Thermodynamic characteristics of sorption of heterocyclic compounds in capillary gas chromatography

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Dependences of sorption energies of sulfur-, oxygen-, and nitrogen-containing heterocyclic compounds on the nature of heteroatoms, structure of substituents and their position in the ring were studied. The contributions of heteroatoms, functional and alkyl groups to the energy of dispersive interaction of position isomers with nonpolar stationary phases were determined for imidazoles, piperidines, morpholines, thiomorpholines, dioxalanes, oxathiolanes, dithiolanes, thiophenes, and furans. The nonequivalence of contributions of the same substituents to the sorption energy of each of the heterocyclic compounds, depending on the nature of the heteroatom and position of the substituent, was shown. The obtained values of contributions of heteroatoms and substituents can be used for *a priori* calculation of retention indices of position isomers of five- and six-membered heterocycles containing one or two heteroatoms in the ring.

Key words: capillary gas chromatography, thermodynamic characteristics of sorption, heterocyclic compounds.

Quantitative thermodynamic characteristics of sorption are the basis for understanding chromatographic processes. The method of gas chromatography is the most convenient for studying the thermodynamics of interaction of a dissolved volatile substance with a nonvolatile solvent[1] and for determination of partial molar free energies of sorption ΔG and $\delta\Delta G$ as characteristics of properties of a sorbate.[2] Several structural sorption regularities, which make it possible to predict the chromatographic behavior of aliphatic compounds, have been established on the basis of thermodynamic characteristics of sorption.[3—6]

The odor of food substances is caused to a great extent by heterocyclic compounds.[7] The identification of the substituted heterocycles is made difficult by the possible position and structural isomerism. For example, mass spectra of 2-alkyl-1,3-dioxolanes are almost identical and contain very low-intensity (0—2 %) peaks of molecular ions independently of the length of the alkyl group.[8,9] Mass-spectral identification of isomeric substituted thiophenes and furans is also difficult, because mass spectra of α- and β-isomers are almost identical.[10—13] Modern capillary chromatography makes it possible to separate isomers of heterocyclic compounds; however, a great number of compounds (standards) should be synthesized to obtain experimental values of retention indices of all isomers.

The purpose of this work is to study the effect of structure of heterocyclic compounds on thermodynamic parameters of their sorption on nonpolar stationary phases under the conditions of capillary GLC and to establish regularities of sorption to predict retention parameters and to extend the database for computer identification of the components of complex mixtures.

Experimental

The retention parameters of sulfur- and oxygen-containing compounds were determined on a Hewlett Packard 5710A chromatograph on quartz capillary columns with SE-30 (50 m×0.32 mm, d_f = 0.25 μm) and SPB-1 (60 m×0.32 mm, d_f = 0.25 μm) stationary phases under isothermal conditions at 100, 110, 120, and 130 °C for five-membered heterocycles and 120, 130, 140, and 150 °C for substituted furans and thiophenes. *N*-Alkylimidazoles, piperidines, morpholines, and thiomorpholines were analyzed on a Pye Unicam 104 chromatograph on glass capillary columns with OV-101/KF stationary phase (50 m×0.3 mm, d_f = 0.2 μm) under isothermal conditions at four temperatures in the range from 90 to 160 °C. Portions of 0.5 μL of solutions of compounds in an organic solvent were analyzed at the split ratio of the carrier gas (helium) flow of 1 : 50. The "dead time" was determined experimentally under the conditions of analysis of compounds by the retention of methane. The partial molar free energy of sorption ΔG with accuracy to the constant at a temperature of analysis T was calculated as follows[14]:

$$\Delta G = -RT\ln k'\beta, \quad (1)$$

$$k' = (t_x - t_0)/t_0, \quad (2)$$

where k' is the retention factor (average of 5 to 7 measurements), t_x is the retention time of a compound, t_0 is the retention time of the nonsorbed gas (methane), "dead time,"

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$$\beta = V_g/V_l, \quad (3)$$

β is the phase ratio calculated from geometric parameters of the chromatographic column on the basis of the model of two cylinders inserted into each other:

$$\beta = (d_c - 2d_f)^2/4(d_c d_f - d_f^2), \quad (4)$$

where d_c is the inner diameter of the capillary column, d_f is the film thickness of the stationary phase on the walls of the capillary column. In this case,

$$V_g = 1/4\pi L(d_c - 2d_f)^2, \quad (5)$$

$$V_l = V - V_g,$$

where $V = 1/4\pi L d_c^2$ is the volume of an empty capillary at the column length L.

Formula (1) for calculation of ΔG of a compound in the capillary column was directly used[15] to determine ΔG values at various temperatures of analysis:

$$\Delta G^T = -RT\ln k' \frac{(d_c - 2d_f)^2}{4(d_c d_f - d_f^2)}. \quad (6)$$

Entropy and enthalpy components of the energy of sorption for sorbates on each stationary phase were calculated by solving the series of Eqs. (7), for which ΔG values were experimentally determined at four temperatures of analysis by Eq. (6), and by averaging obtained ΔH and ΔS values.

$$\Delta G_i^{T_1} = \Delta H - T_1\Delta S, \quad \Delta G_i^{T_3} = \Delta H - T_3\Delta S,$$
$$\Delta G_i^{T_2} = \Delta H - T_2\Delta S, \quad \Delta G_i^{T_4} = \Delta H - T_4\Delta S. \quad (7)$$

Results and Discussion

The ΔG^T value is a quantitative characteristics of the structural sorption properties of the analyzed compound, the energy of its interaction with a given stationary phase at a temperature of analysis. Enthalpy and entropy components of the ΔG value make it possible to judge the heat of sorption of a molecule and the number of degrees of freedom under GC conditions.

In the temperature range studied, the linear dependence of $\log k'$ on $1/T$ was fulfilled, and the ΔH and ΔS values were almost constant for each i-th compound analyzed on the same column at several temperatures. This method was applied for comparative estimation of the influence of the nature of heteroatoms in the cycle and the effect of the molecular conformation on thermodynamic parameters of sorption of alkyl-substituted compounds in which alkyl is directly attached to the carbon atom or heteroatom of the cycle. The following alkylcyclohexanes, five- and six-membered heterocyclic compounds were studied: dioxolanes, oxothiolanes, dithiolanes,[8,9] furans and thiophenes,[10—13] piperidines, morpholines, thiomorpholines,[16,17] and imidazoles.[18]

The results of studies of three homologous series are presented in Fig. 1 as an example: alkylcyclohexanes, *N*-alkylmorpholines, and thiomorpholines.[16,17] The dependences of the partial molar free energy of sorption ΔG on the length of the alkyl substituent m at 110 °C are plotted for alkylcyclohexanes (curve *1*), in which the alkyl group is directly bound to the carbon atom of the ring, for *N*-alkylmorpholines (curve *2*), and *N*-alkylthiomorpholines (curve *3*). All these compounds have chair conformations, but all bonds in cyclohexane are equivalent (1.54 Å), while in morpholine two C—O and two C—N bonds are shortened: 1.43 and 1.47 Å, respectively. The thiomorpholine chair has two long C—S bonds equal to 1.82 Å and two C—N bonds (1.47 Å). As seen from Fig. 1, only the dependence of the first homolog in the series of alkylcyclohexanes, methylcyclohexane, insignificantly deviates from linearity, and its energy of sorption is lower than follows from the linear dependence of ΔG on the mass of the homolog. In two series of heterocycles, dependences for methyl and ethyl homologs (in which substituents are directly bound to the nitrogen atoms) deviate from linearity, and, unlike methylcyclohexane, they have higher energies of sorption than was predicted on the basis of the linear dependences of the other homologs. The existence of the second bulky heteroatom (S) in the ring along with the nitrogen atom increases the deviation from linearity toward higher energies of sorption. Thus, the existence of heteroatoms in six-membered rings and substitution of the C—alkyl bond by the N—alkyl bond results in an increase in the energy of dispersion interaction of heterocyclic compounds with the stationary phase compared to alkylcyclohexanes. Conformation differences in the structure of cycle probably affect the energy of interaction of cycloalkanes and heterocycles with the stationary phase rather than the distribution of electron density in the ring with heteroatoms.

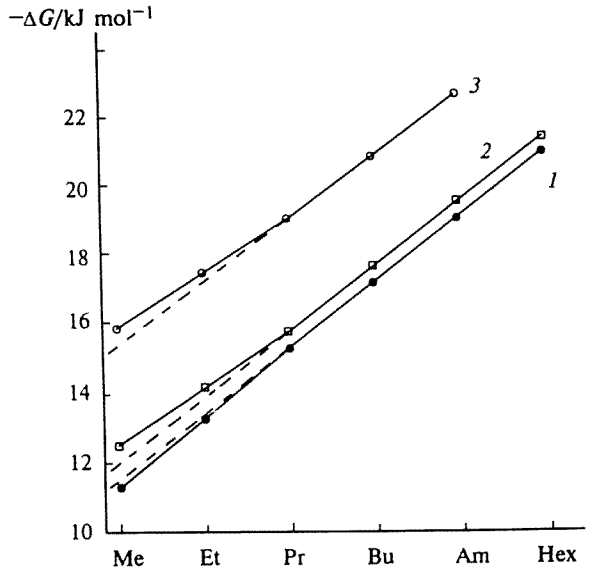


Fig. 1. Change in ΔG values of homologs of alkylcyclohexanes (*1*), *N*-alkylmorpholines (*2*), and *N*-alkylthiomorpholines (*3*) at 110 °C.

Table 1. Thermodynamic parameters of sorption of homologs of alkyl-substituted cyclic compounds (OV-101)[17]

Alkyl in ring	$-\Delta G$(Alk)* /kJ mol^{-1}	$-\Delta H$(Alk) /kJ mol^{-1}	$-\Delta S$(Alk) /J mol^{-1} deg^{-1}	$T\Delta S$ (% from ΔH)
		n-Alkylcyclohexanes		
Methyl	11.33	28.33	44.30	59.7
Ethyl	13.45	32.63	49.85	58.6
Propyl	15.30	36.48	55.10	57.8
Butyl	17.19	40.50	60.60	57.3
Pentyl	19.10	44.39	65.75	56.8
Hexyl	21.01	48.52	71.50	56.8
		N-*n*-Alkylpiperidines		
Methyl	12.09	29.50	45.50	58.9
Ethyl	13.70	32.76	49.80	58.4
Propyl	15.27	35.95	54.05	57.6
Butyl	17.12	39.68	58.95	56.9
Pentyl	18.99	43.55	64.20	56.5
Hexyl	20.87	47.26	69.00	55.9
		N-*n*-Alkylmorpholines		
Methyl	12.40	30.46	47.05	59.0
Ethyl	14.16	34.41	52.80	58.7
Propyl	15.81	37.78	57.30	57.9
Butyl	17.68	41.65	62.60	57.4
Pentyl	19.58	45.72	68.15	57.0
Hexyl	21.48	48.80	71.25	55.9
		N-*n*-Alkylthiomorpholines		
Methyl	15.84	34.44	48.45	53.7
Ethyl	17.48	37.35	51.70	53.0
Propyl	19.05	40.59	56.05	53.0
Butyl	20.89	44.45	61.30	52.8
Pentyl	22.75	48.14	66.05	52.5

* Accuracy for determination of ΔG is 0.04 kJ mol^{-1}, T = 110 °C.

We compared the values of enthalpy ΔH and entropy $T\Delta S$ components of homologs of alkylcyclohexane and *N*-alkylheterocycles. The calculated values for four series are presented in Table 1 as an example. The contribution (%) of the entropy component to the heat of sorption is presented in the latter column. The entropy contribution can be ~60 % (see Table 1). The ΔG value decreases sharply due to this contribution.

The effect of the nature of heteroatoms on thermodynamic parameters of sorption can be estimated by comparison of methyl-substituted heterocyclic compounds. As can be seen from Table 2, when the N atom is introduced to the cyclohexane ring and the C—Me bond is substituted by the N—Me bond in piperidine, the enthalpy increases by 1.4 kJ mol^{-1} and the entropy increases by 1.20 e.u. When the second O heteroatom is introduced to the ring, the enthalpy increases by 2.13 kJ mol^{-1}. The effect of the nature of the second heteroatom is distinctly pronounced, although the molecular weight of the morpholine ring increases only by two units compared to that of piperidine. The enthalpy of methylthiomorpholine increases especially consider-

Table 2. Effect of the nature of heteroatoms on thermodynamic parameters of sorption of *N*-methyl-substituted heterocycles[17]

Compared compounds	$-\delta\Delta H$ /kJ mol^{-1}	$-\delta\Delta S$ /J mol^{-1} deg^{-1}
N-Methylpiperidine — methylcyclohexane	1.17	1.20
N-Methylmorpholine — methylcyclohexane	2.13	2.75
N-Methylthiomorpholine — methylcyclohexane	6.11	4.15
N-Methylmorpholine — *N*-methylpiperidine	0.96	1.55
N-Methylthiomorpholine — *N*-methylpiperidine	4.94	2.95
N-Methylthiomorpholine — *N*-methylmorpholine	3.98	1.40

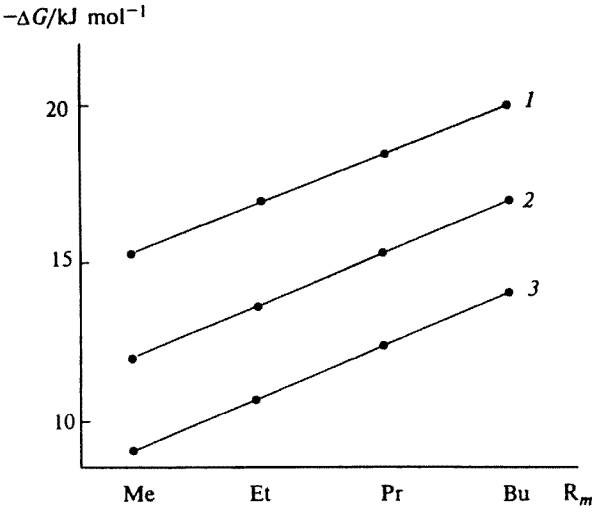
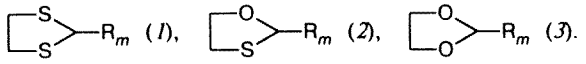


Fig. 2. Change in ΔG values of sorption of *N*-alkyl-substituted five-membered sulfur- and oxygen-containing heterocycles at 130 °C:



ably (by three times compared to methylmorpholine), and the entropy increases by two times. The energy contributions of one heteroatom (O or S) can be calculated comparing methyl derivatives of piperidine and morpholine. The maximum and minimum contributions to $\delta\Delta H$ are made by the introduction of the S and O atoms, respectively, and the values of the contributions differ by five times, although the molecular mass of S differs from that of O only by two times. Thus, this is the nature of the heteroatom and, probably, the differences in conformations of the rings that increase the energy of dispersion interaction with the stationary phase. This makes it possible to predict the retention indices of analogous compounds that differ only in the nature of the heteroatom in the ring.

We studied the GC-behavior of homologous series of 2-alkyl-substituted five-membered heterocyclic compounds containing two heteroatoms in the ring by an example of homologous series of 2-alkyl-1,3-dioxolanes, oxathiolanes, and dithiolanes.[8,9] The plots of a change in ΔG values for three homologous series, in which the alkyl substituent is attached to the ring *via* the C atom, are presented in Fig. 2. All members of the series, including methyl-substituted homologs, obey linear dependences, the maximum values of ΔG are observed for 2-alkyl-1,3-dithiolanes and the minimum values are observed for 2-alkyl-1,3-dioxolanes. The entropy contributions of $T\Delta S$ are 60 and 24 % of the value of ΔH for methyl-substituted oxothiolanes and dithiolanes, respectively.

The effect of the heteroatom nature in five-membered heterocycles on thermodynamic properties of sorption is seen from the comparison of alkyl-substituted compounds. The calculated values of $\delta\Delta G$, $\delta\Delta H$, and $\delta\Delta S$ per alkyl substituent are presented in Table 3.[13] It

Table 3. Contributions of alkyl substituents to the total energy and to enthalpy and entropy components of the energy of sorption of 1,3-dioxolanes, 1,3-oxathiolanes, and 1,3-dithiolanes (SE-30)[13]

2-Alkyl in ring	$-\Delta G$(Alk)* /kJ mol^{-1}	$-\Delta H$(Alk) /kJ mol^{-1}	$-\Delta S$(Alk) /J mol^{-1} deg^{-1}	$T\Delta S$ (% from ΔH)
		4-Methyl-2-alkyl-1,3-dioxolanes		
Methyl	0.73	2.58	4.6	71.7
Ethyl	2.79	8.14	13.3	65.8
Propyl	4.69	12.89	20.4	63.8
Butyl	6.50	16.66	25.2	61.0
		2-Alkyl-1,3-oxathiolanes		
Methyl	0.65	1.58	2.3	58.8
Ethyl	2.51	5.50	7.5	55.2
Propyl	4.28	9.44	12.8	54.7
Butyl	6.10	13.23	17.7	53.9
		2-Alkyl-1,3-dithiolanes		
Methyl	0.37	0.50	0.3	24.0
Ethyl	2.14	4.48	5.8	52.2
Propyl	3.83	8.79	12.3	56.4
Butyl	5.59	12.04	16.0	53.4
		4-Methyl-2-alkyl-1,3-dithiolanes		
Methyl	0.35	0.39	0.1	10.3
Ethyl	1.64	4.38	6.8	62.6
Propyl	3.74	8.62	12.1	56.6
Butyl	5.59	12.69	17.6	55.9

* T = 130 °C.

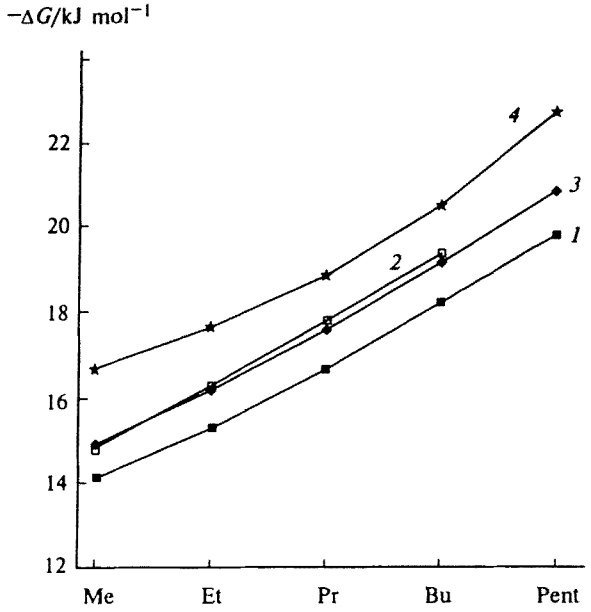


Fig. 3. Dependence of ΔG of sorption of *N*-alkylimidazoles on the position of the Me group in the ring (*1*) and for the substitution at positions 2 (*2*), 4 (*3*), and 5 (*4*).

follows from these data that the contribution of the Me group to the energy of sorption of methyl-substituted dioxolanes, oxathiolane, and dithiolane is only −0.75 to 0.35 kJ mol^{-1}, while in hydrocarbons this contribution is equal to −1.8 kJ mol^{-1}. This is likely caused by the peculiarities of enthalpy and entropy components of the ΔG(Me) value per Me group. The $\delta\Delta H$(Me) value in dioxolane is six times higher than in methyldithiolane, and the entropy component $\delta\Delta S$(Me) is 46 times higher than that in methyldithiolane. It is likely that the introduction of the Me group to dioxolane results in a substantial change in the conformational mobility of the molecule. The minimum contribution to the energy of dispersion interaction with the stationary phase is made by the Me group at the α-position to two S heteroatoms. This contribution is measured in index units (i.u.): δI(Me) = 18, while for methyldioxolane δI(Me) = 38 i.u., and for cyclopentane, which does not contain heteroatoms, δI(Me) = 63 i.u. Thus, there is a distinct influence of the heteroatom nature on the energy of dispersion interaction of the alkyl substituent at the α-position to the heteroatom in five-membered heterocycles.

We also studied five-membered aromatic heterocyclic compounds. The calculation of ΔG values for position isomers of methyl-substituted imidazoles shows that the contributions per methyl group at positions 2 and 5 of the imidazole ring are equivalent, and this is not associated with steric hindrances (see Fig. 2).[18] As seen from Fig. 3, energies of sorption of all alkyl-substituted imidazoles with the methyl group at position 5 are higher than those of imidazoles substituted at positions 2 and 4. Thus, the contributions of two Me groups introduced to the α- and α″-positions relative to the N atom

Table 4. Contributions of different substituents, δI, and $\delta(\Delta G)$ values of sorption of substituted furans, thiophenes, and benzenes on an OV-101 nonpolar stationary phase[10—13]

Compound	Substituent, its position	δI (i.u.)	$\delta(\Delta G)$ /kJ mol^{-1}
	Furans		
2-Methyl	α-Me	93	1.77
3-Methyl	β-Me	112	2.13
2,5-Dimethyl	α-Me (α′-Me)	102	1.94
2-Methyl-5-formyl	α-Me (α′-CHO)	130	2.44
3-Methyl-2-formyl	β-Me (α-CHO)	128	2.41
2-Methyl-5-acetyl	α-Me (α-COMe)	123	2.31
2-Formyl	α-CHO	306	5.75
2-Methyl-5-formyl	α-CHO (α′-Me)	341	6.41
2-Acetyl	α-COMe	387	7.27
2-Methyl-5-acetyl	α-COMe (α′-Me)	415	7.80
2-Formyl-5-acetyl	α-CHO (α′-COMe)	232	4.45
2-Formyl-5-acetyl	α-COMe (α′-CHO)	313	5.86
2-CH_2SH	α-CH_2SH	398	7.48
2-CH_2SMe	α-CH_2SMe	484	9.09
	Thiophenes		
2-Methyl	α-Me	102	1.95
3-Methyl	β-Me	107	2.02
2,5-Dimethyl	α-Me (α′-Me)	93	1.78
2-Methyl-5-formyl	α-Me (α′-CHO)	114	2.14
3-Methyl-2-formyl	β-Me (α-CHO)	117	2.20
2-Formyl	α-CHO	305	5.73
3-Formyl	β-CHO	292	5.48
2-Methyl-5-formyl	α-CHO (α′-Me)	318	5.96
3-Methyl-2-formyl	α-CHO (β-Me)	315	5.91
2-Acetyl	α-COMe	392	7.34
3-Acetyl	β-COMe	384	7.20
2-SH	α-SH	262	4.91
2-SMe	α-SMe	356	6.68
3-SH	β-SH	282	5.30
3-SMe	β-SMe	387	7.27
Toluene	Me	105	2.00
Benzaldehyde	CHO	285	5.37
Acetophenone	COMe	386	7.25
Acetylpyrazine	COMe	283	5.32

in the aromatic ring are nonequivalent. The nonequivalence of the contributions is evidence for the asymmetric electron density distribution in the ring.

The study of the GC-behavior of substituted furans and thiophenes[10—12] shows that the energy contributions of the methyl group and other functional groups in position isomers are not equivalent. This should be taken into account in *a priori* calculations of retention parameters.

As can be seen from Table 4, β-methylthiophene and β-methylfuran are retained longer than the α-isomers, and the contribution of the Me group to the retention index of β-methylthiophene is equal to that of methylbenzene. The O atom exerts a greater effect on the sorption contribution of the Me group than the S atom, because the difference in retention indices of α- and β-methylfurans is greater than that for the same isomers of thiophene.

Unlike derivatives of furan and thiophene with methyl, mercapto-, and sulfide substituents, the retention of α-formyl and α-acetylthiophenes is longer than β-substituted isomers. This is the difference between formyl and acetyl-substituted thiophenes and other heterocycles, for example, acetylpyrazine, in which the contribution of the acetyl group is lower by almost 100 i.u.

Thus, carbonyl-containing substituents are characterized by two types of α-effects that depend on the heteroatom nature: a nonadditive decrease in contributions of α-groups in the nitrogen-containing rings (let it be called the "negative" α-effect) and an increase in the contribution of the same α-group in sulfur-containing thiophenes and furans ("positive" α-effect). When formyl and acetyl substituents move to β-positions of thiophene and furan, the $\delta\Delta G$ values of substituents become equal to those in benzaldehyde and acetophenone (see Table 4). This makes it possible to consider substituents at the more remote β-positions of thiophene and furan as isolated substituents, which are not subjected to the effect the heteroatom nature. The mutual effect of heteroatoms and α-substituents leads to the electron density redistribution over them and to an increase in the dispersion interaction of the substituent with the nonpolar stationary phase. This is indicated by the comparison of IR spectra of α- and β-formylthiophenes and α- and β-acetylthiophenes obtained in the gas phase by the GC—IR Fourier spectroscopy method.[12,13] The shifts of the characteristic absorption bands of the thiophene ring and carbonyl groups are observed for the α-substituted isomers.

The introduction of the second methyl group to the α′-position of furan or thiophene results in a nonadditive increase in retention indices on nonpolar stationary phases: by 102 and 96 i.u., respectively. When methylfuran or methylthiophene has the formyl or acetyl group instead of the methyl group as the second substituent, the energy of sorption increases also nonadditively, and this effect is more considerable in derivatives of furan. For example, δI(Me) in 2-methyl-5-formylthiophene is 12 i.u. higher than that in 2-methylthiophene. The contribution of the methyl group in 2-methyl-5-formylfuran is higher by 35 i.u. than in 2-methylfuran. A similar behavior of substituents is observed for 2-methyl-5-acetylfuran and 2-methyl-5-acetylthiophene. This unusual effect contradicts the common concept of a decrease in retention of substituted compounds due to screening of heteroatoms by substituents in α- and α′-positions.

On the basis of the contributions of various substituents (see Tables 1—4) it is possible to perform *a priori* calculations of retention indices with accuracy up to ±2 i.u. for substituted heterocyclic compounds and to use calculated values in the databank for computer identification. Efficiency and reliability of identification of several heterocyclic compounds by the GLC method on the basis of structural sorption characteristics are confirmed by the study of components of odor of food substances.[13] These studies are evidence that GLC is especially sensitive to the structure of a molecule and its geometry, although the latter exerts a lesser effect on retention parameters compared to those manifested in gas adsorption chromatography, for which the method for calculation of geometric parameters of a molecule with consideratrion of the geometry of the adsorbent surface was developed.[19]

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