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LETTERS TO THE EDITOR

Molecular Complexes of Heteroaromatic *N*-Oxides with 2,4-Dinitrophenylhydrazine

A. V. Ryzhakov

Institute of Water Problems, Northern Karelia Scientific Center, Russian Academy of Sciences,
pr. A. Nevskogo 50, Petrozavodsk, 185003 Russia
e-mail: ryzhakov@nwpi.krc.karelia.ru

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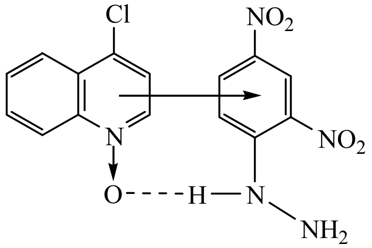
Extending the previously reported study on nucleophilic substitution of heteroaromatic *N*-oxides with weak nucleophiles [1], we attempted to carry out the reaction of 4-chloroquinoline *N*-oxide with 2,4-dinitrophenylhydrazine. However, the solid complex of reactants was isolated instead of expected product of chlorine substitution. The complex formation was surprising, because 2,4-dinitrophenylhydrazine is known as very weak electron acceptor ($E_{1/2}^{\text{red}}$ of –0.93 V [2]) and is not considered as π-acceptor. Herein, preparation and spectral features of 2,4-dinitrophenylhydrazine complexes with other quinoline and isoquinoline *N*-oxides are reported.

The molecular complexes were formed in the course of the reactants interaction in saturated solution in dioxane during 12 h. According to elemental analysis, the complexes were of 1 : 1 stoichiometry. Obtained with relatively high yield, the complexes were stable and melted without decomposition at 127 to 198°C.

The high stability of the prepared molecular complexes could hardly be explained exclusively by formation of the charge-transfer bond (similar to that in the complexes of *N*-oxides with tetrabromoquinone or tetracyanoethylene [3]), as 2,4-dinitrophenylhydrazine was weak electron acceptor. We suppose that the complexes were stabilized by hydrogen bonding between the *N*-oxide oxygen atom and the NH proton of 2,4-dinitrophenylhydrazine (Scheme 1).

Scheme 1.



Heteroaromatic *N*-oxides are known to readily form hydrogen bonds with proton-containing compounds (water, alcohols, phenols, and carboxylic acids) [4]. Acidity of the NH proton of 2,4-dinitrophenylhydrazine is enhanced by the electron accepting 2,4-dinitrophenyl group.

The observed spectra did not contradict the suggested complex structure. In the IR spectra, the band assigned to the N→O stretching was somewhat shifted towards lower frequency as compared with the spectra of the parent *N*-oxides, typical of hydrogen bond formation by the oxygen atom. The observed shift (15–20 cm^{-1}) was significantly smaller than that in the cases of *N*-oxides salts with strong hydrogen halide acids (200 cm^{-1}). At the same time, in the cases of solid molecular complexes of *N*-oxides with halogenanils (hydrogen bond cannot be formed), the N→O band was shifted by no more than 5–7 cm^{-1} due to the complexes formation.

The bands assigned to charge transfer were not detected in electronic absorption spectra of the studied complexes. In our opinion, they were masked due to overlapping with stronger absorption bands of 2,4-dinitrophenylhydrazine at 350–420 nm. Indeed, electron accepting properties of the hydrazine were weak, and the charge-transfer bands of its complexes could be expected at lower wavelength as compared to the complexes of stronger acceptors (for instance, tetracyanoethylene).

Yield of the complex with 2-methylquinoline *N*-oxide was significantly lower (21%) than those of other *N*-oxides. That likely pointed at steric hindrance due to the presence of methyl groups.

The complexes decomposed into the starting compounds in the course of silica gel chromatography.

4-Chloroquinoline *N*-oxide complex with 2,4-dinitrophenylhydrazine. 90 mg (0.5 mmol) of 4-chloroquinoline *N*-oxide was added to warm saturated solution of 99 mg (0.5 mmol) of 2,4-dinitrophenylhydrazine in 2.5 mL of anhydrous dioxane. The mixture was stirred till complete dissolution of the *N*-oxide and then incubated at room temperature. After 12 h of incubation, the so formed yellow precipitate was centrifuged off, washed with dioxane (2 mL) and diethyl ether (3 × 2 mL), and dried in air. Yield 70%, mp 197–198°C. IR spectrum, cm^{-1}: 1285 ($\nu_{N\to O}$). Electronic absorption spectrum, λ_{max}, nm (log ε): 250 sh, 270 sh 347 (4.28), 408 sh. Found, %: C 47.50, 47.80; H 3.31, 3.28; N 18.32, 18.35; $C_9H_6ClNO\cdot C_6H_6N_4O_4$. Calculated, %: C 47.68; H 3.18; N 18.54.

Complexes of other *N*-oxides were prepared similarly.

Quinoline *N*-oxide complex with 2,4-dinitrophenylhydrazine. Yield 57%, mp 172–173°C. IR spectrum, cm^{-1}: 1262 ($\nu_{N\to O}$). Electronic absorption spectrum, λ_{max}, nm (log ε): 263 sh, 340 (4.31), 408 sh.

4-Methylquinoline *N*-oxide complex with 2,4-dinitrophenylhydrazine. Yield 58%, mp 162–163°C. IR spectrum, cm^{-1}: 1305 ($\nu_{N\to O}$). Electronic absorption spectrum, λ_{max}, nm (log ε): 245 sh, 268 sh, 350 (4.11), 408 sh.

4-Methoxyquinoline *N*-oxide complex with 2,4-dinitrophenylhydrazine. Yield 61%, mp 127–128°C. IR spectrum, cm^{-1}: 1280 ($\nu_{N\to O}$). Electronic absorption spectrum, λ_{max}, nm (log ε): 250 (4.3), 268 sh, 349 (4.30), 410 sh.

Isoquinoline *N*-oxide complex with 2,4-dinitrophenylhydrazine. Yield 49%, mp 158–159°C. IR spectrum, cm^{-1}: 1248 ($\nu_{N\to O}$). Electronic absorption spectrum, λ_{max}, nm (log ε): 257 (4.55), 297 (4.13), 307 (4.11), 348 (4.18), 408 sh.

Elemental analysis confirmed the 1 : 1 stoichiometry of the complexes.

IR spectra (Vaseline oil) were recorded using the UR-20 spectrometer. Electronic absorption spectra (acetonitrile solutions) were recorded using the Specord UV-Vis spectrophotometer.

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