 70 | 570 | 7.47 |
| Propyl ether | $C_6H_{14}O$ | 782 | | 700 + 70 | 770 | 0.15 |
| Butyl ether | $C_8H_{18}O$ | 971 | | 900 + 70 | 970 | 0.1 |
| Pentyl ether | $C_{10}H_{22}O$ | 1163 | 1161 | 1100 + 70 | 1170 | 0.6 |
| Hexyl ether | $C_{12}H_{26}O$ | 1368 | 1359 | 1300 + 70 | 1370 | 0.15 |
| Octyl ether | $C_{16}H_{34}O$ | 1763 | | 1700 + 70 | 1770 | 0.39 |
| Allyl sulfide | $C_6H_{10}S$ | | 1151 | 800 + 256 + 2 × 40 | 1136 | 1.3 |
| (2-Ethylhexyl) vinyl ether | $C_{10}H_{20}O$ | | 1168 | 1100 + 70 + 40 − 50 | 1160 | 0.68 |
| Butyl sulfide | $C_8H_{18}S$ | | 1256 | 1000 + 256 | 1256 | 0 |
| *tert.*-Butyl disulfide | $C_8H_{18}S_2$ | | 1323 | 1200 + 377 − 2 × 75 | 1727 | 0.23 |
| Anisole | $C_7H_8O$ | 1340 | | 800 + 350 + 190 | 1340 | 0 |
| 1,2-Dibutoxyethane | $C_{10}H_{22}O_2$ | | 1348 | 1200 + 2 × 70 | 1340 | 0.59 |
| Isopentyl sulfide | $C_{10}H_{22}S$ | | 1359 | 1200 + 256 − 2 × 50 | 1356 | 0.22 |
| Propyl disulfide | $C_6H_{14}S_2$ | 1377 | | 1000 + 377 | 1377 | 0 |
| Phenetole (ethoxybenzene) | $C_8H_{10}O$ | | 1383 | 900 + 350 + 190 − 50 | 1390 | 0.5 |
| Isobutyl disulfide | $C_8H_{18}S_2$ | | 1428 | 1200 + 377 − 2 × 50 | 1477 | 3.32 |
| Benzyl ethyl ether | $C_9H_{12}O$ | | 1438 | 1000 + 350 + 70 | 1420 | 1.25 |
| *m*-Methylanisole | $C_8H_{10}O$ | | 1441 | 900 + 350 + 190 | 1440 | 0.07 |
| Butyl disulfide | $C_8H_{18}S_2$ | | 1567 | 1200 + 377 | 1577 | 0.63 |
| *o*-Dimethoxybenzene | $C_8H_{10}O_2$ | | 1715 | 1000 + 350 + 2 × 190 | 1730 | 0.87 |
| Bis(2-butoxyethyl)ether | $C_{12}H_{26}O_3$ | | 1727 | 1500 + 3 × 70 | 1710 | 0.98 |
| 1,3-Dimethoxybenzene | $C_8H_{10}O_2$ | | 1737 | 1000 + 350 + 2 × 190 | 1730 | 0.4 |
| Pentyl disulfide | $C_{10}H_{22}S_2$ | | 1768 | 1400 + 377 | 1777 | 0.51 |
| Phenyl ether | $C_{12}H_{10}O$ | 2055 | | 1300 + 2 × 350 + 70 | 2070 | 0.72 |
| Phenyl sulfide | $C_{12}H_{10}S$ | | 2287 | 1400 + 2 × 350 + 256 | 2356 | 2.97 |
| *o*-Phenylanisole | $C_{13}H_{12}O$ | | 2246 | 1400 + 2 × 350 + 190 | | |
| Benzyl ether | $C_{14}H_{14}O$ | | 2356 | 1500 + 2 × 350 + 70 | 2270 | 3.65 |
| *p*-Phenoxyanisole | $C_{13}H_{12}O_2$ | | 2438 | 1500 + 2 × 350 + 190 + 80 | 2470 | 1.3 |

[a] See footnote in Table III. Average *GRF* value for the alkyl ether linkage = 69.50 ± 7.01.

alcoholic –OH group on polar column. The *GRF* for the aliphatic amino $-NH_2$ group is +416 as against +647 for the aliphatic primary alcoholic –OH group. Plotting the *I* values of the homologous primary amines against *Z* yields a straight line, as shown in Fig. 1. The *A* and *GRF* values for the aliphatic amines are given in Table I.

The aliphatic primary amino ($-NH_2$) group has a column difference of about +280. When the $-NH_2$ group is attached to a secondary or a tertiary carbon atom, the *GRF* is reduced to +350 or +229, respectively. The *GRF* value of the imino groups in the N,N-dialkyl-substituted secondary amines, such as dibutylamine, is about +180 but that for the N-alkyl-N-aralkyl substituted secondary amines is about +260. The *GRF* values for the tertiary N atom in N,N,N-trialkylsubstituted amines may vary with the size of the substituted alkyl groups.

TABLE XIII

COMPARISON OF OBSERVED AND PREDICTED *I* VALUES OF ALIPHATIC ALDEHYDES AND KETONES[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) "peripheral" aliphatic aldehyde or ketone group = +388, (2) "inner" keto group or 4 position of the carbon chain = +355, (3) chain branching = −50, (4) non-terminal C=C double bond = +60, (5) conjugatio $-C=C-C=O$ group in alkane chain = +53.

| Compound | Formula | $I_{obs}$ | Lit. | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Acetone | $C_3H_6O$ | 816 | | 400 + 388 | 788 | 3.43 |
| Propanal | $C_3H_6O$ | 782 | | 400 + 388 | 788 | 0.76 |
| 2-Methylpropanal | $C_4H_8O$ | | 824 [15] | 500 + 388 − 50 | 838 | 1.67 |
| 2-Butanal | $C_4H_8O$ | | 910 [16] | 500 + 388 | 888 | 2.42 |
| 3-Methyl butanal | $C_5H_{10}O$ | | 928 [15] | 600 + 388 − 50 | 938 | 1.07 |
| 3-Pentanone | $C_5H_{10}O$ | | 977 [16] | 600 + 388 | 988 | 1.11 |
| 2-Pentanone | $C_5H_{10}O$ | | 992 [15] | 600 + 388 | 988 | 0.4 |
| 2-Methyl-3-pentanone | $C_6H_{12}O$ | | 1000 [16] | 700 + 355 − 50 | 1005 | 0.5 |
| 4-Methyl-2-pentanone | $C_6H_{12}O$ | | 1019 [15]<br>1012 [16] | 700 + 388 − 50 | 1038 | 1.83 |
| 2-Butenal | $C_4H_6O$ | | 1038 [16] | 500 + 388 + 60 + 53 | 1001 | 3.56 |
| 3-Hexanone | $C_6H_{12}O$ | | 1048 [16] | 700 + 355 | 1055 | 0.66 |
| 2-Methyl-3-hexanone | $C_7H_{14}O$ | | 1066 [16] | 800 + 355 − 50 | 1105 | 3.53 |
| 2-Hexanone | $C_6H_{12}O$ | | 1078 [16] | 700 + 388 | 1088 | 0.92 |
| Hexanal | $C_6H_{12}O$ | | 1094 [15] | 700 + 388 | 1088 | 0.54 |
| Heptanal | $C_7H_{14}O$ | | 1195 [15] | 800 + 388 | 1188 | 0.59 |
| 2-Heptanone | $C_7H_{14}O$ | | 1194 [15]<br>1180 [16] | 800 + 388 | 1188 | 0.5 |
| 3-Heptanone | $C_7H_{14}O$ | | 1124 [16] | 800 + 355 | 1155 | 2.68 |
| 3-Octanone | $C_8H_{16}O$ | | 1252 [16] | 900 + 355 | 1255 | 0.24 |
| Octanal | $C_8H_{16}O$ | | 1297 [15] | 900 + 388 | 1288 | 0.69 |
| 5-Nonanone | $C_9H_{18}O$ | | 1325 [16] | 1000 + 355 | 1355 | 2.21 |
| Nonanal | $C_9H_{18}O$ | | 1400 [15] | 1000 + 388 | 1388 | 0.86 |
| Decanal | $C_{10}H_{20}O$ | | 1504 [15] | 1100 + 388 | 1488 | 1.06 |
| 2-Heptadecanone | $C_{17}H_{34}O$ | | 2148 [15] | 1800 + 388 | 2188 | 1.83 |

[a] See footnote in Table III. Average *GRF* value for the aldehyde group = 387.92 ± 17.55.

The functionality of the tertiary amino groups in triethylamine, N,N-diethylbenzylamine, tributylamine, tripentylamine, tribenzylamine, etc. decreases with increasing size of the substituent groups. Plotting the *GRF* difference, namely ($I_{obs} - I_p$), of the tertiary amines against $Z$ yields a linear relationship, as shown in Fig. 2. This means that bulky substituents tend to diminish *I*, and the *GRF* of the tertiary amino group decreases in proportion to the bulkiness of the substituents. This finding is in accord with an early observation that the highly substituted amines behave chromatographically as *n*-alkanes [1]. Table XV shows the observed a predicted *I* values of some alkyl and alicyclic amin

*Aromatic amines*

Aromatic amino groups in aniline, anisidi toluidine, etc. have higher *GRF* values than aliphatic amino groups, owing to co-planar c figuration of the molecule as a result of conjugati with the phenyl ring. In the planar configuration primary aromatic amino group is retained longer the column and has a *GRF* of +667, considera higher than that of the aliphatic primary am

TABLE XIV

COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF ALICYCLIC AND AROMATIC ALDEHYDES AND KETONES[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) 5-membered alicyclic ring = +122, (2) alicyclic carbonyl C=O group = +465, (3) 6-membered alicyclic ring = +123, (4) chain branching = −50, (5) cyclopentene ring = +163, (6) conjugation of –C=C–C=O group in 5-membered ring = +106, (7) cycloheptane ring = +183, (8) O atom in 5-membered ring = +80, (9) phenyl ring = +350, (10) aryl or alkyl C=O group = +388, (11) cyclohexene ring = +208, (12) quaternary C atom = −100, (13) conjugation of C=C C=O group in 6-membered ring = +40, (14) phenolic –OH group = +900, (15) *ortho* effect *b* between –OH and –$COCH_3$ groups = −"870", (16) aryl Br atom = +426, (17) *ortho* effect *b* between –Br and –CHO groups = −"126", (18) alkyl Br atom adjacent to C=O group = +386, (19) aryl ether –O– linkage = +190, (20) extended conjugation between –$OCH_3$ to –CHO groups in *para* positions of phenyl ring = +60, (20) alkyl –$NH_2$ group = +417, (21) ring fusion = +60, (22) tertiary amino Ar–$N(CH_3)_2$ group = +260, (23) *para* effect for the extended conjugation from –$N(CH_3)_2$ to –CHO = +360.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Cyclopentanone | $C_5H_8O$ | | 1187 | 600 + 122 + 465 | 1187 | 0 |
| Cyclohexanone | $C_6H_{10}O$ | | 1289 | 700 + 123 + 465 | 1288 | 0.8 |
| 2-Methylcyclohexanone | $C_7H_{12}O$ | | 1305 | 800 + 123 + 465 − 50 | 1338 | 2.47 |
| 3-Methylcyclohexanone | $C_7H_{12}O$ | | 1324 | 800 + 123 + 465 − 50 | 1338 | 1.05 |
| 4-Methylcyclohexanone | $C_7H_{12}O$ | | 1339 | 800 + 123 + 465 − 50 | 1338 | 0.07 |
| 2-Cyclopenten-1-one | $C_5H_6O$ | | 1347 | 600 + 163 + 465 + 106 | 1334 | 0.97 |
| Cycloheptanone | $C_7H_{12}O$ | | 1417 | 800 + 183 + 465 | 1448 | 2.14 |
| 2-Furaldehyde | $C_5H_4O_2$ | | 1456 | 700 + 122 + 80 + 465 | 1455 | 0.07 |
| Benzaldehyde | $C_7H_6O$ | 1517 | 1513 | 800 + 350 + 388 | 1538 | 1.36 |
| 3,5,5-Trimethyl-2-cyclohexen-1-one | $C_9H_{14}O$ | | 1577 | 1000 + 208 + 465 + 40 − 100 | 1613 | 2.23 |
| 3,5-Dimethyl-2-cyclohexen-1-one | $C_8H_{12}O$ | | 1597 | 900 + 208 + 465 + 40 − 50 | 1563 | 2.13 |
| Acetophenone | $C_8H_8O$ | 1643 | | 900 + 350 + 388 | 1638 | 0.3 |
| Salicylaldehyde | $C_7H_6O_2$ | | 1665 | 900 + 350 + 900 + 388 − "870" | 1668 | 0.18 |
| Propiophenone | $C_9H_{10}O$ | | 1712 | 1000 + 350 + 388 | 1738 | 1.49 |
| *p*-Isopropylbenzaldehyde | $C_{10}H_{12}O$ | | 1767 | 1100 + 350 + 388 − 50 | 1788 | 1.17 |
| 2′-Hydroxyacetophenone | $C_8H_8O_2$ | | 1784 | 1000 + 350 + 900 + 388 − "870" | 1768 | 0.9 |
| 2-Bromobenzaldehyde | $C_7H_5BrO$ | | 1838 | 800 + 350 + 388 + 426 − "126" | 1838 | 0 |
| Benzylacetone | $C_{10}H_{12}O$ | 1851 | | 1100 + 350 + 388 | 1838 | 0.7 |
| *o*-Anisaldehyde | $C_8H_8O_2$ | | 1941 | 1000 + 350 + 388 + 190 | 1928 | 0.67 |
| 2-Bromoacetophenone | $C_8H_7BrO$ | | 1971 | 900 + 350 + 388 + 386 | 2024 | 2.62 |
| *p*-Anisaldehyde | $C_8H_8O_2$ | 2014 | 2000 | 1000 + 350 + 388 + 190 + 60 | 1988 | 0.6 |
| *p*-Methoxypropiophenone | $C_{10}H_{12}O_2$ | | 2179 | 1200 + 350 + 388 + 190 | 2128 | 2.34 |
| 2-Aminoacetophenone | $C_8H_9NO$ | | 2187 | 1000 + 350 + 388 + 417 | 2155 | 1.46 |
| 1-Naphthaldehyde | $C_{11}H_8O$ | | 2364 | 1200 + 2 × 350 + 60 + 388 | 2348 | 0.68 |
| Benzophenone | $C_{13}H_{10}O$ | 2457 | | 1400 + 2 × 350 + 388 | 2488 | 1.25 |
| *p*-Dimethylaminobenzaldehyde | $C_9H_{11}NO$ | 2459 | | 1100 + 350 + 388 + 260 + "360" | 2458 | 0.04 |

[a] See footnote in Table III.

group. Secondary aromatic amines with two aryl substituents or with one alkyl and one aryl substituent on N atoms have *GRF*s of +586 or +523, respectively. Tertiary aromatic amino groups with one aryl and two alkyl substituents on N atom as in N,N-dimethylaniline, have a *GRF* of about +310, which may vary with the bulkiness of the substituents.

Table XVI shows the comparison of observed and predicted $I$ values of some aromatic amines.

### *Heterocyclics*

Ring compounds containing nitrogen and oxygen heteroatoms are functionally complex, which renders the prediction of *I* difficult. The number and position of aza and oxo atoms in the ring, ring size, degree of saturation, aromaticity, conjugation, position of substituents, etc. can all affect the *A* and *GRF* values. These compounds are difficult to chromatograph, because traces of moisture and unexpected interaction with the stationary phase can cause large variations. The oxo rings are less complex than the aza rings. The nitrogen atom in the ring, being trivalent, can bond as secondary and tertiary amines, and together with the ring function and conjugation, these groups can contribute differently to *I*. In comparison, the bivalent oxygen atom has its bonding orbitals completely satisfied in ring formation.

The ring oxygen is assigned a *GRF* value of +80 per atom in the 5-membered ring and +160 per atom in the 6-membered ring. Since the number of oxo compounds studied is small, these values are only tentative.

The *GRF*s of the functional groups in the aza rings are difficult to assess individually and independently because of the lack of homologs for comparative study. In the following we rank the aza moieties present in 5-membered and 6-membered rings according to their contribution to the *I* of the analyte: (i) Aza and diaza moieties in 5-membered rings:

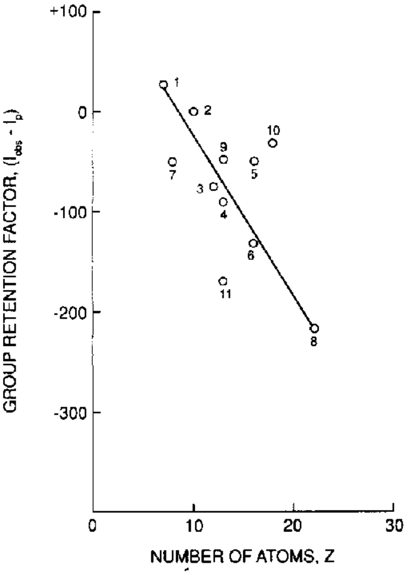
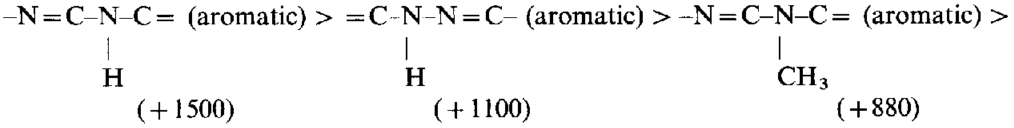
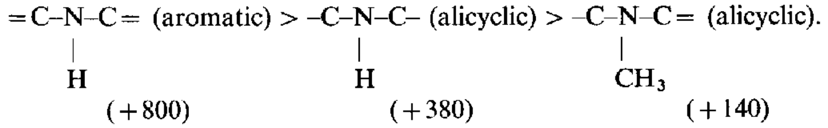


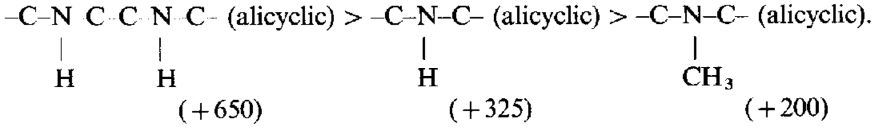
Fig. 2. The relationship between the *GRF*s of tertiary amine function and the size of substituent groups, expressed as the number of atoms (*Z*) in N,N,N-trisubstituted alkylamines. *Z* and *GRF* are given sequentially in parentheses following the name of the tertiary amine. The points plotted are: 1 = triethylamine (7, +27); 2 = N,N-dimethylbenzylamine (10, 0); 3 = N,N-diethylbenzylamine (12, −76); 4 = tributylamine (13, −93); 5 = N-methyldibenzylamine (16, −49); 6 = tripentylamine (16, −131); 7 = N,N-dimethylaniline (9, −50); 8 = tribenzylamine (22, −215); 9 = 2,2′,2″-trimethyltriallylamine (13, −46); 10 = N-methyldioctylamine (18, −30); 11 = N,N-dimethylnaphthylamine (13, −170).


$$-\mathrm{N{=}C{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}}\mathrm{{-}C{=}}\ \text{(aromatic)} > \mathrm{{=}C{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}}\mathrm{{-}N{=}C{-}}\ \text{(aromatic)} > \mathrm{{-}N{=}C{-}}\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{N}}\mathrm{{-}C{=}}\ \text{(aromatic)} >$$
$$(+1500)\qquad (+1100)\qquad (+880)$$


$$\mathrm{{=}C{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}}\mathrm{{-}C{=}}\ \text{(aromatic)} > \mathrm{{-}C{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}}\mathrm{{-}C{-}}\ \text{(alicyclic)} > \mathrm{{-}C{-}}\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{N}}\mathrm{{-}C{=}}\ \text{(alicyclic)}.$$
$$(+800)\qquad (+380)\qquad (+140)$$

(ii) Aza and diaza moieties in 6-membered rings:

=C–N=N–C= (aromatic) > =C–N=C–N= (aromatic) > –N=C–C=N– (aromatic) =C–N=C– (aroma
(+760) (+320) (+270) (+240)


$$\mathrm{{-}C{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}}\mathrm{{-}C{-}C{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}}\mathrm{{-}C{-}}\ \text{(alicyclic)} > \mathrm{{-}C{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}}\mathrm{{-}C{-}}\ \text{(alicyclic)} > \mathrm{{-}C{-}}\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{N}}\mathrm{{-}C{-}}\ \text{(alicyclic)}.$$
$$(+650)\qquad (+325)\qquad (+200)$$

The *GRF*s of the aza moieties are listed in parentheses below each structural moiety. The *GRF*s of these functional groups are specific for the 5- and 6-membered ring structures. A breakdown in terms of contributions from individual functions is given in Tables XVII and XVIII. These *GRF*s have not been widely tested on other aza compounds besides those listed. The general trend is for the highly conjugated N atoms in the ring to contribute the most to the RI, followed by the imino -NH- group connected to two double bonds and then the tertiary amine nitrogen. Similar aza moieties in 5-membered rings have higher *GRF*s than in 6-membered rings, and additional ring N atoms introduce new *GRF*s to increase *I*. The *I* values of pyridines and quinolines are more readily predicted than those of diazines and diazoles. A comparison of the observed and predicted *I* values of 5-membered and 6-membered heterocyclics is given in Tables XVII and XVIII.

Water gives a peak with a *I* of 1066 on polar column with thermal conductivity detector. This peak may appear when a hygroscopic sample is chromatographed.

### *Alkyl halides*

The *I* values of chloroalkanes, bromoalkanes and

TABLE XV

COMPARISON OF OBSERVED AND PREDICTED *I* VALUES OF ALIPHATIC AMINES[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) $-CH_2-NH_2$ group = +417, (2) tertiary amino group = + "27", = + "27", − "30", − "46", − "93" (see text), (3) $-C-NH_2$ group = +229, (4) $-CH-NH_2$ group = +350, (5) quaternary C atom = −100, (5) chain branching = −50, (6) alkyl ether -O- linkage = +70, (7) terminal $C{=}C$ double bond = +40, (8) alkyl imino -NH-R group = +180.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| *n*-Propylamine | $C_3H_9N$ | 816 | | 400 + 417 | 817 | 0.12 |
| *n*-Butylamine | $C_4H_{11}N$ | 908 | | 500 + 417 | 917 | 0.98 |
| *n*-Pentylamine | $C_5H_{13}N$ | 1018 | | 600 + 417 | 1017 | 0.1 |
| *n*-Hexylamine | $C_6H_{15}N$ | 1113 | | 700 + 417 | 1117 | 0.36 |
| *n*-Heptylamine | $C_7H_{17}N$ | 1213 | | 800 + 417 | 1217 | 0.33 |
| *n*-Decylamine | $C_{10}H_{23}N$ | 1522 | | 1100 + 417 | 1517 | 0.33 |
| *n*-Dodecylamine | $C_{12}H_{27}N$ | 1716 | | 1300 + 417 | 1717 | 0.06 |
| *n*-Octadecylamine | $C_{18}H_{39}N$ | 2330 | | 1900 + 417 | 2317 | 0.56 |
| Triethylamine | $C_6H_{15}N$ | 727 | | 700 + "27" | 727 | 0 |
| *tert.*-Butyl amine | $C_4H_{11}N$ | 729 | | 500 + 229 | 729 | 0 |
| *sec.*-Butyl amine | $C_4H_{11}N$ | 864 | | 500 + 350 | 850 | 1.62 |
| 2-Amino-3,3-dimethylbutane | $C_6H_{15}N$ | 948 | | 700 + 350 − 100 | 950 | 0.21 |
| Isoamylamine | $C_5H_{13}N$ | 989 | | 600 + 417 − 50 | 967 | 2.22 |
| 2-Amino-1-methoxypropane | $C_4H_{11}NO$ | 1050 | | 600 + 70 + 350 | 1020 | 2.86 |
| Dibutylamine | $C_8H_{19}N$ | | 1092 | 900 + 180 | 1080 | 1.1 |
| 2-Aminoheptane | $C_7H_{17}N$ | 1158 | | 800 + 350 | 1150 | 0.69 |
| 3-Aminoheptane | $C_7H_{17}N$ | 1137 | | 800 + 350 | 1150 | 1.13 |
| Tributylamine | $C_{12}H_{27}N$ | 1207 | 1206 | 1300 − "93" | 1207 | 0 |
| Tripentylamine | $C_{15}H_{33}N$ | 1469 | | 1600 − "131" | 1469 | 0 |
| 2,2′,2″-Trimethyltriallylamine | $C_{12}H_{21}N$ | | 1224 | 1300 + 3 × 40 − 3 × 50 − "46" | 1224 | 0 |
| N-Ethylbenzylamine | $C_9H_{13}N$ | | 1543 | 1000 − 350 + 180 | 1530 | 0.84 |
| N-Propylbenzylamine | $C_{10}H_{15}N$ | | 1624 | 1100 − 350 + 180 | 1630 | 0.37 |
| N-Butylbenzylamine | $C_{11}H_{17}N$ | | 1726 | 1200 − 350 + 180 | 1730 | 0.23 |
| N-Methyldioctylamine | $C_{17}H_{37}N$ | | 1770 | 1800 − "30" | 1770 | 0 |
| Dibenzylamine | $C_{14}H_{15}N$ | | 2473 | 1500 + 2 × 350 + 180 | 2380 | 3.76 |

[a] See footnote in Table III.

TABLE XVI

COMPARISON OF OBSERVED AND PREDICTED *I* VALUES OF AROMATIC AMINES[a]

The *GRF*s ($m_i$ and $n_i$) have the following values: (1) cyclohexane ring = +123, (2) alicyclic primary $-NH_2$ group = +350, (3) chain branching = −50, (4) tertiary Ar-$NR_2$ group = +310, (5) tertiary amino group = "0", −"30", −"50", −"170", −"49" or −"215" (see text), (6) -N-$C_2H_5$ group = −60, (7) ortho effect b between $-CH_3$ and $-N(C_2H_5)_2$ = −"300", (8) aralkyl alkyl imino -NH- group = +260, (9) alkyl $-NH_2$ group = +417, (10) aryl alkyl imino -NH group = +523, (11) aryl $-NH_2$ group = +667, (12) ortho effect b between $-C_2H_5$ and $-NH_2$ groups = −"70", (13) aryl $-OCH_3$ group = +190, (14) ortho effect b between $-OCH_3$ and $-NH_2$ groups = "160", (15) quaternary C atom = −100.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| Cyclohexylamine | $C_6H_{13}N$ | 1222 | 1155 | 700 + 123 + 350 | 1173 | 1.53 |
| 3-Methyl cyclohexylamine | $C_7H_{10}N$ | 1400 | | 800 + 123 + 350 − 50 | 1450 | 3.49 |
| N,N-Dimethylbenzylamine | $C_9H_{13}N$ | | 1350 | 1000 + 350 + "0" | 1350 | 0 |
| N,N-Diethyl-*o*-toluidine | $C_{11}H_{17}N$ | | 1428 | 1200 + 350 + 310 − 2 × 60 − 300 | 1440 | 0.83 |
| N,N-Dimethylaniline | $C_8H_{11}N$ | 1510 | 1538 | 900 + 350 + 310 − 50 | 1510 | 0 |
| N-Ethylbenzylamine | $C_9H_{13}N$ | 1577 | | 1000 + 350 + 260 − 60 | 1550 | 1.72 |
| Phenethylamine | $C_8H_{11}N$ | 1638 | | 900 + 350 + 417 | 1667 | 1.74 |
| N,N-Diethylaniline | $C_{10}H_{15}N$ | 1660 | 1620 | 1100 + 350 + 310 − 2 × 60 | 1640 | 1.2 |
| N,N-Dimethyl-*o*-toluidine | $C_9H_{13}N$ | | 1679 | 1000 + 350 + 310 | 1660 | 1.13 |
| N-Methylaniline | $C_7H_9N$ | 1686 | 1711 | 800 + 350 + 523 | 1673 | 0.77 |
| Aniline | $C_6H_7N$ | 1710 | 1740 | 700 + 350 + 667 | 1717 | 0.41 |
| N-Ethylaniline | $C_8H_{11}N$ | 1761 | 1717 | 900 + 350 + 523 − 60 | 1713 | 2.73 |
| N-Methyl-dioctylamine | $C_{17}H_{37}N$ | | 1770 | 1800 − "30" | 1770 | 0 |
| N-Methyl-*p*-toluidine | $C_8H_{11}N$ | | 1780 | 900 + 350 + 523 | 1773 | 0.39 |
| *o*-Toluidine | $C_7H_9N$ | 1800 | 1789 | 800 + 350 + 667 | 1817 | 0.94 |
| N-Ethyl-*m*-toluidine | $C_9H_{13}N$ | | 1802 | 1000 + 350 + 523 − 60 | 1813 | 0.6 |
| *p*-Toluidine | $C_7H_8N$ | 1822 | | 800 + 350 + 667 | 1817 | 0.27 |
| *m*-Toluidine | $C_7H_8N$ | 1849 | 1831 | 800 + 350 + 667 | 1817 | 1.73 |
| *o*-Ethylaniline | $C_8H_{11}N$ | | 1848 | 900 + 350 + 667 − 70 | 1847 | 0.05 |
| N-Butylaniline | $C_{10}H_{15}N$ | | 1893 | 1100 + 350 + 523 | 1973 | 4.05 |
| 2,4-Dimethylaniline | $C_8H_{11}N$ | 1903 | | 900 + 350 + 667 | 1917 | 0.73 |
| *o*-Anisidine | $C_7H_9NO$ | 1946 | | 900 + 350 + 190 + 667 − "160" | 1947 | 0.05 |
| *p*-*tert*.-Butylaniline | $C_{10}H_{15}N$ | | 2011 | 1100 + 350 + 667 − 100 | 2017 | 0.3 |
| N,N-Dimethylnaphthylamine | $C_{12}H_{13}N$ | | 2100 | 1300 + 2 × 350 + 60 + 310 − "170" | 2100 | 0 |
| *m*-Anisidine | $C_7H_9NO$ | | 2176 | 900 + 350 + 190 + 667 | 2107 | 3.17 |
| N-Methyldibenzylamine | $C_{15}H_{17}N$ | | 2251 | 1600 + 2 × 350 − "49" | 2251 | 0 |
| N-Benzyl-N-methylaniline | $C_{14}H_{15}N$ | | 2430 | 1500 + 2 × 350 + 260 | 2460 | 1.22 |
| N,N-Diphenylmethylamine | $C_{13}H_{13}N$ | | 2450 | 1400 + 2 × 350 + 310 | 2410 | 1.63 |
| Dibenzylamine | $C_{15}H_{15}N$ | 2427 | 2473 | 1500 + 2 × 350 + 260 | 2460 | 0.53 |
| Diphenylamine | $C_{12}H_{11}N$ | 2586 | | 1300 + 2 × 350 + 586 | 2586 | 0 |
| Tribenzylamine | $C_{21}H_{21}N$ | 3035 | | 2200 + 3 × 350 − "215" | 3035 | 0 |

[a] See footnote in Table III.

iodoalkanes are predicted by assuming the *GRF*s for chlorine, bromine and iodine atoms to be +464, +592 and +710, respectively. These are the averages of the $\Delta m_f$ values of the halo atoms in chloroalkanes, bromoalkanes and iodoalkanes, as shown in Table XIX. The individual $\Delta m_f$ values of each halo atom show a gradual increase within the series with chain lengthening. Plotting the $\Delta m_f$ values against the number of carbon atoms yields a straight line, with the slope increasing from chloro-

TABLE XVII

COMPARISON OF OBSERVED AND PREDICTED *I* VALUES OF HETEROCYCLIC COMPOUNDS[a]

In the 5-membered ring the *GRF*s ($m_i$ and $n_i$) have the following values: (1) cyclopentadiene ring = +210, (2) O atom in the ring = +80, (3) alicyclic aldehyde group = +465, (4) S atom in the ring = +200, (5) cyclopentane ring = +122, (6) –N($CH_3$)– group in the ring = +140, (7) imino –NH– group in the ring = +380, (8) cyclopentene ring = +163, (9) one C=C bond in azole ring = +40, (10) two C=C bonds in azole ring = +190, (11) C=C–NH–C=C group in the ring = +800, (12) additional N atom at the α position of the ring = +300, (13) methyl group *ortho* to ring N = −70, (14) phenyl ring = +350, (15) additional N atom at the β position of the N-methylated azole ring = +550, (16) additional N atom at the β position of the azole ring = +700.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| *Furan group* | | | | | | |
| Furan | $C_4H_4O$ | 800 | | 500 + 210 + 80 | 790 | 1.25 |
| {Water | $H_2O$ | 1066 | | (See text)} | | |
| 2-Furaldehyde | $C_5H_4O_2$ | | 1447 | 700 + 210 + 465 + 80 | 1455 | 0.51 |
| 5-Methylfuraldehyde | $C_6H_6O_2$ | | 1562 | 800 + 210 + 465 + 80 | 1555 | 0.45 |
| *Thiophene group* | | | | | | |
| Thiophene | $C_4H_4S$ | 1022 | 1025 | 600 + 210 + 200 | 1010 | 1.17 |
| *Pyrrolidine group* | | | | | | |
| 1-Methyl pyrrolidine | $C_5H_{11}N$ | 861 | | 600 + 122 + 140 | 862 | 0.12 |
| Pyrrolidine | $C_4H_9N$ | 1003 | | 500 + 122 + 380 | 1002 | 0 |
| Perhydroindole | $C_8H_{15}N$ | 1468 | | 900 + 123 + 122 + 380 | 1525 | 3.88 |
| 3-Pyrroline | $C_4H_5N$ | 1066 | | 500 + 163 + 380 + 40 | 1083 | 1.57 |
| *Pyrrole group* | | | | | | |
| 1-Methyl pyrrole | $C_5H_7N$ | 1142 | 1139 | 600 + 210 + 140 + 190 | 1140 | 0.18 |
| Pyrrole | $C_4H_5N$ | 1511 | 1508 | 500 + 210 + 800 | 1510 | 0.07 |
| Pyrazole (1,2-diazole) | $C_3H_4N_2$ | 1826 | | 500 + 210 + 800 + 300 | 1810 | 0.88 |
| 3-Methyl pyrazole | $C_4H_6N_2$ | 1863 | | 600 + 210 + 800 + 300 − 70 | 1840 | 1.23 |
| 4-Methyl pyrazole | $C_4H_6N_2$ | 1929 | | 600 + 210 + 800 + 300 | 1910 | 0.98 |
| Indazole | $C_7H_6N_2$ | 2556 | | 900 + 350 + 210 + 800 + 300 | 2560 | 0.16 |
| 1-Methyl imidazole | $C_4H_6N_2$ | 1700 | 1638 | 600 + 210 + 140 + 190 + 550 | 1690 | 0.59 |
| 2-Methyl imidazole | $C_4H_6N_2$ | 2238 | | 600 + 210 + 800 + 700 − 70 | 2240 | 0.09 |
| Imidazole (1,3-diazole) | $C_3H_4N_2$ | 2254 | | 500 + 210 + 800 + 700 | 2210 | 1.51 |
| 4-Methyl imidazole | $C_4H_6N_2$ | 2289 | | 600 + 210 + 800 + 700 | 2240 | 2.14 |

[a] See footnote in Table III.

alkanes to bromoalkanes to iodoalkanes, as shown in Fig. 3.

The increase in the slope of these linear plots of haloalkanes and the increase of the $\Delta m_f$ value in ascending each series are associated with the change in polar-to-non-polar moiety ratio on chain lengthening and electronic effects of the halo atom. The halo atom can exert mesomeric and inductive effects. The mesomeric effect and hyperconjugation may dominate in the lower haloalkanes and the inductive effect in the higher ones. That the three lower iodoalkanes show marked deviation from the linear relationship in Fig. 3 may be attributed to these factors.

The *GRF* of the halo atoms is influenced by the presence of other functional groups in the molecule. For example, the *GRF*s of the halo atoms in haloarenes or haloalicyclics are smaller than those in haloalkanes. It may be noted that the *GRF*s of the halo atoms include not only the *GRF*s but also the carbon atom equivalency of the halo atoms. The implication of this inclusion will be discussed in a future communication [20].

## TABLE XVIII

## COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF HETEROCYCLIC COMPOUNDS[a]

In the 6-membered ring the *GRFs* ($m_i$ and $n_i$) have the following values: (1) cyclohexane ring = +123, (2) O atom in the ring = +160, (3) phenyl ring = +350, (4) cyclopentane ring = +122, (5) O atom in 5-membered ring = +80, (6) $-N(CH_3)-$ in the ring = +200, (7) a second imino $-NH-$ group in the ring containing $-N(CH_3)-$ group = +240, (8) imino $-NH-$ group in the ring = +325, (9) methyl group ortho to ring N = −70, (10) chain branching = −50, (11) cycloheptane ring = +183, (12) tertiary $-N=$ in the ring = +240, (13) 1,4-diaza group = +30, (14) 1,3- diaza group = +80, (15) 1,2-diaza group = +520, (16) *trans* isomer–*cis* isomer = −60, (17) N atom in the iso position of fused heterocyclic rings = +40, (18) methyl group in *peri* position to ring N = −100, (19) methyl group in the *para* position of ring N = +70, (20) aryl ether $-O-$ linkage = +190.

| Compound | Formula | $I_{obs}$ | Lit. [16] | $100Z + \Sigma m_i - \Sigma n_i$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| *Dioxane group* | | | | | | |
| 1,4-Dioxane | $C_4H_8O_2$ | 1059 | | 600 + 123 + 160 × 2 | 1043 | 1.51 |
| S-Trioxane | $C_3H_6O_3$ | 1167 | | 600 + 123 + 160 × 3 | 1203 | 2.99 |
| 1,4-Benzodioxane | $C_8H_8O_2$ | | 1800 | 1000 + 350 + 123 + 160 × 2 | 1793 | 0.39 |
| 1,3-Benzodioxole | $C_7H_6O_2$ | | 1531 | 900 + 350 + 122 + 80 × 2 | 1573 | 2.67 |
| *1-Methylpiperidine group* | | | | | | |
| 1-Methyl piperidine | $C_6H_{13}N$ | 1020 | | 700 + 123 + 200 | 1023 | 0.29 |
| 1-Methyl piperazine | $C_5H_{12}N_2$ | 1262 | 1204 | 700 + 123 + 200 + 240 | 1263 | 0.08 |
| *Piperidine group* | | | | | | |
| Piperidine | $C_5H_{11}N$ | 1049 | | 600 + 123 + 325 | 1048 | 0.09 |
| 2-Methyl piperidine | $C_6H_{13}N$ | | 1017 | 700 + 123 + 325 − 70 − 50 | 1028 | 1.07 |
| 2,6-Lupetidine | $C_7H_{15}N$ | | 1009 | 800 + 123 + 325 − 70 × 2 −50 × 2 | 1008 | 0.1 |
| 4-Methyl piperidine | $C_6H_{13}N$ | 1075 | | 700 + 123 + 325 − 50 | 1100 | 2.29 |
| 3-Methyl piperidine | $C_6H_{13}N$ | 1081 | | 700 + 123 + 325 − 50 | 1100 | 1.73 |
| Hexamethylene imine | $C_6H_{13}N$ | 1178 | | 700 + 183 + 325 | 1208 | 2.48 |
| Piperazine | $C_4H_{10}N_2$ | 1391 | | 600 + 123 + 325 × 2 | 1373 | 1.29 |
| Homopiperazine | $C_5H_{12}N_2$ | 1525 | | 700 + 183 + 325 × 2 | 1533 | 0.25 |
| *Pyridine group* | | | | | | |
| Pyridine | $C_5H_5N$ | 1191 | | 600 + 350 + 240 | 1190 | 0.08 |
| Pyrazine (1,4-diazine) | $C_4H_4N_2$ | 1224 | | 600 + 350 + 240 + 30 | 1220 | 0.33 |
| Methyl pyrazine | $C_5H_6N_2$ | | 1259 | 700 + 350 + 240 + 30 − 70 | 1250 | 0.71 |
| Pyrimidine (1,3-diazine) | $C_4H_4N_2$ | 1276 | 1257 | 600 + 350 + 240 + 80 | 1275 | 0.31 |
| 4-Methyl pyrimidine | $C_5H_6N_2$ | 1328 | | 700 + 350 + 240 + 80 − 70 | 1300 | 2.11 |
| Pyridazine (1,2-diazine) | $C_4H_4N_2$ | 1716 | | 600 + 350 + 240 + 520 | 1710 | 0.35 |
| 3-Methyl pyridazine | $C_5H_6N_2$ | 1750 | | 700 + 350 + 240 + 520 − 70 | 1740 | 0.57 |
| 2-Picoline | $C_6H_7N$ | | 1210 | 700 + 350 + 240 − 70 | 1220 | 0.82 |
| 3-Picoline | $C_6H_7N$ | | 1283 | 700 + 350 + 240 | 1290 | 0.54 |
| 4-Picoline | $C_6H_7N$ | | 1300 | 700 + 350 + 240 | 1290 | 0.08 |
| 2,6-Lutidine | $C_7H_9N$ | | 1241 | 800 + 350 + 240 − 70 × 2 | 1250 | 0.72 |
| 3,5-Lutidine | $C_7H_9N$ | | 1400 | 800 + 350 + 240 | 1390 | 0.71 |
| *Quinoline group* | | | | | | |
| Perhydro isoquinoline | $C_9H_{17}N$ | 1520 *trans*) | | 1000 + 123 × 2 + 325 − 60 | 1511 | 0.59 |
| (*cis* + *trans*) | | 1560 (*cis*) | | 1000 + 123 × 2 + 325 | 1571 | 0.7 |
| Quinoline | $C_9H_7N$ | 1942 | | 1000 + 350 × 2 + 240 | 1940 | 0.1 |
| Isoquinoline | $C_9H_7N$ | 1980 | | 1000 + 350 × 2 + 240 + 40 | 1980 | 0 |
| 8-Methylquinoline | $C_{10}H_9N$ | 1959 | | 1100 + 350 × 2 + 240 − 100 | 1940 | 0.97 |
| Quinaldine (2-methylquinoline) | $C_{10}H_9N$ | 1970 | | 1100 + 350 × 2 + 240 − 70 | 1970 | 0 |
| 7-Methyl quinoline | $C_{10}H_9N$ | 2053 | | 1100 + 350 × 2 + 240 | 2040 | 0.63 |
| 6-Methyl quinoline | $C_{10}H_9N$ | 2062 | | 1100 + 350 × 2 + 240 | 2040 | 1.07 |
| 4-Methyl quinoline (lepidine) | $C_{10}H_9N$ | 2108 | 2080 | 1100 + 350 × 2 + 240 + 70 | 2110 | 0.09 |
| 6-Methoxyquinoline | $C_{10}H_9NO$ | | 2353 | 1200 + 350 × 2 + 240 + 190 | 2330 | 0.98 |

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[a] See footnote in Table III.

TABLE XIX

CALCULATION OF $\Delta m_f$ AND COMPARISON OF OBSERVED AND PREDICTED $I$ VALUES OF 1-HALOALKANES[a]

The *GRF*s have the following values: (1) chlorine atom in R–CH$_2$–Cl = +464, (2) bromine atom in R–CH$_2$–Br = +592, (3) bromine atom connected to secondary carbon atom = +492, (4) iodine atom in R–CH$_2$–I = +710.

| Compound | Formula | $I_{obs}$ | 100$Z$ | $\Delta m_f$ | $I_p$ | Difference (%) |
|---|---|---|---|---|---|---|
| *1-Chloroalkanes* | | | | | | |
| 1-Chloropropane | $C_3H_7Cl$ | 739 | 300 | 439 | 764 | 3.27 |
| 1-Chlorobutane | $C_4H_9Cl$ | 842 | 400 | 442 | 864 | 2.55 |
| 1-Chloropentane | $C_5H_{11}Cl$ | 945 | 500 | 445 | 964 | 1.97 |
| 1-Chlorohexane | $C_6H_{13}Cl$ | 1050 | 600 | 450 | 1064 | 1.32 |
| 1-Chloroheptane | $C_7H_{15}Cl$ | 1154 | 700 | 454 | 1164 | 0.86 |
| 1-Chlorooctane | $C_8H_{17}Cl$ | 1262 | 800 | 462 | 1264 | 0.16 |
| 1-Chlorononane | $C_9H_{19}Cl$ | 1364 | 900 | 464 | 1364 | 0 |
| 1-Chlorodecane | $C_{10}H_{21}Cl$ | 1474 | 1000 | 474 | 1464 | 0.68 |
| 1-Chlorotetradecane | $C_{14}H_{29}Cl$ | 1889 | 1400 | 489 | 1864 | 1.32 |
| 1-Chlorohexadecane | $C_{16}H_{33}Cl$ | 2094 | 1600 | 494 | 2064 | 1.43 |
| 1-Chlorooctadecane | $C_{18}H_{37}Cl$ | 2294 | 1800 | 494 | 2264 | 1.31 |
| | | | Average | 464.27 ± 20.72 | | |
| *1-Bromoalkanes* | | | | | | |
| 1-Bromobutane | $C_4H_9Br$ | 955 | 400 | 555 | 992 | 3.87 |
| 1-Bromopentane | $C_5H_{11}Br$ | 1042 | 500 | 542 | 1092 | 4.58 |
| 1-Bromohexane | $C_6H_{13}Br$ | 1163 | 600 | 563 | 1192 | 2.43 |
| 1-Bromoheptane | $C_7H_{15}Br$ | 1256 | 700 | 556 | 1292 | 2.79 |
| 1-Bromooctane | $C_8H_{17}Br$ | 1385 | 800 | 585 | 1392 | 0.5 |
| 1-Bromononane | $C_9H_{19}Br$ | 1496 | 900 | 596 | 1492 | 0.27 |
| 1-Bromodecane | $C_{10}H_{21}Br$ | 1578 | 1000 | 578 | 1592 | 0.88 |
| 1-Bromoundecane | $C_{11}H_{23}Br$ | 1717 | 1100 | 617 | 1692 | 1.46 |
| 1-Bromododecane | $C_{12}H_{25}Br$ | 1818 | 1200 | [618] | 1792 | 1.43 |
| 1-Bromotetradecane | $C_{14}H_{29}Br$ | 2037 | 1400 | 637 | 1992 | 2.1 |
| 1-Bromohexadecane | $C_{16}H_{33}Br$ | 2237 | 1600 | 637 | 2192 | 2.01 |
| 1-Bromooctadecane | $C_{18}H_{37}Br$ | 2447 | 1800 | 647 | 2392 | 2.17 |
| | | | Average | 592.00 ± 35.63 | | |
| *2- and 3-Bromoalkanes* | | | | | | |
| 2-Bromobutane | $C_4H_9Br$ | 905 | 400 | 505 | 892 | 1.44 |
| 2-Bromopentane | $C_5H_{11}Br$ | 984 | 500 | 484 | 992 | 0.81 |
| 3-Bromopentane | $C_5H_{11}Br$ | 994 | 500 | 494 | 992 | 0.2 |
| 2-Bromoheptane | $C_7H_{15}Br$ | 1173 | 700 | 473 | 1192 | 1.59 |
| 2-Bromodecane | $C_{10}H_{23}Br$ | 1493 | 1000 | 493 | 1492 | 0.07 |
| 2-Bromododecane | $C_{12}H_{25}Br$ | 1702 | 1200 | 502 | 1692 | 0.59 |
| | | | Average | 491.83 ± 11.82 | | |
| *1-Iodoalkanes* | | | | | | |
| 1-Iodoethane | $C_2H_5I$ | 876 | 200 | 676 | 910 | 3.74 |
| 1-Iodopropane | $C_3H_7I$ | 965 | 300 | 665 | 1010 | 4.46 |
| 1-Iodobutane | $C_4H_9I$ | 1065 | 400 | 665 | 1110 | 4.05 |
| 1-Iodopentane | $C_5H_{11}I$ | 1175 | 500 | 675 | 1210 | 2.89 |
| 1-Iodohexane | $C_6H_{13}I$ | 1286 | 600 | 686 | 1310 | 1.83 |
| 1-Iodoheptane | $C_7H_{15}I$ | 1400 | 700 | 700 | 1410 | 0.71 |
| 1-Iodooctane | $C_8H_{17}I$ | 1508 | 800 | 708 | 1510 | 0.13 |
| 1-Iodononane | $C_9H_{19}I$ | 1621 | 900 | 721 | 1610 | 0.68 |
| 1-Iododecane | $C_{10}H_{21}I$ | 1734 | 1000 | 734 | 1710 | 1.38 |
| 1-Iodoundecane | $C_{11}H_{23}I$ | 1842 | 1100 | 742 | 1810 | 1.74 |
| 1-Iodododecane | $C_{12}H_{25}I$ | 1953 | 1200 | 753 | 1910 | 2.2 |
| 1-Iodohexadecane | $C_{16}H_{33}I$ | 2400 | 1600 | 800 | 2310 | 3.73 |
| | | | Average | 710.42 ± 41.32 | | |

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[a] See footnote in Table III.

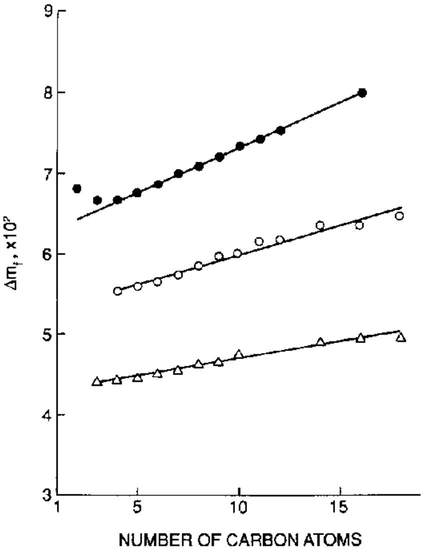

Fig. 3. Linear plots of the *GRF* increment or the functionality constant ($\Delta m_f$) *vs.* the number of carbon atoms in 1-haloalkanes. ● = 1-Iodoalkanes; ○ = 1-bromoalkanes; △ = 1-chloroalkanes.

## CONCLUSIONS

The retention mechanism in gas chromatography is complex and may involve a number of factors, such as partition between the gas phase and the stationary liquid phase, adsorption at the gas-liquid interface, H-bonding and dipolar interaction with the stationary phase, the electronic nature and configuration of the analyte molecule, etc. [5]. In a homologous series, each member differs from its near neighbors by a methylene group, which allows the same retention mechanism to prevail for all members of the series and leads to a linear relationship between *I* and the number of carbon and carbon equivalent atoms (*n* or *Z*). This is the theoretical basis for the prediction of *I*, using *A*, *Z* and *GRF* values.

Accurate *A* and *GRF* values are essential to the prediction. In many cases, the gradual change of the polar-to-non-polar moiety ratio in ascending or descending the homologous series exerts a definite effect on *GRF*. The effect is less on non-polar than on polar stationary phases and may be augmented in certain homologous series. As the polar-to-non-polar ratio decreases to near zero, the *I* value of the analyte will approach the base value. This explains why substituted compounds such as acid esters, tertiary amines and silylated derivatives show chromatographic characteristics similar to that of aliphatic hydrocarbons.

The *I* values of a wide range of compounds, such as acids, alcohols, amines, acid esters, aldehydes, ketones, ethers, aromatic hydrocarbons, alicyclics, heterocyclics, etc. on polar column are predicted by this method to within 3% error. The procedure used for prediction of *I* is similar to that for non-polar columns. In general, the *I* values of compounds of monofunctionality are accurately predicted. The *I* values of compounds of polyfunctionality are difficult to predict, because the functional groups often interact intramolecularly to alter the *GRF* and also the *A* values, as in the case of α-amino acids and acid amides. To apply the rule of additivity without the correct *A* and *GRF* values will lead to either over- or under-estimate of *I*. For example, the free and substituted acid amides have an *A* value that is considerably less than 100 (see Table VIII); the methyl substitution at the *ortho* position to the nitrogen atom in heterocyclics contributes only a fraction of the full *I* increment. According to an early report, methyl substitutions at the α, β, and γ positions of the pyridine ring contribute differently to *I* [21]. Substituents at the *ortho* positions of the phenyl ring tend to interact with each other to lower *I* generally by hydrogen bonding or steric hindrance. Substitutions at the *para* positions may cause an increase in *I*. In addition, identical N-containing moieties in 5-membered and 6-membered aza and diaza rings yield different *GRF* values. The ring constraint in the 5-membered rings accentuates the *GRF*s of these moieties. The effect of multi-substitution and poly-functionality on *GRF* are not well understood, but studies using homologous series may clarify some of these complexities.

From the structure–retention index relationship, one can derive a set of general rules to guide the prediction of *I*. These are as follows: (i) molecules which contain multiple O and N atoms will have high *I* values in comparison to molecules that do not, (ii) molecules which have highly conjugated systems containing N and O atoms tend to give higher *I* values than those that do not, (iii) molecules which contain quaternary carbon atoms and functional groups connected to secondary or tertiary carbon atoms have lower $I$ values than those that do not, and (iv) highly substituted molecules tend to yield lower $I$ values than those that are not.

Strong electron attracting and donating substituents that contain F, N and O atoms can generate unusual $A$ and $GRF$ values. This may also include atoms connected to multi-substituent groups. The magnitudes of the $GRF$ value and the column difference depend upon the polarity and polarizability of the substituent group and the stationary phase. The well-known Rohrschneider and McReynolds constants may be mentioned as examples of utilizing the $GRF$ related parameters and column differences ($\Delta I$ values) of selected compounds to characterize the selectivity and the polarity and polarizability of chromatographic stationary phases [22–24]. According to our method, the ratio of the $GRF$ values for a given functional group or substituent on various chromatographic stationary phases can probably yield direct information about the polarity of the stationary phases and the magnitude of the $I$ values of the analytes.

The structure retention–index relationship formulated thus far for non-polar and polar stationary phases allows us to link chemical structures to chromatographic data. It can predict from a glance of the structure the approximate $I$ to prevent gross errors in assigning unreasonable $I$ values to an analyte. The method of predicting $I$ from structure and *vice versa* is useful, especially in tentatively identifying unknown products formed from parent molecules in a chemical reaction. We have applied this method with success in identifying radioactive by-products in tritium labeling by radiation-induced methods and in elucidating the associated labeling mechanisms.

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