Physical Chemistry

Quantum-chemical analysis of the cluster models of coordination of imidazoline nitroxides on the silica surface

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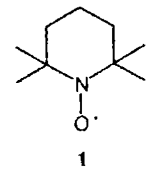
The results of ESR-spectroscopic and quantum-chemical studies of the coordination of 2,2,4,5,5-pentamethyl-3-imidazoline-*N*-oxyl and 2-phenyl-2,4,5,5-tetramethyl-3-imidazoline-*N*-oxyl with the surface acid sites (AS) of silica are analyzed. Cluster models of AS, corresponding to one- and two-point coordination and accepted in radiospectroscopy on the basis of *g*-factors and constants of hyperfine splitting at the N nuclei in the resulting donor-acceptor complexes, are discussed. Within the framework of the unrestricted Hartree—Fock method using the MNDO approach, a comparative quantum-chemical analysis of the structural, spin, electrostatic, energy, and radiospectroscopic characteristics of the coordination of the model cluster AS to the imidazoline nitroxide probes is performed. For the two-center adsorption, three types of AS structures are considered, together with the paramagnetic surface complexes they form. A consistent semi-quantitative interpretation of the whole set of features found experimentally for the coordination of imidazoline nitroxides to the surface AS on silica is given.

Key words: quantum-chemical calculations, MNDO, silica, acid sites, imidazoline nitroxides, surface donor-acceptor complexes, structural, magnetic resonance, electrostatic, and energy characteristics of coordination.

Methods for investigation of the paramagnetic surface complexes (PSC) formed by probe molecules with active sites of solids are successfully used to study the structures and properties of oxide surfaces.[1–6] ESR spectroscopy makes it possible to determine reliably a number of physicochemical characteristics of PSC and, resorting to methods of quantum chemistry, to gain an insight into the coordination phenomena occurring on oxide surfaces.[1–5]

Stable nitroxides such as di-*tert*-butylnitroxyl and 2,2,6,6-tetramethylpiperidin-*N*-oxyl (**1**) (TEMPO) are used most often as paramagnetic probe molecules in studies of the acidic properties of oxide surfaces. These radicals form fairly stable PSC with the acid sites (AS) at the surface. The ESR spectra of these PSC exhibit hyperfine structure due to interaction with the N



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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1081—1086, June, 1998.

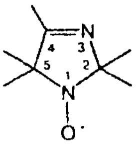
1066-5285/98/4706-1048 \$20.00 © 1998 Plenum Publishing Corporation

nucleus of the nitroxyl group; in the case of interaction of radicals with Lewis acid sites (LAS), the ESR lines are additionally split due to the magnetic nuclei of the metal atom. Analysis of the parameters of the corresponding ESR spectra makes it possible to draw conclusions about the number, nature, strength, and structure of the AS.[1-5,7]

In recent year, the interest in the use of stable nitroxides of the imidazoline and imidazolidine series has increased.[8] This is due to the fact that these "bifunctional" radicals possess two electron-donating centers, which normally compete for the formation of PSC; therefore, the ESR spectra of these compounds provide more detailed information.

The possibility for a "bifunctional" nitroxide to be coordinated simultaneously by both electron-donating centers can be used for studying the mutual arrangement of the surface AS of oxides at the molecular level. In particular, ESR has been used to study[2,3] the coordination of nitroxides of the imidazoline and imidazolidine series to the surface of silica gel with various degrees of dehydroxylation. The magnetic resonance parameters determined in this study and the temperature dependences of the rotational mobility of coordinated radicals were qualitatively interpreted by assuming that the two electron-donating centers of nitroxides form donor-acceptor bonds with two neighboring AS of a silica surface.

Since the structural information obtained in radiospectroscopic studies can be scarce, ambiguous, or indirect,[2,3] we attempted to verify the adequacy of the accepted notions using quantum-chemical calculations of model PSC. This work deals with quantum-chemical analysis of the ESR data on the coordination of nitroxides of the imidazoline series, namely, 2,2,4,5,5-pentamethyl-3-imidazolin-*N*-oxyl (**2**) and 2-phenyl-2,4,5,5-tetramethyl-3-imidazolin-*N*-oxyl (**3**), to the surface AS of partially dehydroxylated silica gel



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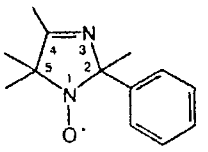

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Structure and properties of surface AS on SiO_2 according to ESR data

ESR spectra (spectral pattern, anisotropic splitting, temperature dependence) provide information about the mechanism of coordination of nitroxides of the imidazoline series to the surface AS of silica.[2,3] The most convenient method for investigating the type of coordination consists in the measurement of the correlation time τ_c of the rotational mobility of an adsorbed radical. When imidazoline radicals are adsorbed on a silica surface, their rotational mobility normally sharply decreases, their ESR spectra change from isotropic to anisotropic, and the correlation time τ_c decreases by several orders of magnitude.[2,3]

It is well known that the adsorption sites on the silica surface are usually represented by silanol groups. In view of this fact, it appears quite reasonable to assume that it is these AS on the SiO_2 surface that react first of all with imidazoline radicals. This assumption is supported by the fact that the hyperfine splitting (HFS) constants ($A_{\parallel}^{N}$) for nitroxides coordinated on SiO_2 are close to those for the same radicals forming hydrogen bonds, involving electron-donating NO groups, with solvent molecules in vitrified solutions.[2,3]

However, it should be borne in mind that imidazoline radicals **2** and **3** contain the second electron-donating center, the N(3) atom. The rotational mobility of these radicals adsorbed on silica, measured experimentally under similar conditions (~720 K, ~10^{-3} Pa),[3] is substantially lower than that of radical **1** containing only one electron-donating group. Based on this result, it was concluded[2] that imidazoline radicals are adsorbed on SiO_2 *via* two-point interaction; this was also confirmed by the results of electron spin echo studies[9] of the orientational motion of nitroxides coordinated to a surface.

As the temperature increases, the rotational mobility of imidazoline radicals increases; the corresponding ESR spectral patterns and correlation times τ_c indicate that the two-point coordination on the surface AS of silica gel is transformed into one-point coordination.[2] This process is reversible, *i.e.*, a dynamic equilibrium between the fast and slowly rotating forms of adsorbed imidazoline radicals is established. The temperature dependence of the ratio between these two adsorption forms can be used to determine the thermodynamic characteristics of this process. In particular, the standard enthalpies of the transition ($\Delta H^\circ \approx 7-9$ kcal mol^{-1}) are fairly close to the heats of formation of hydrogen bonds between the AS of silica and typical electron-donating molecules, while the gain in entropy ΔS° is ~20 cal mol^{-1} K^{-1}, indicating that during the transformation in question the number of degrees of freedom considerably changes.[2]

Based on the analysis of the ESR spectral patterns and the magnitudes of anisotropic HFS constants in imidazoline radicals, it was concluded[2] that the hydrogen bonds between the oxygen atoms of the radical NO groups and the hydrogen atoms of the silica surface AS are cleaved. It is noteworthy that the presence of bulky substituents in the imidazoline ring (*cf.* radicals **2** and **3**) has virtually no effect on the characteristics of the dynamic equilibrium between the two forms of coordination. The transition from the one-point coordination to the two-point form is always accompanied by the formation of PSC of the same type, attesting that the concentration of the surface AS on partially dehydroxylated silica gel is relatively high.

The whole set of experimental data[2,3] indicates that the surface of silica gel, even when it has been dehydroxylated under severe conditions, contains closely located "paired" silanol groups. It has been assumed[10] that geminal OH groups can act as the adsorption AS. The distance between the "paired" AS can be estimated without difficulty from the geometric parameters of nitroxides assuming that the angle O—H···X is equal to 180°. According to these estimates, this distance is close to ~7—8 Å. Judging from the published data,[11] this arrangement of "paired" AS seems quite possible not only for a silica surface dehydroxylated at moderate temperatures (~720 K) but also for that dehydroxylated under more severe conditions (~970 K).

Thus, nitroxides of the imidazoline series can be coordinated to a silica surface by both electron-donating centers through interaction with "paired" AS, whereas the donor-acceptor binding with the surface LAS on Al_2O_3, as shown in previous studies,[1,3] involves only one of these competing positions, and the outcome of this competition is determined by the combination of the factors of basicity and steric accessibility for each of these sites. In the present work, the structural and energy characteristics of the assumed AS and of their binding to imidazoline nitroxides are studied theoretically at the molecular level, in order to obtain a substantiated interpretation of the ESR spectral data[2,3] pointing to the formation of PSC on the silica surface.

Procedure for quantum-chemical calculations of the PSC on SiO_2

The efficiency of various quantum-chemical methods in studies of the coordination of stable nitroxides by the surface LAS of alumina has been discussed previously.[12,13] A number of nonempirical and semiempirical calculations for model systems were carried out[12,13] in terms of the unrestricted Hartree—Fock (UHF) approach. Nonempirical calculations were performed using the STO-3G, STO-6G, 3-21G, and 6-31G basis sets, and semiempirical calculations were carried out in the MNDO, AM1, and PM3 valence approximations.[14]

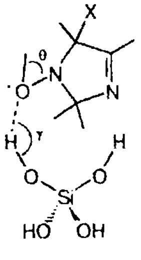
Comparative analysis of the calculated[12,13] structural, magnetic resonance, electrostatic, and energy characteristics showed that the semiempirical MNDO method is often as adequate in describing these properties of the model cluster PSC as are the nonempirical methods. Since this approximation requires much less computation time, it was preferred for the analysis of complex nitroxide PSC on Al_2O_3, studied[1,3,4] by ESR spectroscopy. In addition, comparison of various methods of cluster simulation of the surface LAS demonstrated that the best agreement between the calculated and experimental radiospectroscopic and energy values is attained when the geometric parameters found for the oxide by crystallographic methods are fixed for the model cluster.

Taking the foregoing into account, it would be reasonable to use a similar procedure in the cluster quantum-chemical analysis of the ESR data on the coordination of imidazoline radicals 2 and 3 on the surface AS of partially dehydroxylated silica gel.[2,3] Therefore, in this work, we first used the semiempirical MNDO method and, second, regarded the "structurally rigid" geometric parameters of the cage of the model cluster AS as "frozen" (invariable).

According to the commonly accepted approach,[15,16] the covalent clusters simulating the surface AS on SiO_2 were built of regular silicon-and-oxygen tetrahedra with an intra-cluster interatomic distance *R*(Si—O) equal to 1.62 Å (X-ray diffraction data). Free valences at the borders of these clusters were saturated with H atoms. The structural parameters of the coordinated imidazoline radicals and of the OH groups directly contacting with them as well as the Si—O—Si angles between "connected" silicon-and-oxygen tetrahedra were varied. For the ^{14}N nucleus, the Hartree—Fock magnitude[17] for the coefficient of proportionality between the spin population ρ_s^N of the valence s-AO and isotropic HFS constant a^N_{iso} was used.

Results of quantum-chemical analysis of the cluster PSC on SiO_2

To verify the hypotheses and conclusions involved in the interpretation of the ESR spectra of imidazoline PSC on the silica surface,[2,10] we analyzed the free nitroxides **2** and **3** themselves, their one-point (at O and N(3)) forms of coordination to the model cluster AS $Si(OH)_4$ (**4**, **5**), and the PSC formed upon binding of both electron-donating atoms (O and N(3)) to a "pair" of AS represented by geminal (**4**, **5**), vicinal (**6**), and "tetrahedron-separated" (**7**) silanol groups. Tables 1 and 2 present the results of MNDO-UHF calculations of the following parameters: hydrogen (H···X) and nitroxyl (N(1)—O) bond lengths; θ, γ, and φ angles characterizing bending of the H···O—N(1) fragment (**4**), nonlinearity of hydrogen bonds (**4**—**6**), and the "pyramidality" of the N(1) atom; the a^N_{iso} constants of isotropic HFC with the $^{14}N(1)$ nucleus; atomic spin populations ρ^A and charges Q^A; the Q^R values reflecting the electron transfer from the imidazoline radicals to the model cluster



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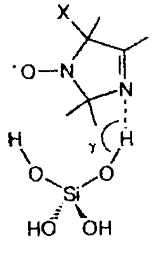

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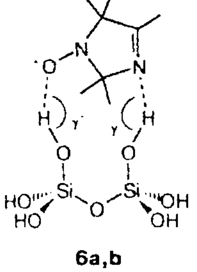

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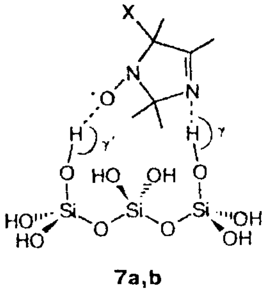

7a,b

X = Me (**a**), Ph (**b**)

Table 1. Structural, magnetic resonance, electrostatic, and energy characteristics of free imidazoline radicals and their PSC with the model cluster AS $Si(OH)_4$

Parameter	**2**	**3**	**4a**	**4b**	**5a**	**5b**
$R(H\cdots X)$/Å	—	—	1.79	1.83	1.92	1.95
$R(N(1)-O)$/Å	1.22	1.22	1.22	1.22	1.22	1.22
θ/deg	—	—	19	22	—	—
γ/deg	—	—	180	180	180	180
φ/deg	17	18	11	12	16	16
$a^N{}_{iso}$/G	19	20	22	22	19	20
$\rho^{N(1)}$	0.40	0.41	0.57	0.56	0.41	0.41
ρ^O	0.59	0.59	0.44	0.46	0.58	0.59
$Q^{N(1)}$	−0.12	−0.11	−0.04	−0.06	−0.13	−0.13
$Q^{N(3)}$	−0.23	−0.22	−0.23	−0.22	−0.25	−0.25
Q^O	−0.25	−0.26	−0.23	−0.24	−0.25	−0.25
Q^R	0	0	0.25	0.25	0.25	0.26
$\|\mu\|$/D	2.5	2.4	5.6	5.4	3.7	3.7
$-\Delta E_c$ /kcal mol^{-1}	—	—	9.1	8.9	16.1	15.9

Table 2. Structural, magnetic resonance, electrostatic, and energy characteristics of coordination of imidazoline radicals to two AS of the model cluster $Si_3O_{10}H_8$ (**7**)

Parameter	**2**	**3**	Parameter	**2**	**3**
$R(H\cdots O)$/Å	1.82	1.86	ρ^O	0.46	0.44
$R(H\cdots N(3))$/Å	1.93	1.96	$Q^{N(1)}$	−0.05	−0.06
$R(N(1)-O)$/Å	1.22	1.22	$Q^{N(3)}$	−0.27	−0.26
θ/deg	58	60	Q^O	−0.24	−0.25
γ/deg	179	178	Q^R	0.27	0.28
γ'/deg	176	178	$\|\mu\|$/D	6.8	6.5
φ/deg	12	14	$-\Delta E_c$ /kcal mol^{-1}	24.3	23.7
$a^N{}_{iso}$/G	22	22			
$\rho^{N(1)}$	0.54	0.55			

AS; electric dipole moments $|\mu|$, and the energies of formation of PSC (ΔE_c).

It can be seen from Table 1 that all the parameters calculated for non-coordinated radicals **2** and **3** differ only slightly and that the ratio of spin populations ρ^O : ρ^N is in both cases ~0.6 : 0.4, which appears to be typical of most of the known free nitroxides. The negative charges on the O and N(3) atoms in structures **2** and **3** are greater than that on N(1). Attention is attracted by the fact that the presence of a bulky substituent in position 2 of the ring has almost no effect on the characteristics under consideration. This result is supported by the data[2] according to which the nature of the ring is much more significant for the main properties of nitroxides than the variation of the substituent.

Table 1 also presents the corresponding values for the PSC (**4a,b** and **5a,b**) formed by nitroxides **2** and **3** with the model cluster AS $Si(OH)_4$ in the case of coordination through the O atom. It can be readily seen that the geometric parameters such as the N—O bond length and the φ angle characterizing the degree of "pyramidality" of the N atom of the nitroxyl group (the angle between the C(2)—N(1)—C(5) plane and the N(1)—O axis) do not change significantly upon complex formation. As should be expected, the fragment with the hydrogen bond formed is linear. The imidazoline radical itself is coordinated to the cluster AS nonlinearly, as indicated by the magnitudes of the θ angle (**4**) presented in Table 1.

Our calculations, in agreement with the experimental results,[2,3] lead to increased constants of isotropic HFS $a^N{}_{iso}$ for the cluster PSC in which radicals **2** and **3** are coordinated through the nitroxyl O atom. The calculations provide a correct qualitative representation of the increase in the spin population on the N(1) atom detected experimentally upon this type of coordination; this increase is so significant that it results in an inverted ρ^O : $\rho^{N(1)}$ ratio (see Table 1). A similar inversion has been observed[12,13] in the case of coordination of these radicals to the surface LAS of alumina.

The calculated negative charges on the N(1) atom in the PSC with coordination through the O atom (**4**) are much smaller than that in free radicals **2** and **3**, whereas the charges on the N(3) and O atoms almost do not change (see Table 1). The fact that in both cases large positive charges are accumulated on the radical fragments of these PSC ($Q^R \approx 0.25$) implies considerable transfer of the electron density from the imidazoline radical to the model cluster AS. Comparison of the dipole moments of the radicals ($|\mu| \approx 2.5$ D) and the PSC in question ($|\mu| \approx 5.5$ D) also points to a substantial electron density redistribution.

It is of interest that although a similar type of coordination[12,13] of the O atom to the "frozen" cluster LAS $Al(OH)_3$ results in nearly the same positive charge ($Q^R \approx 0.26$) on imidazoline radicals **2** and **3**, the dipole moments of the corresponding PSC are much larger ($|\mu| \approx 9$ D). It is also noteworthy that these radicals are bound to the above-mentioned model LAS ~3 times stronger ($\Delta E_c \approx -30$ kcal mol^{-1})[12,13] than to the AS $Si(OH)_4$ discussed here (see Table 1). The values estimated in this work ($\Delta E_c \approx -9$ kcal mol^{-1}) indicate that both PSC contain a relatively strong hydrogen bond, N—O···H—O—Si (**4**).

Owing to their "bifunctional" properties, imidazoline radicals **2** and **3** are capable of one-point coordination to the same model AS $Si(OH)_4$ by the other electron-donating center, the N(3) atom (**5**). In this case, all the structural and magnetic resonance characteristics of the nitroxyl group in the PSC (see Table 1) are practically identical to those for free radicals **2** and **3**; this is due to the fact that the nitroxyl group is relatively insensitive to the coordination by the remote N(3) atom. It is noteworthy that the N···H—O—Si hydrogen bonds in this type of PSC (**5**) are still linear but are much longer than those arising in the case of coordination through the O atom (**4**).

According to the data presented in Table 1, the positive charge Q^R induced on the imidazoline radical does not depend on which of the electron-donating sites

(O or N(3)) is involved in the one-point coordination to the model cluster AS $Si(OH)_4$. However, the electric dipole moments $|\mu|$ for the PSC of different types differ by almost 2 D. It is noteworthy that in the case of coordination *via* N(3) (**5**), the ratios of the charges on the O, N(1), and N(3) atoms in the PSC formed are approximately the same as those in free radicals **2** and **3**.

The calculated energies of complex formation ΔE_c (see Table 1) point to a markedly (by ~7 kcal mol^{-1}) higher stability of those one-point adsorption forms in which the imidazoline radicals are bound by their second electron-donating position (**5**) rather than by the nitroxyl group (**4**). This is also unambiguously indicated by the temperature dependences[2,3] of line shapes in the corresponding ESR spectra and of anisotropic HFS constants. It is especially interesting that in the case of the model LAS $Al(OH)_3$, unlike the AS $Si(OH)_4$ analyzed here, the energies of complex formation in the case of binding of radicals **2** and **3** through the O and N(3) atoms are roughly the same[12,13] and are close to ~30 kcal mol^{-1}.

Since imidazoline radicals are preferably coordinated to the surface AS *via* the N(3) atom of the five-membered ring, it is quite reasonable to assume that the transformation of the ESR spectra of imidazoline PSC on silica observed[3] with increasing temperature reflects the transition from the two-point to one-point adsorption, which results in the formation of a more mobile surface structure **5** after cleavage of the hydrogen bond with the nitroxyl group. In the quantum-chemical analysis of the experimentally studied[2,3] two-center coordination of radicals **2** and **3** to the surface of partially dehydroxylated silica gel, we used the three above-mentioned model cluster structures containing geminal (**4**, **5**), vicinal (**6**), and "tetrahedron-separated" (**7**) OH groups. The starting models for all the PSC considered corresponded to the presence of two hydrogen bonds, N···H—O—Si and N—O···H—O—Si with lengths of ~1.9 and ~1.8 Å, respectively, in each of them.

Our MNDO calculations showed that the two-center coordination of imidazoline radicals **2** and **3** to geminal silanol groups is impossible (there is no minimum on the potential energy surface), which can be explained exclusively by geometric reasons. In fact, the distance between the O and N(3) atoms in the radical is 3.5 Å, *i.e.*, it is even somewhat longer than twice the Si—O bond length. Therefore, in these PSC, there are no structural prerequisites for the occurrence of the energetically most favorable linear configurations of the two hydrogen bonds.

Vicinal silanol groups on the silica surface are sufficiently remote from each other; therefore, the conclusion about their ability to form two-center nitroxyl PSC (**6**) can be drawn only with allowance for the energy criterion. The quantum-chemical calculations carried out here indicate that in this case, too, the two-center coordination of imidazoline radicals is impossible, because the starting two-point form of adsorption (**6**) is modified during the full geometry optimization into the one-point form (γ = 180°) bound through the N(3) atom. Moreover, when the lengths of both hydrogen bonds in the PSC were not varied, and their magnitudes were equal to those given in Table 1, this "forced" two-center coordination of radicals **2** and **3** to vicinal silanol groups (**6**) proved to be energetically unfavorable by more than 10 kcal mol^{-1}.

The insertion of an additional silicon-and-oxygen tetrahedron between the vicinal silanol groups substantially increases the distance between these surface AS. The structural, magnetic resonance, electrostatic, and energy parameters found by MNDO calculations for the coordination of imidazoline radicals **2** and **3** simultaneously to both AS of the model $Si_3O_{10}H_8$ cluster (**7**) are listed in Table 2. By comparing the data given in Tables 1 and 2, one can easily see that both hydrogen bonds, H···O and H···N(3), in the two-center PSC (see Table 2) are somewhat longer than those in the corresponding one-center PSC (see Table 1) and are slightly non-linear (γ and γ' differ from 180°), indicating that this type of adsorption is associated with some steric hindrance. However, the degrees of "pyramidality" (φ) of the N(1) atom in one-point- and two-point-adsorbed radicals **2** and **3** are nearly identical.

From comparison of Tables 1 and 2, it follows that the constants of isotropic HFS $a^{N(1)}{}_{iso}$, the spin populations $\rho^{N(1)}$, ρ^{O}, and the charges $Q^{N(1)}$ and Q^{O} on the N(1) and O atoms in the two-center PSC (see Table 2) are nearly equal to the corresponding values for one-center complexes with X = O (see Table 1). Thus, the coordination of imidazoline radicals through the N(3) atom has only a slight effect on their structural, radiospectroscopic, and electrostatic parameters.

It should be noted that although the ratios of spin populations $\rho^{N(1)} : \rho^{O}$ are inverted (see Table 2) with respect to those typical of free radicals **2** and **3** (see Table 1), the fraction of spin transfer from O to N(1) in this case is somewhat lower than that observed in the case of the one-center coordination by the O atom. This implies that the two-center PSC contain weaker hydrogen bonds N—O···H—O—Si than the one-center PSC. The fact that the positive charges Q^{R} on the radical fragments incorporated in the model PSC with two hydrogen bonds (see Table 2) and in the absence of one of them (see Table 1) are fairly close to each other deserves special attention.

In accordance with the calculated complex formation energies ΔE_c (see Table 1 and 2), the two-point adsorption of imidazoline radicals on the surface AS of silica should be much more favorable than the one-point adsorption. The differences between the ΔE_c values indicating the higher efficiency of the coordination of radicals **2** and **3** by both electron-donating centers compared to the coordination *via* the N(3) atom alone amount to ~8 kcal mol^{-1} and are in good agreement with the experimentally determined[2] enthalpies of transition of the slowly rotating imidazoline adsorption forms into the rapidly rotating ones. The fact that the calculated radiospectroscopic and energy characteristics of PSC are actually insensitive to the presence of the rather bulky phenyl group in the imidazoline ring was also confirmed experimentally.

Thus, the results of our quantum-chemical calculations demonstrate that nitroxides of the imidazoline series are capable of forming both one-center and two-center PSC with different AS of partially dehydroxylated silica gel. Judging from the calculated complex formation energies ΔE_c, in the case of one-point adsorption, these radicals are preferentially coordinated to these AS *via* the electron-donating N(3) atom of the five-membered ring rather than *via* the nitroxyl group, whereas for similar imidazoline PSC formed with "structurally rigid" LAS on Al_2O_3 this energy difference is not so pronounced.[12,13] In addition, the stabilization energy for the one-point coordination of these radicals to the "minimum"[18] cluster LAS $Al(OH)_3$ is even larger than that found for the simultaneous coordination to the two AS of the extended cluster $Si_3O_{10}H_8$ (**7**).

We would like to stress that it is this "optimal" cluster that makes it possible to find easily an adequate quantum-chemical interpretation of the whole combination of available radiospectroscopic and thermochemical data[2,3] concerning the adsorption of paramagnetic imidazoline derivatives on the surface of silica. Simpler cluster structures containing only vicinal or, especially, geminal silanol groups are not suitable for this purpose, as they are incapable of accomplishing two-center coordination of nitroxides of the imidazoline series because of substantial steric hindrances. The results obtained upon extension of the cyclic cluster model **7** by adding one more silicon-and-oxygen tetrahedron followed by analogous calculations with partial geometry optimization (optimization of the Si—O—Si angles between the "paired" tetrahedra) were practically identical to the results presented in Table 2.

This work was supported by the Russian Foundation for Basic Research (Project No. 95-03-08196a).

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Received October 27, 1997