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EFFECT OF THE STATIONARY PHASE ON THE RETENTION INDICES OF DIMETHYLFORMAMIDINES, DIMETHYLACETAMIDINES AND PRIMARY AMINES*

JANUSZ OSZCZAPOWICZ*, JERZY OSEK, WALDEMAR KRAWCZYK and BOŻENA KIELAK
Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw (Poland)
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SUMMARY

The retention indices of 70 compounds comprising series of N¹,N¹-dimethylformamidines [R_xN=CH-N(CH₃)₂], N¹,N¹-dimethylacetamidines [R_xN=C(CH₃)-N(CH₃)₂], primary amines (R_xNH₂) and substituted hydrocarbons (R_xH), each containing the same set of 22 variable substituents R_x on the nitrogen atom, were measured on a polar OV-225 column. They were then correlated with those of the same compounds measured under identical conditions on a non-polar GE SE-30 column. The changes in retention indices upon changing the polarity of the column depend on the type of substituent R_x (*n*-alkyl or substituted phenyl). Good linear correlations were obtained between retention indices measured on the two columns for the compounds of each series, but the slope and the intercept of the correlation line depend not only on the series of compounds, but also on the type of substituent R_x at the nitrogen atom.

INTRODUCTION

In the course of our study on the applicability of gas chromatography (GLC) to amidines²⁻⁴, we have shown that the retention indices of amidines R_x-N=CR'-N(R_y)₂ containing a variable substituent, R_x, at the imino nitrogen atom, measured on a non-polar column, can be predicted with satisfactory accuracy on the basis of retention indices of corresponding standard compounds (Std) using a linear regression of the type:

$$I(\text{amidine}) = a \cdot I(\text{Std}) + b \quad (1)$$

It was also pointed out² that the additivity rule, used for prediction of retention indices of organic compounds, should be regarded as a very special case of linear regression, where the slope, *a*, of the correlation line is by definition equal to unity.

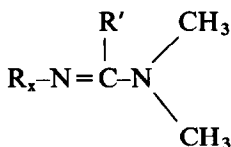
* Amidines, Part XXV; for Part XXIV see ref. 1.

As the standard compounds, primary amines R_xNH_2 or substituted hydrocarbons R_xH were chosen²⁻⁴.

The retention index of a compound depends on its structure, as well as on the polarity of the stationary phase. It seemed probable that eqn. 1 could be applied also for the prediction of retention indices on a polar column. On the other hand, on the basis of literature data^{5,6}, it could be assumed, that for series of compounds X, containing certain functional groups, the retention indices, $P(X)$, on a polar column are related to their retention indices, $P^p(X)$, on a non-polar column by the relationship 2

$$P(X) = a \cdot P^p(X) + b \quad (2)$$

where parameters a and b depend on both the nature of the stationary phase and the type of functional group. Thus the question arose as to whether the retention indices of amidines on a polar column can be predicted using similar relationships, and which type of relationship provides the best results. In this work the retention indices of series of N^1, N^1 -dimethylformamidines (FDM) and N^1, N^1 -dimethylacetamidines (ADM), each containing 22 compounds with the same substituents R_x at the imino nitrogen atom, were determined on a polar OV-225 column.



$R' = H$: N^1, N^1 -dimethylformamidines
 $R' = CH_3$: N^1, N^1 -dimethylacetamidines

For comparison, the retention indices of primary amines R_xNH_2 were determined on the same column. The substituents R_x are listed in the Table I.

EXPERIMENTAL

Materials

Amidines were synthesized and isolated in our laboratory as described elsewhere: FDM⁷, ADM⁸. The amines and hydrocarbon derivatives were of commercial grade, C_{12} - C_{20} *n*-alkanes and the stationary phase OV-225 (25% phenyl, 25% cyanopropyl, methyl silicone) were purchased from Applied Science Labs.

Gas chromatography

A Chromatron Model GCHF 18.3.4 gas chromatograph (VEB Chromatron, Berlin, G.D.R.) equipped with a flame ionization detector and a 3.6 m \times 3 mm I.D. column filled with 10% OV-225 on Chromosorb W AW (60-80 mesh) was used. The column temperature was maintained at 240°C for formamidines and acetamidines and at 180°C for primary amines and substituted hydrocarbons. The carrier gas (nitrogen) flow-rate was 25 ml/min. Samples (1 μ l) of 0.3 *M* solutions in ethanol (or

n-pentane for hydrocarbons) were injected by means of a 10- μ l Hamilton syringe.

The retention indices and dead times were determined by regression analysis by the method of Grobler and Bálizs⁹ as improved by Haken *et al.*¹⁰ using the series of nine C₁₂-C₂₀ *n*-alkanes, each time under the same conditions as for the sample studied.

The retention times were recorded by means of a KB 5503 electronic integrator (COBRABID, Poland) with an accuracy of ± 0.5 s.

RESULTS AND DISCUSSION

The retention index is slightly dependent on the temperature. Therefore, for more accurate correlations, we attempted to determine all the retention indices of the compounds studied, at least within the given series, at one temperature. The most suitable temperature for formamidines (FDM) and acetamidines (ADM) was 240°C and for primary amines (R_xNH₂) and substituted hydrocarbons (R_xH) it was 180°C. The retention indices of these compounds on a non-polar column^{2,3} were determined at exactly the same temperatures.

TABLE I

RETENTION INDICES OF DIMETHYLFORMAMIDINES (FDM), DIMETHYLACETAMIDINES (ADM), PRIMARY AMINES (R_xNH₂) AND SUBSTITUTED HYDROCARBONS (R_xH) ON AN OV-225 POLAR COLUMN

No.	R _x	FDM*	ADM*	R _x NH ₂ **	R _x H**
1	<i>n</i> -C ₅ H ₇	1071 \pm 0	1584 \pm 0		300***
2	<i>n</i> -C ₆ H ₉	1159 \pm 0	1690 \pm 8		400***
3	<i>n</i> -C ₆ H ₁₁	1233 \pm 0	1799 \pm 6		500***
4	<i>n</i> -C ₆ H ₁₃	1393 \pm 0	1888 \pm 0	1021 \pm 0	600***
5	<i>n</i> -C ₇ H ₁₅	1512 \pm 0	1990 \pm 0	1107 \pm 4	700***
6	<i>n</i> -C ₈ H ₁₇	1628 \pm 0	2091 \pm 0	1211 \pm 3	800***
7	<i>n</i> -C ₉ H ₁₉	1710 \pm 0	2188 \pm 2	1313 \pm 2	900***
8	<i>n</i> -C ₁₀ H ₂₁	1805 \pm 0	2286 \pm 1	1413 \pm 1	1000***
9	C ₆ H ₅	1982 \pm 5	1954 \pm 0	1503 \pm 2	887 \pm 24
10	C ₆ H ₅ CH ₂	1919 \pm 13	1875 \pm 9	1447 \pm 0	
11	3-CH ₃ -C ₆ H ₄	2077 \pm 0	2026 \pm 0	1596 \pm 4	948 \pm 0
12	4-CH ₃ -C ₆ H ₄	2070 \pm 7	2061 \pm 11	1582 \pm 6	
13	3-OCH ₃ -C ₆ H ₄	2375 \pm 3	2294 \pm 3	1875 \pm 2	1215 \pm 0
14	4-OCH ₃ -C ₆ H ₄	2331 \pm 4	2315 \pm 6	1830 \pm 3	
15	3-OC ₂ H ₅ -C ₆ H ₄	2398 \pm 4	2327 \pm 3	1917 \pm 1	1242 \pm 0
16	4-OC ₂ H ₅ -C ₆ H ₄	2373 \pm 5	2350 \pm 8	1877 \pm 2	
17	3-Cl-C ₆ H ₄	2257 \pm 6	2195 \pm 7	1830 \pm 2	1126 \pm 0
18	4-Cl-C ₆ H ₄	2256 \pm 6	2210 \pm 3	1824 \pm 3	
19	3-Br-C ₆ H ₄	2394 \pm 4	2329 \pm 6	1959 \pm 1	1243 \pm 0
20	4-Br-C ₆ H ₄	2398 \pm 5	2347 \pm 6	1950 \pm 3	
21	3-NO ₂ -C ₆ H ₄	2746 \pm 3	2622 \pm 5	2498 \pm 3	1598 \pm 3
22	4-NO ₂ -C ₆ H ₄	2921 \pm 4	2784 \pm 3	2780 \pm 0	

* Measured at 240°C.

** Measured at 180°C.

*** By definition.

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. We attempted to correlate the retention indices, P , measured on the polar OV-225 column with the

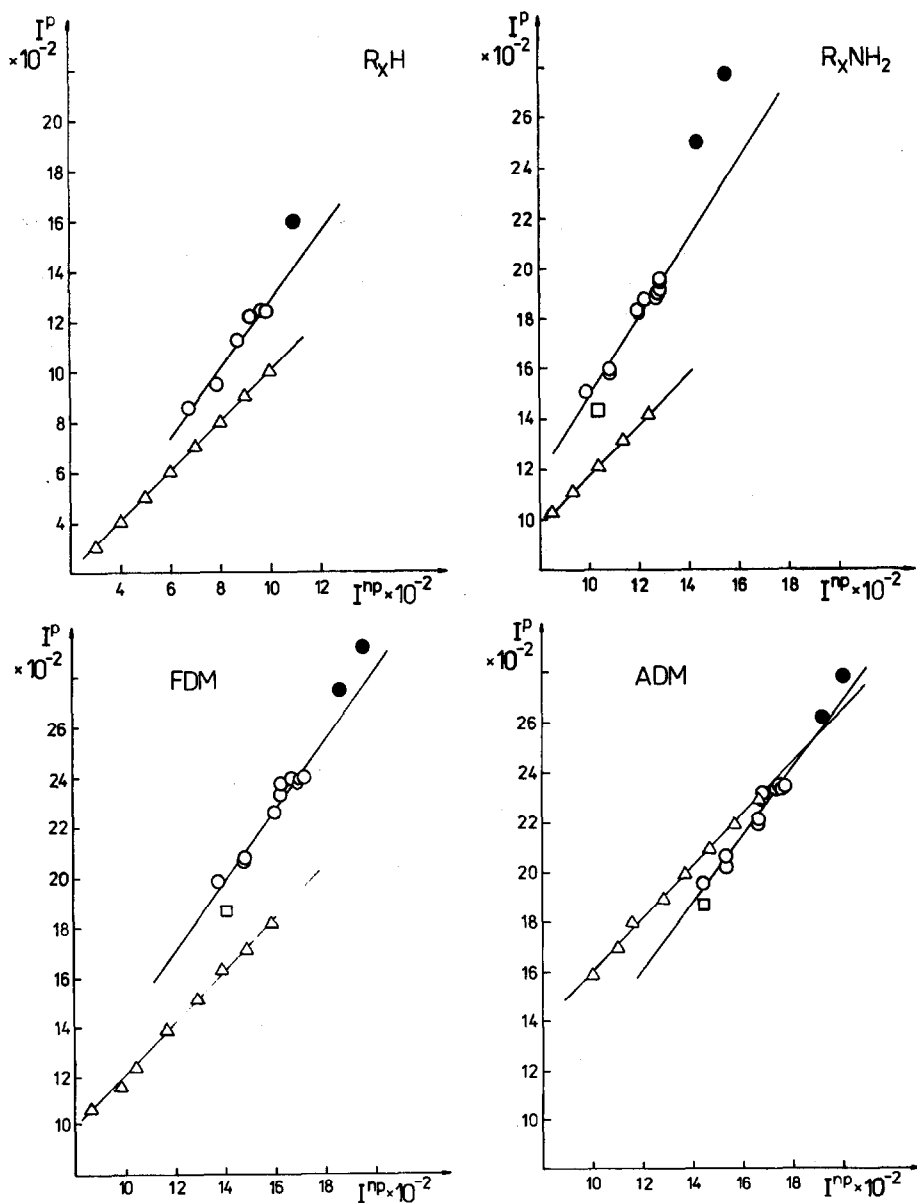


Fig. 1. Plots of retention indices, P , on a polar OV-225 column versus retention indices, P^{np} , measured under the same conditions on a non-polar GE SE-30 column for substituted hydrocarbons (R_xH), primary amines (R_xNH_2), N^1,N^1 -dimethylformamidines (FDM) and N^1,N^1 -dimethylacetamidines (ADM). Δ , *n*-Alkyl derivatives; \circ , phenyl derivatives; \bullet , nitrophenyl derivatives; \square , benzyl derivatives.

retention indices, I^{np} , of the same compounds measured under the same conditions on a non-polar GE SE-30 column (Fig. 1).

For each series studied two separate correlation lines are obtained: one for compounds in which R_x is *n*-alkyl and the other for those in which R_x is a substituted phenyl ring. It should also be noted that the retention indices of *p*- and *m*-nitrophenyl derivatives considerably deviate from the correlation lines.

Thus it was evident that the correlations for these two kinds of derivatives should be calculated separately. The calculations were made by means of a least squares method. The regression coefficients, *a* and *b* in eqn. 1, the confidence intervals for *a*, calculated at a significance level of 0.05, and the correlation coefficients, *r*, and Exner's ψ function¹¹ are given in Table II.

The slopes of the correlation lines for compounds containing *n*-alkyl groups are close to unity (1.050 for FDM, 1.039 for ADM and 1.002 for R_xNH_2). For compounds containing substituted phenyl rings the value are much higher (1.650 for FDM, 1.501 for ADM and 2.295 for R_xNH_2). The correlations obtained for the *n*-alkyl derivatives are of much higher quality than those for the phenyl derivatives. This is most probably due to the fact that all the *n*-alkyl substituents exert the same inductive effect, whereas the mesomeric effect of a substituent at the phenyl ring depends to a considerable extent on its position and the structure of the functional group to which the phenyl ring is bonded. Thus it can be concluded that a general equation for the prediction of retention indices of various types of compounds on a polar column from the retention indices on a non-polar one, should include some terms describing the mutual influence of polar groups in the molecule.

We have also correlated the retention indices of formamidines (FDM) and acetamidines (ADM) on the polar OV-225 column with those of primary amines R_xNH_2 and substituted hydrocarbons R_xH , measured on the same column in order to find out whether eqn. 3 can be applied for the prediction of retention indices of amidines on a polar column, and which type of relationship, 2 or 3, is more suitable for this purpose:

$$I^p(\text{amidine}) = a \cdot I^p(\text{Std}) + b \quad (3)$$

The regression parameters, calculated separately for *n*-alkyl derivatives and phenyl derivatives, are given in Table III. For both series of amidines, the quality of

TABLE II

REGRESSION PARAMETERS OF RETENTION INDICES ON A POLAR OV-225 COLUMN VS. RETENTION INDICES ON A NON-POLAR GE SE-30 COLUMN

Standard	Series	<i>a</i>	<i>b</i>	<i>r</i>	ψ	<i>n</i>
R_xH	R_xH Phenyl deriv.	1.722 ± 0.294	-387	0.9651	0.283	14
R_xNH_2	R_xNH_2 Alkyl deriv.	1.002 ± 0.024	169	0.9999	0.017	5
	R_xNH_2 Phenyl deriv.	2.295 ± 0.360	-932	0.9704	0.261	14
FDM	FDM Alkyl deriv.	1.050 ± 0.069	151	0.9978	0.076	8
	FDM Phenyl deriv.	1.650 ± 0.171	-383	0.9867	0.176	14
ADM	ADM Alkyl deriv.	1.039 ± 0.059	559	0.9984	0.066	8
	ADM Phenyl deriv.	1.501 ± 0.136	-275	0.9897	0.154	14

TABLE III

REGRESSION PARAMETERS OF RETENTION INDICES FOR AMIDINES VS. RETENTION INDICES FOR STANDARDS, BOTH ON AN OV-225 POLAR COLUMN

Standard	Series	<i>a</i>	<i>b</i>	<i>r</i>	ψ	<i>n</i>
R _x H	FDM Alkyl deriv.	1.095 ± 0.089	727	0.9967	0.094	8
	FDM Phenyl deriv.	1.229 ± 0.147	866	0.9825	0.201	14
	ADM Alkyl deriv.	0.998 ± 0.018	1291	0.9998	0.021	8
	ADM Phenyl deriv.	1.094 ± 0.151	969	0.9769	0.231	14
R _x NH ₂	FDM Alkyl deriv.	1.030 ± 0.188	361	0.9951	0.128	5
	FDM Phenyl deriv.	0.742 ± 0.083	919	0.9844	0.190	14
	ADM Alkyl deriv.	1.003 ± 0.073	872	0.9992	0.051	5
	ADM Phenyl deriv.	0.655 ± 0.102	1026	0.9709	0.259	14
FDM	ADM Alkyl deriv.	0.905 ± 0.084	638	0.9957	0.107	8
	ADM Phenyl deriv.	0.891 ± 0.052	195	0.9958	0.099	14

the correlations with primary amines and those with hydrocarbons is comparable, as indicated by the correlation coefficients, *r*, as well as by the Exner's ψ functions. The regression coefficients, *a*, are different for the two types of derivatives, but the differences are less distinct than in the case of correlations with retention indices on a non-polar column. The correlations between the retention indices of the two series of amidines are of very high quality, thus providing support for the aforesaid conclusion concerning the mutual influence between substituents.

The correlation parameters, *r* and ψ , obtained indicate that for the prediction of retention indices of N¹,N¹-dimethyl-formamidines and -acetamidines, and perhaps other amidines as well, on a polar column, either of the relationships 2 or 3 can be used as they provide similar, satisfactorily results.

The question remains as to whether it is possible to find relations enabling the prediction of the regression parameters, *a* and *b* for eqns. 2 or 3, and thus whether it will be possible to precalculate the retention indices on a polar column for a larger variety of amidines. This question requires further studies on appropriate series of compounds.

CONCLUSIONS

The results presented indicate that the retention indices of N¹,N¹-dimethylamidines [R_x-N=CR'-N(CH₃)₂] on a polar OV-225 column can be predicted either on the basis of their retention indices measured on a non-polar GE SE-30 column (eqn. 2, parameters from Table II) or on the basis of retention indices of corresponding standard series (R_xNH₂ or R_xH) measured on the same polar column (eqn. 3, parameters from Table III).

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