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Thermodynamic characteristics of adsorption of nitrogen-containing heterocycles on graphitized thermal carbon black derived from molecular statistical calculation

1. Azines

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Thermodynamic characteristics of adsorption (TCA) for six-membered aromatic nitrogen-containing heterocycles (azines), *viz*., pyridine, pyridazine, pyrimidine, and 1,3,5-triazine, on graphitized thermal carbon black (GTC) were experimentally determined and theoretically calculated. The best coincidence of the experiment and calculation is achieved using atom-atomic potential functions of intermolecular interactions, which allow for a decreased π-electron density in the aromatic system. The N atoms in the azine molecules are nonequivalent in terms of the adsorption behavior. The GTC surface very selectively adsorbs azines with different molecular structures, and this selectivity can be used for separation and chromatographic analysis of these compounds. The dependence of TCA of azines on the degree of aromaticity of their molecules has been established for the first time.

Key words: azines, π-electron density, structural aromaticity indices, atomic polarizability, atomic diamagnetic susceptibility, atom-atomic potentials, adsorption, graphitized thermal carbon black, molecular statistical calculations, Henry´s constant, molar differential heat of adsorption.

Semiempirical molecular statistical theory of adsorption (SMSTA) based on the atom-atomic approximation for description of intermolecular interactions is of great significance for prediction of the chromatographic behavior of compounds and investigation of their electronic and geometric structures.[1] It is convenient to match the calculated values with experimental thermodynamic characteristics of adsorption (TCA) obtained on adsorbents with the planar chemically uniform surface, for example, on graphitized thermal carbon black (GTC). It was shown that the TCA obtained on the GTC surface can be used to estimate the geometric structures of organic compounds[1—3] (bond lengths, bond angles, internal rotation angles, *etc*.). However, studies in which the specific features of electronic structures are derived from data on adsorption of GTC are rare.[4,5] At the same time, it is known that a high sensitivity of intermolecular interaction parameters to the valent state of atoms in the adsorbed molecule allows one to determine what contribution to the total energy of adsorption can make atoms of the same element that have different states of electronic shells and environment in the molecule.[1,3,6]

Molecular statistical calculations of the TCA are based on the additive model used for consideration of pairwise intermolecular interactions of atoms in an adsorbed molecule with atoms of the adsorbent surface. The energy of these interactions can quantitatively be estimated by potential functions, which are widely used in the physical chemistry and among which the Lennard-Jones and Buckingham—Corner potentials[7] are most popular as applied to SMSTA. Nitrogen-containing aromatic heterocycles (azines), *viz*., pyridine (**1**), pyridazine (**2**), pyrimidine (**3**), pyrazine (**4**), and 1,3,5-triazine (**5**), are interesting objects for studying the dependence of the potential function of pairwise intermolecular interaction of atoms on their valent state and electron density distribution in the adsorbate molecule. A change in the relative arrangement and in the number of heteroatoms in heteroaromatic systems has a noticeable effect on the electron density distribution in their molecules and on their physicochemical properties.[8—11] In addition, since aromatic heterocycles have no conformers, the corresponding adjustments for internal rotation are not required and this considerably simplifies molecular statistical calculations of the TCA.[7]

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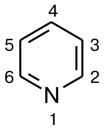

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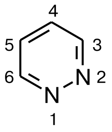

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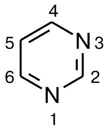

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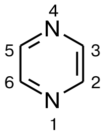

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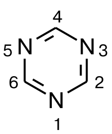

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It seems of interest to study the possibility to apply carbon adsorbents with a small specific surface for efficient and selective separation of aromatic heterocycles in gas chromatography.[12] Sufficient data on the application of GTC for chromatographic separation of heterocyclic nitrogen-,[5,12—17] oxygen-,[6,18,19] sulfur-,[19—21] and selenium-containing[19,21] compounds are presently available. However, the effect of the molecular structure of aromatic heterocycles on their adsorption behavior on the GTC surface was not systematically studied.

The purpose of this work is to determine the parameters of the atom-atomic potential function of pairwise intermolecular interaction (AAP) for nitrogen atoms in azine molecules followed by the molecular statistical calculation of the TCA on GTC. In addition, it was of interest to study the influence of specific features of the molecular structure of these compounds on their chromatographic behavior.

Experimental

Henry's constants ($K_{1,C}$/cm^3 m^{-2}) for pyridine, pyrazine, pyrimidine, and 1,3,5-triazine molecules were experimentally determined on a Tsvet-100M chromatograph with a flame-ionization detector, accepting that $V_g^T \approx K_{1,C}$ at an infinitely small coverage of the adsorbent surface (Henry region).[1,7] Nitrogen was used as a carrier gas. Separation was carried out on a glass micropacked column 0.7 m × 1.5 mm in size. Graphitized thermal carbon black (Sterling MT trade mark) with a specific surface of 7.6 m^2 g^{-1} and a weight of 0.85 g was used as an adsorbent. The size of the adsorbent pellets was 0.18—0.25 mm. Analyzed substances were sampled from the gas phase. The experimental $K_{1,C}$, $\Delta\bar{U}_1$, and $\Delta\bar{S}_1$ values were carried out using a known procedure.[1,7] The experimental and calculated TCA values are presented in Table 1, the error of determination of the experimental TCA values being at most 3.5%.

The molecular statistical calculation was based on semiempirical AAP in the form of the Buckingham—Corner potential[1,7,15]

$$\varphi = -C_1r^{-6} - C_2r^{-8} + B\exp(-qr) = \\ = -C_1r^{-6}(1 + C_2/(C_1r^2)) + B\exp(-qr), \qquad (1)$$

where C_1 and C_2 are the parameters of attraction forces, and B and q are the parameters of repulsion forces.

The parameters of attraction forces (C_1 and C_2) and repulsion forces (B) can be calculated using the quantum-chemical Kirkwood—Müller formulas[7]

$$C_1 = -6m_ec^2\frac{\alpha_a\alpha_b}{(\alpha_a/\chi_a)+(\alpha_b/\chi_b)}, \qquad (2)$$

$$C_2 = \frac{45h^2}{32\pi^2m_e}\alpha_a\alpha_b\left[\frac{1}{2\left(\dfrac{\alpha_b/\chi_b}{\alpha_a/\chi_a}+1\right)}+\frac{1}{2\left(\dfrac{\alpha_a/\chi_a}{\alpha_b/\chi_b}+1\right)}\right], \qquad (3)$$

$$B = \frac{6C_1\exp(qr_0)}{qr_0{}^7}\left(1+\frac{4C_2}{3C_1r_0{}^2}\right), \qquad (4)$$

where h is the Planck constant, m_e is the mass of an electron, α_i is the atomic polarizability, χ_i is the atomic diamagnetic susceptibility, r_0 is the equilibrium distance between the interacting force centers, and q is the parameter of universal repulsion forces accepted to be 35.7 nm^{-1}.

To determine polarizabilities of atoms and molecules (α) of compounds under study (they are necessary for the molecular statistical calculation of the TCA), we used the molecular re-

Table 1. Thermodynamic characteristics of adsorption for nitrogen-containing heterocycles **1**—**5** on GTC

Compound	$\ln K_{1,C} = A + B/T$		$\Delta\bar{U}_1$ /kJ mol^{-1}		$K_{1,C}$/cm^3 m^{-2}				
	$-A$	B			350 K		373 K		423 K[a]
			a	b	a	b	a	b	
1	11.72	4684	38.9	41.0	5.26	5.24	2.30	2.28	0.52
2	—	—	—	—	—	8.76 [c]	—	3.94 [c]	—
3	11.52	4446	37.0	37.0	3.25	3.27	1.49	1.51	0.36
4	11.29	4372	36.3	—	3.32	3.30	1.54	1.53	0.39
5	11.02	4010	33.3	35.0	1.55	1.57	0.75	0.73	0.21

[a] Data of this work.
[b] See Refs. 5 and 13.
[c] See Refs. 5 and 15.

Table 2. Initial values of atomic (α_A) and molecular (α_M) polarizabilities used for the calculation of the parameters of pairwise intermolecular interaction of the N and C atoms of azines with the C atoms of the basis face of GTC

Compound	Method	α_A/m^3·10^{30}						n_D^t	d_4^t	α_M/m^3·10^{30}	
		1	2	3	4	5	6			Experiment[a]	Calculation[b]
1	I[c]	2.269	1.027	1.027	1.027	1.027	1.027	1.5102	0.9831	9.554	10.216
	II[d]	2.289	1.021	1.026	1.022	1.026	1.021				
	III[e]	0.809	1.319	1.319	1.319	1.319	1.319				
	IV[f]	0.917	1.287	1.312	1.290	1.312	1.287				
2	I[c]	1.478	1.478	1.027	1.027	1.027	1.027	1.5231	1.1054	8.783	8.937
	II[d]	1.494	1.494	1.018	1.020	1.020	1.018				
	III[e]	0.894	0.894	1.319	1.319	1.319	1.319				
	IV[f]	0.980	0.980	1.269	1.283	1.283	1.269				
3	I[c]	1.528	1.027	1.528	1.027	1.027	1.027	1.4998	1.0517	8.884	8.937
	II[d]	1.547	1.015	1.547	1.016	1.024	1.016				
	III[e]	0.944	1.319	0.944	1.319	1.319	1.319				
	IV[f]	1.045	1.254	1.045	1.258	1.305	1.258				
4	I[c]	1.607	1.027	1.027	1.607	1.027	1.027	1.4953	1.0254	9.042	9.319
	II[d]	1.622	1.020	1.020	1.622	1.020	1.020	(60°C)	(60°C)		
	III[e]	1.023	1.319	1.319	1.023	1.319	1.319				
	IV[f]	1.102	1.280	1.280	1.102	1.280	1.280				
5	I[c]	1.170	1.027	1.170	1.027	1.170	1.027	—	—	7.880[c]	7.924
	II[d]	1.182	1.015	1.182	1.015	1.182	1.015				
	III[e]	0.878	1.319	0.878	1.319	0.878	1.319				
	IV[f]	0.944	1.252	0.944	1.252	0.944	1.252				

[a] Calculated from the experimental data on molecular refraction.[11,22]

[b] See Ref. 25.

[c] At the atomic polarizability of carbon (α_C) in benzene equal to $1.027 \cdot 10^{-30}$ m^3.

[d] At $\alpha_C = 1.027 \cdot 10^{-30}$ m^3 taking into account the π-electron density distribution in the aromatic ring.

[e] At α_C in benzene $1.319 \cdot 10^{-30}$ m^3.

[f] At $\alpha_C = 1.319 \cdot 10^{-30}$ m^3 taking into account the π-electron density distribution in the aromatic ring.

fraction (MR) values obtained from the experimentally determined refraction index (n_D^t) and density (d_4^t).[22,23] The experimental values of polarizability for atoms and molecules were calculated using a known procedure.[24] The corresponding n_D^t and d_4^t values along with the molecular (α_M) and atomic (α_A) polarizabilities calculated from these values are presented in Table 2. The geometric parameters of the compounds under study used in the molecular statistical calculation were determined by the electron diffraction method in the gas phase.[26–30] The π-electron densities and charges on atoms, used to estimate the π-electron balance and to take into account peculiarities of the molecular structures of azines under study, were taken from the literature.[8,11,31,32]

Results and Discussion

The published[5,13–17] and obtained in this work experimental values of TCA for some azines on GTC are presented in Table 1. The ΔU values and Henry´s constants obtained by different authors are close, which indicates that the experimental data are reliable.

The values of Henry´s constants in the series of azines under study predict the following order of elution of azines on a column packed with GTC: pyridazine > pyridine > > pyrimidine > pyrazine > 1,3,5-triazine. The molar differential heats of adsorption decrease in the same order (see Table 1). The plot of Henry´s constants *vs.* inverse temperature is linear in a wide temperature interval (350—453 K) for all compounds studied in the work and can be approximated by the known expression[1,7,33]

$$\ln K_{1,C} = \frac{\Delta\bar{S}_1 + R}{R} - \frac{\Delta\bar{U}_1}{RT} \approx A + \frac{B}{T}, \qquad (5)$$

where $\Delta\bar{S}_1$ is the change in the molar differential entropy of adsorption (J mol^{-1} K^{-1}), and $\Delta\bar{U}_1$ is the change in the molar differential heat of adsorption (J mol^{-1}).

The A and B parameters in Eq. (5) obtained from the experimental $K_{1,C}$ values are presented in Table 1. In the studied temperature interval, the molar differential heats of adsorption for azines are temperature independent ($\Delta\bar{U}_1 \neq f(T)$, $\Delta\bar{C}_1 = 0$), and molecules of these compounds in the adsorbed state should be considered as a dimeric ideal gas characterized by the loss of only one degree of translation on the transition of an adsorbate molecule from the gas phase to the adsorbed state.[33]

At the same time, it seems impossible to provide an exact physicochemical substantiation for the observed order of elution of azines on a column packed with GTC in the framework of the classical additive approach when considering pairwise intermolecular interactions. For example, in the opinion of several authors, a decrease in retention on going from pyridine to 1,3,5-triazine is probably related to the nonplanar configuration of the pyrimidine, pyrazine, and 1,3,5-triazine molecules in the adsorbed state.[1,5,13,17] However, available data on X-ray diffraction analysis in the crystalline phase[34] and electron diffraction study in the gas phase[26—30] of the structures of these compounds directly indicate the planar structure of their molecules. Moreover, the adsorption potential of GTC is apparently high enough to change the geometry of the azines adsorbed nonspecifically on its surface.[1,7,33] Thus, the published experimental data allow an unambiguous conclusion to be drawn on the planar conformation of the azines in the adsorbed state. A weaker intermolecular interaction of pyrimidine, pyrazine, and 1,3,5-triazine with the GTC surface can be explained by the features of their electronic structure, which directly defines the polarizability of molecules and, hence, the energy of dispersion interactions of the adsorbate with the GTC surface. The influence of the electronic structure of adsorbate molecules on their chromatographic behavior can quantitatively be estimated using the AAP, whose discrete character makes it possible to discriminate rigidly atoms of chemical elements with respect to their electronic state in the adsorbate molecule.

Six-membered aromatic nitrogen-containing heterocycles are among compounds with a reduced π-electron density on the carbon atoms of the cycle compared to the π-system in benzene.[32,35] The planar arrangement of the unshared electron pair of nitrogen relatively to the aromatic ring plane results in the situation when the nitrogen atom does not manifest the electron-donating function and withdraws a substantial fraction of the π-electron density of the aromatic system due to a higher electronegativity compared to that of the carbon atom.[8—11] π-Deficiency of azines is determined, to a great extent, by the number and relative arrangement of heteroatoms in the aromatic system. The total π-deficiency of the heterocycle is determined by the total positive π-charge remaining on the carbon atoms of the aromatic ring after some π-electron density partially shifted to the heteroatom. It numerically equals the negative π-charge concentrated on the heteroatom and changes in the series of pyridine and noncondensed polyazines as follows: 1,3,5-triazine > > pyrimidine > pyridazine > pyridine.[32] As for pyrazine, results of different quantum-chemical methods differ strongly.[8—11] For example, the π-approximation methods allow us to place pyrazine between pyrimidine and pyridazine, while the σ,π-approximation methods indicate that the total π-deficiency of pyrazine is lowest in the series of all noncondensed azines.[8,32] A fairly complicated situation appears for the experimental study of the π-electron balance of the azines. For example, different experimental methods (^{15}N NMR,[11,36] ^{13}C NMR,[37] photoionization (PI),[11,38] IR spectroscopy[11,32]) do not provide the complete objective pattern of π-electron density distribution in the heterocyclic system, because they are affected by both σ-electronic and π-electronic distributions that can hardly be divided into components.[8] Some data on the π-electron balance of the azines considered in this work are presented in Tables 3 and 4.

The concept of π-deficiency is tightly related to the phenomenon of cyclic conjugation of π-electrons, *i.e.*, aromaticity of heterocycles, which is also rather difficult to estimate quantitatively.[32] In this work, we used the geometric parameters of the molecular structures of azines in the gas phase to calculate Julg´s structural aromaticity indices (A_1 (%)), which characterize the degree of alignment of peripheral bonds in the aromatic ring.[8,39] The physical sense of the A_1 index becomes clear on the assumption that the introduction of a heteroatom into the aromatic system results in a decrease in the uniformity of the electron density distribution in the molecule, perturbation of conjugation, and deviation of bond lengths to this or another side from the standard length of the aromatic C—C bond in the benzene molecule equal to 1.40 Å.[8] The A_1 parameter was determined using the expression

$$A_1 = 1 - \frac{225}{n}\sum_{(\mathrm{rs})}(1 - d_{\mathrm{rs}}/\bar{d})^2, \qquad (6)$$

where d_{rs} is the bond length between the atoms r and s, $\bar{d}$ is the mean length of peripheral bonds, and n is the number of π-electrons in the ring.

Table 3. Experimental bond lengths[26—30] and π-charges in azines **1**—**5** calculated using the RHM method[8—10]

Parameter	1	2	3	4	5
Bond			d/Å		
1—2	1.344	1.330	1.340	1.403	1.337
2—3	1.399	1.341	1.340	1.339	1.337
3—4	1.398	1.393	1.340	1.403	1.337
4—5	1.398	1.393	1.393	1.403	1.337
5—6	1.399	1.393	1.393	1.339	1.337
1—6	1.344	1.341	1.340	1.403	1.337
Position			q/C		
1	−0.195	−0.124	−0.199	−0.147	−0.203
2	0.077	−0.124	0.155	0.074	0.203
3	−0.004	0.077	−0.199	0.074	−0.203
4	0.050	0.047	0.126	−0.147	0.203
5	−0.004	0.047	−0.009	0.074	−0.203
6	0.077	0.077	0.126	0.074	0.203

Table 4. Initial π-electron densities in azines **1—5** and atomic (χ_A) and molecular (χ_M) diamagnetic susceptibilities used for calculation of the parameters of atom-atomic potentials of the C and N atoms in azines with the C atoms of the basis face of graphite

Compound	Position	π-Electron density[a]	χ_A[b]	χ_M[c]	$\chi_M - n_H\chi_H$[d]	Λ[e]
			m^3 · 10^{36}			
1	1	1.29	−5.97	−81.70	−57.39	3.04
	2, 6	0.91	−10.27			
	3, 5	0.98	−10.30			
	4	0.92	−10.28			
2	1, 2	1.24	−3.37	−67.25	−47.80	1.44
	3, 6	0.86	−10.26			
	4, 5	0.90	−10.27			
3	1, 3	1.28	−5.55	−71.57	−52.12	3.02
	2	0.82	−10.24			
	4, 6	0.83	−10.25			
	5	0.96	−10.29			
4	1, 4	1.23	−0.96	−62.44	−42.99	2.11
	2—4, 6	0.89	−10.27			
5	1, 3, 5	1.19	−5.88	−62.94	−48.35	−3.16
	2, 4, 6	0.81	−10.24			

[a] See Ref. 31.

[b] Calculated in the this work using the additive scheme that takes into account the π-electron density on the atoms of the heterocyclic system.

[c] See Ref. 11.

[d] The expression $n_H\chi_H$ denotes the contribution χ per H atoms in the molecule ($\chi_H = -4.86 \cdot 10^{-36}$ m^3).[7]

[e] Exaltation of diamagnetic susceptibility corresponding to the difference between the calculated and experimental χ_M values.

However, as follows from the data in Table 5, the A_1 indices for the azines are very close to each other and differ slightly from that for benzene. In addition, for the 1,3,5-triazine molecule the A_1 index is equal to unity (100%), which corresponds to the aromaticity index of the unsubstituted benzene molecule. The latter contradicts the available experimental data on aromaticity of azines, according to which the 1,3,5-triazine molecule is least aromatic of all considered heterocyclic systems.[8—11,32] Therefore, the *A* parameter was also calculated in this work

$$A = A_1A_2, \quad (7)$$

Table 5. Structural aromaticity indices calculated using Julg´s method[8,39]

Compound	A_1	A_2	A
		%	
1	0.92	0.91	0.84
2	0.90	0.95	0.86
3	0.92	0.75	0.69
4	0.89	0.90	0.80
5	1.00	0.56	0.56

The *A* parameter takes into account (through the adjustment factor A_2) the resistance exerted by the cyclic circulation of π-electrons by charges localized on the atoms of the heterocycle. The A_2 factor was calculated using the formula[8,32,39]

$$A_2 = \prod_{(ij)}\left[1 - (\Delta q_{ij}/d_{ij})^2\right], \quad (8)$$

where Δq_{ij} is the difference in π-charges on the adjacent atoms, and d_{ij} is the distance between them.

The *A* and A_2 parameters calculated using formulas (7) and (8) are presented in Table 5. Comparing *A* and A_1, one can see that the use of the *A* parameter makes it possible to describe the aromaticity of the azines under study more correctly, taking into account both the structural component of aromaticity and the distribution of π-electron charges in the heterocyclic system. Based on the obtained *A* indices, we can conclude that the aromaticity of the heterocyclic ring of the azines under study decreases in the sequence: pyridazine > pyridine > > pyrazine > pyrimidine > 1,3,5-triazine. The *A* parameter for pyridazine is higher than for pyridine. As a whole, the aromaticity of the azines considered in this work decreases with an increase in the number of nitrogen atoms in the heterocycle.

Using the calculated values of aromaticity indices *A* and experimentally determined $K_{1,C}$ values, we studied the correlation dependence of $K_{1,C}$ of azines on the aromaticity of their molecules (Fig. 1). It is shown that the $\ln K_{1,C}$ values change in parallel with the *A* parameter. Probably, the adsorption of azines on the GTC surface is determined to a great extent by the aromaticity of their molecules. The studied correlation dependence of $\ln K_{1,C}$ on *A* makes it possible to correctly predict the order of elution of heterocyclic compounds with similar structures from a chromatographic column.

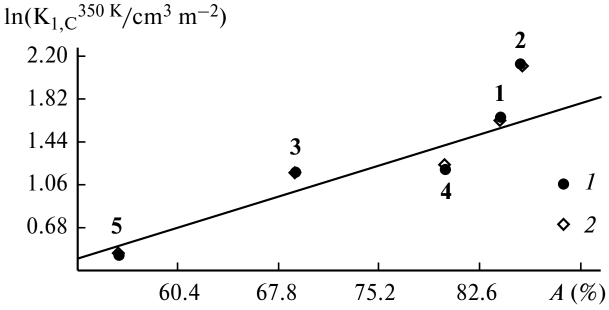

Fig. 1. Dependence of the experimental (*1*) and calculated (*2*) $\ln K_{1,C}^{350\ K}$ values for azines **1—5** on the degree of aromaticity of the heterocyclic molecule (*A*).

The aforementioned features of the electronic state of atoms in molecules of heterocycles are expected to influence the values of the AAP parameters of the N and C atoms in these compounds. In addition, each heterocyclic system is probably characterized by the intrinsic set of values of the AAP parameters.

For the exact molecular statistical calculation of the TCA of a molecule, one has to know its geometry in the GTC-adsorbed state and energetic characteristics of force centers that form the adsorbate molecule.[1,5—7,33] The geometric parameters obtained for the gaseous state of matter (electron diffraction in the gas phase or microwave spectroscopy) are usually used in SMSTA. Atoms entering the composition of the adsorbate and adsorbent are chosen, as a rule, as force centers in the atom-atomic approximation. The AAP values of intermolecular interactions, which are the quantitative characteristic of force centers in the adsorbate—adsorbent system, were determined for many chemical elements (first of all, organogens) in different electronic states.[1,7]

There are few published data on the AAP parameters of intermolecular interaction of the nitrogen atoms of the heterocyclic systems with the carbon atoms of GTC. The influence of variation of the AAP parameters on the results of calculation of Henry´s constants was studied for adsorption of pyridine, pyridazine, pyrimidine, and 1,3,5-triazine on GTC.[15] However, satisfactory agreement between the experimental and calculated TCA values for the studied compounds under assumption of their planar geometry was achieved only for pyridine and pyridazine molecules.[15] In addition, the algorithm for variation of the AAP parameters proposed by the authors is based on the trial-and-error method, due to which the introduction of a correction into the AAP is reduced only to the enumeration of different values of the correction factor. The parameters of the Buckingham—Corner potential proposed[15] for the nitrogen atom in the azines are presented in Table 6.

Table 6. Parameters of the Buckingham—Corner potential calculated for the N atoms in azines for different values of the atomic characteristics[a]

Method	C_1[b]	C_2[c]	B[d] $\cdot 10^{-5}$	$r_{\mathrm{N(azine)...C(GTC)}}$ /nm
		Pyridine		
I	1.341	5.838	1.204	0.340
II	**1.343**	**5.889**	**1.209**	**0.340**
III	0.998	2.081	0.740	0.340
IV	1.047	2.359	0.789	0.340
V[e]	1.640	2.550	1.130	0.340
VI[e]	3.400	5.290	8.680	0.420
		Pyridazine		
I	0.777	3.803	0.589	0.323
II[f]	0.778	3.844	0.592	0.323
II[g]	**1.225**	**6.054**	**0.932**	**0.323**
III	0.699	2.300	0.466	0.323
IV	0.715	2.521	0.484	0.323
V[e]	1.640	2.550	1.130	0.340
VI[e]	**3.400**	**5.290**	**8.680**	**0.420**
		Pyrimidine		
I	1.162	3.931	0.777	0.323
II	**1.166**	**3.980**	**0.781**	**0.323**
III	1.010	2.429	0.6159	0.323
IV	1.044	2.689	0.648	0.323
		Pyrazine		
I	0.252	4.135	0.365	0.323
II[f]	0.253	4.173	0.367	0.323
II[h]	**0.787**	**12.978**	**1.141**	**0.323**
III	0.246	2.632	0.272	0.323
IV	0.247	2.835	0.284	0.323
		1,3,5-Triazine		
I	1.126	3.010	0.771	0.330
II	**1.129**	**3.041**	**0.774**	**0.330**
III	1.021	2.259	0.669	0.330
IV	1.048	2.429	0.694	0.330

[a] In all cases, $q = 35.7$ nm^{-1}.

[b] J nm^6 mol^{-1}.

[c] J nm^8 mol^{-1}.

[d] J mol^{-1}.

[e] See Ref. 15.

[f] Calculated from the data in Tables 2 and 4.

[g] Calculated taking into account the adjustment $\beta = 1.575$.

[h] Calculated taking into account the adjustment $\beta = 3.110$.

In molecular statistical calculations, the AAP for the C atom directly calculated using the quantum-chemical Kirkwood—Müller formulas result in somewhat overestimated (compared to experimental results) $K_{1,\mathrm{C}}$ and $\Delta\bar{U}_1$ values.[1,7] Therefore, adjustment factors (β), which lead to satisfactory correspondence between the experimental and calculated TCA values, are introduced into the calculated AAP parameters. It is shown in this work that at constant r_0 and q parameters and the C_2/C_1 ratio equal to

$$\frac{C_2}{C_1} = \frac{-0.1172h^2}{\pi^2 m_\mathrm{e}^2 c^2}\left(\frac{\alpha_\mathrm{a}}{\chi_\mathrm{a}} + \frac{\alpha_\mathrm{b}}{\chi_\mathrm{b}}\right), \qquad (9)$$

the adjustment introduced into formulas (2)—(4) only corrects the atomic polarizabilities of atoms α_A in the adsorbate molecule because, as seen from Eq. (9), C_2/C_1 = const implies the constant α_i/χ_i ratio. Thus, the α_A values obtained directly from data on molecular refraction should be corrected for using in molecular statistical calculations. For example, for the C atoms in benzene, the α_C value obtained from the data on MR is $1.319 \cdot 10^{-30}$ m^3, and that calculated with the correction to the AAP value is $1.027 \cdot 10^{-30}$ m^3. The choice of appropriate α_Het values is more difficult, because other characteristics necessary for AAP calculations, in particular, r_0

and χ_{Het}, are unknown, as a rule, for heteroatoms. Such an uncertainty can be solved by arbitrary varying one of the parameters (as a rule, r_0)[33,40–42] while maintaining other atomic characteristics (α_{Het} and χ_{Het}) unchanged. Note that the interval of r_0 variation can also be predicted using the corresponding values of the van der Waals radii (r_v) for the heteroatom of the adsorbate and the C atom of the basis face of graphite.

In this work, to determine the AAP parameters, we used four additive schemes of calculation (I—IV) of atomic increments of the α_A and χ_A values from the corresponding molecular values of these characteristics for the azines under study. The same initial α_M and χ_M values equal to the experimentally determined values were taken for all four schemes.

Method I uses the α_C value for the C atom in benzene corrected with adjustment for the AAP values: $1.027 \cdot 10^{-30}$ m^3. The π-electron density distribution was ignored in method I. Since the polarizability values are highly sensitive to the electronic state and environment of the atom in the adsorbed molecule, we also calculated the α_C and α_N values taking into account the π-electron density distribution in the molecules of heterocycles (method II). The α_C values equal to $1.027 \cdot 10^{-30}$ m^3 were used as initial in method II. The algorithm of calculation by method III is similar to that by method I, except for the value of $1.319 \cdot 10^{-30}$ m^3 used as the intial α_C value and directly obtained from the MR data on the benzene molecule. In method IV, $1.319 \cdot 10^{-30}$ m^3 was used as the reference α_C value and the π-electron density distribution in the molecule was also considered. The α_C and α_N values obtained by different methods are presented in Table 2. The χ_C and χ_N values were calculated from the corresponding molecular magnitudes[11] taking into account the π-electron density distribution in the molecules (see Table 4).

Using the determined α_A and χ_A values, we obtained four different sets of AAP parameters for the C and N atoms in the azines under study (see Table 6). Note that the AAP values for the C atoms calculated by methods I and III do not discriminate the C atoms by their ability to intermolecular interactions. This indicates their equivalent adsorption behavior in the framework of a particular molecule. On the contrary, the calculation of the AAP parameters by methods II and IV is based on the fact that the C atoms in the heterocyclic system show different behavior in adsorption and their energetic characteristics of interaction with the graphite surface depend on the number and position of the N atoms in the molecule.

Using the previously proposed method,[40–43] we showed that the optimal $r_{N...C(GTC)}$ value corresponding to the best match of the calculated and experimental TCA values is equal to 0.340 nm for the pyridine molecule, it is 0.323 nm for the pyrimidine and pyrazine molecules, whereas 1,3,5-triazine is characterized by 0.330 nm. The equilibrium distance for the N atom in pyridine virtually coincides with the sum of van der Waals radii of the N and C atoms (r_v(N) + r_v(C) = 0.341 nm),[44,45] which can serve, most likely, as a reliable proof for correctness of the selected $r_{N...C(GTC)}$ values. The values of the AAP parameters for the nitrogen atoms in the azine molecules calculated in this work (I—IV) and published[15] (V, VI) are presented in Table 6. It is seen that the AAP parameters calculated using different approximations differ noticeably. For example, the AAP parameters are reasonably sensitive to the π-electron density distribution as evidenced by comparison of pairs of the corresponding AAP values (I—II and III—IV). For example, the AAP parameters of the N atom in pyridine calculated in this work differ from the values known from the literature. However, a satisfactory agreement for the AAP calculated by methods II and V is observed in the region of a potential minimum. The AAP parameters for N in pyridazine (I—IV) calculated in this work differ strongly from the AAP parameters published previously[15] (VI). In addition, despite somewhat overestimated r_0 value (0.420 nm),[15,46] the potential of VI is appropriate for calculation of the TCA of the pyridazine molecule (see Table 1). For the pyridazine molecule, the calculations of the TCA by the additive scheme II give results comparable with experiment if the corresponding adjustment factor $\beta = 1.575$ is introduced into the initial AAP value. For the N atoms in pyridazine, the same r_0 value as in molecules of other diazines (0.323 nm) was adopted. Evidently, in this case, the need to introduce the adjustment is due to the *ortho*-effect in the pyridazine molecule, resulting, as known, in a remarkable increase in the retention on GTC compared to molecules containing substituents or, as in our case, a heteroatom in the *meta*- and *ortho*-positions.[43,46]

The dependence of the AAP values of the N atom with the C atom of graphite on the distance to the surface of the basic face of graphite for different heterocycles is presented in Fig. 2. Only the AAP giving the best coincidence of the calculated TCA with the experimental values (Table 7) were used in plotting this dependence.

The TCA values of the azines under study calculated by different AAP for the N atom are presented in Table 7. A comparison of the data in Tables 1 and 7 shows that for the pyridine, pyrimidine, and 1,3,5-triazine molecules the best agreement of the experiment and calculation (bold TCA values in Table 7) is observed when using the AAP calculated by method II. This method takes into account the π-electron density distribution in the aromatic system related to the introduction of a heteroatom and also includes the correction to the polarizability of the C atom using formulas (2)—(4). At the same time, analogous (nonrefined) AAP for the N atoms in pyrazine and pyridazine cannot be applied for description of the adsorption behavior of molecules of these substances on the GTC surface. In the case of the pyrazine molecule, the

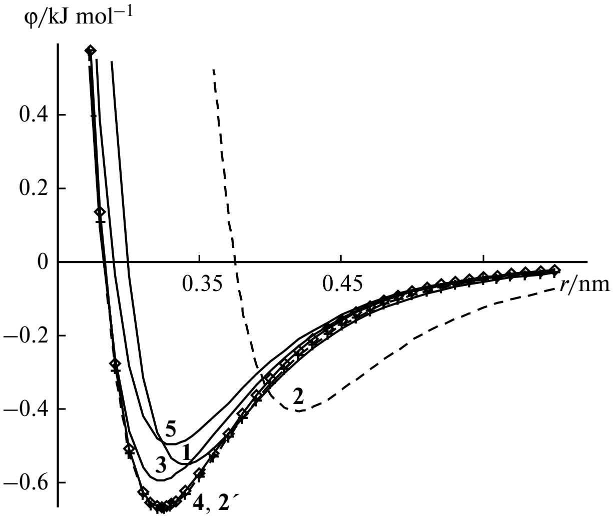

Fig. 2. Atom-atomic potential functions of pairwise intermolecular interaction of the nitrogen atom in different heterocycles with the GTC carbon atom ($\varphi_{N(M)...C(GTC)}$). The $\varphi(r)$ values at $r = r_0$: −0.552 (**1**), −0.407 (**2**),[15] −0.675 (**2′**), −0.596 (**3**), −0.668 (**4**), and −0.498 (**5**) kJ mol^{-1}.

reason for the observed discrepancy lies likely in the fact that the χ_N value, used in the calculation of the AAP parameters and determined by the proposed additive scheme, is much lower than χ_N for molecules of other heterocycles. At the same time, the obtained χ_N value for pyrazine seems to be very realistic because it was determined from the experimental values of molecular diamagnetic susceptibility χ_M, which is also minimal for pyrazine in the series of the considered heterocycles (see Table 4). Therefore, we introduced the adjustment factor (β) into the AAP parameters for N in pyrazine calculated by method II. The algorithm of introduction of this correction is completely analogous to that considered above for the pyridazine molecule and was described in detail.[40—43] The correction was determined using the trial-and-error method and amounted to 3.110. The refined AAP parameters determined by method II for N in the pyrazine molecule are presented in Table 6. It is also noteworthy that the correspondence of experimental and calculated TCA values achieved in this work is observed under assumption of the planar geometry of the azines in the adsorbed state. This agrees well with the structural

Table 7. Thermodynamic chemical adsorption parameters calculated using different AAP values for the N and C atoms in molecules of azines **1**—**5** on GTC

AAP	TCA[a]	T/K	**1**	**2**[b]	**3**	**4**	**5**
I	$K_{1,C}$	350	5.31	1.42	3.30	0.28	1.97
		373	2.32	0.70	1.50	0.15	0.94
		423	0.54	0.19	0.38	0.05	0.26
	$\Delta\bar{U}_1$		38.8	33.5	36.8	27.5	33.7
II	$K_{1,C}$	350	**5.26**	**8.76**	**3.27**	**3.38**	**1.55**
		373	**2.30**	**3.78**	**1.49**	**1.54**	**0.75**
		423	**0.52**	**0.83**	**0.37**	**0.38**	**0.21**
	$\Delta\bar{U}_1$		**38.9**	**40.1**	**36.8**	**36.9**	**33.7**
III	$K_{1,C}$	350	7.35	1.97	3.79	0.49	1.56
		373	3.13	1.06	1.71	0.26	0.76
		423	0.70	0.26	0.42	0.09	0.22
	$\Delta\bar{U}_1$		39.9	34.5	37.1	29.6	33.6
IV	$K_{1,C}$	350	7.48	1.92	3.86	0.46	1.59
		373	3.18	0.92	1.74	0.24	0.77
		423	0.71	0.25	0.43	0.08	0.22
	$\Delta\bar{U}_1$		40.0	34.4	37.2	29.3	33.7
V	$K_{1,C}$	350	5.48	8.13	—	—	—
		373	2.39	3.48	—	—	—
		423	0.55	0.78	—	—	—
	$\Delta\bar{U}_1$		38.9	39.8	—	—	—
VI	$K_{1,C}$	350	5.38	**8.87**	—	—	—
		373	2.36	**3.76**	—	—	—
		423	0.55	**0.83**	—	—	—
	$\Delta\bar{U}_1$		38.6	**40.1**	—	—	—

[a] $K_{1,C}$/cm^3 m^{-2}, $\Delta\bar{U}_1$/kJ mol^{-1}.

[b] For the pyridazine and pyrazine molecules, the calculated TCA values coinciding with the experimental values were obtained using the refined AAP values determined by method II (β = 1.575 and 3.11, respectively).

data for these molecules obtained by the electron diffraction methods in the gas phase.

Thus, analysis of different AAP for N in the azines showed that the best agreement of the calculated and experimental TCA values for the compounds under study is observed if the molecular statistical calculation involves the AAP that allows for the decreased π-electron density in the heterocycle molecule and includes corrections for the approximate character of formulas (2)—(4) (in this case, the adjustment for the polarizability of C in the aromatic system). The molecular statistical calculation of the TCA agrees with experiment if the AAP values take into account both the nonequivalent behavior of the C atoms in the aromatic system and the π-acceptor nature of the N atoms in the molecules. As a whole, we can conclude that the adsorption behavior of the azines depends on the degree of their aromaticity and is determined by the number and relative orientation of the N atoms in the molecules.

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