Chemistry of Heterocyclic Compounds, Vol. 38, No. 12, 2002

ELECTRONIC STRUCTURE, AROMATICITY, AND PHYSICOCHEMICAL CHARACTERISTICS OF CARBENE, RADICAL, AND IONIC FORMS OF COMPOUNDS OF THE IMIDAZOLE SERIES, AND THEIR OXO AND THIO ANALOGS*

Yu. B. Vysotsky, V. S. Bryantsev, and O. A. Gorban

The effects of benzannellation, phenyl substitution at the nitrogen atom, protonation at the carbene carbon, ionization, and the state of the carbene center (σ^2 or π^2) on the electronic structure, diamagnetic susceptibility, induced π-electron ring currents, the ^1H, ^{13}C, and ^{14}N chemical shifts, and the energies of the lowest electronic transitions of imidazol-2-ylidenes and their oxo and thio analogs were examined in the bound version of π-electron perturbation theory. The calculated and experimental data are compared.

Keywords: carbenes, aromaticity, diamagnetic susceptibility, chemical shifts, electronic structure, electronic spectra.

The first report on the synthesis and preparative isolation of 1,3-diadamantylimidazol-2-ylidene – a stable nucleophilic carbene that can be recrystallized at 240-241°C without decomposition – appeared in 1991 [1]. More recently other derivatives of imidazol-2-ylidene with less bulky substituents have successfully synthesized and isolated [2-4] (e.g., 1,3-dimethylimidazol-2-ylidene). This indicates that the high stability of such compounds is due not so much to steric factors as to electronic factors.

In turn, the results of the investigation have prompted a large number of papers on the quantum-chemical investigation of the geometric and electronic structure of singlet nucleophilic heterocarbenes (e.g., see [5-10]). According to data in [5, 6], π-electron delocalization is not the deciding factor in the stabilization of carbenes of the imidazol-2-ylidene type. However, subsequent analysis of the distribution of electrostatic potential and thermodynamic and magnetic characteristics showed [7-10] that the given carbenes and also the corresponding oxo and thio analogs possess additional stabilization compared with saturated and alicyclic carbenes, although the various criteria lead to various assessments of their "aromaticity."

Stable peaks corresponding to the thiazol-2-ylidene radical-cation were recently recorded in the mass spectra [11], and the ESR spectra of a series of radical-anion carbenes have been recorded [12]. It is not, therefore, impossible that the particles also possess aromatic characteristics and may participate as intermediates

---

* The results were presented in part at the First All-Russia Conference on the Chemistry of Heterocycles, Suzdal, 2000.

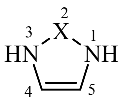
Donbass State Academy of Building and Architecture, Makeevka, Donetsk Region, Ukraine; e-mail: YuB@vysot.dn.ua. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1643-1664, December, 2002. Original article submitted November 30, 2000.

in various chemical processes. In this connection it seemed of definite interest to compare their physicochemical characteristics with the characteristics of both neutral carbenes and noncarbene reactive particles.

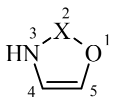
The aim of the present work was to investigate the effect of the state of the carbene center (σ^2- and π^2-carbene), the total charge of the system, the type of heteroatom, and the effects of N-phenyl substitution and benzannellation on the various molecular physicochemical characteristics of the ylidenes in terms of the bound version of perturbation theory by the restricted (for closed electron shells) and unrestricted (for open electron shells) Hartree–Fock methods and also to compare them with the corresponding radicals and ions.

As was demonstrated in [13-16], the physicochemical characteristics and thermal rearrangements of planar singlet π-electron monocyclic carbenes and naphthyl- and phenylcarbenes, having a lacuna both in the π-shell and in the σ-shell, can be described fairly accurately in terms of the π-electron approximation. In this case the coulombic integral of the carbene atom W_C in relation to its state (for a σ^2-carbene $n = 0$, while for a π^2-carbene $n = 2$) is related to the coulombic integral $W_{C^\cdot}$ of the carbon atom supplying one electron to the π-system by the following equation: $W_C = W_{C^\cdot} - (-1)^{n/2} \times \Gamma_{C^\cdot C^\cdot}/2$. Here the resonance integrals and the integrals of interelectronic interaction $\Gamma_{C^\cdot C^\cdot}$ were assumed to be independent of the type of carbon atom. The parameters of the π-electron Hamiltonian for the nitrogen, oxygen, and sulfur atoms correspond to those adopted in [17, 18]. The diamagnetic susceptibilities and π-electron ring currents were calculated as before by the method in [19], the energies of the singlet and doublet transitions were calculated as eigen values of the stability of the Hartree–Fock ground state [20, 21], and triplet transitions were calculated in the Tamm–Dankov approximation [20]. The standard method was used to calculate the physicochemical characteristics of the systems with conjugated bonds in the bound version of π-electron perturbation theory by the unrestricted Hartree–Fock method [21].

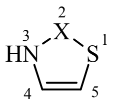
The following carbenes were examined: Imidazol-2-ylidene (**1**); oxazol-2-ylidene (**2**); thiazol-2-ylidene (**3**); benzimidazol-2-ylidene (**4**); benzoxazol-2-ylidene (**5**); benzothiazol-2-ylidene (**6**); 1,2,4-triazol-3-ylidene (**7**); N,N-diphenylimidazol-2-ylidene (**8**); dipyrido[*c*,*e*]imidazol-6-ylidene (**9**). For comparison, apart from actually existing aromatic σ^2-heterocarbenes (compounds **1a**-**9a**), the π^2-carbenes **1d**-**9d** and also the corresponding radical-cations **1b**,**e**–**9b**,**e**, the radical-anions **1c**,**f**–**9c**,**f**, the radicals **1g**-**9g**, and ions with a closed electron shell (compounds **1h**,**i**–**9h**,**i**) were also calculated.



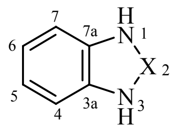
1a–i



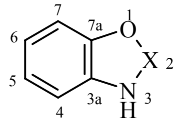
2a–i



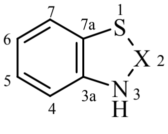
3a–i



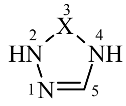
4a–i



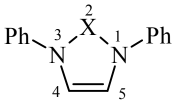
5a–i



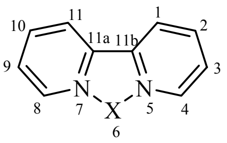
6a–i



7a–i



8a–i



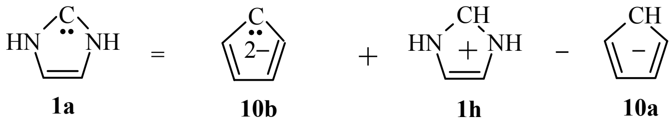
9a–i

a X = σ^2 C: (σ^2-carbene); **b** X = σ^2 $C^{\cdot+}$ (σ^2-radical-cation carbene); **c** X = σ^2 $C^{\cdot-}$ (σ^2-radical-anion carbene);
d X = π^2 C: (π^2-carbene); **e** X = π^2 $C^{\cdot+}$ (π^2-radical-cation carbene); **f** X = π^2 $C^{\cdot-}$ (π^2-radical-anion carbene);
g X = $C^\cdot$ (radical); **h** X = C^+ (cation); **i** X = C^- (anion)

The residual π-electron charges at the atoms of the imidazole, oxazole, and thiazole rings, which are the main structural fragments of the stable singlet conjugated heterocarbenes, were calculated (Table 1). According to the calculations, irrespective of the charge of the system, all the σ^2-carbenes have a large negative residual π-electron charge at the carbene atom, and this corresponds to the experimental evidence for the manifestation of nucleophilic characteristics by the carbenes [1-4]. Here, on the other hand, large positive residual π-electron charges, close in value to the charges at the N atom in the pyrrole molecule ($q_N = 0.371$) and the O atom in the furan molecule ($q_0 = 0.275$), which change to a lesser degree during ionization than the charges at the noncarbene C atoms, are concentrated at the nitrogen and oxygen atoms. For example, the charge on the C=C fragment in imidazol-2-ylidene, equal to -0.161, increases in absolute value to -0.996 in the transition to the radical-anions, while in the radical-cation carbenes it is equal to +0.600, whereas the charge at the nitrogen atoms amounts to 0.349, 0.308, and 0.376 respectively. We note that the electron distribution both in the neutral σ^2-carbenes and in the radical-ions agrees well with the presence of the corresponding ionic resonance structures.

Benzannellation of the neutral σ^2-heterocarbenes **1a-3a** at the 4–5 bond, unlike condensation at the 3–4 or 1–5 bonds (leading to a perceptible increase in the absolute value of the charge at the carbene carbon atom), leads to a decrease (in absolute value) of the residual π-electron charge at the carbene carbon atom and to a less well-defined decrease at all the other atoms of the heteroring. In the case of the radical-cation and radical-anion carbenes, present in both the σ^2- and the π^2-states, annellation at the 4–5 bond leads to a certain increase in the absolute value of the charge at the carbene center, i.e., to increase of its "philicity," which is most clearly seen in the case of the sulfur-containing heterocycles.

As demonstrated earlier in [22], the parameters of the electronic structure of the oxazolium cation can be calculated approximately as the sum of the corresponding charges and the bond orders of pyrrole and furan after deduction of the corresponding values for the cyclopentadienyl anion. This superposition–additive approach is based on the idea of additivity in the contributions from the atoms to the chemical bonds formed by them with the superimposition of several molecular graphs [23]. Thus, for example, the result of the superimposition of the structure of the cyclopentadienyl anion (structure **10a**) and imidazol-2-ylidene (**1a**) coincides with the superimposition of the structure of the imidazolium cation (structure **1h**) and the σ^2-cyclopentadienylene dianion (structure **10b**). This makes it possible to describe the molecular structure and the physicochemical characteristics of one molecule, if the structure and characteristics of three other molecules are known, in particular for the example presented above, according to the following superposition-additive scheme:



Analogous superposition-additive schemes can be written for the other carbenes.

Thus, the charges and bond orders in the σ^2-carbenes **1a-3a** are as follows: σ^2-carbene **1a** $q_1 = 0.277$ (0.349); $q_2 = -0.437$ (-0.535); $q_4 = -0.058$ (-0.081); $P_{12} = 0.611$ (0.594); $P_{34} = 0.414$ (0.424); $P_{45} = 0.801$ (0.837); **2a** $q_1 = 0.165$ (0.274); $q_2 = -0.378$ (-0.498); $q_3 = 0.288$ (0.351); $q_4 = -0.052$ (0.059); $q_5 = -0.021$ (-0.061); $P_{12} = 0.536$ (0.527); $P_{23} = 0.636$ (0.583); $P_{34} = 0.409$ (0.423); $P_{45} = 0.811$ (0.851); $P_{51} = 0.357$ (0.380); **3a** $q_1 = 0.103$ (0.128); $q_2 = -0.431$ (-0.492); $q_3 = 0.309$ (0.393); $q_4 = 0.065$ (0.059); $q_5 = -0.045$ (-0.088); $P_{12} = 0.829$ (0.714); $P_{23} = 0.597$ (0.580); $P_{34} = 0.458$ (0.478); $P_{45} = 0.745$ (0.797); $P_{51} = 0.591$ (0.520).

Comparing the obtained data with the results of direct calculation (in parentheses), we see that the employed approach does give a correct qualitative picture of the electron distribution in the case of carbene particles. In the calculation the residual π-electron charges and bond orders of the cations **1h-3h** (presented in Tables 1 and 2), the σ^2-cyclopentadienylidene dianion ($q_1 = -0.815$; $q_2 = -0.326$; $q_3 = -0.266$; $P_{12} = 0.664$; $P_{23} = 0.573$; $P_{34} = 0.664$, taken from [13]), and the cyclopentadiene anion, determined fully by the symmetry of the task ($q = -0.200$), were used.

According to the presented data, the superposition-additive approach makes it possible to obtain an approximate estimate of the distribution of charges and physicochemical characteristics of the reactive particles (carbenes) on the basis of the characteristics of their stable heterocationic analogs. For example, it follows from the presented superposition-additive scheme that the difference in the charges and also in the ^{13}C chemical shifts at atom 2 in the carbenes **1a-3a** and, accordingly, in the cations **1h-3h** is approximately the same (see below).

TABLE 1. The Residual π-Electron Charges of Carbenes and the Corresponding Radicals and Ions (in a Five-membered Ring)

Compound	P_{ii}	σ^2-Carbenes			π^2-Carbenes			Radicals, ions		
		a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
1	2	3	4	5	6	7	8	9	10	11
1	1	0.349	0.376	0.308	0.120	0.287	0.053	0.259	0.403	0.150
	2	-0.535	-0.352	-0.620	0	0.443	0	-0.333	0.178	-1.000
	4	-0.081	0.300	-0.498	-0.120	-0.009	-0.553	-0.093	0.008	-0.150
2	1	0.274	0.270	0.258	0.089	0.202	0.047	0.198	0.291	0.185
	2	-0.498	-0.320	-0.590	0	0.476	0	-0.308	0.237	-0.932
	3	0.351	0.384	0.312	0.124	0.302	0.050	0.266	0.414	0.072
	4	-0.067	0.318	-0.495	-0.103	0.006	-0.557	-0.073	0.014	-0.228
	5	-0.061	0.347	-0.485	-0.110	0.014	-0.540	-0.084	0.045	-0.097
3	1	0.128	0.282	-0.032	-0.071	0.129	-0.215	0.035	0.229	-0.166
	2	-0.492	-0.319	-0.556	0.100	0.472	0.084	-0.247	0.184	-0.767
	3	0.393	0.407	0.326	0.145	0.311	0.084	0.292	0.435	0.162
	4	0.059	0.376	-0.377	0.010	0.104	-0.406	0.026	0.131	-0.033
	5	-0.088	0.255	-0.361	-0.185	-0.015	-0.547	-0.106	0.021	-0.196
4	1	0.320	0.337	0.332	0.155	0.271	0.109	0.273	0.373	0.271
	2	-0.480	-0.358	-0.623	0.063	0.502	0.015	-0.224	0.245	-0.553
	3a	-0.022	0.192	-0.085	-0.003	-0.026	-0.113	-0.011	-0.032	-0.007

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11
5	1	0.252	0.242	0.269	0.115	0.189	0.084	0.205	0.268	0.213
	2	-0.444	-0.330	-0.592	0.062	0.537	0.016	-0.207	0.303	-0.544
	3	0.322	0.356	0.335	0.156	0.284	0.113	0.273	0.387	0.273
	3a	-0.018	0.221	-0.081	0.000	-0.026	-0.090	-0.008	-0.032	-0.006
	7a	-0.009	0.165	-0.071	0.011	-0.009	-0.122	0.005	-0.011	0.015
6	1	0.127	0.163	0.026	-0.054	0.114	-0.145	0.043	0.210	-0.090
	2	-0.446	-0.377	-0.601	0.155	0.519	0.112	-0.166	0.239	-0.495
	3	0.360	0.402	0.352	0.151	0.293	0.140	0.290	0.407	0.241
	3a	0.044	0.206	0.047	0.034	0.031	0.008	0.0041	0.036	0.062
	7a	-0.048	-0.036	-0.105	-0.046	-0.037	-0.304	-0.030	-0.034	0.004
7	1	-0.304	0.067	-0.566	-0.381	-0.332	-0.632	-0.380	-0.294	-0.602
	2	0.316	0.337	0.269	0.022	0.262	0.015	0.204	0.393	0.009
	3	-0.480	-0.315	-0.597	0.031	0.542	0.004	-0.234	0.306	-0.622
	4	0.346	0.407	0.317	0.217	0.316	0.075	0.336	0.386	0.345
	5	0.122	0.504	-0.424	0.112	0.212	-0.461	0.075	0.209	-0.130
8	1	0.378	0.407	—*	0.236	0.329	—*	0.342	0.429	0.372
	2	-0.533	-0.363	—*	0.093	0.427	—*	-0.250	0.137	-0.448
	4	-0.084	0.206	—*	-0.007	-0.017	—*	-0.079	-0.007	-0.091
9	5	0.447	0.439	0.409	0.341	0.385	0.293	0.438	0.473	0.405
	6	-0.641	-0.462	-0.666	0.149	0.273	0.134	-0.126	-0.112	-0.142
	11a	-0.093	0.002	-0.091	-0.175	-0.082	-0.162	-0.065	-0.046	-0.074

---

* For these systems use of the one-electron approximation is incorrect on account of the partial filling of the degenerate molecular orbitals, and it is necessary to use configuration interaction.

We stress that to obtain satisfactory results in the superposition-additive approach it is necessary also that the state of the carbene center (σ^2 or π^2) and the nature of the rings participating in superposition (aromatic or antiaromatic) in the superimposed structures are identical. If the result of superimposition here can be obtained by different methods, the accuracy of the description increases with increase in the region of intersection of the superimposed molecular graphs (e.g., see [23]).

As shown by analysis of the distribution of charges and bond orders (Tables 1 and 2), the neutral **1d-8d** and negatively charged π^2-carbenes **1f-8f** are unstable with respect to cleavage of the 1–2 or 2–3 bonds, i.e., the possibility of elimination of the carbene atom cannot be ruled out for these systems. This is demonstrated, in part, by the zero or even negative (systems **2f**, **3f**, and **7d**,**e**) values for the orders of the bond with the carbene center and also by the close to zero charges on it. A similar picture is observed for the corresponding anions with closed electron shells **1i-3i**, which as will be demonstrated below are antiaromatic. As expected, increase in the size of the conjugated system (the introduction of N-phenyl substituents or benzannellation) for these systems leads to some stabilization, which corresponds to the increase in the order of the bond between the heteroatom and the carbon atom at which the carbene center is generated. Here, the greatest stabilizing effect is achieved in the anions, e.g., in **1i** $P_{12} = 0$, in **4i** $P_{12} = 0.282$, in **7i** $P_{12} = 0.344$, and in **9i** $P_{56} = 0.528$. Whereas substitution with phenyl affects the strength of the bond with the carbene atom in the radical-anions rather more than in the neutral π^2-carbenes (e.g., for the neutral carbene **7d** $P_{12} = 0.096$, while for the anion-radical **7f** $P_{12} = 0.156$), benzannellation both at bond *d* and at bonds *c* and *e* on the other hand has a greater stabilizing effect on the neutral π^2-carbenes than on their radical-anions (e.g., for the neutral carbene **4d** $P_{12} = 0.065$, while for the radical-anion **4f** $P_{12} = 0.018$).

It is interesting to note that in the respective radicals **1g-3g** and π^2-radical-cation carbenes **1e-3e** (as also in the case of the antiaromatic systems **1d**,**f**,**i**–**3d**,**f**,**i**) the weakest is the heteroatom–X_2 bond. For the uncharged σ^2-carbenes **1a-3a**, as also for their radical-anions **1c-3c** and the corresponding cations **1h-3h**, this is the bond between the heteroatom and the noncarbene carbon atom, and for the σ^2-radical-cation carbenes **1b-3b** it is either the $C_{(4)}$–$C_{(5)}$ bond or the heteroatom–$C_{(2)}$ bond, which are equally strong. All this also holds for the annellated systems **4-6** and for structure **8** with the exception of the radical-cation **8b**, for which the order of the 1–5 bond and not the 4–5 bond is minimum. We note that a weak antibonding effect from the introduction of phenyl groups on the weakest bond arises in the uncharged σ^2-carbenes and cations (cf. structures **1a**,**h** and **8a**,**h**), whereas in structures **1c-g**,**i** phenyl substitution leads to an increase in the strength of this bond. *d*-Benzannellation gives a similar effect, weakening the weakest bonds in the uncharged σ^2-carbenes and cations. At the same time, annellation at bonds *c* and *e* leads to the result that it is they that become the most vulnerable both in the σ^2-carbenes **9a**,**b**,**c** and in the corresponding noncarbene particles **9g**,**h**,**i** (the weakest in the π^2-carbenes **9d-f** is 5–6 bond). As concerns the position of the strongest bonds in structures **4-6**, it is determined by the aromatic characteristics of the annellated substrate; if the initial unannellated five-membered ring is characterized by positive values of *I* (diamagnetic currents), bonds 4–5 or 6–7 are strongest (systems **4a**,**b**,**e**,**h**–**6a**,**b**,**e**,**h**); if the values of *I* are negative (paramagnetic currents), bond 5–6 is strongest (systems **4c**,**d**,**f**,**g**,**i**–**6c**,**d**,**f**,**g**,**i**). Having analyzed the closest bond orders in the five-membered ring, we note that the presence of the pyridine nitrogen in the heteroring (system **7**) leads to the result that the N–N bond is weaker that the noncarbene N–C bond in all the examined forms.

One of the easiest modes of transformation of the antiaromatic states in carbenes is their transition from the σ^2-state to the π^2-state and *vice versa* with the formation of an aromatic system by electron "jumps." In this connection all the examined carbenes will actually exist in the σ^2-forms **1a-9a** and not in the π^2-states **1d-9d**. Calculations by all-valence and *ab initio* methods will also give the geometry of the σ^2-carbenes. At the same time, if an antiaromatic state nevertheless arises, e.g., as transition state, another general possibility for escape from it is a change in the geometry of the molecule, destruction of the cyclicity of the π-electron shell by cleavage of one or several π-bonds (e.g., elimination of an atom or group of atoms), or the formation of a new bond between not directly bonded atoms [24].

TABLE 2. The π-Electron Bond Orders of the Carbenes, Radicals, and Ions*

Compound	P_{ii}	σ²-Carbenes			π²-Carbenes			Radicals, ions		
		a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
1	2	3	4	5	6	7	8	9	10	11
1	1-2	0.576	0.481	0.591	0.000	0.286	0.000	0.302	0.594	0.000
	3-4	0.424	0.549	0.275	0.325	0.435	0.153	0.391	0.488	0.357
	4-5	0.837	0.449	0.389	0.880	0.803	0.553	0.849	0.785	0.850
	1-3	-0.104	-0.125	-0.199	**0.120**	-0.081	**0.053**	-0.015	-0.196	**0.150**
2	1-2	0.527	0.449	0.548	0.002	0.247	0.002	0.272	0.519	0.112
	2-3	0.583	0.484	0.601	0.002	0.308	-0.002	0.314	0.619	-0.070
	3-4	0.423	0.558	0.275	0.334	0.443	0.149	0.401	0.483	0.235
	5-1	0.380	0.460	0.260	0.281	0.375	0.147	0.338	0.431	0.409
	4-5	0.851	0.454	0.390	0.894	0.811	0.451	0.861	0.795	0.835
	1-3	-0.099	-0.111	-0.184	**0.105**	-0.072	**0.049**	-0.017	-0.172	**0.115**
	2-4	-0.227	**0.007**	-0.272	-0.006	-0.213	**0.006**	-0.151	-0.349	**0.229**
	2-5	-0.280	-0.045	-0.300	**0.006**	-0.222	-0.006	-0.139	-0.413	-0.247
3	1-2	0.714	0.555	0.728	0.028	0.404	-0.005	0.417	0.812	0.105
	2-3	0.580	0.498	0.583	0.014	0.274	0.026	0.311	0.580	0.021
	3-4	0.478	0.575	0.284	0.379	0.476	0.221	0.429	0.532	0.386
	5-1	0.520	0.770	0.429	0.307	0.561	0.116	0.466	0.665	0.360
	4-5	0.797	0.451	0.404	0.869	0.761	0.459	0.824	0.729	0.857
	1-3	-0.153	-0.190	-0.255	**0.139**	-0.137	**0.057**	-0.044	-0.298	**0.163**
	3-5	-0.179	-0.089	**0.020**	-0.339	-0.145	-0.185	-0.229	-0.072	-0.361
	2-4	-0.175	**0.036**	-0.150	**0.005**	-0.158	-0.034	-0.078	-0.294	**0.057**
	2-5	-0.288	-0.051	-0.336	**0.078**	-0.169	**0.116**	-0.142	-0.370	**0.050**
4	1-2	0.564	0.497	0.567	0.065	0.308	0.018	0.362	0.601	0.282
	3-3a	0.380	0.462	0.394	0.381	0.386	0.306	0.404	0.407	0.464
	3a-7a	0.595	0.355	0.660	0.562	0.572	0.691	0.573	0.583	0.561
	3a-4	0.601	0.570	0.457	0.640	0.599	0.457	0.606	0.577	0.552
	4-5	0.694	0.726	0.528	0.615	0.692	0.495	0.638	0.714	0.490
	5-6	0.639	0.442	0.730	0.696	0.632	0.750	0.677	0.616	0.760
	1-3	-0.131	-0.143	-0.149	**0.021**	-0.122	**0.064**	-0.095	-0.223	-0.084

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11
5	1-2	0.513	0.473	0.520	0.054	0.262	0.016	0.316	0.518	0.252
	2-3	0.574	0.493	0.576	0.065	0.330	0.020	0.363	0.631	0.285
	3-3a	0.377	0.489	0.393	0.384	0.387	0.317	0.400	0.404	0.465
	1-7a	0.342	0.369	0.362	0.333	0.336	0.269	0.355	0.362	0.419
	3a-7a	0.604	0.378	0.664	0.569	0.577	0.695	0.581	0.586	0.565
	1-3	-0.122	-0.123	-0.138	**0.021**	-0.104	**0.057**	-0.080	-0.194	-0.074
	2-3a	-0.141	**0.004**	-0.245	-0.117	-0.191	-0.042	-0.183	-0.274	-0.307
6	1-2	0.685	0.715	0.678	0.103	0.426	0.037	0.468	0.805	0.345
	2-3	0.588	0.516	0.545	0.061	0.304	0.052	0.363	0.603	0.215
	3-3a	0.407	0.515	0.422	0.380	0.409	0.366	0.405	0.437	0.441
	1-7a	0.445	0.443	0.474	0.391	0.487	0.216	0.467	0.535	0.530
	3a-7a	0.584	0.530	0.579	0.566	0.543	0.479	0.564	0.545	0.535
	1-3	-0.185	-0.127	-0.198	**0.033**	-0.196	**0.030**	-0.131	-0.337	-0.070
	2-7a	-0.197	-0.150	-0.309	-0.039	-0.163	**0.049**	-0.176	-0.291	-0.241
7	2-3	0.615	0.521	0.576	-0.026	0.333	-0.007	0.332	0.664	0.057
	3-4	0.534	0.423	0.604	0.082	0.319	0.016	0.393	0.570	0.361
	4-5	0.464	0.637	0.301	0.491	0.513	0.200	0.521	0.484	0.548
	1-2	0.302	0.423	0.177	0.116	0.268	0.075	0.193	0.351	-0.059
	5-1	0.840	0.397	0.430	0.829	0.784	0.445	0.751	0.814	0.589
	2-4	-0.113	-0.135	-0.205	**0.069**	-0.111	**0.034**	-0.083	-0.203	-0.054
	2-5	-0.223	-0.116	-0.004	-0.156	-0.108	-0.091	-0.091	-0.160	**0.086**
	1-3	-0.226	**0.012**	-0.147	**0.139**	-0.125	**0.036**	0.001	-0.325	**0.388**
	3-5	-0.124	**0.090**	-0.301	-0.186	-0.230	-0.044	-0.325	-0.186	-0.574
8	1-2	0.560	0.469	—*[2]	0.096	0.290	—*[2]	0.369	0.579	0.344
	3-4	0.416	0.533	—*[2]	0.356	0.438	—*[2]	0.408	0.483	0.420
	4-5	0.836	0.525	—*[2]	0.862	0.796	—*[2]	0.835	0.781	0.826
	1-3	-0.097	-0.128	—*[2]	**0.037**	-0.088	—*[2]	-0.064	-0.187	-0.062
9	5-6	0.550	0.482	0.560	0.153	0.241	0.144	0.514	0.506	0.528
	7-11a	0.380	0.417	0.350	0.300	0.389	0.283	0.402	0.445	0.370
	11a-11b	0.614	0.475	0.554	0.726	0.586	0.597	0.471	0.532	0.437
	5-7	-0.052	-0.074	-0.120	**0.019**	-0.054	-0.026	-0.196	-0.130	-0.271

---

* The positive values of the long-range bond orders, arising in the five-membered ring, are shown in bold type.

*[2] See the note in Table 1.

In the first case there is either loss of coplanarity in the conjugated system or the formation of double and single bonds, leading to quinoid structures. As an illustration we will consider the nature of the distribution of the bond orders, to which the bond lengths are closely related, in the condensed benzene rings of systems 4-6. As found, the pattern of the distribution of the bonds is determined by the overall charge of the system and by the type of carbon atom at position 2 and not by the type of heteroatom. In this connection the corresponding π-electron bond orders in the benzene ring for only benzimidazol-2-ylidene (**4**) are given in Table 2 as an illustration. As follows from the calculation, substantial localization of the bond orders in the benzene ring occurs in the σ^2- and π^2-radical-anions, in the σ-radical-cations and anions, i.e., in the rings that are characterized by negative values for the induced π-electron ring currents *I* flowing in them (Table 3) and are, consequently, antiaromatic according to the magnetic criteria. We note also that in systems having weak paramagnetic (or diamagnetic) character and substantial localization of the bonds (e.g., **1c-3c** and **7c**), further optimization of the geometry leads to a decrease of antiaromaticity (an increase of aromaticity) and even to the appearance of weak aromaticity, and this to some extent indicates the possibility of stabilization of such systems. The recording of an ESR spectrum for the radical-anion of the triphenyl-substituted 1,2,4-triazol-3-ylidene can obviously be associated with this fact [12].

In the case of escape from the antiaromatic state by the formation of new bonds, when one of the stages of this reaction is electrocyclic ring closure, the orders of bonds between not directly bonded atoms (the long-range bond orders $P_{ik}(0)$) act as reactivity indices [25]. Here their value determines the rate, while the sign determines the stereospecificity of the reaction. As seen from Table 2, in which all the positive values of the long-range bond orders arising in the five-membered ring are given (shown in bold type), rearrangements of this ring with the subsequent formation of an aromatic system can be realized in the antiaromatic anions, π^2-carbenes and their radical-anions (with the formation of a C–C: or HN–NH(O,S) bond in structures **1d**,**f**,**i-8d**,**f**,**i** and **9d**, in the σ^2-radical-cations (with the formation of the 2–4 bond in **2b**, **3b**, and **5b** and the 1–3 or 3–5 bond in **7b**), and in the σ^2-radical-anions (with the formation of the 3–5 bond in **3c**).

As an example we will present the possible skeletal rearrangements of the oxazolium anion **2i**. In the scheme the orders of the forming $P_{ik}(0)$ and breaking P_{ik} bonds are shown alongside the arrows. The large positive order of the long-range bond 2–4 and also the negative order of the 2–3 bond give rise to the preferred formation of the anion **11i** by path **A**, although the latter may also be formed (less likely) through structure **13i** (path **B**) or through the anions **15i** and/or **17i** (path **C**). The analogous formation of structure **12i**, in which the pyrrole nitrogen atom departs from the ring, is difficult and, with small probability, possibly only by path **D**. As follows from the calculation, the reaction products – the anions **11i** and **12i** – as a result of the aromatic character of their rings (the number of electrons in the ring corresponds to the $2n+2$ rule) are hardly susceptible at all to further rearrangements. (Only for these compounds are the long-range bond orders $P_{ik}(0)$ substantially less than the order of the weakest bond.)

The scheme corresponds not only to a synchronous but also to an asynchronous mechanism of recyclization, when cleavage of the old bonds occurs initially, followed by the formation of new bonds, since calculation of the corresponding π-acyclic forms fully repeats the conclusions made above. (Analogous schemes can easily be obtained from the data in Table 2 for the other examined structures.)

Benzannellation and phenyl substitution of π^2-carbenes and their radical-anions as a rule lead to a substantial decrease in the probability of their recyclization, and it is not at all characteristic for the anions. We note that among the examined π^2-carbenes compounds **7d**, **7b**, and **7i** have the largest values for the long-range bond orders as a result of the destabilizing effect of the pyridine nitrogen.

Passing on to a description of the physicochemical characteristics we will dwell primarily on the diamagnetic susceptibility and π-electron ring currents, which are some of the quantitative criteria of aromaticity–antiaromaticity and make it possible to include the investigated compounds in a single scale of aromaticity–antiaromaticity. The π-electron contributions to the diamagnetic susceptibilities χ^π and the induced π-electron ring currents of the carbene particles investigated in the present work and also their noncarbene

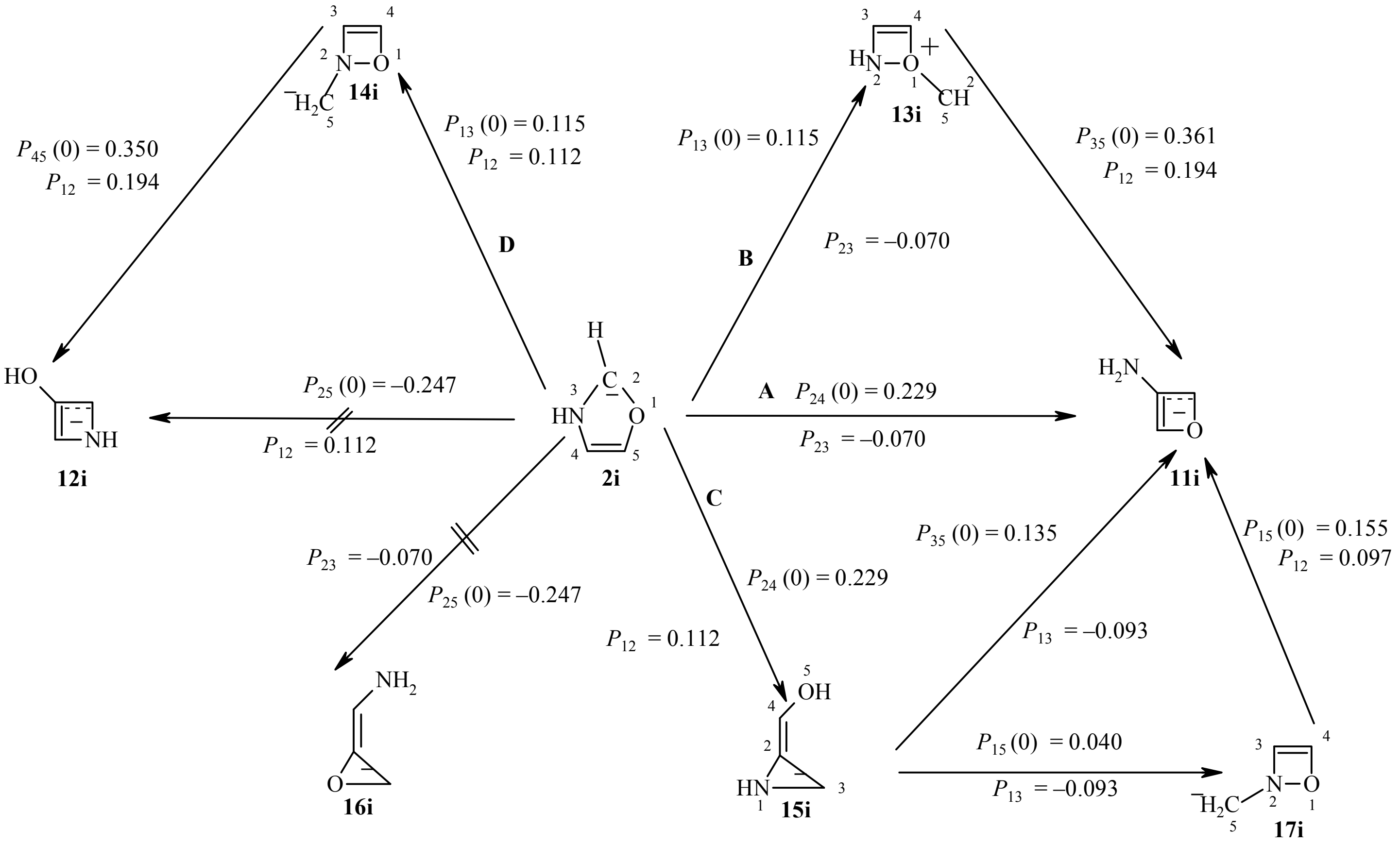

2i
11i
12i
13i
14i
15i
16i
17i
A
B
C
D
$P_{24}(0) = 0.229$
$P_{23} = -0.070$
$P_{13}(0) = 0.115$
$P_{23} = -0.070$
$P_{35}(0) = 0.361$
$P_{12} = 0.194$
$P_{13}(0) = 0.115$
$P_{12} = 0.112$
$P_{45}(0) = 0.350$
$P_{12} = 0.194$
$P_{25}(0) = -0.247$
$P_{12} = 0.112$
$P_{23} = -0.070$
$P_{25}(0) = -0.247$
$P_{24}(0) = 0.229$
$P_{12} = 0.112$
$P_{35}(0) = 0.135$
$P_{13} = -0.093$
$P_{15}(0) = 0.155$
$P_{12} = 0.097$
$P_{15}(0) = 0.040$
$P_{13} = -0.093$

TABLE 3. The π-Electron Contributions to the Diamagnetic Susceptibilities χ^{π} (in -10^{-6} cm^3/mol and the Induced Ring Currents *I** for the Carbenes and the Corresponding Radicals and Ions

Com-pound		σ^2-Carbenes			π^2-Carbenes			Radicals, ions		
		a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
1	χ^{π}	12.70	0.96	–2.71	–18.02	3.98	-4.88	-5.87	17.34	—*[2]
	I	0.615	0.047	-0.131	-0.872	0.193	-0.236	-0.284	0.748	—*[2]
2	χ^{π}	12.47	2.03	-3.11	-18.14	4.19	-5.215	-5.19	15.14	—*[2]
	I	0.604	0.098	-0.150	-0.878	0.203	-0.252	-0.251	0.733	—*[2]
3	χ^{π}	16.59	0.05	-18.12	-30.63	0.54	-8.82	-15.40	19.98	-1479
	I	0.679	0.002	-0.741	-1.253	0.022	-0.361	-0.630	0.818	-60.52
4	χ^{π}	45.13	-158.0	-46.19	1.50	35.22	-133.1	15.43	49.57	-102.9
	I	0.580 (1.062)	-1.212 (-4.263)	0.063 (-1.522)	-0.612 (0.454)	0.319 (0.918)	0.112 (-4.340)	-0.064 (0.537)	0.783 (1.070)	-1.779 (-2.121)
5	χ^{π}	44.78	-146.1	-48.08	2.92	35.65	-133.5	17.89	49.12	-102.0
	I	0.562 (1.063)	-0.848 (-4.122)	0.034 (-1.564)	-0.609 (0.497)	0.320 (0.931)	0.108 (-4.350)	-0.062 (0.675)	0.762 (1.069)	-1.829 (-2.058)
6	χ^{π}	48.46	-166.4	-42.32	-4.16	33.21	-52.75	15.37	54.29	-88.20
	I	0.640 (1.054)	-1.063 (-4.510)	-0.218 (-1.188)	-0.809 (0.501)	0.249 (0.871)	-0.081 (-1.631)	-0.169 (0.627)	0.869 (1.062)	-2.056 (-1.220)
7	χ^{π}	9.51	-3.27	0.28	-16.32	3.970	-3.33	-3.49	11.61	-86.69
	I	0.460	-0.158	0.013	-0.790	0.192	-0.161	-0.169	0.562	-4.196
8	χ^{π}	73.15	50.89	—*	44.32	64.33	—*	54.63	75.90	-38.74
	I	0.571 (0.982)	-0.094 (0.846)	—*	-0.407 (0.845)	0.213 (0.960)	—*	0.086 (0.847)	0.723 (0.976)	-0.462 (-0.469)
9	χ^{π}	72.39	51.22	-129.9	-720	-62.37	-164.2	-266.6	87.71	—*[2]
	I	1.215 (0.758)	0.442 (0.674)	0.010 (-2.085)	-7.352 (-9.103)	-0.846 (-0.720)	-0.671 (-2.409)	-1.933 (-3.632)	1.156 (1.023)	—*[2]

---

* The current flowing in a five-membered ring is given, and the current in a six-membered ring is given in parentheses.

*[2] See the note in Table 1.

analogs are presented in Table 3. From the presented data it is seen that the heterocarbenes in the σ^2-state, like the cations, are characterized by diamagnetic currents, and their aromaticity depending on the type of heteroatom increases in the order: **7a** < **2a** ≤ **1a** < **3a** (**7h** < **2h** < **1h** < **3h** for the cations). The antiaromatic characteristics increase in the same order for the radicals **1g-3g**, **7g**, but the order is different for the aromatic π^2-radical-cation carbenes: **3e** < **7e** ≤ **1e** < **2e**. From the superposition–additive scheme (see above) it follows that the difference in χ^π of the cations and the σ^2-carbenes for structures **1h-3h** and **1a-3a** must be approximately the same. An analogous result should be obtained for their benzannellated forms. According to Table 3, χ^π for the cations **1h-3h** is larger than χ^π for the σ^2-carbenes **1a-3a** by $3.6 \pm 0.7\cdot(-10^{-6}\ \mathrm{cm^3/mol})$, while the value for the cations **4h-6h** is larger than for the σ^2-carbenes by $4.9 \pm 0.7\cdot(-10^{-6}\ \mathrm{cm^3/mol})$.

We note that the full diamagnetic susceptibility χ_m and its anisotropy along the axis perpendicular to the plane of the molecule $\Delta\chi_{zz}$ have been used to estimate the aromaticity of carbenes (e.g., see [8-10]). However, if by aromaticity we mean the tendency of a system to retain the cyclicity of the π-electron shell [24], it is nevertheless more correct to use for this purpose the π-electron contributions to the diamagnetic susceptibility, since the presence of σ contributions in χ_m and $\Delta\chi_{zz}$ can even change the order of the position of the molecules on the aromaticity–antiaromaticity scale.

Of all the examined systems the cations are characterized by the largest values for the π-electron contributions to the diamagnetic susceptibilities (see Table 3). On the other hand, according to the Hückel $4n+1$ rule, the heteroanions and π^2-heterocarbenes must be antiaromatic, and this shows up in the appearance of paramagnetic currents and negative values of χ^π for these systems.

Benzannellation of such structures at the 4–5 bond, like the introduction of phenyl substituents, leads to strengthening of their diatropism or weakening of their paratropism. However, the nature of the change in the current distributions in the rings taken individually here can differ. Thus, during the *d*-annellation of diamagnetic σ^2-carbenes and the cations **4a**,**h**–**6a**,**h**, for the former calculation gives some decrease (by 0.039±0.002), while for the latter it gives an increase of the currents in the heterocyclic ring (by 0.039±0.008). Comparison of the analogous parameters of the π^2-carbene and the anion indicates that, in spite of the mutual decrease of the paratropic currents in the five-membered ring, the differences affect the values and sign of the current flowing in the benzene ring. In the anion it is strongly paratropic and equal to approximately half the value of the current flowing in benzene, which in contradiction to the Hückel rule (which incidentally only holds for monocyclic systems) leads to the appearance of weak diamagnetic characteristics for the π^2-carbenes **4d** and **5d** and, particularly, **8d**, i.e., to some aromaticity in these systems. We note that the σ^2-carbenes **4a-6a** and **8a** are substantially aromatic, while the corresponding dication-carbenes are antiaromatic (e.g., for the dication of structure **8a** $\chi^\pi = -126.5\cdot(-10^{-6}\ \mathrm{cm^3/mol})$].

The benzannellation of the carbene **1a** at bonds *c* and *e* (compound **9a**) has interesting features, as a result of which the current flowing in the σ^2-imidazol-2-ylidene becomes even higher than in benzene. At the same time, the π^2-form (compound **9d**), in contrast to **4d-6d**, is substantially antiaromatic, and for it anomalous values of χ^π and *I* appear in both rings (for the reasons for this, see below). The neutral σ^2-carbene **9a** is aromatic (see Table 3). Its dication, unlike that annellated at the 4–5 bond, is also aromatic to, it is true, a somewhat lesser degree ($\chi^\pi = 25.68\cdot(-10^{-6}\ \mathrm{cm^3/mol})$).

We will examine the diamagnetic characteristics of the radical-ion forms of the carbenes. As follows from Table 3, the radical-cations of carbenes **1-3** in both the σ^2- and the π^2-states have weak diatropism (to a somewhat greater degree in the π^2- than in the σ^2-state). The introduction of phenyl substituents on the whole stabilizes both states. At the same time, their annellation with benzene rings leads to substantially different results. Thus, whereas benzannellation of the radical-cation of the π^2-carbene at the 4–5 bond (compounds **4e-6e**) leads to an increase of the current in the heteroring while the current flowing in the benzene ring is fairly large and diatropic, in the case of the corresponding σ^2-form (structures **4b-6b**) the opposite situation is observed, and the corresponding compounds are paratropic. In order to explain this fact we note that a rough qualitative estimate of the characteristics of the radical-ions can be made on the basis of the characteristics of the neutral molecule and the corresponding diion. (In the Hückel method it is expressed by their half-sum.) Double ionization of the neutral π^2-heterocarbene by analogy with alternant hydrocarbons [26] should strengthen the aromatic characteristics, whereas in the σ^2-state it should weaken the aromatic characteristics or strengthen the antiaromatic characteristics. The latter are less clearly defined in the neutral π^2-carbenes **4d-6d** than in the σ^2-dications and so will be poorly defined in the corresponding radical-cations of the π^2-type compared with those of the σ^2-type (see above). In compound **9**, on the other hand, the σ^2-dication is more aromatic than the π^2-carbene, and the σ^2-state of the radical-cation here is therefore preferred to the π^2-state (see Table 3).

It can be stated on the basis of the presented data that for the radical-cation carbenes (disregarding compound **9**), in contrast to the neutral carbenes, the π^2-state will be more stable according to magnetic criteria. This will bring about a change in the "philicity" of the carbene atom during ionization and so in the whole range of chemical characteristics due to this charge. However, this does not occur in the radical-anions of the carbenes, which are antiaromatic in any state. (The only exception is the radical-anion of 1,2,4-triazol-3-ylidene, which in the σ^2-state has clearly defined diatropism.) Their paratropic characteristics are increased even more as a result of benzannellation, clearly demonstrating the reduced stability of such particles.

On the basis of the obtained values of χ^π for the investigated carbenes it is possible to calculate the components of the tensor of the diamagnetic susceptibility χ_m and its anisotropy $\Delta\chi_{zz}$. In view of the absence of the corresponding experimental data for them the calculated values of the components of the tensor of the full diamagnetic susceptibility are compared with the values obtained by any of the *ab initio* methods, such as the ILGO/II/MP2/6-31G(d) method used in [9, 10] to calculate the anisotropy of diamagnetic susceptibility in a series of heterocarbenes. For the case of $\Delta\chi_{zz}$ we will demonstrate that our employed simple approach reproduces sufficiently reliably the results from calculation by the above-mentioned nonempirical method. As before (see, for example, [22]), we will include the diamagnetic characteristics of the σ–core on the basis of an additive scheme, in which the C–H and C–C bonds are assumed to be magnetically equivalent, while the additive additions to the pyrrole nitrogen ($\chi^N_{xx} = 4.2$; $\chi^N_{yy} = 9.35$; $\chi^N_{zz} = 8.1\cdot(-10^{-6})$ cm^3/mol), furan oxygen ($\chi^O_{xx} = 3.0$ $\chi^O_{yy} = 11.0$; $\chi^O_{zz} = 7.3\cdot(-10^{-6})$ cm^3/mol), and thiophene sulfur ($\chi^S_{xx} = 13.4$; $\chi^S_{yy} = 18.0$; $\chi^S_{zz} = 22.6\cdot(-10^{-6})$ cm^3/mol) were selected from experimental data on pyrrole [27], furan, and thiophene [28]. A prerequisite for using the scheme is good agreement between the calculated and experimental [29, 30] (in parentheses) components of the tensor of the diamagnetic susceptibility of oxazole, on the basis of which we obtained $\Delta\chi_{xx} = -19.1$ (-19.6 ± 1.5); $\Delta\chi_{yy} = -15.8$ (-17.6 ± 1.7); $\chi_m = 39.6$ (38.0) and thiazole $\Delta\chi_{xx} = -23.0$; $\Delta\chi_{yy} = -24.8$; $\chi_m = 52.6$ (50.6) (in units of -10^{-6} cm^3/mol). Assuming that the additive addition at the carbene carbon atom $\Delta^C\chi_{zz} = 10.8\cdot10^{-6}$ cm^3/mol, we obtain good agreement with the values for the anisotropy of diamagnetic susceptibility $\Delta\chi_{zz}$ of imidazol-2-ylidene 27.4 (27.7), oxazol-2-ylidene 23.5 (25.0), and thiazol-2-ylidene 34.2 (32.3) (in units of -10^{-6} cm^3/mol) calculated by the ILGO/II [10] (in parentheses). It should be noted, however, that the obtained values should be regarded as absolute, since the ILGO method gives only a qualitative assessment of the magnetic characteristics of carbenes [31].

On the basis of the calculation of the charge and current distributions according to the procedure in [17, 18], adapted to molecular systems containing a carbene atom [32], it is possible to calculate the chemical shifts of ^{13}C, ^{1}H, and ^{14}N (^{15}N) in stable σ^2-heterocarbenes **1a-9a** (see Table 4).

The effect of the molecular σ-core, steric factors, and unshared electron pairs during comparison with existing experiment on heterocarbenes [2, 31, 33-35] was included in terms of the additive scheme previously approved for the case of conjugated hydrocarbons [36]. Here, the additional additive constants, due to the induced currents of the unshared electron pair of the carbene carbon atom at the screened nuclei, were equal to: 166 ppm for the carbene center and -321 ppm for the ^{14}N (^{15}N) atom adjacent to the σ^2-carbene center. The interaction of the unshared electron pairs, located at the *o*-positions, in our case the unshared electron pair of the carbene atom and the sulfur atom, leads as before (for the sulfur atom and the pyridine nitrogen, see [18]) to an additional downfield shift of the chemical shifts by 30 ppm [37].

TABLE 4. The ^{1}H, ^{13}C, and ^{14}N NMR Spectra of a Series of Imidazol-2-ylidenes, the Phenyl-substituted and Benzannellated Forms, and Their Heteroanalogs

Compound	Chemical shifts, δ, ppm				Compound	Chemical shifts, δ, ppm			
	Atom	π-Electron contributions		Calculation		Atom	π-Electron contributions		Calculation
		δ_{curr}	δ_{loczd}				δ_{curr}	δ_{loczd}	
1	$C_{(2)}$	2.12	-81.56	214.4	**6**	$C_{(2)}$	1.64	-67.87	257.9
	$C_{(4)}$	2.12	284.44	115.6		$C_{(4a)}$	5.62	-6.74	125.8
	$N_{(1)}$	2.12	-12.48	-204.6		$C_{(7a)}$	5.65	-7.41	125.5
	$N(H_{(5)})$	-0.50	-0.42	11.71		$C_{(4)}$	30.6	2.43	128.8
	$H_{(4)}$	-0.50	0.03	6.36		$C_{(5)}$	3.26	-2.46	123.9
2	$C_{(4)}$	2.08	-10.37	117.69		$C_{(6)}$	3.26	2.13	128.3
	$C_{(5)}$	2.08	-9.39	136.41		$C_{(7)}$	3.02	-7.72	119.2
	$N_{(3)}$	2.08	286.1	-195.9		$N_{(3)}$	0.59	293.4	-187.9
	$N(H_{(2)})$	-0.57	-0.45	11.81		$N(H_{(3)})$	-0.75	-0.26	11.28
	$H_{(4)}$	-0.48	-0.01	6.36		$H_{(4)}$	-1.43	-0.04	7.28
	$H_{(5)}$	-0.48	0.02	7.44		$H_{(5)}$	-1.27	0.00	4.62
3	$C_{(2)}$	2.28	-74.84	250.5		$H_{(6)}$	-1.27	0.00	4.62
	$C_{(4)}$	2.26	7.3	136.2		$H_{(7)}$	-1.42	-0.03	7.28
	$C_{(5)}$	2.28	-13.46	114.3	**7**	$C_{(3)}$	1.59	-73.02	223.2
	$N_{(3)}$	2.26	320.3	-161.9		$C_{(5)}$	1.59	18.43	157.4
	$N(H_{(3)})$	-0.47	-0.32	11.71		$N_{(2)}$	1.59	257.54	-224.0
	$H_{(4)}$	-0.47	-0.18	6.54		$N_{(1)}$	1.59	-247.8	209.8
	$H_{(5)}$	-0.43	0.04	7.02		$N_{(4)}$	1.59	281.99	-199.6
4	$C_{(2)}$	1.38	-73.07	223.5		$N(H_{(2)})$	-0.43	-0.26	12.33
	$C_{(3a)}$	5.50	-3.54	129.6		$H_{(5)}$	-0.37	-0.24	7.87
	$C_{(4)}$	3.15	-6.68	119.8	**8**	$C_{(2)}$	1.45	-80.38	215.7
	$C_{(5)}$	3.32	-2.04	124.0		$C_{(4)}$	1.85	-12.97	117.1
	$N_{(1)}$	0.89	260.8	-227.1		$N_{(1)}$	1.14	311.33	-170.9
	$N(H_{(2)})$	-0.90	-0.37	11.32		$H_{(4)}$	-0.43	0.02	6.78
	$H_{(6)}$	-1.39	0.03	7.31	**9**	$C_{(6)}$	2.84	-97.79	198.2
	$H_{(7)}$	-1.27	0.06	7.22		$C_{(11a)}$	6.02	-13.99	118.3
5	$C_{(3a)}$	5.44	-2.95	130.3		$C_{(4)}$	1.62	3.33	131.8
	$C_{(7a)}$	5.44	-1.52	149.5		$C_{(3)}$	2.02	-5.10	122.7
	$C_{(4)}$	3.16	-6.54	119.9		$C_{(2)}$	2.01	-3.51	124.1
	$C_{(5)}$	3.32	1.30	124.8		$C_{(1)}$	1.52	-0.29	127.7
	$C_{(6)}$	3.32	1.60	124.5		$N_{(5)}$	6.24	364.3	-121.9
	$C_{(7)}$	3.16	-6.07	120.4		$H_{(4)}$	-1.35	-0.11	7.13
	$N_{(3)}$	0.99	262.43	-218.6		$H_{(3)}$	-1.06	0.01	6.96
	$N(H_{(3)})$	-0.88	-0.39	12.07		$H_{(2)}$	-1.08	0.03	7.0
	$H_{(4)}$	-1.38	0.02	7.36		$H_{(1)}$	-1.47	0.02	7.38
	$H_{(5)}$	-1.27	0.04	7.12					
	$H_{(6)}$	-1.27	0.05	7.11					
	$H_{(7)}$	-1.38	0.03	7.24					

As seen from the calculation, the chemical shift of the noncarbene carbon atom adjacent to the heteroatom changes little during generation of the carbene center in the system; we compare, for instance, the chemical shifts of carbenes **1a-3a** (see Table 4) with the ^{13}C chemical shifts in imidazole $\delta(^{13}C_{(4)}) = 115.8$, oxazole $\delta(^{13}C_{(4)}) = 120.3$ and $\delta(^{13}C_{(5)}) = 138.2$, and thiazole $\delta(^{13}C_{(4)}) = 144.8$ and $\delta(^{13}C_{(5)}) = 120.8$ ppm [17, 18, 38]. Thus, the ^{13}C chemical shifts are only affected by the nearest environment. We note that benzannellation at position 4-5 leads to a downfield shift of the chemical shifts of the carbene center (see Table 4). Thus, for compounds **1a** and **4a** respectively $\delta(^{13}C_{(2)}:) = 214.4$ and $\delta(^{13}C_{(2)}:) = 223.5$ ppm, and for compounds **3a** and **6a** respectively $\delta(^{13}C_{(2)}:) = 250.5$ and $\delta(^{13}C_{(2)}:) = 257.9$ ppm. At the same time benzannellation at position 3-4 (system **9a** leads to an upfield shift of the signal ($\delta(^{13}C_{(6)}:) = 198.2$ ppm)).

The insertion of the σ^2-carbene center into the heteroaromatic system gives rise in the ^{1}H NMR spectra to some upfield shift of the resonance signals (Table 4) for the carbenes **1a**-**8a** compared with imidazole ($\delta\ (^1H_{(4)}) = 6.52$), oxazole ($\delta(^1H_{(4)}) = 7.09$, $\delta(^1H_{(5)}) = 7.69$), and benzothiazole ($\delta(^1H_{(4)}) = 7.94$, $\delta(^1H_{(6)}) = 7.23$ ppm). However, this does not change the principal relationships governing the effect of the type of heteroatom on proton magnetic screening.

We note that the protonation of carbene systems (the transition to the cations **1h**-**9h**) leads to an upfield shift of the ^{13}C signals. (The $\delta(^{13}C_{(2)})$ values for the cations **1h** and **8h** are 155.4 and 151.29 ppm respectively.) Here for the imidazole systems **1a**-**h** and **8a**-**h** the difference in chemical shifts between the carbene and the protonated forms $\Delta\delta(^{13}C_{(2)})$ amounts to approximately 61 ppm (for the pair **8a**-**h** the experimental value is $\Delta\delta(^{13}C_{(2)}) = 60.88$ ppm [38]); for thiazole systems calculated without substituents **3a**-**3h** and with a phenyl substituent at the nitrogen atom **3a**(Ph)-**3h**(Ph) $\Delta\delta(^{13}C_{(2)}) = {\sim}96$ ppm. At the same time protonation of the carbene systems **1a**-**3a**, **8a** moves the $^{13}C_{(4(5))}$, $^1H_{(4(5))}$ chemical shift downfield. For example, for the cations **1h** and **8h**: $\delta(^{13}C_{(4(5))})$ is equal respectively to 129.8 and 126.5 ppm (**1a** 115.6, **8a** 117.1 ppm) and $\delta(^1H_{(4(5))})$ 7.58 and 7.43 ppm (**1a** 6.36, **8a** 6.78 ppm); for the cation **3h** $\delta(^{13}C_{(4)}) = 147.9$, $\delta(^{13}C_{(5)}) = 131.4$, $\delta(^1H_{(4)}) = 7.6$, $\delta(^1H_{(5)}) = 8.1$ ppm (**3a** $\delta(^{13}C_{(4)}) = 136.2$, $\delta(^{13}C_{(5)}) = 114.3$, $\delta(^1H_{(4)}) = 6.54$, $\delta(^1H_{(5)}) = 7.02$ ppm) and for **3h**(Ph) $\delta(^{13}C_{(4)}) = 145.3$, $\delta(^{13}C_{(5)}) = 131.2$, $\delta(^1H_{(4)}) = 7.59$, $\delta(^1H_{(5)}) = 8.06$ ppm, compared with **3a**(Ph): $\delta(^{13}C_{(4)}) = 134.1$, $\delta(^{13}C_{(5)}) = 115.09$, $\delta(^1H_{(4)}) = 6.28$, $\delta(^1H_{(5)}) = 7.3$ ppm. (The chemical shifts of the carbenes, Table 4, are given in parentheses for comparison.) We note that the chemical shifts of the $^{14}N_{(3)}$ nuclei of the positively charged and π-delocalized imidazolium systems **1h** and **8h** are shifted upfield compared with the corresponding carbenes (cf. the data in Table 4 and the calculated values of the ^{14}N chemical shifts of the cations **1h** and **8h**, for which $\delta(^{14}N_{(3)}:) = -209.0$ and -185.5 respectively). Since the experimental values of the chemical shifts of the ^{14}N and ^{15}N nuclei are fairly close, the data in Table 4 can be used to determine the chemical shifts of the ^{15}N nuclei.

The calculated values of the chemical shifts agree well with the experimental values for the series of stable carbenes and their protonated forms. We compare, for example, the data in Table 4 for the imidazole systems **1a**, **4a**, and **8a** with the experimental chemical shifts of 1,3,4,5-tetramethylimidazol-2-ylidene $\delta(^{13}C_{(2)}) = 215.2$, $\delta(^{13}C_{(4)}) = 115.6$, $\delta(^{14}N_{(3)}) = -197.5$, $\delta(^{15}N_{(3)}) = -197.3$ ppm [31]; 1,3-di(1-adamantyl)benzimidazol-2-ylidene $\Delta(^{13}C_{(2)}) = 223.0$, 1,3-diphenylimidazol-2-ylidene $\delta(^{13}C_{(2)}) = 215.8$, $\delta(^{13}C_{(4)}) = 118.8$, $\delta(^{14}N_{(3)}) = -171$, $\delta(^1H_{(4)}) = 6.96$ ppm [33]; for the triazole system **7a** with the chemical shift of 1,3,4-triphenyl-1,2,4-triazolin-5-ylidene $\Delta(^{13}C_{(2)}) \sim 220$ ppm [34]; for the thiazole system **3a** with the chemical shifts of 3-(2,6-diisopropylphenyl)-4,5-dimethylthiazol-2-ylidene $\delta(^{13}C_{(2)}) = 254.3$, $\delta(^{13}C_{(4)}) = 131.5$, $\delta(^{14}N_{(3)}) = -148.62$, $\delta(^{15}N_{(3)}) = -148.7$ ppm [35]; the calculated values of the chemical shifts for the protonated forms **1i** and **3i**, presented above, with the experimental values of the chemical shifts of the 1,3-dimesitylimidazolium cation $\delta(^{13}C_{(2)}) = 154.92$, $\delta(^{13}C_{(4)}) = 125.8$, $\delta(^1H_{(4)}) = 7.02$, $\delta(^{15}N_{(3)}) = -179.3$ ppm [38]; the 1,3,4,5-tetramethylimidazolium cation $\delta(^{13}C_{(2)}) = 135$, $\delta(^{13}C_{(4)}) = 126.8$, $\delta(^{14}N_{(3)}) = -206.6$ ppm [31]; the 3-(2,6-diisopropylphenyl)-4,5-dimethylthiazolium cation $\delta(^{13}C_{(2)}) = 157.61$, $\delta(^{13}C_{(4)}) = 142.1$, $\delta(^{13}C_{(5)}) = 132.09$ ppm [35].

We note that the differences between the calculated values (Table 4) and the experimental values are due primarily to the fact that the substituents were not taken into account during calculation of the chemical shifts of the model systems. It is natural that their inclusion will lead to an improvement in the agreement with experiment. In fact, direct calculation of structure (**3a**) with a phenyl substituent at the nitrogen atom, for example, gives $\delta(^{14}N_{(3)}) = -148.8$ ppm, which almost coincides with the experimental value for 3-(2,6-diisopropylphenyl)-4,5-dimethylthiazol-2-ylidene.

We emphasize that as in the case of heteroaromatic systems the values of the ^{13}C and ^{14}N (^{15}N) chemical shifts are determined mainly by the π-electron density at the screened nucleus and by the effect of the unshared pairs, in our case the nitrogen, sulfur, oxygen atoms and the carbene carbon atom in the σ^2-state.

TABLE 5. The Energies of the Lowest Singlet, Doublet, and Triplet Electronic Transitions (eV) of the Carbene, Radical, and Ionic Forms

		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
σ^2-Carbenes										
a	λ^s_1	5.01	5.06	4.84	4.41	4.44	4.30	5.24	.51	2.70
	λ^s_2	7.11	7.19	5.86	5.70	5.79	5.14	7.55	5.08	2.97
	λ^t_1	3.82	3.86	3.80	3.60	3.63	3.47	3.80	3.65	1.63
	λ^t_2	5.76	5.80	5.17	4.18	4.16	4.04	7.17	3.66	1.88
b	λ^d_1	4.32	4.83	3.19	1.54	1.61	1.62	3.96	1.81	1.70
	λ^d_2	5.33	5.60	3.65	2.13	2.04	1.92	4.82	1.93	2.02
c	λ^d_1	2.64	2.64	2.32	1.06	2.05	1.98	2.92	—*	0.79
	λ^d_2	3.92	3.98	2.85	2.20	2.22	2.24	5.66	—*	1.29
π^2-Carbenes										
d	λ^s_1	2.44	2.57	2.37	2.68	2.80	2.72	2.19	2.14	0.52
	λ^s_2	8.07	8.13	7.94	3.06	3.15	3.34	8.43	2.40	1.30
	λ^t_1	1.15	1.19	1.25	1.93	2.03	2.13	1.10	1.19	0.03
	λ^t_2	5.17	5.15	5.09	2.08	2.15	2.52	4.82	2.07	0.58
e	λ^d_1	2.48	2.46	2.48	2.15	2.17	2.05	2.37	2.08	1.25
	λ^d_2	4.84	5.27	5.41	3.01	3.05	2.63	4.60	2.24	1.62
f	λ^d_1	—	-3.88	3.33	0.97	0.98	1.28	—*	—*	-0.02
	λ^d_2	—*	0.32	3.49	1.19	1,23	2.62	—*	—*	0.81
Radicals, ions										
g	λ^d_1	1.60	1.59	1.65	1.99	2.00	1.92	2.06	1.62	1.16
	λ^d_2	3.53	3.62	3.40	2.81	2.89	2.74	4.74	2.08	1.26
h	λ^s_1	5.84	5.78	5.51	4.36	4.28	3.80	6.27	4.39	3.24
	λ^s_2	7.50	7.64	6.22	4.40	4.36	4.13	7.85	4.60	3.59
	λ^t_1	3.92	3.79	3.77	3.28	3.26	2.95	3.93	3.62	2.35
	λ^t_2	4.35	4.33	4.35	3.64	3.55	3.40	5.26	3.78	2.44
i	λ^s_1	-0.06	0.24	0.44	1.11	1.13	1.31	1.80	0.87	0.15
	λ^s_2	7.31	7.43	4.78	3.01	3.09	2.88	7.57	1.00	1.68
	λ^t_1	-0.75	-0.81	-0.22	0.41	0.38	0.77	-0.44	-0.22	-0.51
	λ^t_2	4.14	4.14	4.38	0.77	0.78	1.12	4.48	0.83	0.40

---

*See the note in Table 1.

Passing on to a description of the spectral characteristics, we note that the paramagnetic contributions to the diamagnetic susceptibilities and the induced π-electron ring currents are expressed in the form of dispersion sums among the excited states [24]. Therefore, the anomalous values of χ^π and *I* in the series of antiaromatic systems, calculated in the present work (see Table 3), are due to the proximity of the lowest electronic transitions to zero. As a result of this, in the geometrically similar structures the energies of the electronic transitions are as a rule greater in aromatic systems than in antiaromatic systems [24]. A good example of this is the calculated values of the energies of the lowest singlet, doublet, and triplet transitions $\lambda^{s,d,t}$ of the investigated heterosystems (Table 5). Thus, the largest values $\lambda_1^{s,d,t}$ and $\lambda_2^{s,d,t}$ are characteristic respectively of aromatic cations and σ^2-carbenes, while the smallest (with the exception of compound **3f)** are characteristic of antiaromatic radical-anion carbenes of the π^2-type and anions, for which the appearance of negative λ^d and λ^t frequencies, indicating internal and triplet instability of the Hartree–Fock solutions, is also possible [39]. Comparing the σ^2- and π^2-analogs, we see that the carbenes in the σ^2-state are characterized by higher values for the energies of the π–π*-electronic transitions than in the π^2-form. The exception is the radical-cations **4b,f–6b**,**f** and **8b**,**f** for which, as mentioned above, the π^2-state is preferred to σ^2 according to the magnetic criteria. It should, however, be noted that if the diamagnetic characteristics of the examined compounds are close there should not be a direct relation between χ^π and the energies of the lowest transitions, as is seen in the case of the N-, O-, and S-heterocycles of π^2-carbenes and cations. Attention is drawn also to the fact that *d*-annellation and phenyl substitution at the nitrogen atom for the neutral π^2-carbenes and radicals leads not to long-wave, as in the other cases, but to short-wave shift of the absorption bands. This can clearly be explained by the antiaromatic character of the radicals and π^2-carbenes **1d**,**g–3d**,**g** and by the strong stabilizing effect of the annellated or N-substituted benzene ring, leading to a substantial decrease of the paratropism and to the appearance of diamagnetic characteristics in such systems. We note that approximately the same shift of the bands, independent of the type of heteroatom in the system during the transition from the cations to the carbenes, is also observed in the case of the electronic spectra in accordance with the idealogy of the superposition-additive approach. Thus, for systems **1-3** and **7** the difference in energies for the λ_1^s transition amounts to 0.81±0.12; $\Delta\lambda_2^s = 0.38\pm0.04$; $\Delta\lambda_1^t = 0.03\pm0.08$; $\Delta\lambda_2^t = -1.40\pm0.29$.

In conclusion we draw attention to the good agreement between the π-electronic ionization potential of imidazol-2-ylidene (8.33 eV) calculated according to Koopman's theorem and the second transition in the photoelectron spectrum of 1,3-di-*tert*-butylimidazol-2-ylidene (8.22 eV) [40]. Calculation for the other carbenes gives: **2a** 8.52; **3a** 8.75; **4a** 8.55; **5a** 8.66; **6a** 8.70; **7a** 9.54; **8a** 8.21; **9a** 6.57; **10d** 7.88 eV. The first observed ionization potential of **1a** is due to the removal of an electron from the unshared pair of the carbene carbon (σ^2-carbene) and cannot be calculated in terms of the employed π-electron approximation. We note also that the second π-electronic transition in the photoelectron spectrum, assigned in [40] to a value of 11.27 and separated from the first by 3 eV corresponds rather to the π^2-state of the radical-cation carbene than to the σ^2-state, as seen from comparison of the corresponding energies of the lowest doublet transitions λ^d (2.48 for **1e** and 4.32 eV for **1b**).

REFERENCES

1. A. J. Arduengo, R. L. Harlow, and M. Kline, *J. Am. Chem. Soc.*, **113**, 361 (1991).
2. A. J. Arduengo, H. V. R. Dias, R. L. Harlow, and M. Kline, *J. Am. Chem. Soc.*, **114**, 5530 (1992).
3. A. J. Arduengo, *Accounts Chem. Res.*, **32**, 913 (1999).
4. D. Bourissou, O. Guerret, F. P. Gabbaie, and G. Bertrand, *Chem. Rev.*, **100**, 39 (2000).
5. D. A. Dixon and A. J. Arduengo III, *J. Chem. Phys.*, **95**, 4180 (1992).
6. J. Cioslowski, *Int. J. Quantum Chem.: Quantum Chem. Symp.*, **27**, 309 (1993).
7. C. Heinemann and W. Thiel, *Chem. Phys. Lett.*, **217**, 11 (1994).

8. C. Heinemann, T. Muller, Y. Apeloig, and H. Schwarz, *J. Am. Chem. Soc.*, **118**, 2023 (1996).
9. C. Boehme and G. Frenking, *J. Am. Chem. Soc.*, **118**, 2039 (1996).
10. G. Boche, P. Andrews, K. Harms, M. Marsch, K. S. Rangappa, M. Schimeczek, and C. Willeke, *J. Am. Chem Soc.*, **118**, 4925 (1996).
11. G. A. McGibbon, J. Hrusak, D. J. Lavorato, H. Schwarz, and J. Terlouw, *Chem. Eur. J.*, **3**, 232 (1997).
12. D. Enders, K. Breuer, G. Raabe, J. Simonet, A. Ghanimi, H. B. Stegmann, and J. H. Teles, *Tetrahedron Lett.*, **38**, 2833 (1997).
13. Yu. B. Vysotsky and Ya. V. Zaikovskaya, *Teor. Eksp. Khim.*, **29**, 41 (1993).
14. Yu. B. Vysotsky, *Teor. Eksp. Khim.*, **32**, 147 (1996).
15. Yu. B. Vysotsky, Ya. V. Zaikovskaya, and O. A. Gorban, *Teor. Eksp. Khim.*, **32**, 157 (1996).
16. Yu. B. Vysotsky, Ya. V. Zaikovskaya, and O. A. Gorban, *Zh. Org. Khim.*, **35**, 559 (1999).
17. Yu. B. Vysotsky and L. N. Sivyakova, *Teor. Eksp. Khim.*, **21**, 293 (1985).
18. Yu. B. Vysotsky, E. A. Zemskaya, B. P. Zemskii, and V. I. Dulenko, *Khim. Geterotsikl. Soedin.*, 544 (1987).
19. Yu. B. Vysotsky, *Zh. Strukt. Khim.*, **31**, 36 (1990).
20. M. M. Mestechkin, *Density Matrix Method in the Theory of Molecules* [in Russian], Naukova Dumka, Kiev (1977).
21. A. V. Luzanov and V. E. Umanskii, *Zh. Strukt. Khim.*, **18**, 3 (1977).
22. Yu. B. Vysotsky, N. A. Kovach, and O. P. Shvaika, *Khim. Geterotsikl. Soedin.*, 1186 (1977).
23. Yu. B. Vysotsky, Ya. V. Zaikovskaya, and I. N. Solonskii, *Zh. Org. Khim.*, **37**, 111 (2001).
24. Yu. B. Vysotsky, N. A. Kovach, and O. P. Shvaika, *Izv. Sibirsk. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, No. 2, Part 1, 3 (1980).
25. K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **39**, 2116 (1966).
26. Yu. B. Vysotsky and N. N. Solonskii, *Ukr. Khim. Zh.*, **62**, 31 (1996).
27. D. H. Sutter and W. H. Flygare, *J. Am. Chem. Soc.*, **91**, 6895 (1969).
28. D. H. Sutter and W. H. Flygare, *J. Am. Chem. Soc.*, **91**. 4063 (1969).
29. J. R. Davidson, A. K. Burnham, B. Siegel, P. Beak, and W. H. Flygare, *J. Am. Chem. Soc.*, **96**, 7394 (1974).
30. M. Cook and A. R. Katritzky, in: *Adv. Heterocycl. Chem.* (Ed. A. R. Katritzky, A. J. Boulton), Academic Press, **17**, 255 (1974),
31. A. J. Arduengo, D. A. Dixon, K. K. Kumashiro, C. Lee, W. P. Power, and K. W. Zilm, *J. Am. Chem. Soc.*, **116**, 6361 (1994).
32. Yu. B. Vysotski, Yu. G. Skrypnic, Ya. Zaikovskaya, O. Gorban, and S. Lyashchuk, in: *Abstracts of Polish-American Workshop on Reactive Intermediates*, Zakopane, Poland (1995), p. 21.
33. M. I. Korotkikh, G. F. Raenko, and O. P. Shvaika, *Dopovidi NAN Ukraini*, No. 2, 135 (2000).
34. M. I. Korotkikh, G. F. Raenko, and O. P. Shvaika, *XVIII Ukrainian Conference on Organic Chemistry*. Book of Abstracts, Dnepropetrovsk (1998), p. 132.
35. A. J. Arduengo, J. R. Goerlich, and W. J. Marshall, *Liebigs Ann. IRecl.,* 365 (1997).
36. Yu. B. Vysotsky, *Zh. Strukt. Khim.*, 498 (1972).
37. Yu. B. Vysotsky and O. A. Gorban, *New Advances of NMR in Structural investigations. Abstracts of Third All-Union Conference* [in Russian], Kazan (2000), p. 45.
38. A. J. Arduengo, H. V. R. Dias, J. C. Calabrese, and F. Davidson, *Inorg. Chem.*, **32**, 1541 (1993).
39. M. M. Mestechkin, *Instability of Hartree-Fock Equations and the Stability of Molecules* [in Russian], Naukova Dumka, Kiev (1986).
40. A. J. Arduengo. H. Bock, H. Chen. M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, and R. West, *J. Am. Chem. Soc.*, **116**, 6641 (1994).