

# Calculation of the Proton Affinities of Primary, Secondary, and Tertiary Amines Using Semiempirical and *ab initio* Methods

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The proton affinities of some primary, secondary, and tertiary amines have been calculated with different semiempirical and nonempirical quantum chemical methods. We were particularly interested in the question which of the most popular semiempirical methods yield good overall correlations between calculated and experimental values and, therefore, allow a reliable prediction of hitherto unknown proton affinities. We found that some of the most frequently used semiempirical methods result in good correlations only within the groups of primary, secondary and tertiary amines, while the overall correlation is even worse than the one obtained with the noniterative EHT method. Among the more recent methods which allow geometry optimizations (MINDO/3, MNDO, AM1, PM3, MSINDO) the best results have been calculated with the MSINDO method. Testing for the influence of geometry optimization we surprisingly found that two of these methods (MINDO/3, AM1) perform even better when geometry optimizations are omitted and standard bonding parameters are used instead. Superior results, however, have been obtained with the CNDO/2- and the INDO method. Finally, the best correlations between semiempirically calculated and experimental proton affinities have been achieved with the spectroscopic parametrizations of these methods, CNDO/2S and INDO/2S, respectively. The correlations resulting in these cases are close to those reached at the ZPE+MP2/6-311++G\*\*//HF/6-311++G\*\* level of *ab initio* theory and with a comparable DFT method.

A preliminary investigation revealed that an improvement in the semiempirical calculation of proton affinities might be obtained if different  $U_{\mu\mu}$  parameters are used for the nitrogen atoms of primary, secondary, and tertiary amines.

**Key words:** Proton Affinities; Amines; Semiempirical Methods.

## 1. Introduction

One of the most important chemical processes is the protonation reaction. It does not only play an important role in general chemistry but is also of highest physiological relevance. Therefore, a secure computational prediction of proton affinities (PA) is of utmost importance. Since many of the physiologically active compounds are of a size that still prohibits treatment on a reasonable *ab initio* level, one is confined to semiempirical quantum chemical methods in these cases. Thus, a demand to be made on a reliable quantum chemical semiempirical method is that calculated and measured proton affinities correlate.

In order to see which of the commonly used semiempirical methods fulfill this requirement, we calculated the proton affinities of a variety of organic amines with the PM3 [1], AM1 [2], MNDO [3], MINDO/3 [4], MSINDO [5], CNDO/2 [6], INDO [7], CNDO/2S [8], INDO/2S [9], and the EHT [10] method. In addition we performed calculations with two density functional (DFT) methods. The semiempirical results have been compared not only with experimental values [11] but also with the proton affinities calculated at the ZPE+MP2/6-311++G\*\*//HF/6-311++G\*\* level of *ab initio* theory.

We further examined possible reasons for the failure of some semiempirical methods to repro-

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Table 1. Measured ( $PA_{ex}$ ) and calculated proton affinities (in kcal/mol). The values listed in the column headed 6-311++G\*\* have been calculated at the ZPE+MP2/6-311++G\*\*//HF/6-311++G\*\* level. All proton affinities except the STO3-G values have been calculated for completely optimized geometries.

No.	Molecule	$PA_{ex}$	6-311++G**	STO-3G	B-P86/ TZVP	B-P86/ SV(P)
1	NH <sub>3</sub>	207.0	204.7	259.8	205.2	207.5
2	MeNH <sub>2</sub>	218.4	215.3	267.5	215.2	215.1
3	EtNH <sub>2</sub>	221.4	218.0	270.9	218.6	218.1
4	<i>n</i> -PrNH <sub>2</sub>	222.8	219.0	272.4	219.5	219.1
5	<i>n</i> -BuNH <sub>2</sub>	223.3	219.6	273.1	220.2	218.7
6	Me <sub>2</sub> NH	224.8	222.2	272.7	221.4	219.6
7	MeEtNH	227.3	224.6	275.4	224.0	222.3
8	Et <sub>2</sub> NH	229.4	226.9	278.0	227.3	225.5
9	Me <sub>3</sub> N	228.6	226.4	276.7	224.9	221.7
10	Me <sub>2</sub> EtN	230.9	228.7	278.6	228.0	225.0
11	MeEt <sub>2</sub> N	233.3	230.9	281.0	230.7	227.8
12	Et <sub>3</sub> N	235.5	233.3	283.2	233.6	230.7

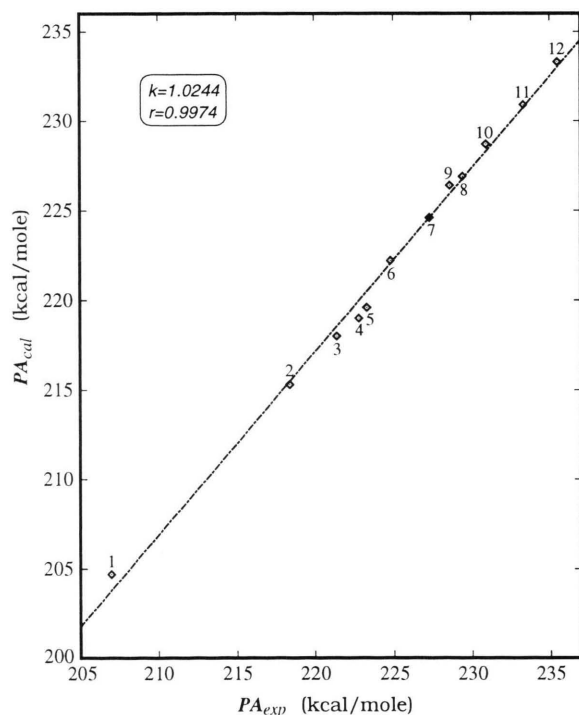


Fig. 1. Plot of calculated proton affinities ( $PA_{cal}$ , 298 K, ZPE+MP2/6-311++G\*\*//HF/6-311++G\*\*) vs. experimental values ( $PA_{exp}$ ) in kcal/mol. (1: NH<sub>3</sub>, 2: MeNH<sub>2</sub>, 3: EtNH<sub>2</sub>, 4: *n*-PrNH<sub>2</sub>, 5: *n*-BuNH<sub>2</sub>, 6: Me<sub>2</sub>NH, 7: MeEtNH, 8: Et<sub>2</sub>NH, 9: Me<sub>3</sub>N, 10: Me<sub>2</sub>EtM, 11: MeEt<sub>2</sub>N, 12: Et<sub>3</sub>N).

duce the experimentally observed trend and tried to improve the performance of these computa-

tional methods in the calculation of proton affinities.

## 2. Computational Methods

All *ab initio* calculations have been performed using the GAUSSIAN98 suite of quantum chemical routines [12], while TURBOMOLE (version 5) [13] has been employed to obtain the DFT results. The MOPAC6.0 package [14] has been used for the MINDO/3-, MNDO-, AM1-, and PM3 calculations, while the personal computer version of CNINDO [15] has been employed for the CNDO/2- and INDO- and the DZDO program [16] for the INDO/2S- and CNDO/2S computations. Finally, calculations with the modified SINDO1 method have been performed with the MSINDO (version 1.0) program [17]. The proton affinities have been calculated using the semi-classical approximation  $PA_{cal} = -\Delta E_{prot} + \frac{5}{2}RT$ .  $\Delta E_{prot} = E_{tot}(BH^+) - E_{tot}(B)$  is the difference between the total energies of the cation ( $BH^+$ ) and the base (B) and includes the correlation- and zero point vibrational energy for the structures optimized at the *ab initio*- and the DFT level. Calculated and measured proton affinities are compiled in Tables 1 - 4. The corresponding correlation lines are shown in Figures 1 - 10.

## 3. Results and Diskussion

*Ab initio* methods including correlation- as well as zero point energy (ZPE) and employing medium-sized basis sets (ZPE+MP2/6-311++G\*\*//HF/6-311++G\*\*) allow calculation of proton affinities which agree nicely with the corresponding measured values (Table 1, Figure 1). Although the calculated proton affinities are systematically smaller than their experimentally determined counterparts, the correlation coefficient is 0.9974 and the slope of the least-squares line ( $k$ ) is close to one. In this case the mean difference between the calculated ( $PA_{cal}$ ) and measured ( $PA_{ex}$ ) values ( $\Delta PA = \langle |PA_{ex} - PA_{cal}| \rangle$ ) is 2.8 kcal/mol. Correlations of similar quality have been obtained by Klessinger *et al.* at the ZPE+MP2(fc)/6-311+G\*\*//HF/6-31G\* and ZPE+MP2(fc)/6-311+G\*\*//HF/6-31G\* levels of *ab initio* theory [18]<sup>a)</sup>. Moreover, Smith and Radom used the G2(MP2,SVP) method to calculate the proton affinities of MeNH<sub>2</sub>, Me<sub>2</sub>NH, Me<sub>3</sub>N,

<sup>a)</sup>fc = frozen core, i.e. core excitations omitted.

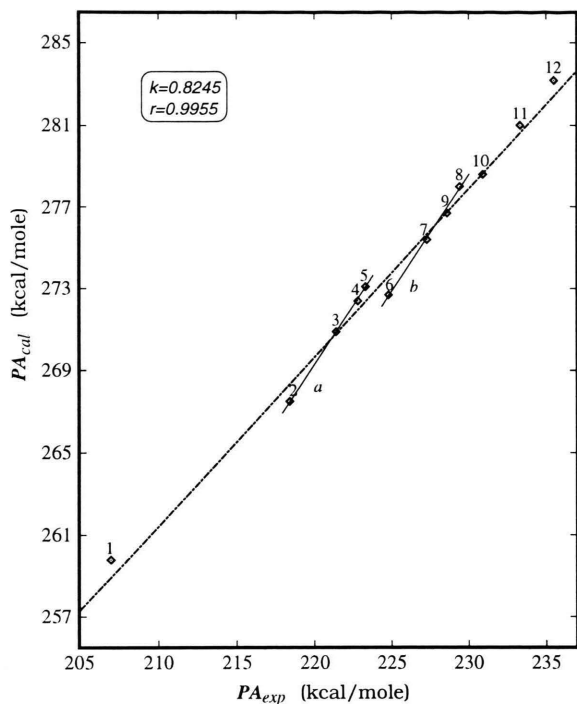


Fig. 2. Plot of calculated proton affinities ( $PA_{\text{cal}}$ , 298 K, HF/STO-3G, standard geometries) vs. experimental values ( $PA_{\text{exp}}$ ) in kcal/mol. Lines *a* and *b* show the correlations within the groups of primary and secondary amines. For numbering of compounds see Figure 1.

and  $\text{EtNH}_2$  [19]. Their values (215.1, 221.7, 227.1, and 218.2 kcal/mol) are essentially identical with our results.

Nonempirical calculations at the Hartree-Fock level employing standard structural parameters [20] and minimal basis sets like STO-3G result in values which also correlate nicely ( $r = 0.9955$ ) with the experimental proton affinities (Fig. 2) although they are much higher than the corresponding experimental values ( $\Delta PA = 48.9$  kcal/mol, see also [21, 22]). Moreover, the correlations within the groups of the primary (line *a*) and secondary amines (line *b*) are better than the overall correlation.

Complete geometry optimizations at the DFT level employing the B-P86 functional [23] and a valence triple- $\zeta$  basis set (TZVP) including polarization functions result in an overall correlation ( $r = 0.9966$ ,  $k = 0.9931$ ) which is only slightly worse than the one obtained at the ZPE+MP2/6-311++G\*\*//HF/6-311++G\*\* level of conventional *ab initio* theory (Table 1, Fig. 3), while the mean difference between

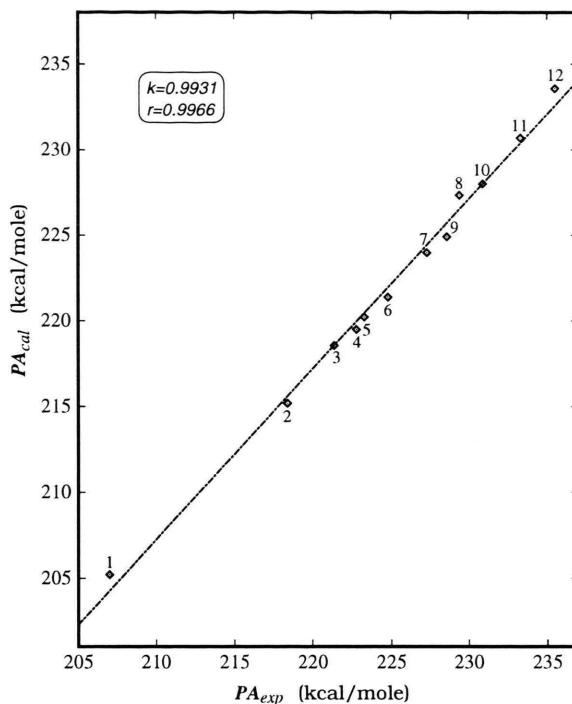


Fig. 3. Plot of calculated proton affinities ( $PA_{\text{cal}}$ , 298 K, ZPE+B-P86/TZVP//B-P86/TZVP) vs. experimental values ( $PA_{\text{exp}}$ ) in kcal/mol. For numbering of compounds see Figure 1.

measured and calculated values is the same ( $\Delta PA = 2.8$  kcal/mol).

To test for the influence of the basis set we repeated these calculations using the same functional but a somewhat smaller split valence basis set including polarization functions for the heavy atoms (SV(P)). These calculations result in a somewhat less satisfying correlation ( $r = 0.9867$ ,  $k = 0.7926$ ). Moreover, the mean difference between measured and calculated values is somewhat higher ( $\Delta PA = 4.4$  kcal/mol) and the correlations within the groups of the secondary (line *b*) and tertiary amines (line *c*) are significantly better than the overall correlations (Table 1, Figure 4).

The results shown in Fig. 5 and listed in Table 2 have been calculated with the most popular semiempirical methods employing fully optimized geometries.

The best correlation between calculated and measured proton affinities has been obtained with the MSINDO method. MINDO/3, MNDO, AM1, and PM3 result in *good correlations within the groups*

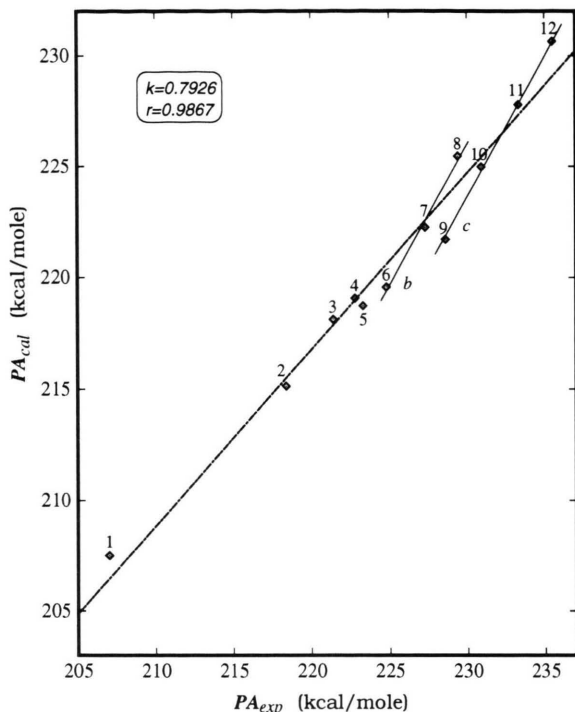


Fig. 4. Plot of calculated proton affinities ( $PA_{cal}$ , 298 K, ZPE+B-P86/SV(P)//B-P86/SV(P)) vs. experimental values ( $PA_{exp}$ ) in kcal/mol. Lines *b* and *c* show the correlations within the groups of secondary and tertiary amines. For numbering of compounds see Figure 1.

of the primary (line *a*), secondary (line *b*), and tertiary amines (line *c*), while the *overall correlations are rather poor*. The only method besides MSINDO which correctly predicts the order of the proton affinities of the mono-, di-, and trimethyl- and ethyl amines ( $RNH_2 < R_2NH < R_3N$ ) is AM1 [24], while the overall correlation is still rather poor. PM3 also gives the correct order for the ethyl amines, however the calculated proton affinities of the corresponding methyl compounds erroneously decrease in the order  $MeNH_2 > Me_2NH > Me_3N$ . Both MINDO/3 [21, 25] and MNDO [26] yield proton affinities which increase from the mono- to the dimethyl- and the diethyl compounds. However, with both methods the proton affinities are lower for the tri- than for the dialkyl bases. Thus these two methods yield gas phase proton affinities which correlate with the observed order of *basicities* in aqueous solution  $pK_b(RNH_2) > pK_b(R_2NH) < pK_b(R_3N)$ , where  $R = Me, Et, n-Pr$  [27].

Table 2. Measured ( $PA_{ex}$ ) and calculated proton affinities (in kcal/mol). All proton affinities have been calculated for completely optimized geometries.

No.	Molecule	$PA_{ex}$	MINDO/3	MNDO	AM1	PM3	MSINDO
1	$NH_3$	207.0	178.7	157.2	158.6	198.6	225.5
2	$MeNH_2$	218.4	184.6	158.9	160.3	196.6	241.0
3	$EtNH_2$	221.4	189.2	161.0	162.6	198.3	247.8
4	$n-PrNH_2$	222.8	190.5	161.5	163.0	198.7	250.4
5	$n-BuNH_2$	223.3	191.3	161.8	163.3	198.9	251.8
6	$Me_2NH$	224.8	185.6	159.2	161.6	194.6	256.0
7	$MeEtNH$	227.3	188.6	160.8	165.2	197.6	260.0
8	$Et_2NH$	229.4	191.3	162.3	168.6	200.5	262.5
9	$Me_3N$	228.6	184.1	158.2	162.7	193.0	270.9
10	$Me_2EtN$	230.9	186.3	159.1	166.3	196.0	273.7
11	$MeEt_2N$	233.3	188.3	159.9	169.7	199.0	276.2
12	$Et_3N$	235.5	190.8	161.0	173.5	201.6	278.6

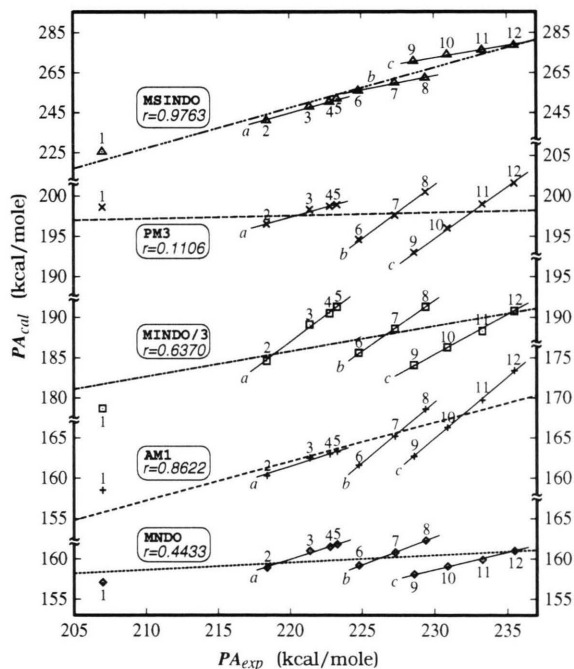


Fig. 5. Plots of proton affinities ( $PA_{cal}$ , 298 K) calculated with the most common semiempirical methods (MSINDO, PM3, AM1, MNDO, MINDO/3) vs. experimental values ( $PA_{exp}$ ) in kcal/mol. Lines *a*, *b*, and *c* show the correlations within the groups of primary, secondary and tertiary amines. For numbering of compounds see Figure 1.

To evaluate the effect of geometry optimization we repeated these semiempirical calculations using standard structural parameters [20] (Table 3, Figure 6).

It is interesting to note that the MINDO/3- and AM1 results obtained using standard geometries cor-

Table 3. Measured ( $PA_{\text{ex}}$ ) and calculated proton affinities (in kcal/mol). All proton affinities have been calculated for standard geometries.

No.	Molecule	$PA_{\text{ex}}$	MIN DO/3	MN DO	AM1	PM3	MSI NDO	EHT NDO
1	NH <sub>3</sub>	207.0	179.0	157.9	158.3	198.7	224.0	148.8
2	MeNH <sub>2</sub>	218.4	186.6	157.5	160.5	196.1	239.2	150.8
3	EtNH <sub>2</sub>	221.4	191.1	159.7	162.6	197.9	244.9	151.3
4	<i>n</i> -PrNH <sub>2</sub>	222.8	193.5	160.5	163.2	198.5	247.5	151.3
5	<i>n</i> -BuNH <sub>2</sub>	223.3	194.7	160.8	163.6	198.7	248.9	151.3
6	Me <sub>2</sub> NH	224.8	190.7	156.4	161.9	193.4	254.3	152.2
7	MeEtNH	227.3	192.6	157.1	164.7	196.0	256.3	152.5
8	Et <sub>2</sub> NH	229.4	194.3	157.8	167.4	198.5	257.9	152.8
9	Me <sub>3</sub> N	228.6	192.3	154.8	162.7	190.8	269.1	153.2
10	Me <sub>2</sub> EtN	230.9	193.8	155.4	165.2	193.3	270.1	153.5
11	MeEt <sub>2</sub> N	233.3	194.9	155.8	167.6	195.7	270.8	153.7
12	Et <sub>3</sub> N	235.5	196.1	156.2	169.9	198.0	271.6	153.9

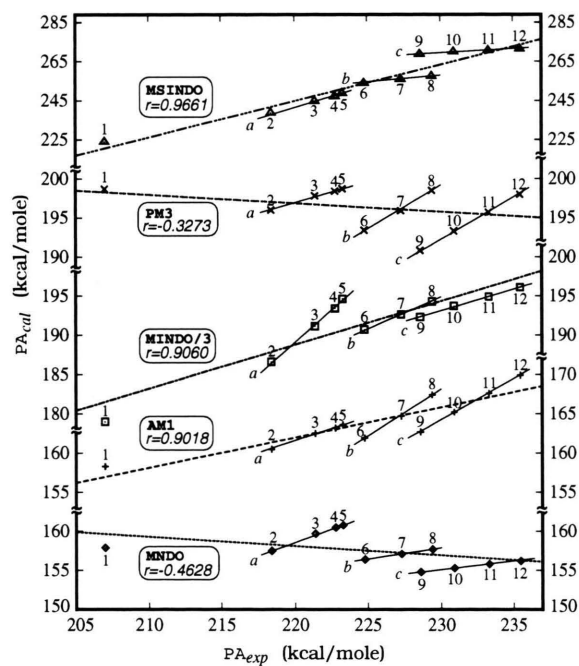


Fig. 6. Plots of proton affinities ( $PA_{\text{cal}}$ , 298 K) calculated with the most common semiempirical methods employing standard geometries (MSINDO, PM3, AM1, MINDO/3, MNDO) vs. experimental values ( $PA_{\text{exp}}$ ) in kcal/mol. Lines a, b, and c show the correlations within the groups of primary, secondary and tertiary amines. For numbering of compounds see Figure 1.

relate slightly (AM1) or significantly (MINDO/3) better with the experimental values than those obtained from fully optimized structures. Note that at this level

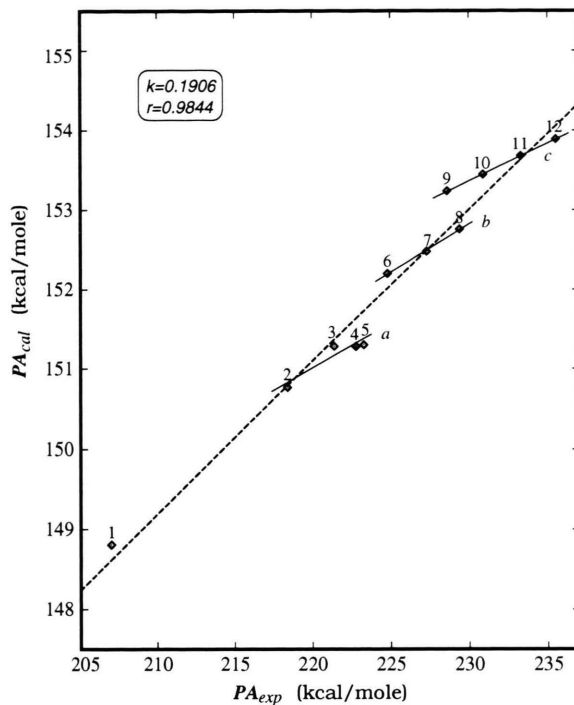


Fig. 7. Plots of proton affinities ( $PA_{\text{cal}}$ , 298 K) calculated with the non-iterative EHT method employing standard geometries vs. experimental values ( $PA_{\text{exp}}$ ) in kcal/mol. Lines a, b, and c show the correlations within the groups of primary, secondary and tertiary amines. For numbering of compounds see Figure 1.

MINDO/3 also gives the correct order of proton affinities for RNH<sub>2</sub>, R<sub>2</sub>NH, and R<sub>3</sub>N (R = Me, Et). We therefore conclude that geometry optimizations are of no general advantage in the calculation of proton affinities of amines with either the MINDO/3- or AM1 method. The overall correlation obtained with MSINDO remains essentially unchanged while the MNDO- and PM3 results are significantly worse when standard geometries are used.

Surprisingly, even the noniterative extended Hückel theory yields an overall correlation which is much better than those obtained with MINDO/3, MNDO, AM1, and PM3 (Table 3, Fig. 7) ( $\Delta PA = 73.1$  kcal/mol). Again, the measured order of the proton affinities of the methyl- and ethyl amines is reproduced correctly.

Surprising results have also been obtained with the CNDO- and INDO methods (Table 4, Figure 8). While the absolute values of the proton affinities calculated by means of the CNDO/2-, INDO-, CNDO/2S-,

Table 4. Measured ( $PA_{\text{ex}}$ ) and calculated proton affinities (in kcal/mol). All proton affinities have been calculated for standard geometries. The CNDO/2' values have been calculated using reoptimized parameters for H, C, and N.

No. Molec.	$PA_{\text{ex}}$	CNDO/2	INDO	CNDO/2S	INDO/2S	CNDO/2'
1 $\text{NH}_3$	207.0	291.8	312.9	496.7	522.0	
2 $\text{MeNH}_2$	218.4	304.5	323.8	502.0	527.0	301.1
3 $\text{EtNH}_2$	221.4	311.9	331.3	504.0	528.8	308.6
4 $n\text{-PrNH}_2$	222.8	314.7	334.1	505.1	529.8	311.3
5 $n\text{-BuNH}_2$	223.3	316.0	335.4	505.6	530.3	312.6
6 $\text{Me}_2\text{NH}$	224.8	313.8	331.3	506.3	531.2	315.7
7 $\text{MeEtNH}$	227.3	318.0	335.1	507.8	532.4	319.8
8 $\text{Et}_2\text{NH}$	229.4	321.7	338.6	509.2	533.5	323.5
9 $\text{Me}_3\text{N}$	228.6	320.8	336.3	509.7	534.9	321.4
10 $\text{Me}_2\text{EtN}$	230.9	324.2	339.5	511.1	536.0	324.8
11 $\text{MeEt}_2\text{N}$	233.3	327.3	342.4	512.6	537.1	327.9
12 $\text{Et}_3\text{N}$	235.5	330.2	345.2	513.9	538.1	

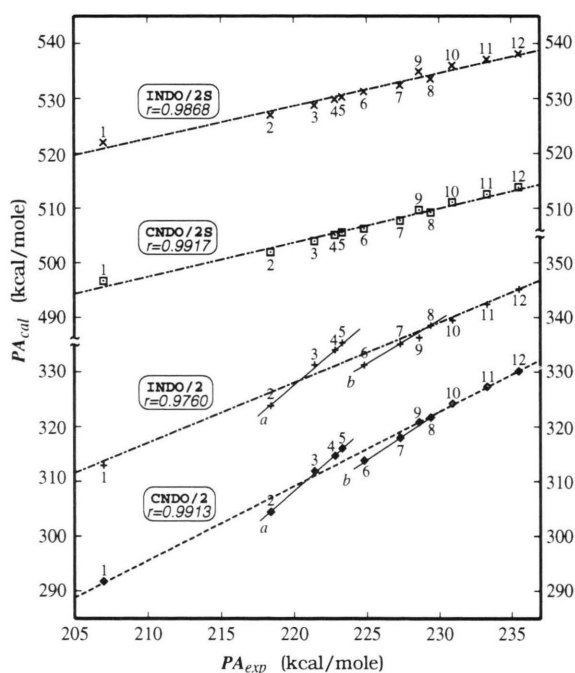


Fig. 8. Plots of proton affinities ( $PA_{\text{cal}}$ , 298 K) calculated with the semiempirical methods CNDO/2, INDO/2, CNDO/2S, and INDO/2S employing standard geometries vs. experimental values ( $PA_{\text{exp}}$ ) in kcal/mol. Lines *a* and *b* show the correlations within the groups of primary and secondary amines. For numbering of compounds see Figure 1.

and INDO/2S theory using standard geometries differ significantly from their experimental counterparts ( $\Delta PA = 91.0, 108.6, 281.8,$  and  $306.5$  kcal/mol), the overall correlations are *much better* than those ob-

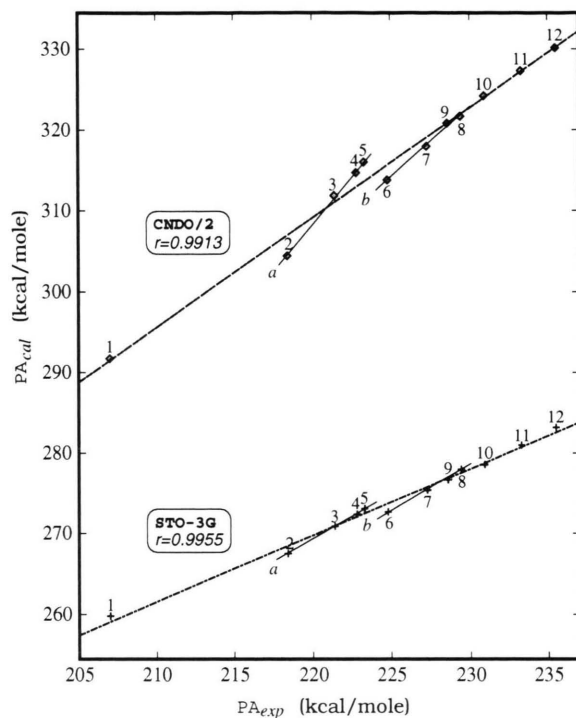


Fig. 9. Comparison of correlations obtained at the HF/STO-3G and CNDO/2 level. Proton affinities in kcal/mol. Lines *a* and *b* show the correlations within the groups of primary and secondary amines. For numbering of compounds see Figure 1.

tained with MINDO/3, MNDO, AM1, and PM3. Especially the order of the proton affinities of  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$ , and  $\text{R}_3\text{N}$  ( $\text{R} = \text{Me}, \text{Et}$ ) is reproduced correctly by all four methods. Similar<sup>b)</sup> CNDO/2 proton affinities have been obtained by Tollenaere and Moereels [28]. The same authors also report the results of PCILO calculations for a variety of amines which resulted in an excellent correlation between measured and calculated proton affinities. Most of the PCILO PAs are slightly higher than the corresponding CNDO/2 values.

The overall correlation obtained with the CNDO/2 method is strikingly similar to that from our HF/STO-3G calculations (Fig. 9). This might be due to the fact that the CNDO/2 parameters have been chosen in such a way as to reproduce some results of nonempirical calculations using a minimal basis set [20].

<sup>b)</sup>The CNDO/2 proton affinities in [28] are on the average 3.8 kcal/mol higher than our values, since the N-H bond lengths in the cations have been optimized.

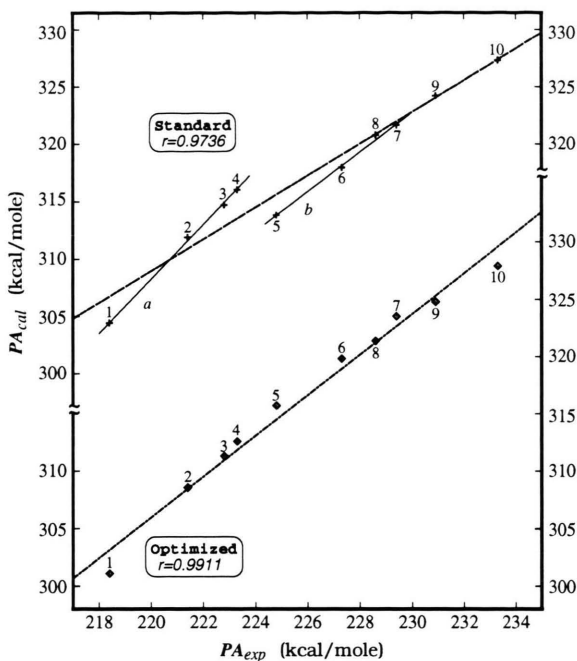


Fig. 10. Comparison of correlations obtained with the CNDO/2 method employing standard (upper line) an re-optimized  $U_{\mu\mu}$  parameters (lower line). Proton affinities in kcal/mol. Lines *a* and *b* show the correlations within the groups of primary and secondary amines. For numbering of compounds see Figure 1.

We now turned our attention to the question why some of the semiempirical methods perform poorly in the calculation of proton affinities. Within the framework of most semiempirical methods it is assumed that the basis set consists of Löwdin orbitals ( $\chi^L$ ) although this is merely reflected by the neglect of certain integrals containing differential overlap. However, the

Table 5. Optimized CNDO/2  $U_{\mu\mu}$  parameters for the hydrogen-, carbon-, and nitrogen atoms of primary, secondary, and tertiary amines together with the standard values (in e. V.).

Parameter	Primary	Secondary	Tertiary	Standard
$U_{1s1s,H}$	-6.966	-6.966	-6.966	-7.1761
$U_{2s2s,C}$	-14.057	-14.057	-14.057	-14.051
$U_{2p2p,C}$	-5.819	-5.819	-5.819	-5.572
$U_{2s2s,N}$	-19.978	-18.745	-19.134	-19.3163
$U_{2p2p,N}$	-7.523	-7.123	-7.223	-7.275

fact that a Löwdin orbital of an atom has satellites at its neighbours is neglected when atomic parameters are derived. Thus, for example, the same parameter  $U_{\mu\mu}$  is used for the orbital  $\mu$  of a nitrogen atom regardless whether this atom is part of a primary, secondary, or tertiary amine. To take into account the different nature of primary, secondary and tertiary nitrogen atoms we then reoptimized the  $U_{\mu\mu}$  parameters for  $\mu = 1sH, 2sC, 2pC, 2sN,$  and  $2pN$  regarding the proton affinities. In this way we determined the separate values for the N atoms in primary, secondary, and tertiary amines which are listed in Table 5. Use of these new parameters results in the proton affinities given in the last column of Table 4. The corresponding correlation is shown in Fig. 10 (lower line). In order to demonstrate the improvement we also included the corresponding plot obtained using standard CNDO/2 parameters (upper line).

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