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# Basicity of {(2-Amino)- and (2-Aminomethyl)bicyclo[2.2.1]hept-3-yl}anilines in Nitromethane

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**Abstract**—Ionization constants of {(2-amino)-bicyclo[2.2.1]-hept-3-yl}anilines and {(2-aminomethyl)bicyclo [2.2.1]-hept-3-yl}anilines in nitromethane have been determined by potentiometric titration. Due to high values of $pK_{a1}^{BH+}$ and $pK_{a2}^{BH+}$ (close to known adamantane-containing diamines) the studied compounds are promising candidates for preparation of (co)polyimides with a complex of excellent utilitarian properties.

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For diamines, a strong correlation exists between $pK_a$ and logarithms of the rate constant of acylation with tetracarboxylic acid dianhydrides [1]. Therefore, determination of diamines basicity is an important stage in predicting their reactivity in nucleophilic substitution reactions.

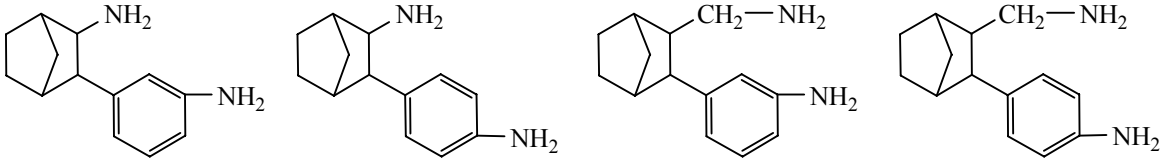
In this work, we took advantage of potentiometric titration [2] to determine basicity of compounds **I–VII** in nitromethane.

The organic solvent, nitromethane, was chosen due to several reasons. First, the studied bicyclic and adamantane-containing diamines were insoluble in water. Second, nitromethane was a weak acid itself; it made possible titration of even very weak bases in nitromethane medium. Finally, contrary to acetic acid and similar acidic solvents, in nitromethane medium the basicity of diamines did not level off.

The experimental results are collected in the table.

For all the studied bicyclic diamines, $pK_{a1}^{BH+}$ varied from 15.8 to 16.8. The higher basicity was observed in the cases of compounds containing the amino group separated from the bicyclic fragment with methylene bridge. The $pK_{a2}^{BH+}$ were in the range of 9.0–9.9.

Thus, {(2-amino)- and (2-aminomethyl)bicyclo-[2.2.1]hept-3-yl}anilines were sufficiently strong bases in nitromethane. However, most of the studied diamines were somewhat weaker bases than linear aliphatic amines {for butylamine in $CH_3NO_2$, $pK_a^{BH+}$ = 16.86 [3]} or alicyclic amines {for cyclohexylamine in $CH_3NO_2$, $pK_a^{BH+}$ = 16.79 [3]}. We suppose that it was




**I**



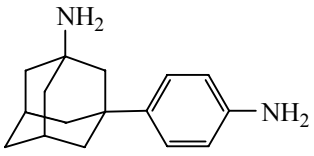

**II**



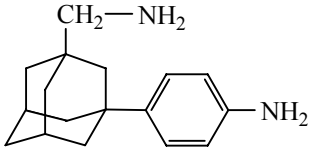

**III**



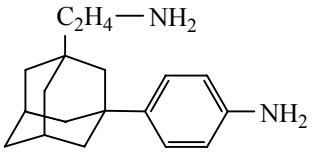

**IV**




**V**




**VI**




**VII**

Basicity ($pK_a^{BH+}$) and $\sigma^-$ constants of adamantane-containing and bicyclic diamines in nitromethane

| Comp. no. | $pK_{a1}^{BH+}$ | $pK_{a2}^{BH+}$ | $\sigma^-(H_3N^+–X–Alk)$ |
|---|---|---|---|
| **I** | 15.8 | 9.1 | –0.05 |
| **II** | 16.0 | 9.0 | –0.02 |
| **III** | 16.8 | 9.9 | –0.26 |
| **IV** | 16.8 | 9.9 | –0.26 |
| **V** | 16.0 | 9.4 | –0.13 |
| **VI** | 16.3 | 9.9 | –0.26 |
| **VII** | 16.9 | 10.1 | –0.31 |

caused by special features of solvation of the bicyclic ammonium cations with nitromethane molecules.

As follows from the tabulated results, the studied bicycle-containing diamines were close (**II** and **V**) or somewhat stronger (**IV** and **VI**) in basicity than the adamantane-containing diamine analogs. Higher $pK_{a1}^{BH+}$ in the cases **III** and **IV** as compared to **VI** could be due to less steric hindrance by the cage fragment.

Having known $pK_a^{BH+}$ values of diamines, we could calculate the corresponding $\sigma^-$ constants of substituents, and thus, to quantify their electronic effect.

As all the studied compounds could be regarded as anilines with complex substituents $H_3N^+$–X–Alk, for calculation of $\sigma^-$ constants we used the Hammett dependence reported for anilines in $CH_3NO_2$ [4].

$$\sigma^-(H_3N^+–X–Alk) = [9.22 – (pK_{a2}^{BH+} + 0.3)]/3.81.$$

Results of calculations are presented in the table.

In the cases of all the studied diamines, $\sigma^-(H_3N^+–X–Alk)$ was negative. Thus, bicyclic fragment acted as electron-donating group even after protonation of the aliphatic $NH_2$ {for aniline in $CH_3NO_2$, $pK_a^{BH+}$ = 9.07 [2]}.

In general, $pK_{a2}^{BH+}$ of bicyclic and adamantane-containing non-symmetric diamines was determined by the interplay of alicyclic fragment electron-donating effect (increasing the basicity of aromatic $NH_2$ as compared to unsubstituted aniline) and the possibility of transmission of the protonated amino group electronic effects along the carbon chain (decreasing $pK_{a2}^{BH+}$).

The lowest $pK_{a2}^{BH+}$ (and, consequently, absolute values of $\sigma^-$) was found for **I** and **II,** with amino group directly bound to bicyclic fragment ($\sigma^-$ of –0.05 to –0.02). The introduction of methylene bridge between the amino group and bicyclic fragment (**III** and **IV**) shielded the electronic effects from the protonated amino group and, thus, increased the electron-donating effect of alkyl ($\sigma^-$ of –0.26).

Comparison of $pK_{a2}^{BH+}$ and $\sigma^-$ values of bicycle-containing **III** and **IV** ($\sigma^-$ –0.26) and of adamantane-containing diamine **V** ($\sigma^-$ –0.13) with four σ–bonds separating the amino groups revealed seemingly less efficient transmission of electronic effects along the bicyclic backbone as compared to adamantylene. It was probably due to the possibility of additional through-space transmission of electronic effect in the latter case [5].

The highest $pK_{a2}^{BH+}$ (and, consequently, absolute values of $\sigma^-$) was observed in the case of adamantane-containing diamine **VII** with ethylene bridge separating the aliphatic amino group and adamantylene fragment. Evidently, in that case $pK_{a2}^{BH+}$ was exclusively determined by the electron-donating effect of the cage fragment {for *p*-toluidine in $CH_3NO_2$, $pK_a^{BH+}$ = 9.80 [2]}.

To conclude, the introduction of methylene bridge between the amino group and caged backbone of adamantane- and bicycle-containing diamines significantly increased their basicity (both $pK_{a1}^{BH+}$ and $pK_{a2}^{BH+}$). Sufficiently high basicity suggests that the studied bicyclic diamines reactivity in formation of polyamidoacids and polyimides should be close to that of known adamantane-containing diamines. Therefore, the (co)polyimides possessing a complex of perfect utilitarian properties can likely be prepared based on {(2-amino)- and (2-aminomethyl)bicyclo[2.2.1]hept-3-yl}anilines.

## EXPERIMENTAL

Bicycle-containing diamines **I**–**IV** were prepared according to [6–8]. Adamantane-containing diamines **V**–**VII** were prepared according to [9].

Potentiometric measurements were performed using I-130M ionometer with glass ESL-43-07 and silver chloride EVL-1M3 electrodes. All measurements were carried out at 25±0.5°C in thermostatted cell.

Solutions of $HClO_4$ in nitromethane ($c$ ≈0.1 mol/L) were used as titrants. $HClO_4$ was obtained by distillation of the 57% commercial pure grade acid [10]. For titration, 10 mL of solution of the studied

diamine (0.0025 mol/L) was used. The titrant was added in 0.02 mL portions, at constant stirring.

In [2], reversibility of glass electrode performance in nitromethane was showed, thus the absolute value of diphenylguanidine p$K_a$ (17.2) could be determined. Therefore, in this work the results were reduced to standard conditions.

To calculate the first and the second ionization constants (p$K_{a\,1}^{BH+}$ and p$K_{a\,2}^{BH+}$), the pH values at 50% and 150% neutralization ($pH_{0.5}$ and $pH_{1.5}$) were used. The presented data was averaged from 3–4 independent measurements; p$K_a$ reproducibility was of 0.05–0.1.

## ACKNOWLEDGMENTS

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