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RETENTION INDICES OF DIMETHYLBENZAMIDINES AND BENZYLIDENEAMINES ON A NON-POLAR COLUMN*

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SUMMARY

The retention indices of 207 compounds comprising four series of dimethylbenzamidines, $R_xN=C(C_6H_4Z)N(CH_3)_2$ (BDM), and five series of benzylideneamines, $R_xN=CHC_6H_4Z$ (BA), each containing the same set of 23 variable substituents R_x on the imino nitrogen atom, have been measured on a non-polar GE SE-30 column. The retention indices obtained were correlated with those of corresponding model simple compounds, such as substituted hydrocarbons R_xH, primary amines R_xNH_2, ethyl benzoates ZC_6H_4COOEt for BDM and substituted benzaldehydes ZC_6H_4CHO for BA. Further support is provided for earlier conclusions on the limitation of additivity rules in the prediction of retention indices and that the correlation method should be used instead for this purpose. It has been found that the retention indices of both dimethylbenzamidines and benzylideneamines obey a diparameter linear equation with the retention indices of corresponding model compounds as an independent variable.

INTRODUCTION

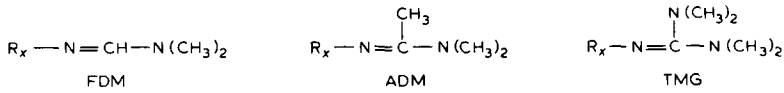
In the course of studies on the applicability of gas chromatographic analysis to amidines[1,2], it was found that the prediction of the retention indices for dimethylformamidines (FDM), dimethylacetamidines (ADM) and tetramethylguanidines (TMG) from the retention indices of corresponding substituted hydrocarbons, R_xH, cannot be based on the additivity rule. It was shown that linear correlations of the form

$$I_{\text{amidine}} = aI_{\text{Std}} + b \quad (1)$$

where I are the Kováts retention indices[3,4] of amidine and a standard (Std) may be successfully applied for this purpose. The additivity rule may be used only when the slope of the correlation line is equal to unity.

* Amidines, Part XIX.

It was concluded that the additivity rule should be used very carefully, because at least in some instances it may cause considerable errors. For example, for the FDM series *vs.* R_xH, $a = 1.28$.



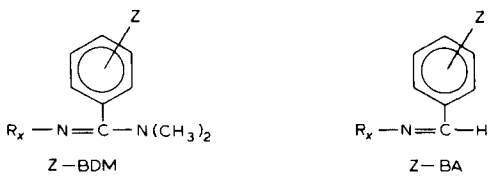
Thus the question arose of whether for the prediction of retention indices for compounds containing two or more substituents (Cpd) a multiparameter regression of the type

$$I_{\mathrm{Cpd}} = \sum_i a_i I_{\mathrm{Std}_i} + b \tag{2}$$

can be applied or whether in some instances a more complex equation should be used, taking into account changes in one of the coefficients, a_i, similar to those observed in correlations of other physico-chemical properties of molecules[5,6], following a change in substituent at a certain site in the molecule.

In this work, the retention indices for four series of dimethylbenzamidines (BDM) and five series of benzylideneamines (BA), each including 23 compounds with the same substituents R_x at the imino nitrogen atom, were determined on a non-polar GE SE-30 column.

The compounds investigated have the general formulae



Benzamidines:

Z = H	N^1,N^1-dimethylbenzamidines (H-BDM)
Z = *p*-CH_3	N^1,N^1-dimethyl-*p*-methylbenzamidines (*p*-Me-BDM)
Z = *p*-OCH_3	N^1,N^1-dimethyl-*p*-methoxybenzamidines (*p*-MeO-BDM)
Z = *p*-Cl	N^1,N^1-dimethyl-*p*-chlorobenzamidines (*p*-Cl-BDM)

Benzylideneamines:

Z = H	benzylideneamines (H-BA)
Z = *p*-CH_3	*p*-methylbenzylideneamines (*p*-Me-BA)
Z = *p*-OCH_3	*p*-methoxybenzylideneamines (*p*-MeO-BA)
Z = *p*-Cl	*p*-chlorobenzylideneamines (*p*-Cl-BA)
Z = *p*-Br	*p*-bromobenzylideneamines (*p*-Br-BA)

The substituents R_x are listed in the Table I.

Using the same column, the retention indices of the ethyl esters of corresponding substituted benzoic acids (ZC_6H_4COOEt) and substituted benzaldehydes (ZC_6H_4CHO) were determined for comparative purposes.

EXPERIMENTAL

Benzamidines were synthesized accordingly to a procedure described elsewhere[7]. Benzylideneamines were obtained by mixing equimolar amounts of aldehyde and amine. Aldehydes were commercial samples. C_{12}–C_{20} *n*-alkanes were purchased from Applied Science Labs.

Gas chromatography

A Chromatron Model GCHF 18.3.4 gas chromatograph with a flame ionization detector, equipped with a 3 m × 3 mm I.D. column filled with 15% GE SE-30 silicone gum rubber on Chromosorb W AW (60–80 mesh), was used. The column temperature was maintained at 280°C for amidines and benzylideneamines and at 180°C for benzaldehydes and ethyl esters of substituted benzoic acids. The carrier gas was nitrogen at a flow-rate of 25 ml/min. Samples of 1 μl of 0.1 *M* solutions in methanol (or pentane for hydrocarbons) were injected by means of a 10-μl Hamilton syringe.

Retention indices and dead times were determined by regression analysis by the method of Grobler and Bálizs[8] as improved by Haken *et al.*[9] using the series of nine C_{12}–C_{20} *n*-alkanes, each time under the same conditions as for the studied sample.

Retention times were recorded by means of a Cobrabid KB 5503 electronic integrator with an accuracy to ± 0.5 sec.

RESULTS AND DISCUSSION

The retention indices obtained with confidence intervals at a significance level of 0.05, calculated from at least five measurements, are given in Table I and those of ethyl esters of substituted benzoic acids and benzaldehydes are given in Table II.

The retention index depends to a small extent on temperature. Therefore, for the sake of higher accuracy of correlations, we attempted to determine all retention indices of the compounds studied at one temperature. The most suitable temperature for both benzamidines and benzylideneamines appeared to be 280°C and for the standards 180°C.

We correlated the retention indices of the compounds of each series studied with those of corresponding substituted hydrocarbons (R_xH) and primary amines (PA) in order to establish whether the slopes (*a* in eqn. 1) are equal to unity for both correlations and which of the standards ensure a higher accuracy of prediction. Calculations were made by means of the least-squares method.

The regression coefficients (*a* and *b*) with confidence intervals calculated at a significance level of 0.05 and the estimators of correlation, *i.e.*, the correlation coefficient (*r*) and Exner's ψ function[10], are given in Table III.

The regressions obtained indicate that for all the series studied the correlations

TABLE I

RETENTION INDICES OF DIMETHYLBENZAMIDINES [$R_xN=C(C_6H_4Z)N(CH_3)_2$; Z-BDM] AND BENZYLIDENEAMINES ($R_xN=CHC_6H_4Z$; Z-BA) ON A GE SE-30 NON-POLAR COLUMN

No.	R_x	R_xH *(180°C)*	*PA (180°C)*	*H-BDM (280°C)*	*p-Me-BDM (280°C)*	*p-MeO-BDM (280°C)*	*p-Cl-BDM (280°C)*	*H-BA (280°C)*	*p-Me-BA (280°C)*	*p-MeO-BA (280°C)*	*p-Cl-BA (280°C)*	*p-Br-BA (280°C)*
1	*n*-C_3H_7	300*	521 ± 2**	1498 ± 0	1583 ± 8	1734 ± 5	1687 ± 5	1270 ± 0	1371 ± 8	1546 ± 5	1457 ± 9	1572 ± 5
2	*n*-C_4H_9	400*	629 ± 2**	1552 ± 0	1627 ± 7	1774 ± 0	1733 ± 4	1368 ± 8	1479 ± 6	1649 ± 7	1565 ± 8	1678 ± 8
3	*n*-C_5H_{11}	500*	712 ± 3**	1637 ± 7	1673 ± 5	1820 ± 5	1778 ± 0	1429 ± 9	1540 ± 6	1706 ± 4	1628 ± 6	1743 ± 7
4	*n*-C_6H_{13}	600*	848 ± 7**	1689 ± 0	1767 ± 5	1915 ± 4	1870 ± 3	1567 ± 6	1682 ± 7	1843 ± 5	1768 ± 5	1884 ± 6
5	*n*-C_7H_{15}	700*	939 ± 3	1789 ± 5	1866 ± 0	2012 ± 2	1966 ± 3	1674 ± 3	1783 ± 3	1936 ± 2	1868 ± 4	1975 ± 1
6	*n*-C_8H_{17}	800*	1038 ± 2	1887 ± 0	1963 ± 3	2111 ± 2	2064 ± 2	1772 ± 3	1881 ± 2	2033 ± 1	1966 ± 2	2074 ± 1
7	*n*-C_9H_{19}	900*	1141 ± 2	1987 ± 0	2063 ± 0	2208 ± 2	2162 ± 2	1873 ± 3	1979 ± 2	2130 ± 2	2065 ± 2	2172 ± 2
8	*n*-$C_{10}H_{21}$	1000*	1241 ± 1	2086 ± 0	2163 ± 0	2306 ± 1	2260 ± 2	1970 ± 3	2076 ± 1	2227 ± 1	2163 ± 1	2269 ± 1
9	cyclo-C_6H_{11}	658 ± 0	857 ± 1**	1725 ± 0	1801 ± 0	1946 ± 0	1904 ± 4	1658 ± 0	1771 ± 3	1939 ± 2	1872 ± 4	1982 ± 3
10	$C_6H_5CH_2$	788 ± 1**	1035 ± 6**	1943 ± 3	2023 ± 3	2169 ± 0	2121 ± 2	1817 ± 0	1929 ± 3	2102 ± 2	2024 ± 3	2143 ± 3
11	C_6H_5	681 ± 2**	995 ± 0**	1842 ± 1	1909 ± 1	2059 ± 1	2013 ± 1	1769 ± 2	1894 ± 3	2052 ± 2	1968 ± 3	2077 ± 3
12	3-$CH_3C_6H_4$	788 ± 1**	1088 ± 5**	1897 ± 3	1960 ± 3	2107 ± 2	2061 ± 0	1866 ± 2	1989 ± 2	2151 ± 3	2056 ± 3	2175 ± 9
13	4-$CH_3C_6H_4$	788 ± 1**	1092 ± 5**	1913 ± 4	1974 ± 3	2122 ± 2	2077 ± 0	1882 ± 4	1998 ± 3	2159 ± 3	2077 ± 3	2192 ± 7
14	3-$CH_3OC_6H_4$	927 ± 1**	1229 ± 6**	2048 ± 2	2111 ± 3	2259 ± 0	2210 ± 1	2003 ± 5	2129 ± 2	2296 ± 4	2198 ± 4	2324 ± 9
15	4-$CH_3OC_6H_4$	927 ± 1**	1199 ± 5**	2060 ± 2	2122 ± 3	2265 ± 1	2224 ± 2	2035 ± 3	2151 ± 3	2315 ± 3	2235 ± 3	2348 ± 7
16	3-$C_2H_5OC_6H_4$	995 ± 2**	1293 ± 1**	2092 ± 2	2154 ± 2	2299 ± 1	2250 ± 0	2058 ± 4	2182 ± 2	2350 ± 3	2249 ± 2	2371 ± 9
17	4-$C_2H_5OC_6H_4$	995 ± 2**	1277 ± 1**	2113 ± 2	2171 ± 2	2315 ± 2	2273 ± 2	2096 ± 3	2212 ± 4	2372 ± 3	2294 ± 3	2407 ± 5
18	3-ClC_6H_4	875 ± 2**	1204 ± 1**	2032 ± 0	2091 ± 0	2234 ± 0	2199 ± 2	1961 ± 3	2093 ± 5	2248 ± 6	2171 ± 3	2272 ± 4
19	4-ClC_6H_4	875 ± 2**	1204 ± 1**	2060 ± 2	2112 ± 0	2263 ± 1	2223 ± 2	1977 ± 4	2096 ± 4	2259 ± 5	2180 ± 4	2289 ± 2
20	3-BrC_6H_4	964 ± 2**	1295 ± 5**	2126 ± 0	2184 ± 0	2320 ± 1	2293 ± 0	2068 ± 3	2202 ± 4	2355 ± 6	2277 ± 4	2382 ± 4
21	4-BrC_6H_4	964 ± 2**	1300 ± 3**	2160 ± 2	2208 ± 1	2360 ± 2	2321 ± 0	2086 ± 4	2202 ± 4	2367 ± 4	2287 ± 4	2399 ± 3
22	3-$NO_2C_6H_4$	1103 ± 6**	1446 ± 3**	2291 ± 1	2341 ± 1	2472 ± 3	2460 ± 1	2212 ± 4	2348 ± 5	2506 ± 8	2428 ± 7	2526 ± 3
23	4-$NO_2C_6H_4$	1103 ± 6**	1560 ± 1**	2415 ± 0	2454 ± 2	2610 ± 2	2578 ± 1	2259 ± 4	2378 ± 4	2542 ± 4	2460 ± 5	2569 ± 4

* By definition.

** According to ref. 1.

TABLE II

RETENTION INDICES OF ETHYL ESTERS OF SUBSTITUTED BENZOIC ACIDS (ZC_6H_4COOEt) AND SUBSTITUTED BENZALDEHYDES (ZC_6H_4CHO) ON A GE SE-30 NONPOLAR COLUMN AT 180°C

Z	*H*	*p-Me*	*p-MeO*	*p-Cl*	*p-Br*
Ester	1178 ± 1	1288 ± 1	1430 ± 3	1327 ± 1	
Aldehyde	974 ± 1	1096 ± 0	1262 ± 1	1137 ± 0	1229 ± 1

with the retention indices of primary amines are of the highest quality, but the correlations with the retention indices of substituted hydrocarbons are still satisfactory.

The differences between the regression coefficients for the series of benzamidines studied were within the confidence intervals, and the test of parallelism gave no basis for treating them differently. The same was observed for the series of benzylideneamines studied. This leads to the conclusion that for the prediction of their retention indices a diparameter linear regression in the form of eqn. 2 may be used, and two standard series are necessary.

As one standard series, for substitution at the imino nitrogen atom, we chose primary amines (PA) because in this instance and also for other amidines[1] they yield correlations of higher quality than substituted hydrocarbons, R_xH. As the second standard series, for substitution at the carbon atom of the C=N group, we have used ethyl esters of benzoic acids (ZC_6H_4COOEt) for benzamidines and benzaldehydes (ZC_6H_4CHO) for benzylideneamines, and also derivatives of benzene (ZC_6H_5) for both groups of compounds.

TABLE III

REGRESSION PARAMETERS OF RETENTION INDICES OF BENZAMIDINES AND BENZYLIDENEAMINES *VS.* RETENTION INDICES OF STANDARDS (EQN. 1)

Standard	*Series*	*a*	*b*	*r*	ψ	*n*
R_xH	H-BDM	1.043 ± 0.115	1105	0.9719	0.246	23
	p-Me-BDM	1.015 ± 0.103	1192	0.9758	0.229	23
	p-MeO-BDM	1.008 ± 0.107	1344	0.9735	0.239	23
	p-Cl-BDM	1.024 ± 0.114	1289	0.9710	0.250	23
	H-BA	1.215 ± 0.105	871	0.9823	0.196	23
	p-Me-BA	1.238 ± 0.115	970	0.9796	0.210	23
	p-MeO-BA	1.224 ± 0.122	1143	0.9769	0.224	23
	p-Cl-BA	1.225 ± 0.110	1062	0.9811	0.202	23
	p-Br-BA	1.217 ± 0.111	1180	0.9804	0.206	23
R_xNH_2	H-BDM	0.887 ± 0.053	980	0.9915	0.136	23
	p-Me-BDM	0.860 ± 0.051	1074	0.9914	0.137	23
	p-MeO-BDM	0.855 ± 0.053	1225	0.9910	0.140	23
	p-Cl-BDM	0.870 ± 0.056	1167	0.9901	0.147	23
	H-BA	1.023 ± 0.059	737	0.9920	0.132	23
	p-Me-BA	1.044 ± 0.063	831	0.9912	0.138	23
	p-MeO-BA	1.033 ± 0.068	1004	0.9898	0.149	23
	p-Cl-BA	1.031 ± 0.063	927	0.9911	0.139	23
	p-Br-BA	1.025 ± 0.065	1046	0.9903	0.145	23

The correlations for series with two variable substituents (all BDM or all BA) are in the form

$$I = a_1 I_{PA} + a_2 I_{Std_2} + b \quad (3)$$

The regression parameters with confidence intervals calculated at a significance level of 0.05 and correlation coefficients are given in Table IV. The parameters obtained indicate that for substituents at a functional carbon atom slightly better correlations are obtained when substituted benzenes are used as standards. However, it seems that this may be due to limitations of the substituents to *p*-substituted phenyl rings and to a small number of substituents. It may be assumed that the use of a larges and more varied set of substituents may reveal that in this instance also, on account of isomerism[1], better correlations are obtained with standards containing functional groups.

TABLE IV

MULTIPLE REGRESSION PARAMETERS OF RETENTION INDICES OF BENZAMIDINES AND BENZYLIDENEAMINES *VS.* RETENTION INDICES OF STANDARDS (EQN. 3)

Series	*Standards*		a_1	a_2	b	r	ψ	n
BDM	R_xNH_2	ZC_6H_5	0.868 ± 0.027	0.883 ± 0.072	389	0.9907	0.138	92
	R_xNH_2	ZC_6H_4COOEt	0.868 ± 0.033	0.879 ± 0.091	−36	0.9860	0.170	92
	R_xH	ZC_6H_5	1.022 ± 0.053	0.883 ± 0.117	510	0.9751	0.225	92
	R_xH	ZC_6H_4COOEt	1.023 ± 0.057	0.879 ± 0.132	85	0.9703	0.246	92
BA	R_xNH_2	ZC_6H_5	1.031 ± 0.027	1.105 ± 0.065	27	0.9920	0.128	115
	R_xNH_2	ZC_6H_4CHO	1.031 ± 0.032	1.076 ± 0.078	−318	0.9885	0.153	115
	R_xH	ZC_6H_5	1.224 ± 0.047	1.105 ± 0.096	109	0.9829	0.187	115
	R_xH	ZC_6H_4CHO	1.224 ± 0.052	1.076 ± 0.104	182	0.9794	0.205	115

The most important feature is the striking difference between the regression coefficients a_1 for benzamidines and benzylideneamines, no matter what kind of standard series, R_xH or R_xNH_2, is used for correlation. This shows that a change in the substituent at a certain site in the molecule, in this instance at the carbon atom of the C=N group, may cause considerable changes in a_i. Therefore, it can be assumed that apparently negligible differences in the coefficient a in monoparameter correlations (eqn. 1) for individual series of benzamidines or benzylideneamines are not coincidental, but are due to substitution at the carbon atom of the C=N group.

The question remains of whether it is possible to find some general equations, common for a wide variety of organic compounds, for the prediction of retention indices. How far the linear multiparameter regression in the form of eqn. 2 can be used, and what kind of compounds are the most suitable as standard series, require further studies on appropriate series of compounds.

CONCLUSIONS

The results presented indicate that the application of the additivity rule for

compounds with a wide range of retention indices may cause considerable errors, and that more accurate results are obtained if a correlation equation is applied. General correlation equations probably should contain terms that take into account the dependence of the regression coefficients a_i on substitution at certain sites of the molecule. However, for some groups of compounds satisfactory results may be obtained using a simple multiparameter equation in the form of eqn. 2.

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