Structure-Retention Relationships in the Gas Chromatography of N,N-Dialkylhydrazones

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Summary

N,N-Dialkylhydrazones [DAHs; $R_1R_2C = {}^1N\text{-}{}^2N(R_3)_2$] were prepared and their Kováts retention indices determined on 100 % dimethylpolysiloxane (HP-1) and 5 % diphenyl and 95 % dimethylpolysiloxane (HP-5) stationary phases. The physico-chemical and retention behaviour of the DAHs depend greatly on whether $R_2 = H$ or an alkyl group. A similar difference is observed in the alkane and oxo homomorphic factors of DAHs formed from aldehydes or ketones. The difference is explained on the basis of NMR and quantum-chemical results by intramolecular interactions between R_2 and the lone pair of the ^2N atom. A single linear equation is suitable for prediction of retention indices if parameters are introduced representing resonance structure (bond angle and electron density) besides I_{oxo} or the van der Waals' surface.

Introduction

Derivatization of an organic compound with a functional group is often necessary for gas chromatographic (GC) analysis when the compound of interest is reactive (unstable under the conditions of analysis), not volatile enough or present in such a low concentration that the analytical method is not sensitive enough. Selective GC detection may be a solution in some cases.

Aldehydes and ketones are often analysed by GC in the form of their 2,4-dinitrophenylhydrazones (DNPHs) [1–3]. Other methods, e.g analysis in the form of a dimedone derivative, are used in biological matrices, where, owing to the low concentration of the compound, e.g. formaldehyde, the use of other methods is often difficult [4]. The N,N-dimethylhydrazones (DMHs, $R_3 = CH_3$) of oxo compounds may be prefered in GC analysis when the DNPHs are not volatile enough and the formation of DMHs occurs under mild reaction conditions [5, 6]. DMH formation proceeds essentially quantitatively, without side-reactions, but the method fails for ketones involving steric hindrance [7].

N,N-Dialkylhydrazones [DAHs; $R_1R_2C = {}^1N\text{-}{}^2N(R_3)_2$] of unsymmetrical ketones ($R_1 \neq R_2$) can exist in E and Z stereoisomeric forms [8], but the Z-DAHs of aldehydes ($R_2 = H$) are not formed for structural reasons [9].

Application of Kováts indices is a well-known method for the identification of different types of compound [10]. We reported recently on the retention indices of DNPHs of aldehydes and ketones [11]. It was concluded that the retention index of a DNPH could be estimated from that of the aldehyde, whereas the additivity rule was not valid for the derivatives of ketones. The difference in behaviour was explained by the difference in intermolecular interactions in DNPHs formed from ketones and aldehydes. For similar reasons, an even more pronounced difference can be expected in the retention behaviour of ketone and aldehyde DAHs. The probable explanation of this difference is the fact [12] that the boiling point difference for isomeric ketone and aldehyde DMHs is much greater than for other classes of compounds (alkane, alkene, aldehyde and ketone isomers). The retention indices of DAHs have not been reported previously.

In the present article, attention is focused on the GC of DMHs, as this class of DAHs is more intensively studied because of possible biological effects [13], structural curiosity [6, 9], synthetic use [6] and the low relative molar mass, which is an advantage in comparative studies. DMHs are more volatile than DNPHs, so they may provide a better opportunity for identification. Ad-

No.	Compound	Boiling point °C	Density g cm^{-3}	n_D^{27}	R_M
1	Methanal DMH	70–72 [12]	0.789	1.4293	23.59
2	Ethanal DMH	93–94 [12]	0.807	1.4349	27.85
3	Propanal DMH	112–113.5 [12]	0.801	1.441^b	33.23
4	2-Propanone DMH	92–93 [12]	0.769	1.4195	32.93
5	Butanal DMH	134–135.5 [12]	0.791	1.4398	38.03
6	2-Methylpropanal DMH	123–125 [12]	0.800	1.4317	37.00
7	2-Butanone DMH	118–119.5 [12]	0.783	1.4260	37.37
8	Pentanal DMH	164, this work	0.794	1.4423	42.75
9	2-Pentanone DMH	131–132 [12]	0.793	1.4100	40.06
10	3-Methyl-2-butanone DMH	120.5–122 [12]	0.782	1.4258	42.00
11	2,2-Dimethylpropanal DMH	132 [17]	0.776	1.4290	43.00
12	Ethanal DEH	125, this work	0.824	1.442^b	36.61
13	2-Propanone DEH	125 [12]	0.78	1.421^b	42.13

[a]DMH: N,N-dimethylhydrazone; DEH: N,N-diethylhydrazone.
[b]Measured at 20 °C [12].

ditionally, more physical constants are available or calculable for DMHs and DEHs than for DNPHs. Thus, they offer a better possibility for the study of structure-retention relationships.

Experimental

DMHs (Table I) were synthesized from N,N-dimethyl-hydrazine and the appropriate aldehydes and ketones (Fluka, Switzerland, and Aldrich, Germany) according to the method described in [14]. N,N-Diethylhydrazones (DEHs, $R_3 = C_2H_5$) were synthesized from N,N-diethyl-hydrazine prepared from the appropriate nitrosoamine [14]. The products were purified first by fractional distillation and afterwards by preparative GC. All of the retention data published here were determined for the E isomers; we did not observe Z isomers (of compounds 7, 9 and 10) in amounts sufficient to allow determination of physical constants and retention data. One DAH (14, Table II) was produced in the thermal and initiated decompositions of an azoalkane [15]; the DAH in the mixture of reaction products was identified by GC-MS.

The Kováts retention index was determined as described in [16]. Fitting parameters and statistics were calculated by PSI-PLOT (Polysoft International, USA) and DRUGIDEA (CheMicro Ltd., Hungary). The apparatus and GC conditions are presented in Table III.

Physical parameters of the DAHs synthesized are listed in Table I, while retention parameters are given in Table II.

Calculations

Fully optimized geometries of the DAHs and the structurally similar olefins were calculated for the estimation of molecular properties at the level of the semi-empirical, quantum-chemical method MNDO [19]. The force matrices at the stationary points were found to be positive definite. Calculations were performed with the program package PcMOL [20a] and MOPAC 6.1 [20b]. Van der Waals' volumes and surface areas were calculated as described earlier [21].

Results and Discussion

Structural Behaviour of DAHs

Interactions between solvent molecules and solute can be characterized by van der Waals' (orientation, induction and dispersion) forces and H-bonding [22, 23]. On an apolar phase, retention is determined mainly by dispersive forces which are a function of the ionization potential (I_p) and polarizability, which, according to the Lorentz equation, finally depends on the molar refraction (R_M).

The I_p values of DAHs are very close to one another, but ketone DAHs have smaller I_p-s. Ketone DMHs and DEHs have somewhat lower R_M-s (polarizability) (Table I) and I_p-s than isomeric aldehyde derivatives.

Theoretical calculations indicate that DAHs are somewhat more polar than alkenes of similar structure, owing to the greater electronegativity of the N atom. The dipole moment does not differ significantly for $R_2 = H$ or $R_2 = $ alkyl group: these values are around 0.7 Debye (D), as compared with about 0.1–0.4 D for alkenes [24]. Calculations show the dipole moments of Z-DAHs to be greater by about 0.1–0.2 D than those of E-DAHs.

The boiling point (t_b) is a physical parameter which is an overall measure of different types of interactions between the same molecules. Nevertheless, literature data

No.	Compound	I_{HP-1}	$\Delta I/\Delta t^c$	I_{HP-5}	ΔI	H^A	H^{oxo}
1	Methanal DMH	593.0	0.07	613.7	20.7	118	n.d.
2	Ethanal DMH	676.0	– 0.04	696.5	20.5	106	310
3	Propanal DMH	765.8	– 0.06	784.9	19.1	97	291
4	2-Propanone DMH	692.3	– 0.11	710.3	18.0	62	220
5	Butanal DMH	859.5	– 0.04	878.9	19.4	94	287
6	2-Methylpropanal DMH	815.0	– 0.07	831.4	16.4	87	273
7	2-Butanone DMH	775.2	– 0.08	793.1	17.9	43	198
8	Pentanal DMH	957.8	– 0.03	971.1	13.3	93	282
9	2-Pentanone DMH	865.6	– 0.08	881.2	15.6	45	199
10	3-Methyl-2-butanone DMH	826.4	– 0.06	837.4	11.0	15	185
11	2,2-Dimethylpropanal DMH	841.0	– 0.07	854.9	13.9	64	257
12	Ethanal DEH	819.7	– 0.13	836.1	16.4	45	454
13	2-PropanoneDEH	825.2	– 0.03	839.1	13.9	1	353
14	Ethanal methylethylhydrazone	758.0	n.d.	n.d.	n.d.	80	382

[a] $I_{hydrazone}$ and I_{oxo} were measured at 60 °C.
[b] For calculation of H^A, I_{alkane} taken from [18], assuming I(squalane) = I(HP-1); I_{oxo} taken from [11].
[c] Determined from index data at 60, 70 and 80 °C.

Table III. Analytical conditions used for Kováts retention index determination.

Apparatus	Hewlett-Packard 5890 Series II GC
GC column	HP-1 (100 % dimethylpolysiloxane gum), 50 m, 0.32 mm, d_f = 0.52 µm HP-5 (5 % diphenyl and 95 % dimethylpolysiloxane), 50 m, 0.32 mm, d_f = 0.52 µm
Injector	split-splitless (in split mode), split ratio 1 : 38, 150 °C
Detector	FID, 150 °C
Carrier gas	N_2, 1.2 cm³ min⁻¹

suggest that its value also represents interactions between different molecules (solute and stationary phase), although the solute is largely diluted in the liquid stationary phase.

The isomeric DMHs studied have very different boiling points (Table I, see e.g. **3** and **4** or **5, 6** and **7**). It is somewhat surprising that the boiling point differences for isomeric hydrazones are larger than those for the corresponding pair of alkenes with similar structure (e.g. **3** and **3C**, where **3C** is an alkene analogue of **3** in which the N atoms are substituted by CH groups). For example:

$$t_b(\mathbf{3}) - t_b(\mathbf{4}) \approx 20 \text{ °C}, t_b(\mathbf{3C}) - t_b(\mathbf{4C}) \approx 5 \text{ °C}$$

NMR investigations showed that in DMHs where R_1 = H, no formation of Z isomers was observed. If R_1, R_2 = alkyl group, the amount of the Z isomer is much lower than that of the E isomer [9]. The low stability of Z isomers was explained by the difference in the electronic structure and by the different overlap of the lone pair and π orbitals, which is a result of the nonbonding repulsions between the dimethylamino and $R_1(R_2)$ groups. On account of the possibility of rotation around the N-N bond, this interaction is not present in the E isomer of aldehyde hydrazones, while when R_1,R_2 = alkyl group, the loss of resonance stabilization is inevitable. The increase in the C=N-N bond angle in the ketone DAH (Table IV) must be due to the interaction of substituents on the C and the lone pair on the N atoms of the dialkylamino group and can cause a loss of the resonance stabilization, as mentioned above. At the same time, the electron density on the imino carbon atom is lower in aldehyde DAHs than that in the ketone DAHs (Table IV). The electron density is not changed significantly on the N atoms of DMHs.

¹⁵N NMR spectra support this observation: there is a constant difference in the chemical shift of the ²N atoms in aldehyde and ketone dialkylhydrazones [25].

From a study of the dimethylamino derivatives containing N-N bonds, it was found that the shorter the bond, the greater the extent of electronic delocalization [25], i.e. a linear correlation exists between the N-N bond length and the $\delta^{15}N$ chemical shift.

In keto hydrazones, the resonance structure is disturbed anyway, modifying the extent of interactions with the stationary phase.

Molecular parameters representing molecular size (V_w, S_w and molar volume) are important variables in the correlation equations [21, 26–28] as the dispersion interactions increase with increasing number of electrons. Theoretically calculated V_w and S_w data for the DAHs

Table IV. Molecular parameters[a] of N,N-dialkylhydrazones calculated from MNDO results

No.	Compound	$10^4\ S_W/pm^2$	$10^6\ V_W/pm^3$	Θ	d_C
1	Methanal DMH	115.9	82.3	116.8	3.909
2	Ethanal DMH	139.7	99.4	116.3	3.954
3	Propanal DMH	162.2	116.2	116.3	3.942
4	2-Propanone DMH	162.1	116.8	118.7	3.991
5	Butanal DMH	186.6	133.9	116.3	3.942
6	2-Methylpropanal DMH	174.7	133.2	116.2	3.933
7	2-Butanone DMH	186.4	133.7	118.8	3.979
8	Pentanal DMH	207.4	151.4	116.3	3.943
9	2-Pentanone DMH	212.6	150.4	118.8	3.980
10	3-Methyl-2-butanone DMH	196.5	151.0	118.9	3.969
11	2,2-Dimethylpropanal DMH	194.9	150.3	116.1	3.924
12	Ethanal DEH	182.7	133.5	117.2	3.965
13	2-PropanoneDEH	206.8	150.7	119.6	3.995
14	Ethanal methylethylhydrazone	164.4	116.8	116.9	3.961

[a] van der Waals' surface areas (S_W) and volumes (V_W); C = N-N bond angle (Θ) in degrees; and electron density (d_C) on C atom of C = N double bond.

and the analogous olefins are listed in Table IV. They do not reveal any significant difference for isomeric ketone and aldehyde DAHs. V_w and S_w are not sensitive enough to the above-mentioned electronic differences.

Retention Behaviour of DAHs

Many examples illustrate [10, 29–31] that the boiling point is a physical parameter that correlates closely with the retention index. This is the case for DMHs and DEHs, also (Eq. (1), Figure 1):

$$I = (310.6 \pm 20.5) + (4.06 \pm 0.17)\ t_b \qquad (1)$$

$$r = 0.991 \quad s = 13.6 \quad F = 573.3 \quad MSC = 3.66 \quad n = 13$$

where r is the correlation coefficient, s is the standard error, F is result of Fischer test, MSC is the model selection criterion parameter, and n is the number of compounds included in the calculation. Equation (1) can alternatively be used to estimate I or t_b.

The Kováts rule [10, 32] stipulates that the ratio $\Delta I : \Delta t_b$ is generally around 5 for several classes of compounds. In the present case, this value (slope of line in Figure 1) is 4.06, in good agreement with the original assumption.

Molar refractivity (polarizability) has been found to be an important descriptor in structure-retention relations. Although the dispersion energy is linearly related to R_M, the reciprocal of R_M [33, 34] has sometimes been found to be a better descriptor than the direct value.

In this case, the I vs. R_M correlations for aldehyde and ketone DMHs and DEHs have similar slopes but different intercepts (Figure 2).

A ketone derivative with a retention index similar to that of an aldehyde (e.g. propanal DMH and 2-butanone DMH) has a higher R_M due to the greater number of

electrons. Consequently, interactions cannot be characterized by dispersive forces only.

Differences in structural and retention behaviour of the members of a homologous series are not common. GC methods may be suitable to explain the structural differences from the retention behaviour.

The difference in I values measured on stationary phases with different polarities is a measure of, for example, polarity differences, and physico-chemical interactions (H-bonding). No H-bonding with the stationary phase can be expected for DAHs. The $\Delta I = I(\text{polar}) - I(\text{apolar})$ values are somewhat higher for aldehyde than ketone DMHs and DEHs (Table II), suggesting a similar trend in polarities, although the polarity of HP-5 is limited.

The homomorphic factor

$$H^A = I_{\text{substance}} - I_{\text{alkane}} \qquad (2)$$

introduced by Schomburg [35] is the difference in I for a compound and an alkane with the same carbon skeleton. H^A depends on several structural parameters, e.g. the number of carbon atoms in the compound, the position of the double bond, geometrical isomerism and column temperature [36–40]. H^A is approximately constant in a homologous series of compounds; it may vary slightly with increasing number of carbon atoms if there is no other structural change in the series.

The H^A data determined for DAHs on the HP-1 column depend on the structure: they decrease gradually with increasing number of carbon atoms in the oxo part of the molecule, but decrease sharply if R_2 is an alkyl group (ketone hydrazone) (Table II, Figure 3). A similar result was obtained when an alkene was chosen as the standard, where the N atom of the hydrazone was substituted
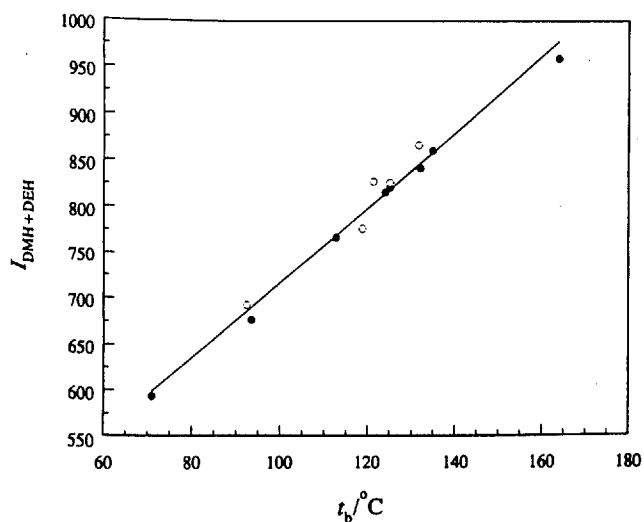
Figure 1

Retention index vs. boiling point for N,N-dialkylhydrazones. (●) = aldehyde hydrazones, (O) = Ketone hydrazones.
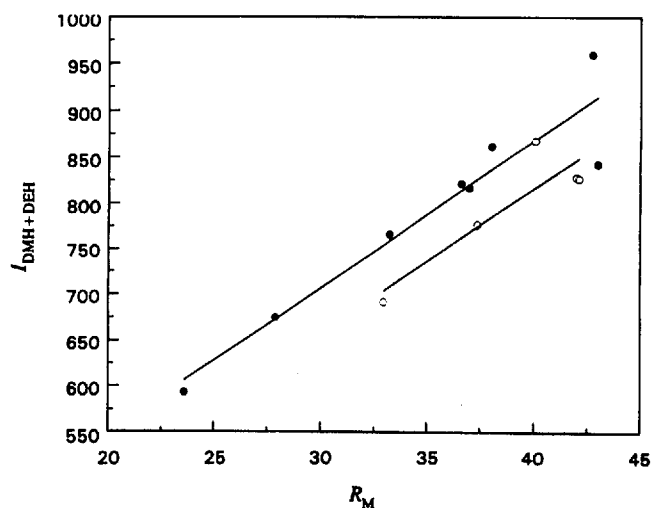

Figure 2

Retention index on HP-1 column vs. molar refraction of N,N-dialkylhydrazones. (●) = aldehyde hydrazones, (O) = ketone hydrazones.
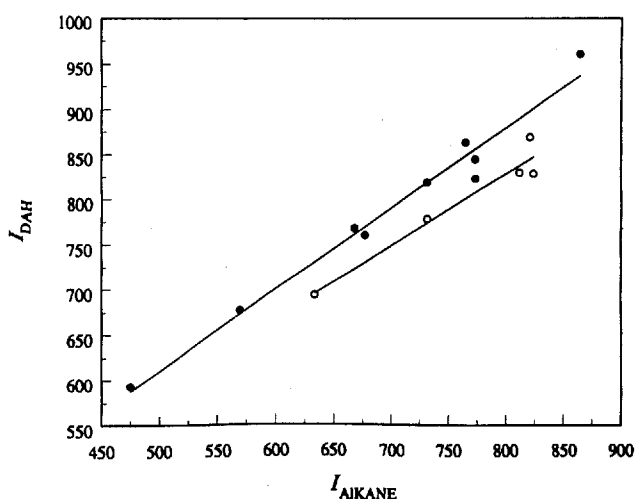

Figure 3

Retention indices of N,N-dimethylhydrazones on HP-1 column vs. retention indices of analogous (standard) alkanes. (●) = aldehyde hydrazones, (O) = ketone hydrazones.
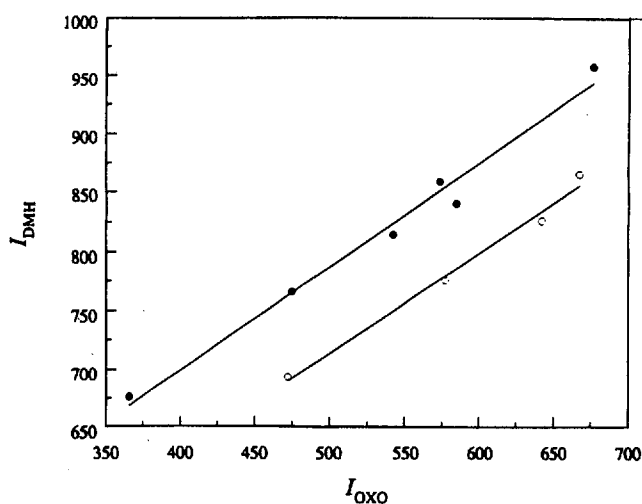

Figure 4

Retention indices of N,N-dimethylhydrazones on HP-1 column vs. retention indices of starting oxo compound. (●) = aldehyde hydrazones, (O) = ketone hydrazones.

with a CH group. The plots in Figures 2 and 3 may reflect the same structural and electronic differences in the ketone and aldehyde DMHs and DEHs. The basic difference in retention behaviour of DAHs is observed when there is branching at the carbon in the C=N double bond. Further branching in the alkyl chain of R_1, R_2 (e.g. 9, 10) does not cause any additional effect.

Which structural characteristics of the molecule, then, are responsible for the differences?

If we choose an oxo compound instead of an alkane as a standard (i.e. H^A is substituted for H^{oxo}), where oxo is the compound from which the hydrazone was synthesized, we also obtain different plots for ketone and aldehyde DMHs (Figure 4). Thus, there is a major difference in retention when R_2 = H and R_2 = alkyl group.

Equation (2) predicts an additivity of retention indices for homologous compounds without structural anomaly. If we allow some systematic deviation from this rule for $(a \neq 1, b = H^A$ or H^{oxo}, Eq. (3) [11]) owing to structural anomaly:

$$I_{substance} = aI_{standard} + b \qquad (3)$$

We observed good additivity $(a \sim 1)$ for the DNPHs of aldehydes, but not for the ketone derivatives $(a < 1)$, when the standard was the analogous oxo compound [11]. The structural differences were analysed by means of a similar equation in the case of amides [41, 42].

The additivity rule (Eq. (3) with $a \sim 1$) is not strictly valid for either type of DMHs $(a < 1)$, and we have two

Table V. Regression parameters in the correlation equation[a] $I = (a \pm \sigma_a) + (b \pm \sigma_b)x + (c \pm \sigma_c)y$.

Compound	x	y	$a\ (\pm \sigma_a)$	$b\ (\pm \sigma_b)$	$c\ (\pm \sigma_c)$	r	s	F	MSC	n
DMHs	I_{oxo}	0	383.1 ± 80.4	0.76 ± 0.14	0	0.884	41.7	28.6	1.12	10
Aldehyde DMHs	I_{oxo}	0	345.5 ± 33.5	0.88 ± 0.06	0	0.990	14.6	206.6	3.30	6
Ketone DMHs	I_{oxo}	0	284.8 ± 37.8	0.86 ± 0.06	0	0.995	9.6	181.8	3.52	4
Aldehyde DAHs	S_w	0	160.7 ± 45.2	3.69 ± 0.26	0	0.983	21.1	196.9	2.93	9
Ketone DAHs	S_w	0	162.6 ± 71.4	3.29 ± 0.37	0	0.982	14.7	79.7	2.52	5
Aldehyde DAHs	V_w	0	234.6 ± 64.7	4.45 ± 0.51	0	0.957	33.2	75.3	2.02	9
Ketone DAHs	V_w	0	200.4 ± 94.2	4.25 ± 0.67	0	0.965	20.2	40.5	1.87	5
DMHs	I_{oxo}	Θ	3810 ± 397	0.88 ± 0.05	−29.8 ± 3.4	0.990	13.0	183.3	3.38	10
DMHs	I_{oxo}	d_C	6048 ± 1511	0.77 ± 0.09	−1433 ± 382	0.963	25.7	44.7	2.02	10
DAH	S_w	Θ	3457 ± 485	3.55 ± 0.20	−28.4 ± 4.2	0.983	18.1	160.1	2.98	14
DAH	S_w	d_C	4796 ± 1370	3.54 ± 0.33	−1172 ± 353	0.957	28.8	59.8	2.05	14

[a] I is retention index of compound indicated, I_{oxo} retention index of selected oxo compound, S_w is the van der Waals' surface area, V_w van der Waals volume, Θ C = N-N bond angle, d_C electron density on C atom of imino group, σ error in parameters a, b and c, respectively, r correlation coefficient, s standard error, F result of Fischer test, and MSC model selection parameter. V_w is in 10^6 pm^3 and S_w is in 10^4 pm^2.

different correlation equations for aldehyde and ketone DMHs (Table V).

The difference of electronic structure of isomers is not reflected in parameters representing molecular size (S_w or V_w), and thus we have different correlation equations for aldehyde and ketone DAHs (Table V).

The basic reason why separate equations are necessary for calculation of retention indices of the two classes of compounds is the different resonance structures in the aldehyde and ketone derivatives. The difference can be eliminated by introducing the C=N-N bond angle or the electron density on the imino C atom into the correlation equation as a measure of the change of resonance in the ketone DAHs because of the above effect (Table V).

Conclusions

DMHs are one of the rare examples where electronic structures of structural isomers differ. This is reflected in retention relations. Retention indices for all DAHs can be estimated from the boiling points. Homomorphic factors and van der Waals' parameters can also be used to predict retention indices for both ketone and aldehyde DMHs, DEHs, separately. The I_{oxo} values of analogous oxo compounds and molecular parameters (van der Waals' surface area, S_w, C = N-N bond angle and electron density) describe the retention behaviour of both classes of DAHs in a single correlation equation.

Acknowledgements

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