

NOTIZEN

A CNDO/2 Study of the Homoconjugation Energies of 4-Substituted Pyridine N-Oxides

Lech Chmurzyński* and Adam Liwo

Institute of Chemistry, University of Gdansk,
80-952 Gdańsk, Poland

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Homoconjugation energies *in vacuo* have been calculated for pyridine N-oxide (PyO) and its 4-methyl- (4 PicO) and 4-nitro- (4-NO₂PyO) derivatives with the use of the CNDO/2 method. Comparison with the experimental homoconjugation constants in some aprotic solvents reveals the opposite order of the stability of homocomplexes than could be expected based on the calculated homoconjugation energies. This formal inconsistency can be explained in terms of the solvation effect.

Introduction

In our recent paper [1] we discussed the influence of the solvation effect on the acid-base equilibria of 4-substituted pyridine N-oxides. As the N-oxides investigated, apart from the simple cations (BH⁺) form also the homoconjugated cations (BHB⁺) with symmetric H-bonds, we thought it worthwhile to extend our study to the influence of the solvation effect on the homoconjugation equilibria. It seems especially interesting to compare the theoretically calculated homoconjugation energies with the experimental homoconjugation constants determined in various solvents.

Methods

We have chosen three model N-oxides of various acidic-basic properties: 4-nitropyridine N-oxide (4 NO₂PyO), pyridine N-oxide (PyO), and 4-methylpyridine N-oxide (4 PicO). The homoconjugation energies (*i. e.* the energies of the reaction BH⁺ + B = BHB⁺ where B denotes a N-oxide molecule) have been calculated in the su-

permolecule approach by the CNDO/2 method [2]. The geometries of N-oxides and their simple cations have been taken from either the crystallographic data [3–5] or estimated by extrapolation, as described previously [1]. As no experimental data exist for the homoconjugated cations investigated, based on the data for 2,6-lutidine N-oxide semiperchlorate [6] we have assumed that the geometry of the ring does not change when compared with free N-oxides, while the N–O bond length increases by 0.05 Å with respect to N-oxides, being still shorter than that of simple cations. Also taking into account the crystallographic data mentioned above [6] the O···O distance has been assigned a value of 2.345 Å and proton was located symmetrically in the bridge.

Results and Discussion

The calculated values of the homoconjugation energy in the systems under study are collected in Table I, together with the values of the homoconjugation constants determined in various aprotic solvents. As shown, the energy and constants values vary in exactly opposite direction: the homoconjugation constants decrease in the series 4 PicO, PyO, and 4 NO₂PyO, while the energies increase. In the case of acetonitrile and acetone the homoconjugation constant of 4 NO₂PyO is even indeterminably small.

Table I. CNDO/2 homoconjugation energies of the compounds studied and their homoconjugation constants in some Parker solvents.

Compound	Homoconjugation energy [eV]	log K _{BHB⁺} AN ^a	PC ^b	NM ^c	AC ^d
4 NO ₂ PyO	2.630	– ^e	1.62	1.91	– ^e
PyO	2.595	3.22	3.08	3.69	2.69
4 PicO	1.964	3.57	3.28	4.27	3.19

^a Acetonitrile, log K values from ref. [7]; ^b propylene carbonate, log K values from ref. [8]; ^c nitromethane, log K values from ref. [9]; ^d acetone, log K values from ref. [9]; ^e values indeterminably small.

The calculated order of the homoconjugation energy *in vacuo* is reasonable, taking into account the changes in the charge density of the species studied. The proton net charge is the greatest for

* Reprint requests to Dr. L. Chmurzyński.



4 NO₂PyOH⁺ and the least for 4 PicOH⁺ (see Table II). Proton is therefore least shielded for 4 NO₂PyO, thus allowing for the effective electrostatic interactions on H-bond formation. We can also observe that there is some correlation between the N-oxide nitrogen net charge and the CNDO/2 homoconjugation energy: for 4 NO₂PyO and PyO which have similar nitrogen charges the energy is also similar, while for 4 PicO which has a much lower charge the energy is lower also. This is due to the fact that on increasing the nitrogen charge the dipole moment of the N–O bond also increases,

making thus a greater contribution to electrostatic energy, as the oxygen net charge does not change as significantly.

The reversal of the experimental ΔG of homoconjugation with respect to the homoconjugation energy *in vacuo* may be due only to the solvation effect. In fact, it has long been observed [10–12] that the homoconjugation constants of N-oxides in aprotic solvents decrease on increasing the acidity of their simple cations. It can therefore be concluded that in aprotic solvents the difference in the solvation energy of the homoconjugated cation and its components shifts to the favour of the latter on increasing the acidity of protonated N-oxide and that this difference cannot be compensated, in general, by increasing the “vacuum” homoconjugation energy which, according to the results of our calculations, increases with decreasing the basicity of N-oxides. Again, the change of the difference in the solvation energy is consistent with the results of the analysis of the charge density of the simple cations (Table II): 4 NO₂PyOH⁺ has the greatest proton net charge and can therefore efficiently interact with Lewis bases such as the Parker solvents molecules. In contrast to this, 4 PicOH⁺ has the least proton net charge, making thus the solvation less effective.

Table II. Selected CNDO/2D net atomic charges of the N-oxides studied and their complexes with proton.

Species studied	atom	4 NO ₂ PyO	PyO charge [e]	4 PicO
N-Oxide	N	0.285	0.286	0.150
	O	-0.404	-0.429	-0.444
Simple cation	N	0.194	0.195	0.101
	O	-0.132	-0.149	-0.137
	H	0.240	0.227	0.222
Homoconjugated cation	N	0.202	0.207	0.066
	O	-0.346	-0.360	-0.332
	H	0.324	0.320	0.324

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