

Quantumchemical Calculations on Nitrogen Bases.

Part 6*: Analysis of the Proton Affinities of Aliphatic Amines Using the Kitaura-Morokuma Scheme and the MINDO/3 Method

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The energy partitioning scheme of Morokuma et al. has been applied to the proton affinities of fourteen aliphatic amines. The electrostatic, the polarization and the charge transfer component of the proton affinities have been calculated using the MINDO/3 method. Two different sets of structural parameters have been used for the complexes of the bases and the attacking proton. Within the framework of the semiempirical method employed here, the electrostatic interaction between an attacking proton and the base was found to be positive as a result of the relative magnitudes of the repulsion terms used in the proton-electron and the proton-core interactions.

In the case of the polarization term our findings roughly parallel those of Morokuma. For one of the two sets of structural parameters a good and almost group overlapping correlation was found between polarization energies and experimental proton affinities: the polarization part was found to decrease with increasing proton affinity. Independent of the choice of the amine geometries, the results for the charge transfer energy contradict the nonempirical data of Morokuma: Contrarily to his results we found values which increase in the order ammonia < methylamine < dimethylamine < trimethylamine.

1. Introduction

Recently we published the results of some semiempirical and *ab initio* studies concerning the proton affinities of aliphatic amines [1–5]. In the course of these investigations we calculated the polarization and the electrostatic part of the energy of interaction between an approaching proton and fourteen bases [5]. We used

$$E_{PL}' = -\frac{1}{2} \sum_i \frac{\alpha_i}{|r_p - r_i|^4}$$

for the contribution of the polarization energy [6] ($|r_p - r_i|$ is the magnitude of the distance between the attacking proton and the atom with number i and polarizability α_i) [4, 5, 7].

The electrostatic part of the proton affinity was calculated according to

$$E_{EST}' = \sum_i \frac{q_i}{|r_p - r_i|}$$

* Part 5 see [5].

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where q_i is the charge of atom i . The interatomic distances were taken from MINDO/3 geometry optimizations, and different sets of polarizabilities have been used in the polarization part. Use of the polarizabilities [4] calculated by means of the MINDO/3-FP method [8] in the expression for the polarization part, and of MINDO/3 charges in the calculation of the electrostatic energy led to values for these components which, in the case of the molecules ammonia, methylamine, dimethylamine, and trimethylamine correlate with the nonempirical 4-31 G results of Morokuma et al. [9, 10]. At the *ab initio* level it was found that the sum of the polarization and the electrostatic energy decreases with increasing proton affinity [10]. This trend could not be reproduced by our semiempirical treatment. The reason for this lies in the fact that successive exchange of the hydrogen atoms of the amino group by methyl substituents caused an increase of the electrostatic part, which could not be compensated by the decreasing polarization term.

In this communication we present the results of further investigations in which we not only recalculated the electrostatic term using a method closer adapted to MINDO/3 theory [11], but also

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determined the polarization part in a way closer related to the method of Morokuma [9, 10, 12]. In addition we calculated the charge transfer contribution to the proton affinity according to that author's method.

2. Computational Method

The electrostatic part was calculated by

$$E_{\text{EST}} = \sum_i (Z_i \Gamma_{iH} - p_{ii} \gamma_{iH}),$$

where Z_i is the core charge of atom i , and p_{ii} the sum of its bondorder matrix diagonal elements. Γ_{iH} and γ_{iH} are the two center core-core and electron-electron repulsion terms used within the MINDO/3 method [11].

In order to calculate the polarization energy, the molecular orbitals of the amines were allowed to be polarized in the field of an attacking proton without permitting any charge transfer between the reactants. This was accomplished by performing the Hartree-Fock calculation only with the atomic orbitals of the amine. The diagonal elements of the H^{core} -matrix had to be modified in the following way:

$$h_{\mu\mu} = h_{\mu\mu}^0 - \gamma_{iH},$$

where $h_{\mu\mu}^0$ is the unperturbed H^{core} -matrix element and γ_{iH} is the two center repulsion integral which is also used in the expression for the electrostatic energy. Furthermore,

$$\sum_i Z_i \Gamma_{iH}$$

had to be added to the core-core repulsion energy on account of the electrostatic interaction between the point charge and the atomic cores of the amine. The total energy (E_2) calculated in this manner can be regarded as the sum of the groundstate energy of the unperturbed system (E_0), the electrostatic part (E_{EST}), and the contribution due to polarization (E_{POL}):

$$E_2 = E_0 + E_{\text{EST}} + E_{\text{POL}}.$$

Finally, the charge transfer energy was determined. For this purpose, we followed Morokuma's method [9, 10, 12] and defined a new basis, ψ , the components of which are the n occupied molecular orbitals of

the amine $\{\chi\}$ plus one hydrogen 1s Slater function:

$$\psi = \begin{pmatrix} \chi_1 \\ \chi_2 \\ \vdots \\ \chi_n \\ 1s \end{pmatrix}.$$

This basis is related to the atomic one by the following transformation (n is the number of the occupied molecular orbitals and m is the number of the atomic orbitals of the amine):

$$\begin{pmatrix} \chi_1 \\ \chi_2 \\ \vdots \\ \chi_n \\ 1s \end{pmatrix} = \tilde{C}' \cdot \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_m \\ 1s \end{pmatrix},$$

$$\tilde{C}' = \begin{pmatrix} \tilde{c}_{11} & \tilde{c}_{12} & \cdots & \tilde{c}_{1n} & 0 \\ \tilde{c}_{21} & \tilde{c}_{22} & \cdots & \tilde{c}_{2n} & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \tilde{c}_{n1} & \tilde{c}_{n2} & \cdots & \tilde{c}_{nm} & 0 \\ 0 & 0 & \cdots & 0 & 1 \end{pmatrix}.$$

The elements \tilde{c}_{ij} are the LCAO-MO coefficients of the occupied molecular orbitals of the neutral base (i and j are the indices of the molecular and atomic orbitals, respectively). After performing an SCF calculation for the amine, the final self consistent bondorder matrix in the atomic basis was extended for zeros in line and column $m+1$:

$$\begin{pmatrix} p_{11} & p_{12} & \cdots & p_{1m} \\ p_{21} & p_{22} & \cdots & p_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ p_{m1} & p_{m2} & \cdots & p_{mm} \end{pmatrix} \rightarrow \begin{pmatrix} p_{11} & p_{12} & \cdots & p_{1m} & 0 \\ p_{21} & p_{22} & \cdots & p_{2m} & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ p_{m1} & p_{m2} & \cdots & p_{mm} & 0 \\ 0 & 0 & \cdots & 0 & 0 \end{pmatrix}.$$

This bondorder matrix was used to calculate an initial Fock matrix (F_k^A , A = atomic, $k=1$ in the first step) of dimension $m+1$, which was then transformed in the following manner:

$$F_k^{\text{MO}} = \tilde{C}' F_k^A C'.$$

From the n occupied eigenvectors of F_k^{MO} a new bondorder matrix of dimension $m+1$ was con-

structed and used to set up a new Fock matrix F_{k+1}^A . This procedure was repeated until the calculation converged. In the case of the molecules examined here no convergency problems occurred. From the final value of the total energy (E_3) the charge transfer energy can be calculated in the following way:

$$E_{CT} = E_3 - E_0 - E_{EST}.$$

The atomic coordinates used in the calculations of the components of the proton affinity have been determined by two different methods. In a first approach (further referred to as method 1) we started from the MINDO/3 optimized structures of the amines, placed an additional proton in a reasonable position above the nitrogen atom of the amino group, and then optimized the position of the proton without changing the geometry of the amine part. The final coordinates of the proton were used to calculate the electrostatic energy and to define the position of the point charge in the calculation of the polarization energy, as well as that of the attacking proton in the calculation of E_3 . The MINDO/3 optimized structures of the tertiary amines are of low reliability. So, e.g. in striking contradiction to the experimental results [13] the environment of the nitrogen atom in trimethylamine is almost planar, and the same is true for the other tertiary amines discussed here. In the optimized cations, however, the geometries of the amine fragments, although still rather flat, are closer to reality than those of the optimized neutral amines. There-

fore, we performed a second set of calculations, in which we used the coordinates of the fully optimized cation for the complex of the neutral base and the attacking proton* (method 2).

Although the geometries of the optimized neutral amines, especially those of the tertiary amines, differ in some cases significantly from the ones used in method 2, the differences between their total energies are relatively small and never exceed 0.4 eV.

3. Results and Discussion

Use of both methods to determine the position of the attacking proton in the complex led to H-N bond distances for which Γ_{NH} is considerably larger than γ_{NH} , so that even the electrostatic interaction between the proton and the nitrogen atom, which carries the largest amount of negative charge in the whole molecule, becomes repulsive. The energy decreasing contributions, which emerge from the interactions between the proton and negatively charged atoms i in such distances, for which Γ_{iH} is

* In the case of the primary cations, the proton lying in the plane which contains the nitrogen and the α -carbon atom and which bisects the H-N-H angle was considered as the attacking one.

For the secondary bases the results of the partitioning procedure were found to be almost identical regardless which of the two hydrogen atoms of the NH_2^+ -group was considered as the attacking proton. The dependency upon the choice of the hydrogen atom was found to be so weak that it could be neglected.

Table 1. Electrostatic (E_{EST}), polarization (E_{POL}), and charge transfer (E_{CT}) component of the proton affinity. In addition the experimental proton affinity (PA_{ex}) and the sum of the electrostatic and polarization part are listed. Results of method 1. All values in eV.

No.	Molecule	E_{EST}	E_{POL}	E_{CT}	PA_{ex}	$E_{EST} + E_{POL}$
1	Ammonia	4.94	- 0.60	- 12.09	8.98	4.34
2	Methylamine	5.06	- 0.72	- 12.08	9.47	4.34
3	Ethylamine	4.99	- 0.81	- 12.09	9.60	4.18
4	n-propylamine	5.00	- 0.85	- 12.08	9.66	4.15
5	i-propylamine	5.06	- 0.88	- 12.07	9.70	4.18
6	n-butylamine	5.00	- 0.87	- 12.08	9.68	4.13
7	t-butylamine	5.00	- 0.95	- 12.09	9.79	4.05
8	Dimethylamine	5.19	- 0.78	- 11.64	9.75	4.41
9	Methylethylamine	5.09	- 0.79	- 11.24	9.86	4.30
10	Diethylamine	5.28	- 0.97	- 11.80	9.95	4.31
11	Trimethylamine	5.44	- 0.87	- 11.19	9.91	4.57
12	Dimethylethylamine	5.52	- 0.97	- 11.44	10.01	4.55
13	Methyldiethylamine	5.50	- 1.02	- 11.24	10.12	4.48
14	Triethylamine	5.70	- 1.16	- 11.66	10.21	4.54

Table 2. Electrostatic (E_{EST}), polarization (E_{POL}), and charge transfer (E_{CT}) component of the proton affinity. In addition the experimental proton affinity (PA_{ex}) and the sum of the electrostatic and polarization part are listed. Results of method 2. All values in eV.

No.	Molecule	E_{EST}	E_{POL}	E_{CT}	PA_{ex}	$E_{\text{EST}} + E_{\text{POL}}$
1	Ammonia	4.79	− 0.51	− 12.16	8.98	4.28
2	Methylamine	4.94	− 0.72	− 12.15	9.47	4.22
3	Ethylamine	4.85	− 0.82	− 12.13	9.60	4.03
4	n-propylamine	4.86	− 0.86	− 12.12	9.66	4.00
5	i-propylamine	4.88	− 0.90	− 12.16	9.70	3.98
6	n-butylamine	4.86	− 0.88	− 12.12	9.68	3.98
7	t-butylamine	4.86	− 0.96	− 12.14	9.79	3.90
8	Dimethylamine	5.08	− 0.88	− 12.10	9.75	4.20
9	Methylethylamine	5.06	− 0.96	− 12.12	9.86	4.10
10	Diethylamine	5.05	− 1.05	− 12.14	9.95	4.00
11	Trimethylamine	5.22	− 1.01	− 12.00	9.91	4.21
12	Dimethylethylamine	5.25	− 1.09	− 12.07	10.01	4.16
13	Methyldiethylamine	5.25	− 1.16	− 12.10	10.12	4.09
14	Triethylamine	5.26	− 1.23	− 12.13	10.21	4.03

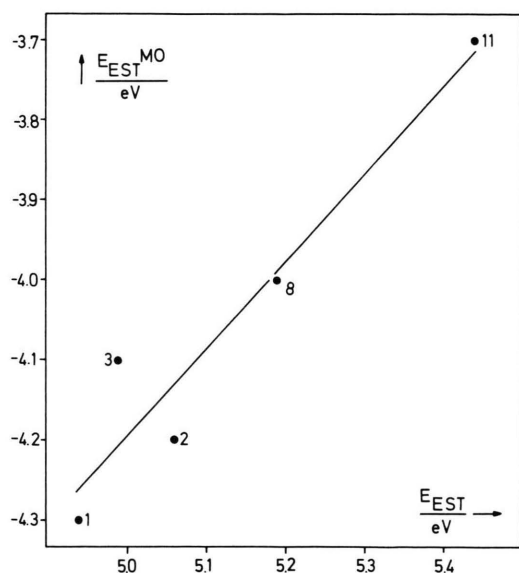


Fig. 1a. Nonempirical electrostatic energies ($E_{\text{EST}}^{\text{MO}}$) vs. the MINDO/3 results (E_{EST} , method 1). All values in eV. (For numbering out the compounds see Table 1.)

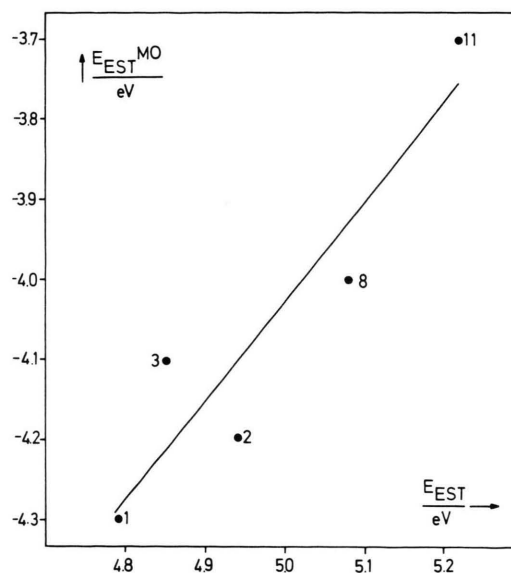


Fig. 1b. Nonempirical electrostatic energies ($E_{\text{EST}}^{\text{MO}}$) vs. the MINDO/3 results (E_{EST} , method 2). All values in eV. (For numbering of the compounds see Table 1.)

small enough, do not compensate the positive contributions, so that, independent of the method used, the total electrostatic term is positive for all molecules under consideration (cf. Table 1 and Table 2).

For all amines method 2 gives smaller electrostatic energies than method 1 (cf. Table 1 and Table 2). Using method 1 no trend can be recognized within the groups of the primary, secondary, and tertiary amines. The same is true for the primary amines in the case of method 2. Among the second-

ary and tertiary amines this method gives trends which, however, contradict each other: Whereas the electrostatic term decreases with increasing weight of the alkyl part in the case of the secondary bases, just the opposite is obtained for the tertiary species (cf. Table 1 and Table 2).

Morokuma et al. have published electrostatic energies for ammonia (− 4.3 eV), methylamine (− 4.2 eV), ethylamine (− 4.1 eV), dimethylamine (− 4.0 eV), and trimethylamine (− 3.7 eV) [9, 10],

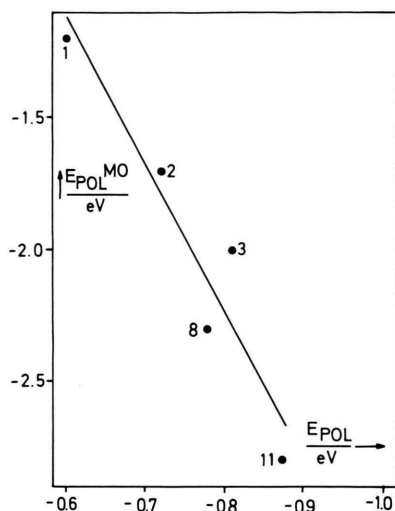


Fig. 2a. Nonempirical polarization energies (E_{POL}^{MO}) vs. the MINDO/3 results (E_{POL} , method 1). All values in eV. (For numbering of the compounds see Table 1.)

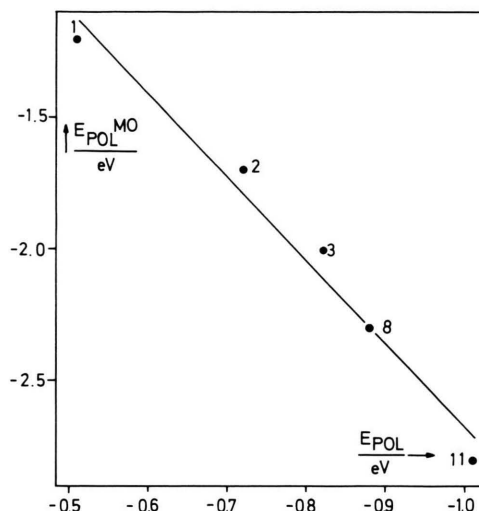


Fig. 2b. Nonempirical polarization energies (E_{POL}^{MO}) vs. the MINDO/3 results (E_{POL} , method 2). All values in eV. (For numbering of the compounds see Table 1.)

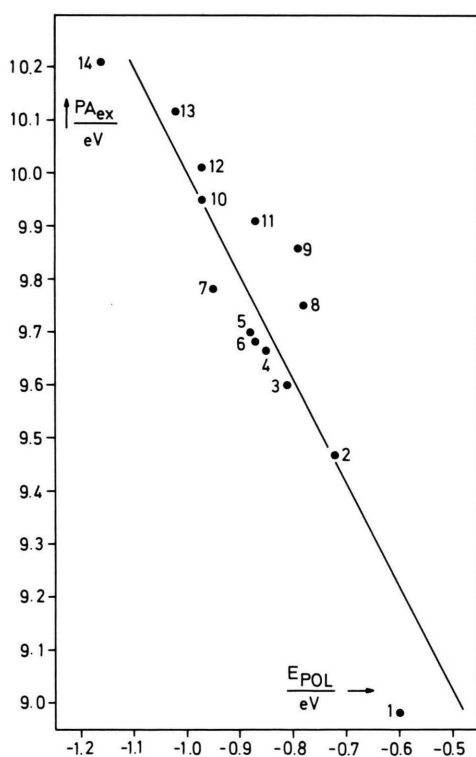


Fig. 3a. Experimental proton affinities (PA_{ex}) vs. the MINDO/3 calculated polarization energies (E_{POL} , method 1). All values in eV. (For numbering of the compounds see Table 1.)

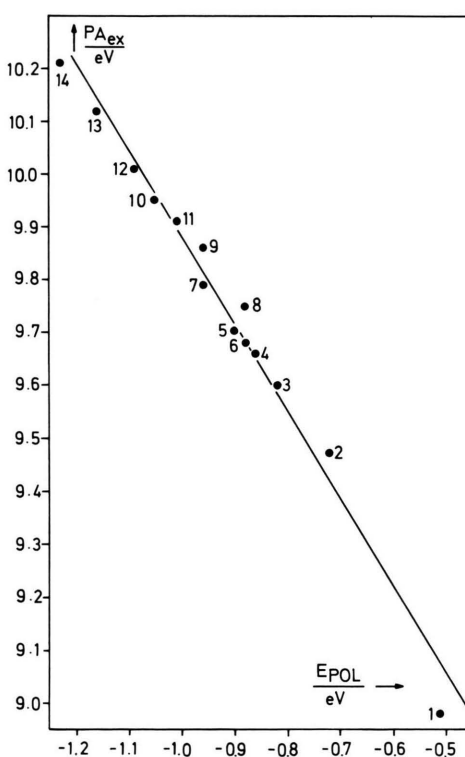


Fig. 3b. Experimental proton affinities (PA_{ex}) vs. the MINDO/3 calculated polarization energies (E_{POL} , method 2). All values in eV. (For numbering of the compounds see Table 1.)

due to the lower flexibility of the basis set used in the MINDO/3 method.

If one considers only the five compounds examined by Morokuma [9, 10], the correlation between his *ab initio* and our MINDO/3 values is satisfying (all values in eV, see Fig. 2a and Figure 2b):

Method 1 $E_{\text{POL}}^{\text{MO}} = 5.556 E_{\text{POL}} + 2.200$; $|r| = 0.944$,

Method 2 $E_{\text{POL}}^{\text{MO}} = 3.185 E_{\text{POL}} + 0.509$; $|r| = 0.989$.

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We tried to correlate the MINDO/3 polarization energies with experimental proton affinities [14, 15] (see Fig. 3a and Figure 3b). The correlation obtained with method 2 is rather satisfying ($|r| = 0.991$), and is also a little bit better than that obtained in [5]. Moreover, the correlation found here is almost group overlapping. The only exception is dimethylamine (8): For this compound the polarization energy (-0.88 eV) is more positive than for *i*-propylamine (5) (-0.90 eV), whereas the

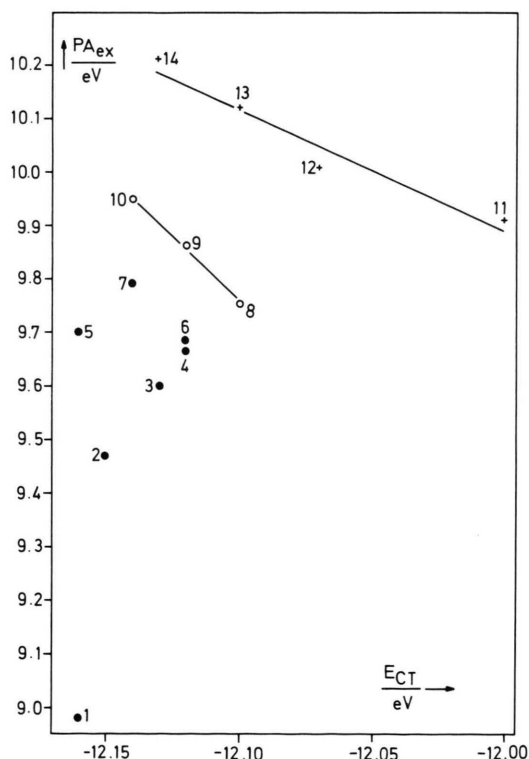


Fig. 5. Experimental proton affinities (PA_{ex}) vs. the MINDO/3 calculated charge transfer energies (E_{CT} , method 2). All values in eV. (For numbering of the compounds see Table I.) ● \equiv primary (plus ammonia), ○ \equiv secondary, + \equiv tertiary amines.

experimental proton affinity of 8 was found to be somewhat higher than that of 5 (cf. Table 2). In the case of the *ab initio* results, the sum of the electrostatic and the polarization energy was found to correlate with the proton affinities in a sense that this sum decreases with increasing energy of protonation. If one restricts oneself to the molecules examined by Morokuma et al. it is realized that this trend is completely failed by the MINDO/3 results from method 1. Although in the case of method 2 $E_{\text{EST}} + E_{\text{POL}}$ decreases in the order ammonia > methylamine > dimethylamine, the value for trimethylamine exceeds that for dimethylamine. That method 2 leads to better results can clearly be seen if one checks the correlation between $E_{\text{EST}} + E_{\text{POL}}$ and the proton affinities within the groups of the primary, secondary, and tertiary compounds (see Fig. 4): No such correlation exists when 1 is used.

Things are even more complicated in the case of the charge transfer energy. Not even a trend can be recognized when method 1 is used (cf. Table 1). In the case of method 2, however, calculation of the charge transfer energy leads to results which are

worth further comments (cf. Table 2 and Figure 5). Among the primary amines only one trend can be seen clearly: The values for the branched molecules are lower than those for the unbranched isomers. Among the secondary and tertiary amines E_{CT} decreases with increasing proton affinity. However, the MINDO/3 values contradict the *ab initio* results in one very important respect: According to Morokuma the charge transfer energy decreases in the order ammonia (− 3.8 eV) > methylamine (− 4.0 eV) > dimethylamine (− 4.1 eV) > trimethylamine (− 4.3 eV). With method 2, just the opposite is found. Moreover, the average value for the primary amines is lower than that for the secondary, which on the other hand, is lower than that for the tertiary species (cf. Table 2 and Figure 5).

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