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CORRELATION OF RETENTION DATA WITH THE CHEMICAL STRUCTURE OF THE SOLUTE MOLECULES

V. M. SAKHAROV

All Union Scientific Research Geological Prospecting Petroleum Institute, VNIGNI, Moscow (U.S.S.R.)

SUMMARY

A method for calculating the retention values of isomeric compounds is proposed, based on the assumption that isomers can be regarded as different energy states of the same substance. The relationships between the retention values of isomers belonging to different classes and their structures are discussed.

INTRODUCTION

The use of gas chromatography for the analysis of complex industrial, natural or synthetic mixtures results in the detection, in each of these mixtures, of scores or even hundreds of compounds that have either been insufficiently investigated or have not been synthetically produced previously. The inadequate efficiency of the classical methods of identification, involving isolation of the unknown compound, study of its structure by physical and chemical methods, synthesis of the expected compound and identification of the synthesized and isolated compounds, becomes particularly evident when such methods are compared with the speed of chromatographic resolution. The synthesis of an extensive set of individual compounds, the presence of which may be expected in the test mixture, becomes difficult when mixtures boiling in the intermediate temperature range are concerned. More effective is the preparation of model mixtures of compounds produced by isomerization, methylene insertion or other stochastic reactions, although the determination of the composition of model mixtures is a separate task.

The combination of gas chromatography with instrumental physical methods (*e.g.*, mass spectrometry) provides an efficient method for the identification of compounds in complex mixtures. A chromatographic–mass spectrometric identification is facilitated by the availability of mass spectra catalogues that give data for thousands of compounds[1].

It should be noted that the rapid increase in the number of isomers with increase in the boiling points of the compounds makes the measurement of physico-chemical and spectral characteristics of the extensive numbers of compounds having a given formula very difficult. Thus many isodecanes and nonenes have not yet been synthesized. No systematic study has been made of the physico-chemical properties of

oxygen-, sulphur- and halogen-containing compounds with more than eight carbon atoms.

The vast number of isomeric compounds detected by detailed chromatographic analysis thus necessitates the use of calculation methods of identification and the estimation of identification parameters of compounds based on their structural formulae. It may be presumed that further success in the application of gas chromatography to the many poorly investigated components of industrial or natural mixtures will depend on the establishment of sufficiently general relationships between identification parameters (retention values) and structures of the compounds. It is desirable to develop some methods for calculating the retention values of large groups of compounds (compounds of similar structure or isomers).

ISOMERS AS DIFFERENT ENERGY STATES OF THE SAME SUBSTANCE

In quantum mechanics, the following procedure is used to arrange the energy levels of a molecule: (1) the atoms composing a molecule are considered to be infinitely distant from each other; (2) the atoms draw nearer to each other and form a molecule; (3) the positive nuclei of the atoms draw still closer to each other until a complete overlapping of nuclei is reached, as a result of which a united atom is formed.

The spectrum of a molecule must include as limiting cases the spectra of the isolated atoms and of the united atom, and all the energy levels of a molecule may be arranged in a series between these two limiting cases. Isomeric compounds with the same number of atoms in a molecule correspond to the same limiting energy states. Accordingly, isomers may be regarded as different energy states of the same united atom. By dividing the charge of the united atom and allocating the partial integral charges obtained, different configurations of the positive skeleton (different positions of nuclei) and different configurations of the electronic cloud surrounding the positive nucleus corresponding to individual isomers may be produced.

The calculation of the retention values of isomers may thus be reduced to the calculation of the interaction of the united atom in different quantum states with the solvent surrounding it (stationary phase).

The concept of isomers as different energy states of the same substance is sometimes used in organic chemistry[3].

THE STATIONARY PHASE AS A CONTINUOUS MEDIUM

When the united atom is placed in the solvent medium, its energy levels must be shifted and split. The energy of interaction of the united atom with the medium is related to the magnitude of the shift of energy levels of the united atom.

The arrangement of energy levels of the united atom depends on the symmetry of the molecular field acting upon the united atom. When the atom is placed into the crystal lattice the shift of levels depends on the type of symmetry of the lattice[4].

Let the stationary phase be considered as a continuous medium surrounding the atom. Such an assumption may be regarded as sufficiently valid if one considers that thermal movement heat averages out the different positions of the united atom and molecules of the stationary phase. The energy levels of the system comprised by the united atom and the continuous medium (stationary phase) will depend in this

case on the symmetry of the united atom electron cloud (geometry of isomer molecules). Thus the energy levels of the system comprised by the isomers and the solvent should vary in parallel with the variation of the energies of the isomers (energy levels of the united atom). Elsewhere[5-7], a linear relationship has been given between the difference of the energies of formation of isomeric compounds from elements and the difference of the logarithms of the retention volumes of iso alkanes, aromatic hydrocarbons and olefins. This relationship may be used for the estimation of thermochemical data from retention values of isomeric compounds detected in a complex mixture which have been either poorly investigated or not produced synthetically. JANÁK AND NOVÁK[8] have considered the dependence of the retention values of Freons on their thermochemical properties from a different point of view.

The interaction of the united atom with oriented molecules (with symmetrical molecular fields), which takes place in the case of gas–solid chromatography or chromatography on liquid crystals, is probably governed by relationships essentially different from those that are operative for liquid phases in which the arrangement of molecules is chaotic owing to heat movement.

CLASSIFICATION OF ENERGY LEVELS OF THE UNITED ATOM

In order to establish the sequence of the retention values for isomeric compounds, the energy levels of the united atom must be arranged in order of precedence. For a classification of energy levels, theoretical group methods are used, e.g., the symmetry group theory[9]. The symmetry of a molecule may be found by determining the symmetry group or the symmetry number of this molecule. In Table I examples

TABLE I

RELATION BETWEEN SYMMETRY NUMBERS, BOILING POINTS AND RETENTION VOLUMES OF ISOMERIC ALKANES AND CHLOROALKANES

Numbers of compounds compared (see Table II)	Ratio of symmetry numbers	Difference of boiling points (°C)	Ratio of retention volumes
Alkanes			
3–4	0.67	8.3	1.35
1–2	0.23	11.2	1.54
4–5	0.028	18.3	1.94
3–5	0.020	26.6	2.64
Chloroalkanes			
8–9	0.33	9.8	1.42
6–7	0.33	9.9	1.75
9–10	0.111	17.0	2.03
8–10	0.036	26.3	2.90

are given that show that the retention values of isomeric compounds are in inverse relationship with the symmetry number of the isomer. Squalane was used as the stationary phase at 20°. Some other examples showing the dependence of retention on the symmetry of molecules are given elsewhere[10].

TABLE II

SYMMETRY NUMBERS OF ISOMERIC ALKANES AND CHLOROALKANES

Number	Compound	σ
1	n-Butane	13
2	2-Methylpropane	81
3	n-Pentane	18
4	2-Methylbutane	27
5	2,2-Dimethylpropane	972
6	1-Chloropropane	3
7	2-Chloropropane	9
8	1-Chlorobutane	3
9	2-Chlorobutane	9
10	2-Methyl-2-chloropropane	81

For large molecules, the symmetry number is not sufficient for complete characterization of their chromatographic behaviour, probably owing to the fact that a large molecule does not interact with the stationary phase as a complete entity if the dimensions of the molecule exceed the radius of intermolecular interaction (several Ångstroms). The retention values of large molecules seem to be related to the symmetry of their separate fragments and to the symmetry of arrangement of these fragments within the molecule. In addition, the existence of rotatory isomerism renders impossible a univocal determination of the symmetry group of a large, flexible molecule.

A more detailed classification of energy levels may be developed if the system of quantum numbers be used.

Quantum numbers are essentially geometric, or, more exactly, topological characteristics of the surface of the electron cloud of an atom. Quantum numbers determine the topological type of the surface (presence of holes, nodes, relative arrangement of the different parts of the surface).

Since the shape of the electron cloud of a molecule follows, in general, the pattern of nuclei, the determination of the geometrical characteristics of the electron cloud surface may be reduced to the determination of the relative arrangement of the nuclei composing the "nucleus" of the united atom. The pattern of the point nuclei system may be found by determining the distances between all the pairs of nuclei and the number of nuclei of each type. These characteristics represent the quantum numbers of the united atom.

MOLECULAR STRUCTURE CHARACTERISTICS

The number of atoms of a given type is an important characteristic when the retention parameters of compounds that are not isomers are being compared. To establish the order of quantum numbers of this type, the concept of the stationary phase as a continuous, structureless medium can be used again.
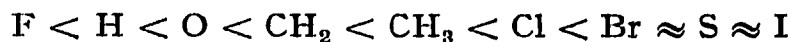
Consider an atom with a polarizability α_i and a Van der Waals' radius r_i located in a medium with a polarizability density ϱ. The average Van der Waals' radius of the stationary phase functional groups is r_0. The energy of the dispersion interaction of atom i with the stationary phase is calculated from the expression:

$$u_i = 0.9 \int_{r+r_0}^{\infty} \tfrac{3}{4} \, hv \, \frac{\alpha_i 4\pi r^2 \varrho}{r^6} \, dr = 0.9\pi hv \, \frac{\alpha_i \varrho}{(r_i + r_0)^3}$$

The term under the integral represents the energy of the dispersion interaction of atom i with the spherical layer of the stationary phase with a thickness dr, which is at a distance r from the centre of the atom i. The factor 0.9 has been introduced to account for the repulsion energy, which is about 10% of the energy of attraction. The Planck constant is h and v is the mean oscillator frequency of molecules of the stationary phase and the atom considered. By polarizability density is meant the ratio of the molecule polarizability to its molecular volume. This value is a function of the refractive index.

Thus the contribution of different atoms to the energy of interaction with the stationary phase will be the larger, the greater is the polarizability or refractive index of the atom and the smaller is the Van der Waals' radius of the atom.

According the value of $\dfrac{\alpha_i}{(r_0 + r_i)^3}$, the functional groups form a series:

$$F < H < O < CH_2 < CH_3 < Cl < Br \approx S \approx I$$

The methylene group, with $r_0 = 1.8$ Å, has been chosen as being typical of groups that occur in stationary phases.

The use of quantum numbers of the type considered is sufficient for a determination of the order of retention parameters of a similar structure containing different functional groups and atoms.

The selectivity of a stationary phase when non-polar isomers are separated increases with an increase in the concentration of heavy atoms in the stationary phase (such as Cl, Br and S) and with a decrease in the concentration of hydrogen atoms. Perfluorinated stationary phases have a very low selectivity in isomer separation since fluorine atoms have a weak ability for dispersion interaction.

There are two types of distances between the atoms within a molecule: those between atoms linked by a chemical bond, and those between atoms not directly linked within the molecule.

The number and type of chemical bonds within a molecule determine the polarity of the substance being analyzed. This characteristic is important when separations of polar and non-polar compounds and isomers of the same formula but containing different functional groups are considered (e.g., acids, esters, keto-alcohols and keto-ethers).

If the mean density of the square of the dipole moment of the functional groups of the stationary phase molecules is μ_2^2/v, the energy of orientation interaction of the dipole of the substance analyzed, μ_1, immersed in the stationary phase medium, will be

$$U_r = \int_{r_1+r_2}^{\infty} \frac{\mu_2^2}{v} \, 4\pi r^2 \, \frac{\mu_1^2}{kT r^6} \, dr = A \, \frac{\mu_2^2}{v} \, \frac{\mu_1^2}{T(r_1 + r_2)^3}$$

where A is the proportionality coefficient, $r_1 + r_2$ is the sum of the Van der Waals' radii of the functional groups, and v is the molecular volume of the stationary phase.

The third type of quantum number allows the determination of the order of the

retention parameters of compounds having similar values of the quantum number as the two types considered above (*i.e.*, isomeric compounds). This type of quantum number permits the structures of the molecules of the separated substances to be described in detail.

The number of similar distances between atoms not bonded chemically within the molecule is closely related to the magnitude of steric effects. These steric effects are related to the degree of branching of the carbon skeleton of the molecule or the degree of screening of a reaction centre by a large substituent. As a measure of steric effects, some empirical quantities are considered (examples of such quantities are the number of "sixths" atoms in the NEWMAN rule[11] or the E_s value in the Hammett–Taft equation[12]). In the most rigorous definition of the value of the steric effect, this value is defined as the sum of the energies of the Van der Waals' interaction of directly non-linked atom pairs within a molecule of the compound considered[13].

Let us consider the order of the retention parameters of isoalkanes and cyclo-alkanes with an equal number of carbon atoms. Some insignificant differences in the quantum numbers of the first and second types compensate each other (alkanes contain two hydrogen atoms more but one carbon–carbon bond less than cycloalkanes). It would be rational to choose as the quantum number of the third type the number

TABLE III

DEPENDENCE OF RETENTION INDICES OF ALKANES AND CYCLOALKANES ON THE NUMBER OF PAIR INTERACTIONS OF *geminal* HYDROGEN ATOMS IN THE MOLECULES OF THESE COMPOUNDS (SQUALANE; 25°)

Hydrocarbons	Retention parameters	
	I	$(H\text{–}H)_I$
C_6		
Cyclohexane	658	6
Methylcyclopentane	624	7
n-Hexane	600	10
2-Methylpentane	569	11
2,2-Dimethylbutane	595	12
C_7		
Cycloheptane	787	7
Methylcyclohexane	720	8
cis-1,2-Dimethylcyclopentane	716	9
n-Heptane	700	11
2-Methylhexane	666	12
2,2-Dimethylpentane	624	14

of the shortest distances between hydrogen atoms linked with the same carbon atom. The steric effect in these compounds will be proportional to the sum of such pair interactions of *geminal* hydrogen atoms and to the quantum number selected.

The accumulation of the number of pair interactions of *geminal* hydrogen atoms leads to a decrease in the retention parameters of cycloalkanes and alkanes (Table III). Consequently, the same cause, that is, a change in steric effects (change in the number of pair interactions of *geminal* hydrogen atoms) produces a decrease in the retention parameters with a branching of the alkane and an increase in the retention parameters with cyclization of the molecule.

The order of quantum numbers of the third type can be established when a calculation is made of the energy of pair interactions of atoms not linked directly within a molecule. Such calculations have been made by using the Lennard–Jones potential[6]. An accumulation within the molecule of mutually attracted atom pairs not linked directly results in a decrease in the retention parameters, while that of mutually repulsed atom pairs produces an increase in the retention parameters. As a rule, the contribution of the mutually repulsed atoms is greater than that of the mutually attracted atoms. The greatest repulsion occurs between atoms with high polarizabilities, which are closely spaced, or between heavy and light atoms that are within a short distance of each other. An increase in the distance between interacting atoms decreases the contribution of the corresponding quantum number to the retention parameters.

In alicyclic compounds containing hydrogen, nitrogen, sulphur or halogens, one should first consider the number of pairs of heteroatoms and hydrogen atoms located near the same carbon atoms, the interactions of methyl groups located near neighbouring carbon atoms and the interactions of ethyl groups with the neighbouring methyl or methylene groups. An accumulation of the above pair interactions results in an increase in the retention of the compound considered. A decrease in retention is produced by interactions of *geminal* hydrogen atoms.

In the series of aromatic heterocyclic compounds, the order of atom pair interactions is given by the sequence:

$$(H{-}\Gamma)_{ortho} > (H{-}\Gamma)_{peri} > (H{-}H)_{ortho} > (H{-}H)_{peri}$$

where Γ is sulphur, nitrogen, oxygen or any other heteroatom in the aromatic nucleus.

Some examples of a correlation of the retention parameters of isomeric compounds and the quantum numbers of the united atom for the major classes of compounds are given in the following sections.

ALKYLCYCLOPENTANES

In addition to the interaction of *geminal* hydrogen atoms in cyclopentane derivatives, the interaction of alkyl radicals linked to the ring must be considered. The closer the mutually repulsed groups are spaced, the greater is the increase in the retention parameters.

If an "envelope" configuration of the cyclopentane pattern is assumed, the distance between the centres of two methyl groups will give the following order:

1,2-*cis* < 1,2-*trans* ⩽ 1,3-*trans* ⩽ 1,3-*cis* < 1,1-

The retention parameters of isomers containing methyl groups in these positions (other conditions being equal) increase in the opposite order.

The retention parameters in Table IV are taken from the literature[14] (retention indices on squalane at 86°).

The contributions to the retention parameters of the interactions of methyl groups in 1,3-*cis* and 1,3-*trans* positions depend to a certain extent on the presence of other methyl groups in neighbouring positions.

Ethyl derivatives generally have higher retention parameters than those of

TABLE IV

RETENTION INDICES OF DIMETHYLCYCLOPENTANES

Substitutuents	Number of interactions of methyl groups in positions					Retention index
	1,2-cis	*1,2-trans*	*1,3-trans*	*1,3-cis*	*1,1-*	
1,1-Dimethyl	0	0	0	0	1	681
1,3-*cis*-Dimethyl	0	0	0	1	0	683.4
1,3-*trans*-Dimethyl	0	0	1	0	0	693.8
1,2-*trans*-Dimethyl	0	1	0	0	0	695.8
1,2-*cis*-Dimethyl	1	0	0	0	0	729.3

the isomeric methyl derivatives since in the ethyl derivative molecules there are fewer interactions of *geminal* hydrogen atoms. In a similar way, propyl derivatives have higher retention volumes than trimethyl derivatives.

The order of elution of methylethylcyclopentanes is similar to that of the corresponding dimethylcyclopentanes (methyl–methyl interactions are replaced by methyl–ethyl interactions of a similar type).

CYCLOHEXANE DERIVATIVES

When considering the steric effects in cyclohexane derivatives, it should be noted that the molecules of cyclohexane derivatives exist in a chair shape, the equatorial substitution of bonds producing more stable compounds.

In *1,2-cis* derivatives, equatorial (*e*) and axial (*a*) bonds are substituted; in *1,2-trans* derivatives, the *e,e* bonds; in *1,3-cis*, the *e,e* bonds; in *1,3-trans*, the *e,a* bonds; in *1,4-cis*, the *e,a* bonds; and in *1,4-trans*, the *e,e* bonds are substituted.

Stereochemical data are taken from the literature[15].

The conformations of *1,2-cis*, *1,3-trans* and *1,4-cis*-substituted compounds are almost equally stable, since in all these cases one substituent is oriented equatorially and the other axially. If it is considered, in addition, that the methyl groups in these compounds are located at different distances (*1,2-cis* < *1,3-trans* ≈ *1,4-cis*), the sequence of retention values of these compounds will be:
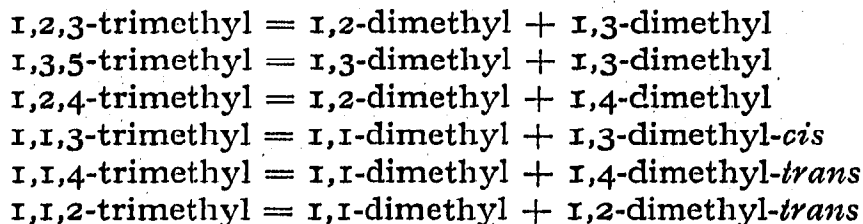
1,2-cis > *1,3-trans* ≈ *1,4-cis*

Let us consider the sequence of elution from the column of *1,4-trans*-, *1,3-cis*- and *1,2-trans*-dimethyl derivatives. The number of equatorial substituents in all these compounds is the same, while the distances between the substituents are different. This distance is the greatest in the *1,4-trans*-substituted, less in the *1,3-cis*-substituted and the least in *1,2-trans*-substituted substances. Hence, the sequence of elution of isomeric dimethylcyclohexanes must be *1,4-trans*, *1,3-cis*, *1,2-trans*, *1,4-cis*, *1,3-trans*, *1,2-cis*, which is in agreement with experimental data.

The order of retention parameters of methylcyclohexanes is similar to that of dimethyl derivatives: 1-methyl-4-ethyl-*trans*; 1-methyl-3-ethyl-*cis*; 1-methyl-2-ethyl-*trans*, 1-methyl-4-ethyl-*cis*, 1-methyl-2-ethyl-*cis*.

The conformations of trimethyl-substituted cyclohexanes contain many similarities with those of dimethyl-substituted cyclohexanes. The conformation of tri-

methyl-substituted cyclohexanes may be regarded as a superposition of two conformations of the respective dimethyl-substituted cyclohexanes in the same *cis–trans* position as those in trimethylcyclohexanes, and represented by:

1,2,3-trimethyl = 1,2-dimethyl + 1,3-dimethyl
1,3,5-trimethyl = 1,3-dimethyl + 1,3-dimethyl
1,2,4-trimethyl = 1,2-dimethyl + 1,4-dimethyl
1,1,3-trimethyl = 1,1-dimethyl + 1,3-dimethyl-*cis*
1,1,4-trimethyl = 1,1-dimethyl + 1,4-dimethyl-*trans*
1,1,2-trimethyl = 1,1-dimethyl + 1,2-dimethyl-*trans*

The order of elution from the column of 1,1-trimethyl-substituted compounds in this case must coincide with that of dimethyl-substituted compounds ($1,1,4 \leqslant 1,1,3 < 1,1,2$; $1,4 \leqslant 1,3 < 1,2$), which has been confirmed experimentally.

AROMATIC COMPOUNDS

The retention parameters of isomeric aromatic compounds can be calculated if the number of interactions of hydrogen atoms not linked directly and located in the *ortho*-position to each other are known.

In naphthalene and phenanthrene derivatives, the number of weaker *peri*-interactions of hydrogen atoms must also be considered.

In heterocyclic aromatic compounds, the number of *ortho*- and *peri*-interactions of the heteroatom with the neighbouring hydrogen atom must also be considered, as well as the number of interactions of hydrogen atoms in *ortho*- and *peri*-positions to each other.

Dimethylpyridines, for instance, have the following retention volumes on silicone oil (according to the data of BAYER[16]) at 140°: 3,5-dimethylpyridine (2;0), 4.07; 2,3-dimethylpyridine (1;2), 3.45; 2,4-dimethylpyridine (1;1), 3.06; 2,5-dimethylpyridine (1;1), 3.06; and 2,6-dimethylpyridine (0;2), 2.31.

The first number in parentheses in each case is the number of interactions of a nitrogen atom with an *ortho*-atom of hydrogen; the second number shows the number of *ortho*-interactions of hydrogen atoms. Two isomers (2,4- and 2,5-dimethylpyridine) have similar structural characteristics and, as a result of this, equal retention volumes.

A more detailed discussion of the dependence of retention parameters of aromatic compounds on steric effects in the molecules of these compounds is given elsewhere[6].

OLEFINS

When calculating the retention parameters of olefins, one should consider the number of pair interactions of *geminal* hydrogen atoms located in the alkyl groups, as well as the numbers of pair interactions of hydrogen atoms located on the same carbon atom of a double bond. The latter characteristic may assume only two values: unity for 1-alkanes, and zero for other olefins. An increase in the number of pairs of α,α'-atoms of hydrogen produces a decrease in the retention parameters. This structural characteristic is denoted below as $(H–H)_{Id}$.

The electronic states of the isomers of unsaturated compounds cannot be considered to be identical. Isomeric olefins have markedly different polarizabilities and ionization potentials, as shown by the magnitudes of the energies of the intermolecular interaction of these compounds with the stationary phase. Thus, for instance, an accumulation of alkyl groups at the double bond results in an increase in the retention parameters of olefinic isomeric compounds, other conditions being equal. This effect is related to the positive induction effect of alkyl substituents increasing the mobility of the electrons of the double bond and its polarizability.

As a result of this, as the third structural characteristic in the calculation of the retention parameters of isomeric olefins, the number of alkyl radicals located at the double bond has been selected. This characteristic (m) has values of 1–4.

The difference between the retention indices of two isomeric olefins (or the difference between logarithms of retention volumes) can be expressed as follows:
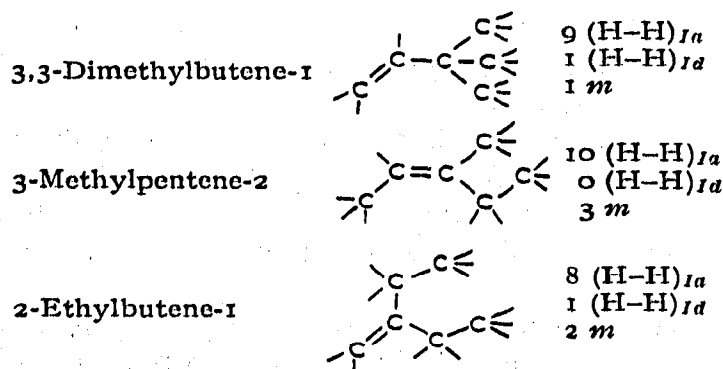
$$\delta I = A(m' - m'') - B\{(H\text{--}H)'_{Ia} - (H\text{--}H)''_{Ia}\} - C\{(H\text{--}H)'_{Id} - (H\text{--}H)''_{Ia}\}$$

A, B and C are coefficients depending on the type of stationary phase and the temperature. Values referring to the first isomer are marked with a single prime and those referring to the second isomer with a double prime.

From experimental data (retention indices of hexenes on squalane at 20°) the mean values of A, B and C were calculated to be 52, 23 and 12, respectively.

The mean error in calculating the differences between the retention indices was 4%, and that in the values of retention indices was 0.8% (ref. 7).

The following examples show the calculation of the structural characteristics of isomeric olefins:

3,3-Dimethylbutene-1   9 $(H\text{--}H)_{Ia}$
                         1 $(H\text{--}H)_{Id}$
                         1 m

3-Methylpentene-2   10 $(H\text{--}H)_{Ia}$
                         0 $(H\text{--}H)_{Id}$
                         3 m

2-Ethylbutene-1   8 $(H\text{--}H)_{Ia}$
                         1 $(H\text{--}H)_{Id}$
                         2 m

CHLORINATED HYDROCARBONS

The number of possible chlorinated hydrocarbons is very great even for molecules with a small number of carbon atoms. For instance, for heptane about two thousand chlorinated derivatives are theoretically possible.

Many of these compounds have either not yet been sufficiently investigated or not produced in a pure state, which makes important an *a priori* calculation of the physico-chemical properties of these compounds.

Of great significance in calculating the retention parameters of chlorinated

hydrocarbons is the number of interactions of the chlorine atoms with the hydrogen atoms located on the same carbon atom. The lower the number of such interactions, the higher are the retention parameters of the isomer. The presence of pairs of *geminal* hydrogen atoms decreases the retention parameters of the isomer.

A discussion of the retention parameters of C_2-C_{10} chlorinated hydrocarbons from this standpoint is given elsewhere[17].

ORGANOSULPHUR AND OXYGENATED COMPOUNDS

The retention of isomeric compounds belonging to these classes depends on the number of interactions of *geminal* hydrogen atoms $(H-H)_I$ and the number of interactions of a heteroatom with a hydrogen atom located on the same carbon atom $(H-S)_I$ or $(H-O)_I$. The former characteristic decreases the retention parameters, the latter increases them (Table V). Steric effects in molecules of aliphatic and cyclic oxygenated compounds and their retention values are discussed elsewhere[18].

TABLE V

DEPENDENCE OF RETENTION VOLUMES OF ALKYLTHIOLS ON SILICONE OIL DC-550 (140°) ON THE NUMBER OF STRUCTURAL INTERACTIONS

Compound	Number of atom pairs $(H-H)_I$	Number of atom pairs $(H-S)_I$	Retention volume
Pentanethiol-1	7	2	30.3
2-Methylbutanethiol-1	8	2	26.8
3-Methylbutanethiol-1	8	2	25.5
Pentanethiol-3	8	1	24.2
Pentanethiol-2	8	1	23.0
3-Methylbutanethiol-2	9	1	22.7
2,2-Dimethylpropanethiol-1	10	2	20.1
2-Methylbutanethiol-2	10	0	18.6

ORDERED SEQUENCES OF COMPOUNDS

The great variety of compounds present in industrial or natural mixtures is due not only to isomerism but also to the existence of compounds with similar structures but with different numbers of substituents.

In the series of methylated aromatic compounds and of chlorinated compounds, it is interesting to note that the order of the retention parameters for polymethyl-(polychloro-) substituted isomers follows the order of the retention parameters for isomers of the same groups of compounds with a small number of substituents. Let us assume that in a compound there are substituents of two types. The replacement of substituents of the first type by those of the second type, and those of the second type by those of the first type, results in a new substance which we shall call "mirrored" with respect to the original substance. The operation of substituent exchange may be considered as a generalization of the "mirrored reflection" operation. Examples of "mirrored" substances are the methylbenzene series (exchange of hydrogen atoms and

methyl groups), the chloroethane series (exchange of hydrogen and chlorine atoms), and the chlorobenzene series (exchange of hydrogen and chlorine atoms) may be cited. The most significant aspect of the "mirrored" substance method is that the order of retention parameters persists when passing from the original isomeric compounds to their "mirrored" analogues, which allows the orders of the retention parameters to be determined for compounds with a large number of substituents (or highly chlorinated compounds) using the retention parameters of readily available substances with a small number of substituents.

The following are examples of the correspondence of "mirrored" substances (exchange of hydrogen and chlorine atoms):

ethane   ↔ hexachloroethane
ethyl chloride   ↔ pentachloroethane
1,1-dichloroethane   ↔ 1,3,3,3-tetrachloroethane
1,2-dichloroethane   ↔ 1,1,2,2,-tetrachloroethane
1,1,1-trichloroethane   ↔ 1,1,1-trichloroethane
1,1,2-trichloroethane   ↔ 1,1,2-trichloroethane
1,1,2,2-tetrachloroethane   ↔ 1,2-dichloroethane
1,3,3,3-tetrachloroethane   ↔ 1,1-dichloroethane
pentachloroethane   ↔ ethyl chloride
hexachloroethane   ↔ ethane

It can be expected that the "mirrored" substance method will be useful in calculating the retention parameters of polysubstituted polynuclear compounds and halogenated organic compounds from the retention parameters of their "mirrored" analogues with a small number of substituents.

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