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Quantum-Chemical Study of Nitrosonium Complexes Derived from Nitrogen-Containing Heterocycles*

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Abstract—The affinities of a series of azines for nitrosonium ion (A_{NO^+}) were calculated by quantum-chemical methods, AM1 and *ab initio*. The A_{NO^+} values were found to increase as the number of nitrogen atoms in the ring decreases and the donor power of substituents increases; ring fusion also increases A_{NO^+}. The best agreement between the calculated and experimental A_{NO^+} values was attained with the use of AM1 calculations and *ab initio* methods with split polarization or diffuse functions. Substituted pyridines showed linear correlations between the calculated A_{NO^+} values and substituent constants σ or σ^+ or overall charges on the NO group in the complex. Linear correlations were also found between the calculated A_{NO^+} values of azines and their experimental proton affinities.

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Nitrosonium complexes of nitrogen-containing organic compounds have been extensively studied over many years [3–15]. Interest in these complexes originates from the fact that they are intermediates in a number of important organic reactions, such as diazotization [16], nitrosation of amides [16] and nitrogen-containing heterocycles [17, 18], and formation [16, 19] and denitrosation [20] of *N*-nitroso amines. In the recent years, nitrosonium complexes have attracted increased attention since a unique role of NO molecule in biological processes has been discovered [21–23]. It is assumed that nitrosonium ion and some parent molecules are responsible for neurotoxic and neuroprotecting effects of nitrogen oxide [24, 25] and cross-linking of DNA [26, 27]. Many chemical, physicochemical, and biological properties of NO^+ are determined by its ability to coordinate neutral ligands. Taking into account quite limited experimental data on the affinity of nitrogen-containing heteroaromatic compounds for nitrosonium ion (A_{NO^+}) [3, 8], calculation of A_{NO^+} values by quantum-chemical methods seems to be an important task.

The goal of the present work was to find most appropriate quantum-chemical methods for estimation of the affinity of six-membered nitrogen-containing heterocycles (azines) for NO^+ ion, determine geometric and electronic parameters of the corresponding nitrosonium complexes, and reveal structural factors affecting the A_{NO^+} values. Experimental data on the structure of azine complexes with nitrosonium ions were reported for only one specific example, 1,10-nitrosophenanthrolinium [13, 15].

In order to estimate the effect of the number and position of nitrogen atoms in the ring, as well as the effects of substituents and fusion, on A_{NO^+}, the following azines were examined: pyridine (**I**), 2-substituted pyridines 2-$\mathrm{XC_5H_4N}$ [**IIa**–**IIj**: X = Me (**a**), Et (**b**), $\mathrm{CF_3}$ (**c**), CN (**d**), MeO (**e**), MeS (**f**), Br (**g**), Cl (**h**), F (**i**), $\mathrm{NH_2}$ (**j**)], 3-substituted pyridines 3-$\mathrm{XC_5H_4N}$ [**IIIa**–**IIIk**: X = Me (**a**), $\mathrm{CF_3}$ (**b**), Ac (**c**), PhCO (**d**), OH (**e**), MeO (**f**), MeS (**g**), Br (**h**), Cl (**i**), F (**j**), $\mathrm{NH_2}$ (**k**)], 4-substituted pyridines 4-$\mathrm{XC_5H_4N}$ [**IVa**–**IVl**: X = Me (**a**), Et (**b**), $\mathrm{CH_2{=}CH}$ (**c**), Ph (**d**), $\mathrm{CF_3}$ (**e**), MeO (**f**), MeS (**g**), Br (**h**), Cl (**i**), F (**j**), $\mathrm{NH_2}$ (**k**), $\mathrm{O_2N}$ (**l**)], disubstituted pyridines $\mathrm{XYC_5H_3N}$ [**Va**–**Vi**: X = 2-Me, Y = 3-Me (**a**), 4-Me (**b**), 5-Me (**c**), 6-Me (**d**); X = 3-Me, Y = 4-Me (**e**), 5-Me (**f**); X = 2-Cl, Y = 4-Me (**g**), 6-Me (**h**), 6-MeO (**i**)], and compounds **VI**–**XIX**. These structures were selected taking into account availability of the corresponding experimental proton affinities [28] with a view to compare A_{NO^+} and *PA* values.

The affinities of azines for nitrosonium ion A_{NO^+} were calculated using both semiempirical AM1 proce-

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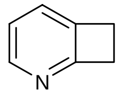
* For preliminary communications, see [1, 2].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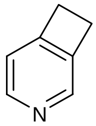
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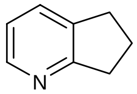
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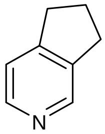
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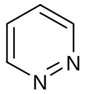
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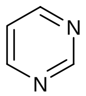
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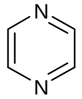
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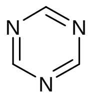
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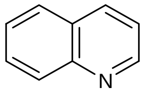
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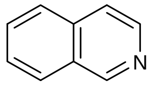
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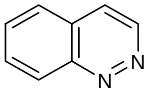
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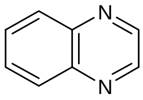
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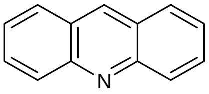
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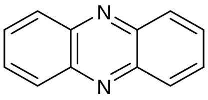
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dure [29] and nonempirical methods [30, 31]. Local minima on the potential energy surfaces were found by calculating Hesse matrices [31]. We initially calculated by different methods the geometric parameters of nitrosonium complexes, charge distribution, and A_{NO^+} values for pyridine, some its derivatives (compounds **IIh**, **IIi**, **IIIa**, **IIIj**, and **IVi**), and heterocycles **X**–**XIX** (Tables 1–3, Fig. 1). The optimized structures of the complexes calculated by different methods were mostly characterized by similar geometric parameters, except for the data obtained by the MP2, B3LYP, and CI methods. When electronic correlation was taken into account, the N–N bond in the ONN^+ fragment appeared considerably longer than the standard N_{sp2}–N_{sp2} bond (1.401 Å) [32]. In going from initial azines to their nitrosonium complexes, most methods predicted

Table 1. Total energies (E_{tot}, a.u.), affinities of pyridine for nitrosonium ion (A_{NO^+}, kJ/mol), some geometric parameters,[a] and Mulliken charges on the NNO oxygen and nitrogen atoms of complex **I**–NO^+, calculated by different quantum-chemical methods

Method	E_{tot}	A_{NO^+}[b]	l_{NO}	l_{NN^1}	$l_{N^1C(N)}$[c]	φ_{ONN^1}	q_{N^1}	q_N(NO)	q_O(NO)
AM1	912.8[d]	167.4	1.132	1.453	1.383	117.7	–0.176	0.388	–0.035
HF/6-31G	–375.497969	260.3	1.164	1.475	1.349	113.5	–0.849	0.487	–0.234
HF/6-31G(*d*)	–375.678049	181.4	1.140	1.474	1.342	112.8	–0.573	0.429	–0.196
HF/6-31G(2*d*)	–375.691974	165.8	1.131	1.477	1.337	112.9	–0.228	0.386	–0.210
HF/6-31G(*d*,*p*)	–375.687310	182.6	1.140	1.474	1.342	112.8	–0.597	0.431	–0.198
HF/6-31G(2*d*,*p*)	–375.704227	167.5	1.132	1.476	1.338	112.9	–0.247	0.390	–0.213
HF/6-31G(3*d*)	–375.703818	164.8	1.132	1.480	1.339	112.8	0.118	0.614	–0.676
HF/6-31G$^+$	–375.505944	251.8	1.166	1.472	1.350	113.6	–0.164	0.173	–0.007
HF/6-31G+(*d*)	–375.683395	168.1	1.139	1.474	1.343	112.9	0.045	0.126	0.013
HF/6-31G+(*d*,*p*)	–375.692737	169.5	1.140	1.473	1.342	112.9	0.042	0.146	0.014
HF/6-31G++	–375.506214	252.1	1.166	1.472	1.350	113.6	–0.147	0.176	0.010
HF/6-31G++(*d*)	–375.683556	168.4	1.139	1.474	1.343	112.9	0.069	0.129	0.030
HF/6-31G++(*d*,*p*)	–375.692917	169.8	1.140	1.473	1.342	112.9	0.059	0.138	0.029
MP2/6-31G	–376.303573	225.2	1.171	1.968	1.359	111.0	–0.766	0.598	–0.104
MP2/6-31G (*d*,*p*)	–376.849385	215.4	1.143	1.873	1.336	110.4	–0.433	0.369	0.075
MP2/6-31G (2*d*)	–376.904015	217.7	1.131	1.874	1.334	110.4	–0.105	0.335	0.071
B3LYP/6-31G(*d*,*p*)	–377.724250	280.9	1.137	1.744	1.341	110.5	–0.445	0.362	–0.020
CI/6-31G (*d*)[e]	–376.452268	329.1[f]					–0.507	0.389	–0.163

[a] Bond lengths *l* are given in Å, and bond angles φ, in deg.

[b] Calculated with correction for ZPE (see the procedure for calculations).

[c] The length of the bond located *syn* with respect to the NO group.

[d] ΔH_f, kJ/mol.

[e] Configurational interactions were taken into account for the compounds whose geometric parameters were optimized by the HF/6-31G(*d*) method.

[f] Calculated with no correction for ZPE.

Table 2. Optimized geometric parameters[a] and Mulliken charges in the ON–N$^+$C(N) fragment of nitrosonium complexes of compounds **I**–**IV** and **X**–**XIX**, calculated by different quantum-chemical methods

Complex no.	Method	l_{NO}	l_{NN^1}	$l_{N^1C(N)}$[b]	φ_{ONN^1}	q_{N^1}	q_N(NO)	q_O(NO)
I–NO$^+$	AM1	1.132	1.453	1.383	117.7	–0.176	0.388	–0.035
	HF/6-31G	1.164	1.475	1.349	113.5	–0.849	0.487	–0.234
	HF/6-31G(*d*)	1.140	1.474	1.342	112.8	–0.573	0.429	–0.196
	HF/6-31G+(*d*)	1.139	1.474	1.343	112.9	0.045	0.126	0.013
	HF/6-31G(2*d*)	1.131	1.477	1.337	112.9	–0.228	0.386	–0.210
	HF/6-31G(*d*,*p*)	1.140	1.474	1.342	112.8	–0.597	0.431	–0.198
	HF/6-31G(2*d*,*p*)	1.132	1.476	1.338	112.9	–0.247	0.390	–0.213
	MP2/6-31G	1.171	1.968	1.359	111.0	–0.766	0.598	–0.104
IIh–NO$^+$	AM1	1.132	1.455	1.384	117.5	–0.186	0.395	–0.034
	HF/6-31G	1.158	1.510	1.353	112.4	–0.866	0.529	–0.222
	HF/6-31G(*d*)	1.133	1.511	1.347	111.8	–0.621	0.463	–0.179
	HF/6-31G+(*d*)	1.134	1.510	1.348	111.9	0.072	0.121	0.082
	HF/6-31G(2*d*)	1.124	1.521	1.342	111.8	–0.314	0.420	–0.186
	HF/6-31G(*d*,*p*)	1.134	1.511	1.347	111.8	–0.633	0.463	–0.180
	HF/6-31G(2*d*,*p*)	1.124	1.519	1.343	111.9	–0.321	0.420	–0.189
	MP2/6-31G	1.168	2.019	1.364	109.7	–0.461	0.443	0.070
IIi–NO$^+$	AM1	1.131	1.456	1.386	117.5	–0.222	0.402	–0.029
	HF/6-31G	1.154	1.532	1.355	111.6	–0.919	0.548	–0.204
	HF/6-31G(*d*)	1.131	1.525	1.352	111.2	–0.684	0.470	–0.164
	HF/6-31G+(*d*)	1.129	1.532	1.351	111.2	–0.196	0.226	0.085
	HF/6-31G(2*d*)	1.121	1.536	1.347	111.4	–0.361	0.429	–0.176
	HF/6-31G(*d*,*p*)	1.131	1.524	1.352	111.2	–0.696	0.471	–0.165
	HF/6-31G(2*d*,*p*)	1.121	1.532	1.347	111.4	–0.368	0.428	–0.179
	MP2/6-31G	1.163	2.043	1.370	110.9	–0.508	0.458	0.097
IIIa–NO$^+$	AM1	1.133	1.452	1.381	117.7	–0.166	0.387	–0.038
	HF/6-31G	1.166	1.470	1.351	113.6	–0.853	0.483	–0.239
	HF/6-31G(*d*)	1.141	1.470	1.345	112.9	–0.575	0.427	–0.201
	HF/6-31G+(*d*)	1.141	1.469	1.345	113.0	0.149	0.057	0.015
	HF/6-31G(2*d*)	1.133	1.472	1.341	113.1	–0.227	0.384	–0.217
	HF/6-31G(*d*,*p*)	1.141	1.469	1.345	112.9	–0.600	0.429	–0.204
	HF/6-31G(2*d*,*p*)	1.133	1.470	1.341	113.1	–0.250	0.386	–0.220
	MP2/6-31G	1.173	1.955	1.356	110.8	–0.481	0.415	0.031
IIIj–NO$^+$	AM1	1.130	1.463	1.377	117.8	–0.152	0.396	–0.020
	HF/6-31G	1.160	1.493	1.347	113.1	–0.855	0.501	–0.215
	HF/6-31G(*d*)	1.136	1.490	1.341	112.5	–0.576	0.441	–0.180
	HF/6-31G+(*d*)	1.136	1.491	1.341	112.6	0.040	0.141	0.032
	HF/6-31G(2*d*)	1.128	1.494	1.336	112.7	–0.227	0.396	–0.194
	HF/6-31G(*d*,*p*)	1.136	1.490	1.341	112.5	–0.602	0.443	–0.182
	HF/6-31G(2*d*,*p*)	1.128	1.492	1.336	112.7	–0.245	0.399	–0.197
	MP2/6-31G	1.169	1.992	1.359	111.1	–0.477	0.430	0.063

Table 2. (Contd.)

Complex no.	Method	l_{NO}	l_{NN^1}	$l_{N^1C(N)}{}^b$	φ_{ONN^1}	q_{N^1}	q_N(NO)	q_O(NO)
IVi–NO^+	AM1	1.133	1.450	1.384	117.7	–0.186	0.389	–0.038
	HF/6-31G	1.164	1.476	1.349	113.4	–0.861	0.491	–0.231
	HF/6-31G(*d*)	1.140	1.471	1.343	112.8	–0.587	0.431	–0.198
	HF/6-31G+(*d*)	1.140	1.470	1.344	112.9	0.065	0.104	0.010
	HF/6-31G(2*d*)	1.132	1.473	1.339	112.9	–0.237	0.386	–0.213
	HF/6-31G(*d*,*p*)	1.140	1.470	1.343	112.8	–0.611	0.432	–0.200
	HF/6-31G(2*d*,*p*)	1.132	1.472	1.339	112.9	–0.261	0.389	–0.216
	MP2/6-31G	1.170	1.975	1.361	111.5	–0.484	0.425	0.051
X–NO^+	AM1	1.122	1.530	1.375	116.0	–0.144	0.472	0.006
	HF/6-31G	1.156	1.521	1.323	111.8	–0.619	0.549	–0.205
	HF/6-31G(*d*)	1.131	1.523	1.313	111.5	–0.342	0.469	–0.162
	HF/6-31G+(*d*)	1.131	1.524	1.313	111.6	0.311	0.004	0.125
	HF/6-31G(2*d*)	1.122	1.530	1.308	111.7	–0.075	0.427	–0.176
	HF/6-31G(*d*,*p*)	1.132	1.522	1.313	111.5	–0.354	0.469	–0.163
	HF/6-31G(2*d*,*p*)	1.123	1.528	1.308	111.7	–0.084	0.428	–0.178
	MP2/6-31G	1.167	2.017	1.359	115.9	–0.299	0.448	0.080
XI–NO^+	AM1	1.132	1.450	1.401	117.7	–0.231	0.395	–0.030
	HF/6-31G	1.161	1.489	1.352	113.2	–0.829	0.499	–0.212
	HF/6-31G(*d*)	1.137	1.487	1.343	112.6	–0.579	0.437	–0.176
	HF/6-31G+(*d*)	1.137	1.487	1.343	112.7	–0.014	0.057	0.029
	HF/6-31G(2*d*)	1.128	1.492	1.337	112.7	–0.226	0.392	–0.190
	HF/6-31G(*d*,*p*)	1.137	1.487	1.343	112.6	–0.600	0.439	–0.178
	HF/6-31G(2*d*,*p*)	1.129	1.490	1.338	112.7	–0.240	0.395	–0.193
	MP2/6-31G	1.165	2.033	1.365	114.0	–0.433	0.433	–0.086
XII–NO^+	AM1	1.128	1.472	1.378	117.6	–0.139	0.399	–0.008
	HF/6-31G	1.155	1.519	1.341	112.6	–0.816	0.512	–0.195
	HF/6-31G(*d*)	1.130	1.525	1.331	111.8	–0.533	0.452	–0.149
	HF/6-31G+(*d*)	1.129	1.527	1.331	111.9	0.007	0.133	0.068
	HF/6-31G(2*d*)	1.120	1.536	1.325	111.9	–0.180	0.409	–0.157
	HF/6-31G(*d*,*p*)	1.130	1.524	1.331	111.8	–0.557	0.453	–0.152
	HF/6-31G(2*d*,*p*)	1.120	1.533	1.326	111.9	–0.200	0.411	–0.161
	MP2/6-31G	1.168	2.018	1.360	110.7	–0.456	0.432	–0.074
XIII–NO^+	AM1	1.131	1.446	1.405	117.8	–0.285	0.404	–0.023
	HF/6-31G	1.156	1.509	1.354	112.6	–0.822	0.521	–0.192
	HF/6-31G(*d*)	1.132	1.507	1.346	112.0	–0.589	0.453	–0.156
	HF/6-31G+(*d*)	1.133	1.505	1.346	112.1	–0.117	0.025	0.058
	HF/6-31G(2*d*)	1.123	1.514	1.341	112.2	–0.231	0.402	–0.165
	HF/6-31G(*d*,*p*)	1.133	1.506	1.346	112.0	–0.607	0.454	–0.159
	HF/6-31G(2*d*,*p*)	1.124	1.510	1.341	112.2	–0.243	0.404	–0.169
	MP2/6-31G	1.161	2.092	1.370	114.6	–0.407	0.457	–0.126

Table 2. (Contd.)

Complex no.	Method	l_{NO}	l_{NN^1}	$l_{N^1C(N)}$^{b}	φ_{ONN^1}	q_{N^1}	q_N(NO)	q_O(NO)
XIV–NO$^+$	AM1	1.137	1.435	1.372	117.6	–0.184	0.377	–0.069
	HF/6-31G	1.173	1.444	1.342	114.1	–1.012	0.495	–0.278
	HF/6-31G(*d*)	1.147	1.447	1.332	113.3	–0.706	0.433	–0.238
	HF/6-31G+(*d*)	1.147	1.148	1.332	113.4	0.056	0.040	0.029
	HF/6-31G(2*d*)	1.139	1.449	1.327	113.5	–0.377	0.394	–0.258
	HF/6-31G(*d*,*p*)	1.147	1.447	1.332	113.3	–0.718	0.433	–0.240
	HF/6-31G(2*d*,*p*)	1.139	1.449	1.328	113.5	–0.383	0.395	–0.259
	MP2/6-31G	1.174	1.980	1.341	110.3	–0.530	0.408	0.027
XV–NO$^+$	AM1	1.135	1.442	1.403	117.7	–0.179	0.374	–0.047
	HF/6-31G	1.170	1.447	1.380	114.0	–0.874	0.467	–0.257
	HF/6-31G(*d*)	1.145	1.546	1.375	113.2	–0.596	0.416	–0.223
	HF/6-31G+(*d*)	1.145	1.446	1.376	113.3	0.229	–0.036	0.011
	HF/6-31G(2*d*)	1.138	1.447	1.371	113.4	–0.238	0.372	–0.242
	HF/6-31G(*d*,*p*)	1.145	1.446	1.375	113.2	–0.622	0.416	–0.225
	HF/6-31G(2*d*,*p*)	1.138	1.446	1.371	113.4	–0.269	0.376	–0.245
	MP2/6-31G	1.175	1.926	1.378	111.5	–0.500	0.410	0.015
XVI–NO$^+$	AM1	1.124	1.502	1.312	120.0	–0.146	0.405	0.017
	HF/6-31G	1.160	1.483	1.299	113.5	–0.779	0.487	–0.197
	HF/6-31G(*d*)	1.133	1.502	1.284	111.7	–0.473	0.415	–0.156
	HF/6-31G+(*d*)	1.133	1.502	1.283	111.8	0.549	–0.215	0.153
	HF/6-31G(2*d*)	1.124	1.507	1.279	111.7	–0.209	0.376	–0.175
	HF/6-31G(*d*,*p*)	1.133	1.502	1.284	111.7	–0.473	0.415	–0.157
	HF/6-31G(2*d*,*p*)	1.124	1.507	1.279	111.7	–0.205	0.377	–0.176
	MP2/6-31G	1.171	2.016	1.383	119.4	–0.360	0.430	0.057
XVII–NO$^+$	AM1	1.134	1.452	1.362	117.4	–0.147	0.386	–0.043
	HF/6-31G	1.166	1.473	1.331	113.2	–0.973	0.512	–0.244
	HF/6-31G(*d*)	1.139	1.483	1.318	112.4	–0.658	0.447	–0.199
	HF/6-31G+(*d*)	1.139	1.485	1.317	112.4	–0.017	0.083	0.056
	HF/6-31G(2*d*)	1.131	1.489	1.312	112.5	–0.323	0.408	–0.215
	HF/6-31G(*d*,*p*)	1.139	1.483	1.318	112.4	–0.670	0.448	–0.200
	HF/6-31G(2*d*,*p*)	1.131	1.487	1.313	112.5	–0.329	0.409	–0.217
	MP2/6-31G	1.173	2.019	1.341	108.6	–0.494	0.411	–0.051
XVIII–NO$^+$	AM1	1.141	1.411	1.410	120.4	–0.206	0.356	–0.103
	HF/6-31G	1.182	1.401	1.400	117.9	–1.146	0.462	–0.337
	HF/6-31G(*d*)	1.154	1.405	1.394	116.8	–0.841	0.415	–0.303
	HF/6-31G+(*d*)	1.155	1.404	1.394	116.8	0.016	–0.107	0.017
	HF/6-31G(2*d*)	1.147	1.406	1.390	116.8	–0.547	0.399	–0.330
	HF/6-31G(*d*,*p*)	1.154	1.405	1.394	116.9	–0.840	0.415	–0.304
	HF/6-31G(2*d*,*p*)	1.147	1.405	1.391	117.0	–0.544	0.405	–0.336
	MP2/6-31G	1.174	1.981	1.377	114.8	–0.576	0.393	–0.013

Table 2. (Contd.)

Complex no.	Method	l_{NO}	$l_{\mathrm{NN^1}}$	$l_{\mathrm{N^1C(N)}}$[b]	$\varphi_{\mathrm{ONN^1}}$	$q_{\mathrm{N^1}}$	q_{N}(NO)	q_{O}(NO)
XIX–NO$^+$	AM1	1.138	1.423	1.403	120.4	–0.181	0.363	–0.081
	HF/6-31G	1.177	1.417	1.389	117.0	–1.116	0.475	–0.309
	HF/6-31G(*d*)	1.149	1.427	1.380	115.9	–0.799	0.423	–0.268
	HF/6-31G+(*d*)	1.150	1.426	1.380	115.9	–0.063	–0.065	0.039
	HF/6-31G(2*d*)	1.141	1.430	1.376	116.0	–0.498	0.412	–0.297
	HF/6-31G(*d,p*)	1.149	1.427	1.380	115.9	–0.798	0.424	–0.369
	HF/6-31G(2*d,p*)	1.141	1.429	1.376	116.0	–0.490	0.412	–0.297
	MP2/6-31G	1.172	2.022	1.375	115.0	–0.548	0.401	0.036

[a] Bond lengths *l* are given in Å, and bond angles φ in deg.

[b] The length of the bond located *syn* with respect to the NO group.

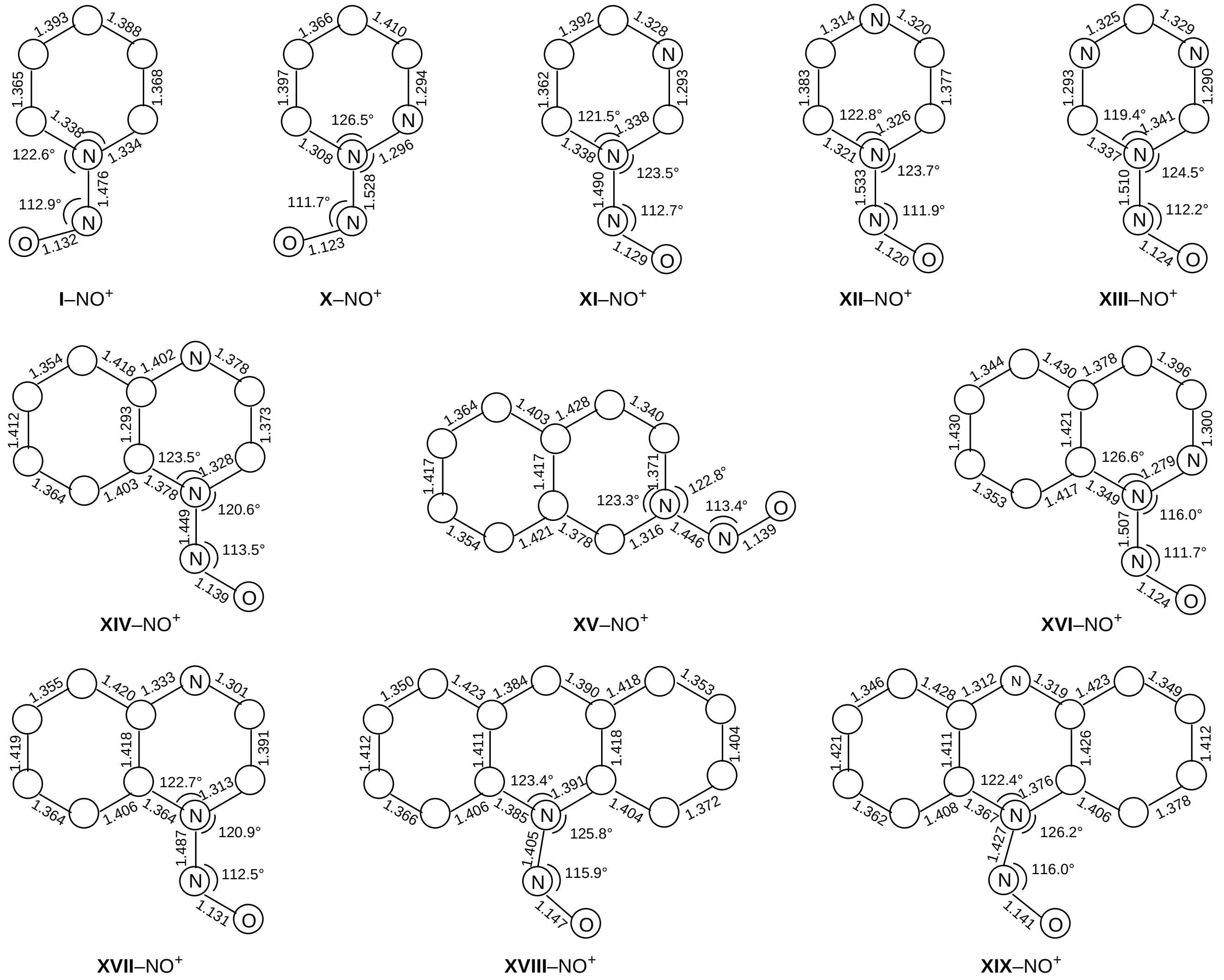
Table 3. Affinities of compounds **I**, **IIh**, **IIi**, **IIIa**, **IIIj**, **IVi**, and **X**–**XIX** for nitrosonium ion and proton, kJ/mol

Comp. no.	$A_{\mathrm{NO^+}}$ (calcd.)								$A_{\mathrm{NO^+}}$ (exptl.) [8]	*PA* [28]
	AM1	HF/6-31G	HF/6-31G+(*d*)	HF/6-31G(*d*)	HF/6-31G	HF/6-31G(2*d*)	HF/6-31G(*d,p*)	MP2/6-31G(2*d,p*)		
I	167.4	260.3	168.1	181.4	165.7	182.6	167.5	225.2	167.8	930.0
IIh	152.0	198.3	117.5	128.4	114.5	129.2	115.6	194.1		900.9
IIi	150.7	186.2	107.2	124.6	112.3	125.4	113.4	182.3		884.6
IIIa	174.5	272.9	181.8	193.7	178.3	195.8	180.3	238.3	172.0	943.4
IIIj	138.3	212.9	134.1	147.8	135.1	148.9	136.4	195.2	156.1	902.0
IVi	156.1	226.8	148.2	158.7	144.4	159.9	145.9	201.3	162.3	916.1
X	114.8	233.2	157.3	168.1	155.1	168.7	156.2	213.1		907.2
XI	143.6	203.0	119.7	131.5	118.3	132.8	119.9	178.8		885.8
XII	121.6	186.6	102.8	114.5	101.5	115.8	103.0	180.5		877.1
XIII	116.0	144.2	70.3	80.4	70.0	81.7	71.3	132.8		848.8
XIV	184.5	270.7	184.8	186.6	184.3	187.5	185.7	239.3		953.2
XV	188.7	293.5	199.0	212.8	197.4	214.0	199.0	249.0		951.7
XVI[a]	125.4	257.0	173.3	186.6	172.8	187.1	173.7	230.9		936.3
XVII	145.8	216.7	123.8	138.0	124.1	139.1	125.6	202.9		903.8
XVIII	212.2	301.8	193.4	209.7	193.0	210.3	194.2	233.0		972.6
XIX	176.1	245.0	138.4	154.9	139.2	155.6	140.4	202.8		938.4

[a] The NO$^+$ group is attached to the N^1 atom.

extension of the endocyclic C–N and N–N bonds including the nitrogen atom to which the NO group is attached. The dihedral angles CNNO are close to zero, indicating almost planar structure of nitrosonium complexes. Exceptions were complexes derived from 2,6-disubstituted pyridines and from compounds **XVIII** and **XIX**. According to the HF/6-31G(2*d,p*) calculations, the dihedral angles CNNO in complexes **Vd**–NO$^+$, **Vh**–NO$^+$, and **Vi**–NO$^+$ are 15, 45, and ~90°, respectively; in addition, the nitroso group in **Vi**–NO$^+$ declines from the pyridine ring plane by an angle of 9°. The same applies to complexes **XVIII**–NO$^+$ and **XIX**–NO$^+$ where the dihedral angle CNNO ranges from 2 to 5° and the NO group deviates from the plane of the polycyclic system. This may be due to spatial interaction between the NO fragment and hydrogen atoms in the *peri* position. The dihedral angle between the planes of the benzene and pyridine rings in complex **IVd**–NO$^+$ is 30.5°.

In the series of substituted pyridines, the N–N bond becomes longer while the N–O bond becomes shorter as the acceptor power of the substituent increases


I–NO^+ **X**–NO^+ **XI**–NO^+ **XII**–NO^+ **XIII**–NO^+

XIV–NO^+ **XV**–NO^+ **XVI**–NO^+

XVII–NO^+ **XVIII**–NO^+ **XIX**–NO^+

Fig. 1. Structures of complexes of compounds **I** and **X**–**XIX** with NO^+ ion optimized by the HF/6-31G(2*d*,*p*) method (bond lengths are given in Å).

(Tables 2, 4). The effect is most pronounced when the substituent occupies position *2* (or *6*) of the pyridine ring. Likewise, replacement of a CH group in pyridine, quinoline, or acridine molecule by nitrogen atom (compounds **X**–**XVII** and **XIX**) leads to extension of the N^1–N bond and shortening of the N–O bond (Fig. 1). Bi- and tricyclic complexes are characterized by alternation of the carbon–carbon bonds (Fig. 1).

According to *ab initio* calculations, in all cases [except for some versions with the use of 6-31G(*d*,*p*) and 6-31G+(*d*) basis sets], the nitrogen atom of the nitroso group retains its positive charge (Table 2). As a rule, all methods, except for MP2/6-31G and HF/6-31G+(*d*), predict increase in the negative charge on the N^1 atom in the pyridinium ring upon introduction of an acceptor substituent; presumably, this is the result of electron density transfer from the NO group (Tables 2, 4).

The calculations of nitrosonium complexes of pyridazine (**X**) and cinnoline (**XVI**) having contiguous nitrogen atoms in the aromatic ring revealed structures **XX**–NO^+ and **XXI**–NO^+ with a lower energy (by 27.6 and 37.2 kJ/mol, respectively), where the oxygen atom

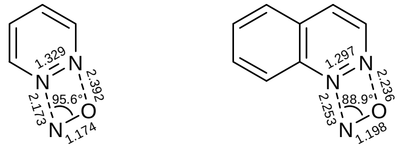

XX-NO^+ **XXI**-NO^+

Fig. 2. Structures of complexes **XX**–NO^+ and **XXI**–NO^+ optimized by the MP2/6-31G method (bond lengths are given in Å).

Table 4. Calculated [HF/6-31G(2*d*,*p*)] affinities of compounds **I**–**XIX** for nitrosonium ion (A_{NO^+}), some geometric parameters of the corresponding nitrosonium complexes, Mulliken charges (*q*) on the NO nitrogen and oxygen atoms, and experimental proton affinities of azines **I**–**XIX** (*PA*) [28]

Complex no.	A_{NO^+}, kJ/mol	*PA*, kJ/mol	l_{NO}, Å	l_{NN^1}, Å	$l_{N^1C^2}$,[a] Å	φ_{ONN^1}, deg	q_{N^1}, a.u.	q_N(NO), a.u.	q_O(NO), a.u.
I–NO$^+$	167.5	930.0	1.132	1.476	1.338	112.9	–0.247	0.390	–0.213
IIa–NO$^+$	177.0	949.1	1.136	1.463	1.346	113.1	–0.326	0.391	–0.237
IIb–NO$^+$	179.1	952.4	1.136	1.461	1.349	113.2	–0.331	0.390	–0.241
IIc–NO$^+$	117.1	887.1	1.046	2.167	1.315	108.5	–0.489	0.683	0.078
IId–NO$^+$	90.2	872.9	1.119	1.541	1.327	111.8	–0.356	0.439	–0.175
IIe–NO$^+$	182.3	934.7	1.134	1.474	1.358	112.3	–0.374	0.409	–0.233
IIf–NO$^+$	151.3	937.8	1.135	1.466	1.348	113.0	–0.303	0.389	–0.233
IIg–NO$^+$	125.5	904.8	1.126	1.507	1.343	112.2	–0.302	0.418	–0.207
IIh–NO$^+$	115.6	900.9	1.124	1.519	1.343	111.9	–0.321	0.420	–0.189
IIi–NO$^+$	113.4	884.6	1.121	1.532	1.347	111.4	–0.368	0.428	–0.179
IIj–NO$^+$	194.6	947.2	1.143	1.421	1.378	114.1	–0.379	0.368	–0.266
IIIa–NO$^+$	180.3	943.4	1.133	1.470	1.341	113.1	–0.250	0.386	–0.220
IIIb–NO$^+$	129.4	892.5	1.129	1.489	1.335	112.7	–0.269	0.401	–0.205
IIIc–NO$^+$	155.9	916.2	1.131	1.482	1.343	112.8	–0.262	0.396	–0.213
IIId–NO$^+$	166.5	934.1	1.132	1.475	1.343	112.9	–0.264	0.393	–0.219
IIIe–NO$^+$	164.3	929.5	1.129	1.488	1.332	112.7	–0.237	0.397	–0.207
IIIf–NO$^+$	175.4	942.7	1.131	1.482	1.335	112.8	–0.235	0.394	–0.213
IIIg–NO$^+$	162.6	936.5	1.132	1.475	1.337	112.9	–0.250	0.390	–0.218
IIIh–NO$^+$	138.7	910.0	1.129	1.488	1.334	112.7	–0.251	0.397	–0.206
IIIi–NO$^+$	134.5	903.4	1.128	1.491	1.334	112.7	–0.249	0.399	–0.202
IIIj–NO$^+$	136.4	902.0	1.128	1.492	1.336	112.7	–0.245	0.399	–0.197
IIIk–NO$^+$	182.4	954.4	1.131	1.479	1.326	112.9	–0.226	0.390	–0.216
IVa–NO$^+$	188.3	947.2	1.135	1.459	1.343	113.2	–0.257	0.382	–0.229
IVb–NO$^+$	191.9	951.1	1.136	1.456	1.341	113.2	–0.256	0.380	–0.232
IVc–NO$^+$	193.0	944.1	1.138	1.447	1.345	113.4	–0.260	0.376	–0.240
IVd–NO$^+$	200.3	939.7	1.139	1.442	1.344	113.5	–0.258	0.373	–0.247
IVe–NO$^+$	128.3	893.9	1.129	1.491	1.332	112.7	–0.253	0.398	–0.200
IVf–NO$^+$	206.9	961.7	1.140	1.438	1.343	113.6	–0.275	0.374	–0.251
IVg–NO$^+$	193.6	955.2	1.139	1.441	1.343	113.5	–0.267	0.374	–0.247
IVh–NO$^+$	149.2	917.8	1.133	1.469	1.339	113.0	–0.258	0.388	–0.218
IVi–NO$^+$	145.9	916.1	1.132	1.472	1.339	112.9	–0.261	0.389	–0.216
IVj–NO$^+$	151.8	913.1	1.132	1.470	1.341	113.0	–0.268	0.391	–0.217
IVk–NO$^+$	233.1	979.7	1.143	1.422	1.354	113.8	–0.284	0.365	–0.268
IVl–NO$^+$	95.2	874.3	1.124	1.511	1.333	112.4	–0.253	0.409	–0.183
Va–NO$^+$	181.9	958.9	1.136	1.463	1.344	113.2	–0.327	0.394	–0.245
Vb–NO$^+$	197.2	962.9	1.139	1.449	1.350	113.4	–0.336	0.384	–0.250
Vc–NO$^+$	189.2	958.8	1.137	1.459	1.350	113.3	–0.330	0.388	–0.243
Vd–NO$^+$	163.1	963.0	1.136	1.458	1.364	114.9	–0.412	0.387	–0.248

Table 4. (Contd.)

Complex no.	A_{NO^+}, kJ/mol	*PA*, kJ/mol	l_{NO}, Å	l_{NN^1}, Å	$l_{N^1C^2}$,[a] Å	φ_{ONN^1}, deg	q_{N^1}, a.u.	q_N(NO), a.u.	q_O(NO), a.u.
Ve–NO$^+$	198.7	957.3	1.136	1.456	1.334	113.2	–0.262	0.382	–0.236
Vf–NO$^+$	191.8	955.4	1.134	1.467	1.336	113.2	–0.253	0.386	–0.228
Vg–NO$^+$	135.5	921.2	1.120	1.546	1.344	112.6	–0.373	0.349	–0.115
Vh–NO$^+$	102.7	908.0	1.130	1.490	1.348	112.2	–0.327	0.408	–0.210
Vi–NO$^+$	146.3	909.9	1.041	2.225	1.321	108.7	–0.535	0.650	–0.167
VI–NO$^+$	181.6	953.9	1.136	1.457	1.355	113.3	–0.269	0.381	–0.237
VII–NO$^+$	198.1	957.5	1.136	1.457	1.356	112.9	–0.346	0.376	–0.226
VIII–NO$^+$	193.1	957.5	1.137	1.456	1.332	113.1	–0.362	0.386	–0.238
IX–NO$^+$	202.7	962.4	1.136	1.455	1.339	113.4	–0.262	0.383	–0.239
X–NO$^+$	156.2	907.2	1.123	1.528	1.308	111.7	–0.084	0.428	–0.178
XI–NO$^+$	119.9	885.8	1.129	1.490	1.338	112.7	–0.240	0.395	–0.193
XII–NO$^+$	103.0	877.1	1.120	1.533	1.326	111.9	–0.200	0.411	–0.161
XIII–NO$^+$	71.3	848.8	1.124	1.510	1.341	112.2	–0.243	0.404	–0.169
XIV–NO$^+$	185.7	953.2	1.139	1.449	1.328	113.5	–0.383	0.395	–0.259
XV–NO$^+$	199.0	951.7	1.138	1.446	1.371	113.4	–0.269	0.376	–0.245
XVI–NO$^+$	173.7	936.3	1.124	1.507	1.279	111.7	–0.205	0.377	–0.176
XVII–NO$^+$	125.6	903.8	1.131	1.487	1.313	112.5	–0.329	0.409	–0.217
XVIII–NO$^+$	194.2	972.6	1.147	1.405	1.391	117.0	–0.543	0.404	–0.334
XIX–NO$^+$	140.4	938.4	1.141	1.429	1.376	116.0	–0.490	0.412	–0.297

[a] The length of the bond located *syn* with respect to the NO group.

of the nitroso group is located close to the ring nitrogen atom (Fig. 2). Such structure for the cinnoline nitrosonium complex occupies a saddle point on the potential energy surface.

The affinity of azines for NO$^+$ was defined as the difference in the energies (ΔE) or enthalpies (ΔH_f) of formation of the initial azine HtH, nitrosonium ion, and nitrosonium complex.

$$A_{NO^+} = \Delta E(\text{HtH}) + \Delta E(\text{NO}^+) - \Delta E(\text{HtH–NO}^+);$$
$$A_{NO^+} = \Delta H_f(\text{HtH}) + \Delta H_f(\text{NO}^+) - \Delta H_f(\text{HtH–NO}^+).$$

It is seen that the closest agreement between the calculated A_{NO^+} value for pyridine and experimental value (167.8 kJ/mol [8]) is obtained by the AM1 method and *ab initio* calculations with basis sets including split polarization [6-31G(2*d*), 6-31G(2*d*,*p*), 6-31G(3*d*)] or diffuse functions [6-31G+(*d*), 6-31G++(*d*), 6-31G+(*d*,*p*), 6-31G++(*d*,*p*)] (Table 1). In the other cases, the difference between the calculated and experimental A_{NO^+} values is very large (14–162 kJ × mol^{-1}). The calculations procedures with account taken of electronic correlation (CI, MP2, DFT-B3LYP) give increased affinity of pyridine for nitrosonium ion, presumably due to overestimation of the contribution of higher excited states for cationic complexes. Although the situation is improved in terms of the MP2 method (6-31G basis set), the difference between the calculated and experimental A_{NO^+} values for pyridine remains quite considerable (65 kJ/mol). Electronic correlation with the use of 6-31G(*d*,*p*) or 6-31G(2*d*) basis set increases this difference.

Variation of basis sets and electronic correlation in the calculations of nitrosonium complexes derived from substituted pyridines **IIIa**, **IIIj**, and **IVi** give rise to a pattern similar to that observed for pyridine. The sums of the absolute deviations of the calculated A_{NO^+} values from those determined experimentally for compounds **I**, **IIIa**, **IIIj**, and **IVi** [8] are as follows, kJ/mol: 23.0 (AM1), 161.6 (6-31G), 27.9 [6-31G+(*d*)], 27.1 [6-31G(*d*)], 28.4 [6-31G(2*d*)], 28.5 [6-31G(*d*,*p*)], 27.0 [6-31G(2*d*,*p*)], 147.1 (6-31G+), 29.9 [6-31G(3*d*)], 147.6 (6-31G++), 26.9 [6-31G+(*d*,*p*)], 26.8 [6-31G++(*d*,*p*)], 27.8 [6-31G++(*d*)]. Insofar as the best consistency between the calculated *ab initio* and experimental A_{NO^+} values for pyridine was obtained in terms of the

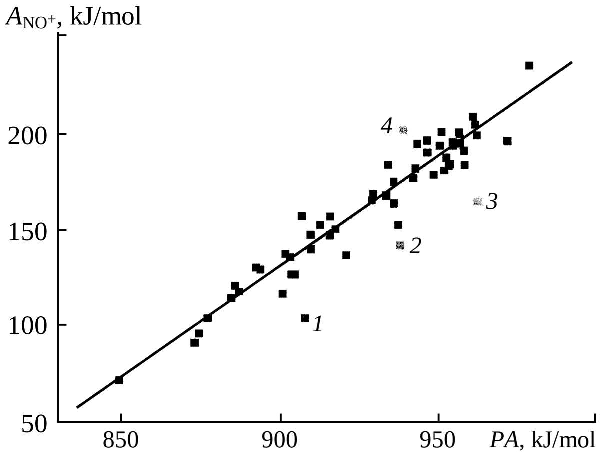
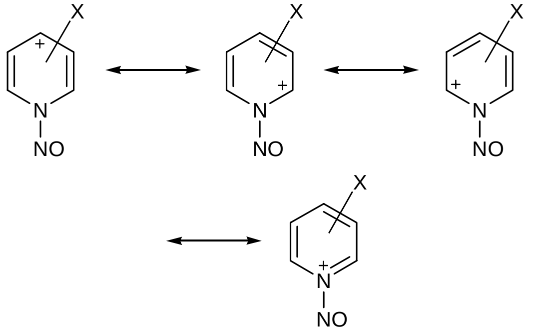


Fig. 3. Correlation between the affinities of compounds **I**–**XIX** for nitrosonium ion (A_{NO^+}, kJ/mol), calculated by the HF/6-31G(2*d*,*p*) method and experimental proton affinities (*PA*, kJ/mol). Points nos. *1*–*4* corresponding to compounds **Vh**, **XIX**, **Vd**, and **IVd** were not included in the statistical processing.

HF/6-31G(2*d,p*) method, it was used subsequently to estimate the effect of structural factors on A_{NO^+}.

Different quantum-chemical methods give qualitatively similar patterns of variation of the affinity of azines for nitrosonium ion, depending on their structure (Tables 3, 4). As expected, the affinity of substituted pyridines increases with rise in the donor power of the substituent; in keeping with the resonance theory, the +*M* effect is maximal when the substituent occupies position *2*, *4*, or *6*.



Comparison of the calculated [HF/6-31G(2*d,p*)] A_{NO^+} values for pyridine and its 3- and 4-substituted derivatives **IIIa**, **IIIb**, **IIIf**–**IIIk**, **IVa**, **IVb**, and **IVd**–**IVl** (Table 4) with the substituent constants σ^+ [33] leads to the following correlation:

$$A_{NO^+} = (163.9 \pm 2.6) - (63.2 \pm 5.3)\sigma^+;$$
$$r = 0.942,\ s = 11.5,\ n = 20.$$

The corresponding correlation for the series of pyridines **I**, **IIIa**–**IIIk**, and **IVa**–**IVl** with the use of substituent constants σ^+ taken from [34] is characterized by a lower correlation coefficient:

$$A_{NO^+} = (177.1 \pm 2.5) - (94.8 \pm 7.6)\sigma^+;$$
$$r = 0.936,\ s = 11.2,\ n = 24.$$

As structural parameter suitable for correlation with A_{NO^+} we selected the charge on the NO group in nitrosonium complexes (q_{NO}). It might be expected that A_{NO^+} should increase with decrease in the positive charge on the NO group, i.e., as the ability of the remaining part of the complex to delocalize positive charge increases. A satisfactory correlation between A_{NO^+} and q_{NO} (Table 4) was obtained for 4-substituted pyridines:

$$A_{NO^+} = (338 \pm 10) - (1067 \pm 61)q_{NO};$$
$$r = 0.984,\ s = 7,\ n = 12.$$

Inclusion of the data for 3-substituted pyridines impairs the correlation:

$$A_{NO^+} = (327 \pm 14) - (960 \pm 81)q_{NO};$$
$$r = 0.933,\ s = 11.6,\ n = 23.$$

Even larger dispersion is observed when the data for different azine series are included.

Increase in the number of ring nitrogen atoms leads to decrease in the affinity of azines for nitrosonium ion according to the following series: **I** > **X** > **XI** > **XII** > **XIII**; **XIV** > **XVI** > **XVII**; **XVIII** > **XIX** (Table 4). In the series of diazines **X**–**XII**, **XVI**, **XVII**, the effect of the second nitrogen atom becomes stronger as the distance to the first nitrogen atom increases. Benzene ring fusion enhances the affinity of azines for NO^+ cation in the series **I** < **XIV** < **XVIII**; **XII** < **XVII** < **XIX**.

Some specificity in the application of different quantum-chemical methods can be revealed by comparing the calculated A_{NO^+} values and experimental proton affinities (*PA*) of azines. Cacace et al. [8] found a linear correlation between the corresponding quantities for a wide series of nitrogen- and oxygen-centered bases. We obtained the following linear correlation between the calculated A_{NO^+} values and proton affinities (Table 4) of azines **I**–**XIX** (Table 5, Fig. 3).

$$A_{NO^+} = a + b\,PA.$$

The coefficients *a* and *b* in this correlation differ from those given in [8]. Presumably, the reason is that the correlations were drawn for series of compounds of

Table 5. Parameters of correlations between the calculated affinities of azines for nitrosonium ions and their experimental proton affinities

Method	Azine series	–*a*	*b*	*r*	*s*	*n*
AM1	**I**–**IX**, **XI**–**XV**, **XVII**–**XIX**[a]	601 ± 44	0.83 ± 0.05	0.923	10.5	55
HF/6-31G	**I**, **IIi**, **IIIa**, **IIIh**, **IIIj**, **IVi**, **X**–**XIX**	939 ± 68	1.27 ± 0.07	0.977	9.5	16
HF/6-31G (*d*)	**I**, **IIi**, **IIIa**, **IIIh**, **IIIj**, **IVi**, **X**–**XIX**	812 ± 87	1.06 ± 0.09	0.948	12.1	16
HF/6-31G + (*d*)	**I**, **IIi**, **IIIa**, **IIIh**, **IIIj**, **IVi**, **X**–**XIX**	824 ± 91	1.1 ± 0.1	0.943	12.7	16
HF/6-31G (2*d*)	**I**, **IIi**, **IIIa**, **IIIh**, **IIIj**, **IVi**, **X**–**XIX**	812 ± 86	1.04 ± 0.09	0.947	12.0	16
HF/6-31G (*d*,*p*)	**I**, **IIi**, **IIIa**, **IIIh**, **IIIj**, **IVi**, **X**–**XIX**	809 ± 88	1.1 ± 0.1	0.947	12.3	16
HF/6-31G (2*d*,*p*)	**I**–**XIX**	872 ± 51	1.11 ± 0.05	0.939	12.2	57
HF/6-31G (2*d*,*p*)	**I**–**XIX**[b]	880 ± 37	1.12 ± 0.04	0.969	8.7	53
MP2/6-31G	**I**, **IIi**, **IIIa**, **IIIh**, **IIIj**, **IVi**, **X**–**XIX**	562 ± 84	0.84 ± 0.09	0.926	11.7	16

[a] The data for compounds **X** and **XVI** were not included, for the deviations of the corresponding points from the regression straight line exceeded 2σ (95% confidence probability) [35].

[b] The data for compounds **IVd**, **Vd**, **Vg**, and **XIX** were not included, for the deviations of the corresponding points from the regression straight line exceeded 2σ.

different natures. On the other hand, the coefficients *a* and *b* in the correlation between A_{NO^+} values calculated by the HF/6-31G(2*d*,*p*) method for H_2O, MeCN, MeCHO, and pyridine and the corresponding proton affinities are fairly similar to the coefficients determined in [8].

The AM1 method underestimated A_{NO^+} for pyridazine (**X**) and cinnoline (**XVI**), so that the points for these compounds were excluded from the correlation. A probable reason is underestimation (by ~40 kJ/mol) of repulsion between lone electron pairs on the contiguous nitrogen atoms in heteroaromatic compounds, which is inherent to semiempirical methods [36–39].

Thus, using the complex of pyridine with nitrosonium ion as an example, we found that the AM1 method and *ab initio* procedures involving 6-31G(2*d*), 6-31G(2*d*,*p*), 6-31G(3*d*), 6-31G+(*d*), 6-31G++(*d*), 6-31G+(*d*,*p*), and 6-31G++(*d*,*p*) basis sets ensure the best agreement between the calculated and experimental affinities for NO^+. Electronic correlation in terms of the MP2/6-31G, MP2/6-31G(*d*,*p*), MP2/6-31G(2*d*), B3LYP/6-31G(*d*,*p*), and CI/6-31G(*d*) methods overestimates A_{NO^+} values. The revealed linear correlation between the calculated A_{NO^+} values and experimental proton affinities for a wide series of nitrogen-containing heteroaromatic compounds, taking into account ready accessibility of the latter quantities, may be used as a basis for estimation of unknown A_{NO^+} values.

Quantum-chemical calculations by the semiempirical AM1 [29] and nonempirical Hartree–Fock (RHF) methods [30, 31] were performed using GAMESS software package [30]. Full geometry optimization of molecular structures corresponding to stationary points (minima, $\lambda = 0$, and saddle points, $\lambda = 1$; here, λ is the number of negative Hessian eigenvalues) on the potential energy surface [31] was executed up to a gradient value of 10^{-5} a.u./bohr. Electronic correlation was taken into account in terms of the Moeller–Plesset second-order perturbation method (MP2) [31], as well as of the CI [31] and B3LYP methods [40, 41]. Corrections for zero-point energy (ZPE) were introduced while calculating A_{NO^+} values; the ZPE correction factors for 6-31G(*d*), 6-31G(*d*,*p*), and 6-31G+(*d*) basis sets were taken from [42], and in the other cases, the following correction factors were applied: 0.9135 [6-31G, 6-31G(2*d*), 6-31G(3*d*)], 0.9181 [6-31G(2*d*,*p*)], 0.9153 [6-31G+, 6-31G+(*d*,*p*), 6-31G++, 6-31G++(*d*), 6-31G++(*d*,*p*)], 0.9661 [MP2/6-31G, MP2/6-31G(*d*,*p*), MP2/6-31G(2*d*)], 0.9806 [B3LYP/6-31G(*d*,*p*)] (cf. [42]).

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REFERENCES

1. Borodkin, G.I. and Shubin, V.G., Abstracts of Papers, *Int. Conf. "Reaction Mechanisms and Organic Intermediates,"* St. Petersburg: Nauch.-Issled. Inst. Khim. Sankt-Peterb. Gos. Univ., 2001, p. 88.
2. Borodkin, G.I. and Shubin, V.G., *Trudy mezhdunarodnoi konferentsii "Sovremennye problemy organicheskoi khimii"* (Proc. Int. Conf. "Current Problems in Organic Chemistry"), Novosibirsk: Sib. Otd. Ross. Akad. Nauk, 2001, p. 70.

3. Borodkin, G.I. and Shubin, V.G., *Usp. Khim.*, 2001, vol. 70, p. 241.
4. Olah, G.A., Olah, J.A., and Overchuk, N.A., *J. Org. Chem.*, 1965, vol. 30, p. 3373.
5. Makhova, N.N., Karpov, G.A., Mikhailyuk, A.N., Bova, A.E., Khmel'nitskii, L.I., and Novikov, S.S., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, p. 226.
6. Lee, K.Y. and Kochi, J.K., *J. Chem. Soc., Perkin Trans. 2,* 1994, p. 237.
7. Freitas, M.A., O'Hair, R.A.J., Schmidt, J.A.R., Tichy, S.E., Plashko, B.E., and Williams, T.D., *J. Mass Spectrom.*, 1996, vol. 31, p. 1086.
8. Cacace, F., de Petris, G., and Pepi, F., *Proc. Natl. Acad. Sci. USA*, 1997, vol. 94, p. 3507.
9. Borodkin, G.I., Shubin, V.G., and Andreev, R.V., *Book of Abstracts of the International Conference on Reactive Intermediates and Reaction Mechanisms*, Ascona, 1998, p. 38.
10. Andreev, R.V., Borodkin, G.I., and Shubin, V.G., Abstracts of Papers, *Molodezhnaya nauchnaya shkola po organicheskoi khimii* (Youth Scientific School on Organic Chemistry), Yekaterinburg, 1999, p. 65.
11. Borodkin, G.I., Andreev, R.V., Elanov, I.R., and Shubin, V.G., *Book of Abstracts of the 7th European Symposium on Organic Reactivity*, Ulm, 1999, p. 136.
12. Lindeman, S.V., Bosch, E., and Kochi, J.K., *J. Chem. Soc., Perkin Trans. 2,* 2000, p. 1919.
13. Andreev, R.V., Borodkin, G.I., Gatilov, Yu.V., and Shubin, V.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, p. 2365.
14. Andreev, R.V., Borodkin, G.I., and Shubin, V.G., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 144.
15. Andreev, R.V., Borodkin, G.I., Gatilov, Yu.V., and Shubin, V.G., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 845.
16. Williams, D.L.H., *Nitrosation*, Cambridge: Cambridge Univ., 1988.
17. Castro, A., Iglesias, E., Leis, J.R., Pena, M.E., Vazquez Tato, J., and Williams, D.L.H., *J. Chem. Soc., Perkin Trans. 2*, 1986, p. 1165.
18. Loeppky, R.N. and Cui, W., *Tetrahedron Lett.*, 1998, vol. 39, p. 1845.
19. Loeppky, R.N., Bao, Y.T., Bae, J., Yu, L., and Shevlin, G., *Nitrosamines and Related N-Nitroso Compounds. Chemistry and Biochemistry*, Loeppky, R.N. and Michejda, C.J., Eds., Washington: Am. Chem. Soc., 1994, p. 52.
20. Williams, D.L.H., *Nitrosamines and Related N-Nitroso Compounds. Chemistry and Biochemistry*, Loeppky, R.N. and Michejda, C.J., Eds., Washington: Am. Chem. Soc., 1994, p. 66.
21. Murad, F., *Angew. Chem., Int. Ed. Engl.*, 1999, vol. 38, p. 1857.
22. Furchgott, R.F., *Angew. Chem., Int. Ed. Engl.*, 1999, vol. 38, p. 1871.
23. Ignarro, L.J., *Angew. Chem., Int. Ed. Engl.*, 1999, vol. 38, p. 1883.
24. Lipton, S.A., Choi, Y.-B., Pan, Z.-H., Lel, S.Z., Chen, H.-S., Sucher, N.J., Loscalzo, J., Singel, D.J., and Stamler, J.S., *Nature*, 1993, vol. 364, p. 626.
25. Stamler, J.S., Singel, D.J., and Loscalzo, J., *Science*, 1992, vol. 258, p. 1898.
26. Kirchner, J.J., Sigurdsson, S.T., and Hopkins, P.B., *J. Am. Chem. Soc.*, 1992, vol. 114, p. 4021.
27. Elcock, A.H., Lyne, P.D., Mulholland, A.J., Nandra, A., and Richards, W.G., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 4706.
28. Hunter, E.P.L. and Lias, S.G., *J. Phys. Chem., Ref. Data*, 1998, vol. 27, p. 413.
29. Dewar, M.J.S., Zoebisch, E.G., Healy, E.F., and Stewart, J.J.P., *J. Am. Chem. Soc.*, 1985, vol. 107, p. 3902.
30. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem.*, 1993, vol. 14, p. 1347.
31. Minkin, V.I., Simkin, B.Ya., and Minyaev, R.M., *Kvantovaya khimiya organicheskikh soedinenii. Mekhanizmy reaktsii* (Quantum Chemistry of Organic Compounds. Reaction Mechanisms), Moscow: Khimiya, 1986, p. 10.
32. Allen, F.H., Kennard, O., Watson, D.G., Brammer, L., Orpen, A.G., and Taylor, R., *J. Chem. Soc. Perkin Trans. 2*, 1987, p. S1.
33. Zhdanov, Yu.A. and Minkin, V.I., *Korrelyatsionnyi analiz v organicheskoi khimii* (Correlation Analysis in Organic Chemistry), Rostov-on-Don: Rostov. Gos. Univ., 1966, p. 110.
34. Hansch, C., Leo, A., and Taft, R.W., *Chem. Rev.*, 1991, vol. 91, p. 165.
35. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972. Translated under the title *Sputnik khimika*, Moscow: Mir, 1976, p. 516.
36. Fos, E., Vilarrasa, J., and Fernandez, J., *J. Org. Chem.*, 1985, vol. 50, p. 4894.
37. Ritchie, J.P., *J. Org. Chem.*, 1989, vol. 54, p. 3553.
38. Del Valle, J.C. and de Paz, J.L.G., *J. Mol. Struct.*, 1992, vol. 254, p. 481.
39. Poplavskaya, Yu.V., Trifonov, R.E., Shcherbinin, M.B., and Koldobskii, G.I., *Russ. J. Org. Chem.*, 2000, vol. 36, p. 1788.
40. Becke, A.D., *J. Chem. Phys.*, 1993, vol. 98, p. 5648.
41. Stephens, P.J., Devlin, F.J., Chablowski, C.F., and Frisch, M.J., *J. Phys. Chem.*, 1994, vol. 98, p. 11623.
42. Scott, A.P. and Radom, L., *J. Phys. Chem.*, 1996, vol. 100, p. 16502.