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Retentions of alkyloxazoles and alkylthiazoles and their prediction based on non-linear additivity concepts in gas chromatography

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ABSTRACT

The gas chromatographic (GC) behaviour of 39 alkyloxazoles and alkylthiazoles was studied on three capillary columns with OV-101–KF, Triton X-305–KF and PEG-40M–KF. The regularities in the thermodynamic characteristics of sorption of azoles having O or S atoms were established. Energy contributions of methyl, ethyl and propyl groups to the partial molar free energy of sorption of alkyloxazoles and alkylthiazoles were determined. It was found that the contributions of the same alkyl group are different and dependent on the nature of the heterocycle and the position of the alkyl group with respect to the heteroatoms in the azole ring. Two methods for the prediction of retention indices on the basis of the analogy of the GC behaviour of azoles and inconstancy of the contributions of the same alkyl groups are given. The predicted retention indices are in good agreement with the experimental values.

INTRODUCTION

Computer programs using sorption–structure correlations considerably increase the number of substances that can be identified [1]. In the development of such programs for the determination of heterocyclic compounds, it is necessary to take into account the influence of the nature of the heterocyclic ring and substituents on sorption properties of substances [1–4]. It has recently been shown that one can predict retention indices of methylpyridines and methylpyrazines in capillary chromatography by taking into account various values of the energy contribution of the same molecular fragment situated in the different positions on the heterocyclic ring [5]. This approach was applied to the prediction of the retention indices of alkylthiazoles on packed columns [6].

Alkyloxazoles and alkylthiazoles with analogous molecular structure have similar physico-chemical properties [7,8]. Some alkyloxazoles and alkylthiazoles have been characterized by retention index values [6,7,9,10] but these data are not sufficient to predict the gas chromatographic (GC) behaviour of a wide range of substituted compounds.

The purpose of this work was to compare the partial molar free energies of

sorption of alkyloxazoles and alkylthiazoles analysed on capillary columns of different polarity, to determine and compare the contributions of methyl, ethyl and propyl groups to the sorption energy of azoles depending on the nature of the heterocycle and the position of the alkyl group with respect to N, O and S heteroatoms and to search for a scheme for the calculation of retention indices of alkyl-substituted oxazoles and thiazoles on the basis of the correlation established.

EXPERIMENTAL

Alkyloxazoles and alkylthiazoles were analysed using a Carlo Erba Mega 5300 gas chromatograph with a flame ionization detector at 110°C, equipped with three glass capillary columns (50 m × 0.3 mm I.D., film thickness 0.4 μm) with OV-101–KF, Triton X-305–KF and PEG-40M–KF as the stationary phases. Potassium fluoride was used to suppress the adsorption of organic bases on the surface of the column and enhance the efficiency of GC separation. It has also been found that potassium fluoride is capable of interacting with organic bases via a donor–acceptor mechanism [11]. Columns were prepared as described previously [12].

For the OV-101–KF column the coating efficiency (*CE*) calculated for *n*-tridecane at 110°C was 80%. To determine the *CE* value the equation

$$CE = \frac{n_{\text{exp}}}{n_{\text{theor}}} \cdot 100\% \tag{1}$$

was used, where n_{exp} and n_{theor} are the numbers of theoretical plates calculated from experimental data and the theory of capillary chromatography, respectively.
For the Triton X-305–KF and PEG-40M–KF columns the *CE* values were 70%; calculations of *CE* were made for *n*-heptadecane at 120°C.

Substances were analysed as 1% solutions in pentane. Sample volumes were 0.1–0.2 μl. The samples were injected into the capillary column through a splitter (50:1). Helium was used as the carrier gas. The 39 compounds involved in this study were oxazole, thiazole and mono-, di- and trisubstituted oxazoles and thiazoles with methyl, ethyl and propyl groups in different positions on the heterocyclic ring. The values of retention indices [13] were calculated with respect to C_5–C_{16} *n*-alkanes. The reproducibilities of retention indices averaged over three to ten measurements were within 2 i.u. for each of the 39 azoles.

RESULTS AND DISCUSSION

Oxazoles and thiazoles are five-membered aromatic heterocyclic molecules with two heteroatoms, *viz.*, N and O and N and S, respectively. The basic properties of these compounds arise from the presence of the N atom in the oxazole and thiazole rings. At the same time the O and S atoms produce a significant effect on the basicity and other physico-chemical properties of oxazoles and thiazoles, such as the polarizability and the dipole moment of the molecule [7,8,14]. As a result, oxazoles and thiazoles of similar structure should show different sorption thermodynamic characteristics. As the mass of a sulphur atom is twice that of oxygen, the energy of dis-

persive interaction of alkylthiazoles with stationary phases should be higher than that of corresponding alkyloxazoles.

The analogy of the GC behaviour of oxygen- and sulphur-containing aliphatic compounds such as alcohols and thiols or ethers and sulphides has been observed previously [15]. Equations to calculate retention index values of one analogous substance from the retention indices of another have been given [15]. We have studied alkyloxazoles and alkylthiazoles with analogous structures. The difference between the partial molar free sorption energies of an alkylthiazole (Tz) and an alkyloxazole (Ox) of analogous structure, $\delta\Delta G(S,O)$, can be calculated using the equation

$$\delta\Delta G(S,O) = \Delta G(Tz) - \Delta G(Ox) = -RT \ln\left[\frac{V_g(Tz)}{V_g(Ox)}\right] \qquad (2)$$

where V_g is the specific retention volume of the compared compounds.

As the comparison of sorption properties was performed on the same column under the same conditions, eqn. 2 becomes

$$\delta\Delta G(S,O) = -RT \ln\left[\frac{t'(Tz)}{t'(Ox)}\right] \qquad (3)$$

where t' is the adjusted retention time of compared compounds.

The $\delta\Delta G(S,O)$ values obtained are given in Table I. According to these values, the pairs of Tz and Ox analogues can be divided into two groups: di- and trisubstituted compounds with the alkyl substituent in the 2-position on the heterocycle (pairs 1–16) and compounds having no substituent in this position (pairs 17–19). Thus, for the OV-101–KF column the average value of $\delta\Delta G(S,O)$ is -3.04 kJ/mol for 2-alkyl-substituted compounds and -3.63 kJ/mol for compounds unsubstituted in the 2-position. On the polar columns the average values of $\delta\Delta G(S,O)$ for the two groups of analogues differ more sharply (see Table I).
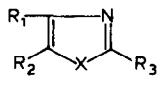
It should be noted that the 2-position in the molecules of studied compounds plays a peculiar role in thiazoles and oxazoles [7,8]. It is the preferred position in nucleophile substitution reactions because of the relatively large positive charge density on the C-2 atom [16]. Therefore, an H atom in the 2-position has relatively high acidity [8]. The $\delta\Delta G(S,O)$ values obtained (Table I) also reflect the presence of an activated H-2 atom capable of donor–acceptor interactions, including hydrogen bonding, with stationary phases. The $\delta\Delta G(S,O)$ values for compounds with a 2-H atom are always higher than those for 2-alkyl-substituted azoles.

The data on the change in sorption energy of azoles allow a linear correlation between retention index values for alkyloxazoles (I_{Ox}) and alkylthiazoles (I_{Tz}) with analogous structures. Thus, the retention indices of di- and trisubstituted alkyloxazoles having an alkyl substituent in the 2-position on the heterocycle can be calculated according to the following equations:

for OV-101–KF:
$$I_{Ox} = 1.01 I_{Tz} - 163 \qquad (4)$$

TABLE I

DIFFERENCE IN PARTIAL MOLAR FREE ENERGIES OF THE SORPTION OF ALKYL-
THIAZOLES AND ALKYLOXAZOLES WITH ANALOGOUS STRUCTURE, $\delta\Delta G(S,O)$, ON
THREE CAPILLARY COLUMNS AT 100°C

No. of pair	Compared pair[a]			$\delta\Delta G(S,O)$ (kJ/mol)		
				OV-101–KF	Triton X-305–KF	PEG-4OM–KF
	R_1	R_2	R_3			
1	Me	H	Me	3.13	3.50	3.53
2	H	Me	Me	3.13	3.35	3.23
3	Me	H	Et	3.02	3.47	3.42
4	Et	H	Me	3.05	3.44	3.32
5	Me	Me	Me	3.05	3.23	3.23
6	H	Me	Et	3.04	3.25	3.31
7	H	Et	Me	3.15	3.34	3.25
8	Me	H	Pr	3.02	3.47	3.40
9	Et	H	Et	2.98	3.26	3.25
10	Pr	H	Me	3.05	3.47	3.35
11	Me	Et	Me	2.96	3.43	3.34
12	Me	Me	Et	3.00	3.27	3.22
13	H	Et	Et	2.94	3.43	3.31
14	Me	Pr	Me	3.08	3.58	3.50
15	H	Et	Pr	2.96	3.47	3.33
16	Me	Pr	Et	3.01	3.55	3.44
Average				3.04	3.41	3.34
17	H	H	H	3.68	4.37	4.29
18	H	Me	H	3.66	4.22	4.11
19	Me	Me	H	3.55	4.12	4.01
Average				3.63	4.24	4.14

[a] X = O for oxazoles and S for thiazoles. Me = Methyl; Et = ethyl; Pr = propyl.

for Triton X-305–KF:

$$I_{Ox} = 0.97I_{Tz} - 138 \qquad\qquad (5)$$

for PEG-40M–KF:

$$I_{Ox} = 0.985I_{Tz} - 164 \qquad\qquad (6)$$

The calculated and experimental values of I_{Ox} are compared in Table II. The experimental retention indices of alkylthiazoles applied for the determination of the coefficients in eqns. 4–6 are also given. The standard deviation of the calculated and experimental values of I_{Ox} (see Table II) is 2.4–5.7 i.u., depending on the polarity of the columns.

Another scheme for the prediction of the retention indices of azoles was found using the energy contributions of alkyl groups to the sorption energies of alkyloxazoles and alkylthiazoles. The energy contribution of an alkyl group, ΔG^{Alk}, was determined according to the following equations from the sorption energies of two compounds, one containing an alkyl group and the other not:

$$\Delta G^{\text{Alk}} = \Delta G(\text{AlkOx}) - \Delta G(\text{Ox}) = -RT \ln \left[\frac{t'(\text{AlkOx})}{t'(\text{Ox})} \right] \tag{7}$$

$$\Delta G^{\text{Alk}} = \Delta G(\text{AlkTz}) - \Delta G(\text{Tz}) = -RT \ln \left[\frac{t'(\text{AlkTz})}{t'(\text{Tz})} \right] \tag{8}$$

where t' (AlkOx) and t' (Ox) are the adjusted retention times of oxazoles containing and not containing an alkyl group, respectively, and t' (AlkTz) and t' (Tz) are corresponding values for thiazoles.

For the comparison of the ΔG^{Alk} contributions of the same alkyl group located at different positions in the oxazole and thiazole molecules, the following indications are accepted because any substituent is in an α-position with respect to one or two heteroatoms:
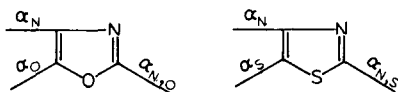
The values of ΔG^{Alk} for methyl, ethyl and propyl groups calculated according to eqns. 7 and 8 in Table III. When eqns. 7 and 8 could not be used because of the absence of standard substituted oxazoles and thiazoles, more complex schemes were applied (see Table III). The contributions of "independent" methyl and ethyl groups calculated from the adjusted retention times of toluene and benzene or ethylbenzene and benzene are also given in Table III.

The comparison of the alkyl group contributions in substituted oxazoles and thiazoles (see Table III) shows that maximum ΔG^{Alk} values are observed for the groups in the 5-position (α_O in oxazole and α_S in thiazole). Moreover, on the non-polar OV-101–KF column the alkyl contributions for α_O and α_S positions do not depend on the nature of the heterocycle, and are equal -2.16 and -2.10 kJ/mol for methyl groups in oxazole and thiazole, respectively. It should be noted that the ΔG^{Me} values for α_O- and α_S-positions are slightly higher than the contribution of the "independent" methyl group in toluene (see Table III).

On transferring any substituent from a α_O- or α_S-position to the α_N-position in an oxazole or thiazole molecule, an α-effect [17] becomes pronounced, i.e., a sharp decrease in the alkyl group contribution arising from its interaction with the N heteroatom is observed. It is interesting that on non-polar and intermediate-polarity columns the ΔG^{Alk} values for the α_N-position of oxazoles and thiazoles are almost equal (Table III). For example, the $\Delta G^{\text{Me}}(\alpha_N)$ values on the OV-101–KF column are -1.44 and -1.43 kJ/mol for oxazoles and thiazoles, respectively; these values are close to the contribution of methyl group in α-picoline [5]. A difference in the $\Delta G^{\text{Alk}}(\alpha_N)$ contributions for oxazoles and thiazoles appears only on the polar PEG-40M–KF column (see Table III).

The values of the contributions of alkyl groups situated in an $\alpha_{N,O}$- or $\alpha_{N,S}$-position, i.e., between the two heteroatoms, depend essentially on the nature of the heterocycle. This dependence manifests itself very clearly on all columns (Table III).
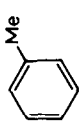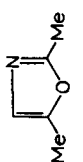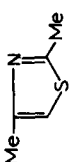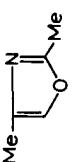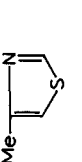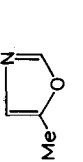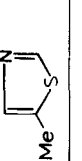
TABLE II

EXPERIMENTAL AND CALCULATED RETENTION INDICES OF ALKYLOXAZOLES BY EQNS. 3–5 FROM RETENTION INDEX VALUES OF ALKYLTHIAZOLES ON THREE COLUMNS AT 110°C

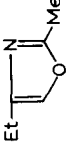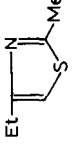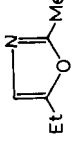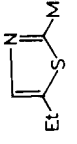| Compound[a]			I_{Ox}						I_{Tz} (exptl.)		
			OV-101–KF		Triton X-305–KF		PEG-40M–KF		OV-101–KF	Triton X-305–KF	PEG-40M–KF
R_1	R_2	R_3	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.			
Me	H	Me	730	733	1043	1050	1094	1108	887	1225	1291
H	Me	Me	765	768	1092	1091	1145	1140	922	1267	1324
Me	H	Et	818	817	1104	1108	1159	1165	970	1285	1349
Et	H	Me	820	821	1111	1114	1171	1172	974	1291	1356
Me	Me	Me	843	844	1150	1141	1200	1195	997	1319	1380
Me	Me	Et	851	851	1155	1147	1204	1203	1004	1325	1388
H	H	Et	855	857	1162	1159	1222	1218	1010	1337	1403
H	Et	Me	901	901	1175	1178	1229	1233	1053	1357	1418
Me	H	Pr	903	901	1172	1165	1228	1224	1053	1343	1409
Et	H	Et	910	912	1198	1201	1247	1243	1064	1380	1428
Pr	H	Me	923	920	1201	1201	1252	1252	1072	1380	1438
Me	Et	Me	926	925	1210	1202	1260	1253	1077	1381	1439
Me	Et	Et	940	938	1222	1222	1279	1277	1090	1402	1463
H	Pr	Me	1000	1006	1269	1275	1319	1328	1157	1457	1515
Me	Et	Pr	1024	1024	1294	1293	1347	1347	1175	1475	1534
Me	Pr	Et	1079	1082	1327	1329	1374	1379	1233	1512	1567
σ^b (i.u.)				2.4		5.2		5.7			
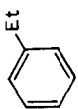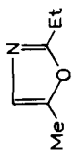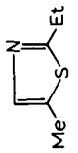
[a] General structure as in Table I.
[b] σ is the standard deviation of the calculated I_{Ox} values.

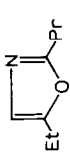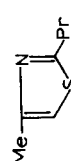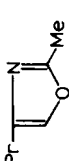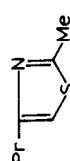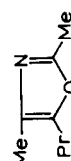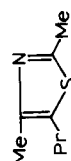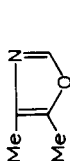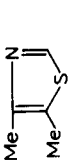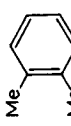TABLE III

ENERGY CONTRIBUTIONS OF ALKYL GROUPS, ΔG^{Alk}, TO THE SORPTION ENERGY OF ALKYLOXAZOLES AND ALKYLTHIAZOLES ON THREE COLUMNS AT 110°C

Starting compounds		Scheme for calculation[a]	Alkyl position[a]	$-\Delta G^{Alk}$ (kJ/mol)		
				OV-101–KF	Triton X-305–KF	PEG-40M–KF
(Tol)	(Bz)	$\Delta G^{Tol} - \Delta G^{Bz}$	Me, Bz	2.06	1.92	1.75
(2)	(1)	$\Delta G^2 - \Delta G^1$	Me($\alpha_{N,O}$), Ox	1.69	1.17	0.76
(4)	(3)	$\Delta G^4 - \Delta G^3$	Me($\alpha_{N,S}$), Tz	1.11	0.29	0.05
(6)	(5)	$\Delta G^6 - \Delta G^5 - \Delta G^{Me(\alpha_{N,O})}$	Me(α_N), Ox	1.44	0.73	0.57
(3)	(7)	$\Delta G^3 - \Delta G^7$	Me(α_N), Tz	1.43	0.74	0.53
(1)	(5)	$\Delta G^1 - \Delta G^5$	Me(α_O), Ox	2.16	1.69	1.47
(8)	(7)	$\Delta G^8 - \Delta G^7$	Me(α_S), Tz	2.10	1.55	1.30

TABLE III *(continued)*

Starting compounds	Scheme for calculation[a]	Alkyl position[a]	$-\Delta G^{Alk}$ (kJ/mol)		
			OV-101]KF	Triton X-305–KF	PEG-40M-KF
(EtBz)	(Bz) $\Delta G^{EtBz} - \Delta G^{Bz}$	Et, Bz	3.94	3.59	3.27
(9)	(1) $\Delta G^9 - \Delta G^1$	Et($\alpha_{N,O}$), Ox	3.43	2.37	1.83
(10)	(8) $\Delta G^{10} - \Delta G^8$	Et($\alpha_{N,S}$), Tz	2.78	1.40	1.03
(11)	(5) $\Delta G^{11} - \Delta G^5 - \Delta G^{Me}(\alpha_{N,O})$	Et(α_N), Ox	3.27	2.05	1.95
(12)	(7) $\Delta G^{12} - \Delta G^7 - \Delta G^{Me}(\alpha_{N,S})$	Et(α_N), Tz	3.17	2.01	1.80
(13)	(5) $\Delta G^{13} - \Delta G^5 - \Delta G^{Me}(\alpha_{N,O})$	Et(α_O), Ox	3.97	3.03	2.86
(14)	(7) $\Delta G^{14} - \Delta G^7 - \Delta G^{Me}(\alpha_{N,S})$	Et(α_S), Tz	3.88	2.88	2.55

No.	Eq.	Expression	Descriptor			
(15)	(5)	$\Delta G^{15} - \Delta G^5 - \Delta G^{Et}(\alpha_0)$	Pr($\alpha_{N,O}$), Ox	5.04	3.69	3.01
(16)	(7)	$\Delta G^{16} - \Delta G^7$	Pr($\alpha_{N,S}$), Tz	4.41	2.81	2.34
(17)	(5)	$\Delta G^{17} - \Delta G^5 - \Delta G^{Me}(\alpha_{N,O})$	Pr(α_N), Ox	5.06	3.72	3.31
(18)	(7)	$\Delta G^{18} - \Delta G^7 - \Delta G^{Me}(\alpha_{N,S})$	Pr(α_N), Tz	4.95	3.70	3.00
(19)	(6)	$\Delta G^{19} - \Delta G^6$	Pr(α_O), Ox	5.41	4.34	4.04
(20)	(4)	$\Delta G^{20} - \Delta G^4$	Pr(α_S), Tz	5.34	4.43	4.01
(21)	(5)	$\Delta G^{21} - \Delta G^5 - \Delta G^{Me}(\alpha_N) - \Delta G^{Me}(\alpha_O)$	ortho-Effect, Ox	0.21	0.37	0.34
(22)	(7)	$\Delta G^{22} - \Delta G^7 - \Delta G^{Me}(\alpha_N) - \Delta G^{Me}(\alpha_S)$	ortho-Effect, Tz	0.09	0.25	0.39
(o-Xyl)	(Bz)	$(\Delta G^{o\text{-}Xyl} - \Delta G^{Bz}){:}2 - \Delta G^{Me\,b}$	ortho-Effect, Bz	0.46	—	0.80

a Me = Methyl; Et = ethyl; Pr = propyl; Tol = toluene; Bz = benzene; EtBz = ethylbenzene; o-Xyl = o-xylene.

b Additional energy of Me group standing in ortho position to another Me-group in benzene.

TABLE IV

COMPARISON OF EXPERIMENTAL RETENTION INDICES OF ALKYLOXAZOLES AND ALKYLTHIAZOLES WITH THE VALUES CALCULATED FROM THE CONTRIBUTIONS OF ALKYL GROUPS

	Compound[a]			OV-101–KF		Triton X-305–KF		PEG-40M–KF	
X	R_1	R_2	R_3	I (calc.)	I (exptl.)	I (calc.)	I (exptl.)	I (calc.)	I (exptl.)
O	Me	Et	Me	927	923	1200	1201	1254	1252
O	Me	H	Pr	896	901	1174	1175	1220	1229
O	Me	Me	Me	847	843	1150	1150	1196	1200
O	Et	Me	H	843	845	1138	1145	1211	1213
O	Me	H	Et	815	818	1105	1104	1154	1159
O	H	Et	Et	942	940	1225	1222	1282	1279
O	Me	Me	Et	934	926	1212	1210	1255	1260
O	Et	H	Et	906	903	1174	1172	1231	1228
O	Me	Pr	Et	1089	1079	1332	1327	1380	1374
S	H	Me	Me	921	922	1267	1267	1334	1324
S	Me	H	Et	970	970	1283	1285	1345	1349
S	Et	H	Et	1057	1053	1349	1343	1410	1409
S	H	Et	Et	1093	1090	1395	1402	1457	1463
S	Me	Me	Et	1080	1077	1377	1381	1433	1439
S	Me	Et	Me	1081	1072	1376	1380	1432	1438
S	H	Me	Pr	1087	1089	1399	1401	1461	1463
S	Me	Me	Me	997	997	1319	1319	1379	1380
S	H	Et	Pr	1176	1175	1469	1475	1530	1534
S	Me	Pr	Et	1240	1233	1515	1512	1569	1567
Average error of calculation				4		3		4	

[a] General structure as in Table I.

The contribution of any alkyl group in an $\alpha_{N,O}$-position in oxazole is considerably greater than that of the same group in an $\alpha_{N,S}$-position in thiazole. Thus, on the non-polar OV-101–KF column the value of $\Delta G^{Me}(\alpha_{N,O})$ is -1.69 kJ/mol but ΔG^{Me} $(\alpha_{N,S})$ is only -1.11 kJ/mol. On polar columns the difference in the $\alpha_{N,O}$ and $\alpha_{N,S}$ contributions of the alkyl groups increases. This can probably be explained by the different dipole moments of oxazole and thiazole molecules [14].

With 4,5-dimethylthiazole and -oxazole, an *ortho*-effect of methyl groups is observed, as shown in Table III. This means that the total contribution of two vicinal methyl groups is higher than the sum of two methyl contributions in 4- and 5-methyl-azoles. Under the influence of the two heteroatoms the *ortho*-effect in 4,5-dimethyl-oxazole and -thiazole is less pronounced than in *o*-xylene (Table III) and in 3,4-dimethylpyridine [5].

The data in Table III, reflecting the inconstancy of the contribution of the same alkyl group because of α-and *ortho*-effects, were used to predict the retention indices of nineteen alkyl-substituted oxazoles and thiazoles other than those listed in Table III. For this purpose oxazole, thiazole and C_5–C_{16} *n*-alkanes were analysed simultaneously under identical GC conditions. The sorption energies, $\Delta G'$, were calculated with the equation [18]

$$\Delta G' = -RT \ln t' \tag{9}$$

where t' is the adjusted retention time of the compound.

The general schemes for the calculation of the sorption energy of alkyloxazole, $\Delta G'_1$, and alkylthiazole, $\Delta G'_2$, to predict retention indices can be formulated as follows:

$$\Delta G'_1 = \Delta G'(Ox) + \Delta G^{Alk}(\alpha_O,Ox) + \Delta G^{Alk}(\alpha_N,Ox) +$$

$$\Delta G^{Alk}(\alpha_{N,O},Ox) + \Delta G^{Me}(\textit{ortho}\text{-effect},Ox) \tag{10}$$

$$\Delta G'_2 = \Delta G'(Tz) + \Delta G^{Alk}(\alpha_S,Tz) + \Delta G^{Alk}(\alpha_N,Tz) +$$

$$\Delta G^{Alk}(\alpha_{N,S},Tz) + \Delta G^{Me}(\textit{ortho}\text{-effect},Tz) \tag{11}$$

where $\Delta G'$ (Ox) and $\Delta G'$ (Tz) are sorption energies determined according to eqn. 9 for oxazole and and thiazole respectively, ΔG^{Alk} are the contributions of alkyl groups in different positions of the heterocycle and ΔG^{Me} (*ortho*-effect) are the additional sorption energies arising from the vicinal position of two methyl groups.

The $\Delta G'_1$ and $\Delta G'_2$ values obtained were converted into retention index units, using the equation given in ref. 19:

$$\Delta G'_i = -RT \left[a' + b'(I_i/100) + \frac{c'}{I_i/100 + d'} \right] \tag{12}$$

where a', b', c' and d' are coefficients determined from values of t' for standard *n*-alkanes, $\Delta G'_i$ is the calculated free energy of sorption of a substance i and I_i is the retention index sought.

Retention index values calculated by eqn. 12 for alkyloxazoles and alkyl-thiazoles are given in Table IV. The average errors of calculation are 3–4 i.u. With the polar columns the accuracy of prediction of retention indices with eqns. 10 and 11 is slightly higher than that when using the analogy of the GC behaviour of thiazoles and oxazoles (eqns. 5 and 6 and Table II).

In conclusion, the thermodynamic sorption characteristics of alkyloxazoles and alkylthiazoles on columns of different polarity were compared. The regularities estab-lished were used to confirm two methods for the prediction of retention indices based on the analogy of the GC behaviour of S- and O-containing azoles and on the un-equal energy contributions of identical alkyl groups. The prediction ability of the methods was found to be accurate within 1% of the mean retention index value (see Tables II and IV). The predicted retention indices of mono-, di- and trisubstituted oxazoles and thiazoles can be used to increase the data bank for computer identifica-tion of complex mixtures of nitrogen-containing bases.

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