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Peculiarities of the effect of the electronic nature of substituents on the basic properties of aliphatic amines

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Changes in the hybrid state of atomic orbitals of nitrogen and p-character of LEP, which occur under the effect of saturated hydrocarbon radicals and polar substituents in aliphatic amines, differ substantially. Therefore, the effect of the both substituents on the basicity constants of amines cannot be described by the single formal type of interaction. The "anomalous" changes in the basicity in the series of primary, secondary, and tertiary alkylamines, which are discussed in the literature, and the correlations $pK_{BH^+} = f(\Sigma\sigma^*)$ and $\Delta G_B = f(\Sigma\sigma^*)$ are, in fact, imaginary, because the alkyl radicals at the N atom do not manifest the electron-donor properties.

Key words: aliphatic amines, basicity, alkyl and polar substituents, steric effects, bond angles, p-character of LEP.

When studying the relation of the structure to the basic properties of alkyl- and arylamines, the influence of the following factors is usually studied: inductive (electron-donor and electron-acceptor) and steric effects, conjugation effect, and solvation of protonated and neutral forms of molecules. In most cases, these effects make it possible to explain rather comprehensively changes occurred in the basicity of amines with variation of their structure. However, exceptions are also known. For example, in order to take into account the effect of alkyl radicals, it was accepted, as a rule, that they possess the electron-donor (+*I*) effect. However, as revealed, this is not always the fact. For example, the basicity gradually increases with the successive substitution of the hydrogen atoms in the ammonia molecule by the methyl radicals and decreases sharply when the third radical is introduced[1]: NH_3 (pK_{BH^+} 9.21) < $MeNH_2$ (pK_{BH^+} 10.64) < < Me_2NH (pK_{BH^+} 10.76) > Me_3N (pK_{BH^+} 9.76). However, this order of changing the basicity in the series primary—secondary—tertiary amine does not always take place. For example, the basic properties are enhanced in the series of isopropyl-substituted derivatives: Pr^iNH_2 (pK_{BH^+} 10.64)[1] < $Pr^i{}_2NH$ < (pK_{BH^+} 11.03)[1] < $Pr^i{}_3N$ (pK_{BH^+} 11.86).[2]

Somewhat different situation is observed in the gas phase. Here the basic properties increase with the successive substitution of the hydrogen atoms in the ammonia molecule by the alkyl radicals, and tertiary amines possess the highest basicity (ΔG_B/kcal mol^{-1})[3,4]: NH_3 (ΔG_B 0.00) < < $MeNH_2$ (ΔG_B 9.1) < Me_2NH (ΔG_B 15.15) < Me_3N (ΔG_B 20.0), *i.e.*, in the absence of a solvent, the basicity changes in parallel with the +*I* effect of the alkyl groups. Long ago this fact favored the assertion of the solvation theory,[3,4] according to which the observed "anomalies" are related to differences in solvation (hydration) of neutral and protonated forms of molecules of primary, secondary, and tertiary amines. However, it was further clarified that an increase in the number of alkyl radicals at the N atom enhances both the basic and acidic properties of these compounds,[5] although the latter should be diminished if the +*I* effect of the alkyl radicals was manifested.

The successive introduction of polar substituents into the ammonia molecule results in the expected (according to their electron-acceptor inductive effect) gradual decrease in the basicity in solutions (Table 1). However, unlike solutions, in the gas phase the same electron-withdrawing substituents do not decrease but, on the contrary, enhance the basic properties on going from primary to secondary and tertiary amines[3,4]: $H_2C{=}CH{-}CH_2NH_2$ (ΔG_B 11.3) < $(H_2C{=}CH{-}CH_2)_2NH$ (ΔG_B 19.3) < < $(H_2C{=}CH{-}CH_2)_3N$ (ΔG_B 24.7) or $HC{\equiv}C{-}CH_2NH_2$ (ΔG_B 6.7) < $(HC{\equiv}C{-}CH_2)_2NH$ (ΔG_B 11.7) < < $(HC{\equiv}C{-}CH_2)_3N$ (ΔG_B 15.0).

Comparison of the presented data shows that the regularities in the behavior of amines as bases in solutions and in the gas phase differ substantially and the influence of substituents does not always agree with the known concepts on their electronic nature.

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Table 1. Basicity constants (pK_{BH^+}), calculated bond angles, and p-character of LEP of the N atom (*p*) in several aliphatic amines

Amine	pK_{BH^+}	Bond angle/deg			*p*
		H—N—H	C—N—H, N—N—H*, O—N—H**	C—N—C	
$MeNH_2$ (**1**)	10.63	108.713	109.748	—	0.748
$C_2H_5NH_2$ (**2**)	10.64	108.653	109.760	—	0.748
Pr^nNH_2 (**3**)	10.64	108.678	109.809	—	0.749
Bu^nNH_2 (**4**)	10.62	108.680	109.811	—	0.749
$H_2C=CH-CH_2NH_2$ (**5**)	9.49	108.723	109.930	—	0.752
$BrCH_2CH_2NH_2$ (**6**)	8.49	109.059	110.033	—	0.757
$HC\equiv C-CH_2NH_2$ (**7**)	8.15	108.956	110.103	—	0.757
$CF_3CFHCH_2NH_2$ (**8**)	7.10	109.498	110.408	—	0.766
$CF_3CH_2NH_2$ (**9**)	5.70	109.866	110.558	—	0.774
$CF_3CF_2CH_2NH_2$ (**10**)	5.70	109.899	110.608	—	0.775
$NCNH_2$ (**11**)	−0.36	111.855	109.495	—	0.772
$(H_2C=CH-CH_2)_2NH$ (**12**)	9.29	—	109.942	112.532	0.786
$(HC\equiv C-CH_2)_2NH$ (**13**)	6.10	—	110.642	112.044	0.794
$(NCCH_2)_2NH$ (**14**)	0.2	—	110.901	112.010	0.799
$(H_2C=CH-CH_2)_3N$ (**15**)	8.31	—	—	112.106	0.820
$(HC\equiv C-CH_2)_3N$ (**16**)	3.09	—	—	112.311	0.826
$(NCCH_2)_3N$ (**17**)	−8.05	—	—	112.865	0.840
NH_2-NH_2 (**18**)	7.95	108.080	106.512	—	0.680
$HO-NH_2$ (**19**)	5.97	109.704	104.283	—	0.651
$MeO-NH_2$ (**20**)	4.85	110.409	103.389	—	0.640

* In hydrazine.

** In hydroxylamine and *O*-methylhydroxylamine.

Extensive literature[2—4,6—11] is devoted to the elucidation of reasons for the observed "anomalies" of the influence of alkyl radicals on the basic properties of amines. However, in most cases, alkyl groups were considered only as carriers of electron-donor properties, *i.e.*, according to the concept of their electron-donor character. In order to retain this concept for plotting the basicity—structure correlations, the authors had to introduce various additional parameters, which impart the influence of various factors (most often, specific[3] or nonspecific (electrostatic)[9] solvation).

The concept on the electron-donor effect of alkyl radicals as their some *a priori* property took root in chemists´ minds to such an extent that remains doubtless even in the recent and best courses of organic chemistry (see Ref. 7).

That is why, evidently, some doubts, which were multiply cast[7,12—15] on such a categorical interpretation of the influence of alkyl radicals on the structure and reactivity of organic compounds (first of all, on the basicity[7,12—15] and nucleophilicity[16] of alkylamines), remained unnoticed. It was established[13] that the inductive effect of hydrocarbon radicals and electron-withdrawing substituents cannot be described by the single formal type of interaction. When plotting and interpreting the correlations $pK_{BH^+} = f(\sigma^*)$, it is recommended[9] to use effects of electron-withdrawing substituents or neglect (consider to be zero)[9,14,15] the inductive electron-donor effect of alkyl radicals. However, in recent reports (see Ref. 17 and literature cited therein), the authors admit that the alkyl radicals are characterized by the inductive effect, although this effect has a steric nature and is genetically related to the steric effect of the alkyl groups. One of the confirmations of the inductive effect of the alkyl groups is considered by these authors to be a gradual increase in basicity in the whole series when the alkyl radicals are successively introduced into the phosphine molecule. It is noteworthy that the influence of two factors was considered when the differences in the order of changing the basic properties in the series of primary, secondary, and tertiary amines were explained: the electron-donor inductive effect of alkyl groups and solvation. It was believed that the influence of solvation, which decreases the basicity, is much lower in the case of phosphines because the phosphorus atom is larger than the nitrogen atom and steric hindrances of solvation of the protonated form of phoshine are insignificant. As a result, the basicity of tertiary phoshines, unlike tertiary amines, does not decrease. However, another approach can be proposed to explain the latter, which will be described below.

In this study, we aimed at revealing reasons for specificity of the influence of hydrocarbon radicals and electron-withdrawing substituents on the basicity of aliphatic amines in solutions and in the gas phase.

Experimental

The bond angles at the N atom in the amines under study were calculated using the MOPAC program by the PM3 method.

The fraction of the p-character of lone electron pair (LEP) of the N atom was estimated using the formula[2] $p = \cos^2\varphi/(\cos^2\varphi - \cos^2\alpha) - 2\cos\alpha/(1 - \cos\alpha)$, where α and φ are the angles between the bonds with the same and different substituents, respectively. In the case of the same substituents, the equation $p = 3\cos\alpha/(1 - \cos\alpha)$ was used.

The basicity constants measured in aqueous solutions at 298 K were taken from the publications.[1,2,18,19]

Results and Discussion

The solution of the stated problem is based on the hypothesis[2,10,11] developed by us, according to which the hybrid state of LEP of the N atom (more exactly, its p-character) instead of the classical inductive effect is the key factor determining the acid-base properties of alkylamines. The influence of the alkyl radicals on the acid-base properties of alkylamines is considered as a result of the change in the bond angles at the N atoms under the steric effect, *i.e.*, the change in the hybrid state of the atomic orbitals of nitrogen and, correspondingly, its LEP rather than the inductively induced redistribution of electrons over the bonding orbitals.

According to these concepts, the change in the basicity constants in the series ammonia < methyl- < dimethyl- > trimethylamine is not an anomaly but a regularity. As shown previously,[2] the gradual substitution of the hydrogen atoms in the ammonia molecule by the methyl radicals increases the band angles at the N atom, *i.e.*, $sp^3 \to sp^2$-rehybridization of its atomic orbitals occurs, the p-character of LEP increases, and, correspondingly, the basic properties are enhanced. However, on going to trimethylamine, the H—N—H bond angles decrease[2] to 108.7°, *i.e.*, the hybrid state of the atomic orbitals of nitrogen becomes close to sp^3, due to which the fraction of the p-character of LEP decreases substantially and, correspondingly, the basicity decreases. In this case, the higher basicity of di- and trisubstituted isopropylamines, for example, compared to that of their methyl analogs, can easily be explained. The introduction of the isopropyl radicals strongly increases the bond angles of the N atom, *i.e.*, its hybridization becomes closer to sp^2, the LEP gains a higher p-character, and the basicity increases on going from the mono- to di- and triisopropyl-substituted derivatives. (The same is observed for alkylphosphines: the consecutive substitution of the alkyl radicals results in a continuous increase[20] in the bond angles at the P atom and, correspondingly, the p-character of LEP is enhanced, due to which the basicity enhances in the whole series of alkylphosphines.)

The application of this approach makes it possible to obtain the one-parameter correlation, which relates the basicity constants of primary, secondary, and tertiary amines measured in water, acetonitrile, and nitromethane to the p-character of LEP of the N atom. This result can prove that the problems of "anomalies" in changes in the basicity of alkylamines are not caused by such factors as solvation and the electron-donor effect of alkyl radicals.

The correlations relating pK_{BH^+} to the calculated steric constants of the alkyl groups (R_s) were obtained[21] separately for primary, secondary, and tertiary alkylamines. Choosing the parameters for the calculation of these constants, the authors assumed that the steric effect of the substituents is mainly associated with the shielding of the reaction site. As known,[12] this does not concern a proton. Then the sense of the presented[21] correlations $pK_{BH^+} = f(R_s)$ is not quite clear. Based on our concepts, this can easily be explained: when the steric effects of the alkyl radicals increase, the hybrid state of the N atom becomes closer to sp^2, the p-character of LEP is enhanced, and, correspondingly, the basicity increases.

The situation is somewhat different in the gas phase. The basic properties of alkylamines depend on the number of the introduced alkyl groups. This can be considered as the natural manifestation of the classical electron-donor effect of alkyl radicals. However, the quantitative analysis[4] shows that on going from ammonia to primary, secondary, and tertiary alkylamines (Alk = Me, Et, Pr^n) the ΔG_B values increase in a ratio of 1 : 1.72 : 2.22 rather than 1 : 2 : 3, *i.e.*, proportionally to the number of the alkyl groups. Therefore, it is difficult to plot the single correlation $\Delta G_B = f(\Sigma\sigma^*)$ for mono-, di-, and trialkylamines (although these attempts took place[22]). The correlations were obtained[8] separately for primary, secondary, and tertiary amines. At the same time, the order of changing the basicity in the amine series for the consecutive introduction of the alkyl radicals[4] indicates that the basic properties of alkylamines in the gas phase depend on the effect of at least two opposite (increasing (prevails) and decreasing basicity) factors.

According to the known concepts,[3,4,7,8] the influence of the alkyl groups on the order of changing the basic properties in the series primary < secondary < tertiary amine is caused by the stabilization (by the polarized environment) of the charge localized on the N atom. This allows one, in particular, to explain why the basicity of primary amines in the gas phase depends on the nature of the alkyl radical at the N atom and is independent of its nature in solutions.

Therefore, in the gas phase for the substitution of the hydrogen atoms in the ammonia molecule by the alkyl radicals, the polarizability effect of the alkyl radicals should enhance the basicity as the +*I* effect. That is why, it is difficult to explain the low basicity of trialkylamines in the gas phase in the framework of these two effects. The use of the above considered concept on the rehybridization of the N atom and its LEP substantially simplifies the interpretation of these experimental data (the influence of the hybrid state of the N atom on the basic properties of the nitrogen-containing organic bases in the gas phase has already been mentioned[23] in the literature). The influence of the polarizability of the alkyl radicals on the basicity competes with their steric effect. In mono- and dialkyl-substituted amines, both effects favor the enhancement of the basic properties, while for tertiary amines the substantial decrease in the fraction of the p-character of LEP remarkably decreases the basic properties.

Let us analyze the basicity constants, bond angles, and p-character of LEP (*p*) for the series of alkylamines with the substituents different in electronic nature (see Table 1) to obtain quantitative data on the influence of the substituents on the hybrid state of the N atom and, correspondingly, on the basicity of aliphatic amines.

As can be seen, in the series of primary amines, the steric effect of the saturated hydrocarbon radicals is independent of their nature: the bond angles and p-character of LEP of the N atom are virtually unchanged (the same results have previously[24] been obtained for a broader series of alkylamines) and, correspondingly, the basicity constants do not almost change, which was also mentioned in Ref. 7. These amines are presented by one point in Fig. 1, where the plots of the basicity constants *vs.* bond angles are shown.

The introduction of the electron-withdrawing substituents (see Table 1) in primary amines results in substantial changes in the bond angles at the N atom and, correspondingly, in the p-character of LEP to change considerably the basicity constants from 9.49 to −0.36 p*K* units. Such substantial changes in the values of the p-character of LEP and pK_{BH^+} can evidently be explained by two simultaneous effects: the bond angle values are affected by both the steric effect of the polar substituents, as in the case of the saturated hydrocarbon radicals, and also their electron-acceptor properties. The latter favor, on the one hand, flattening of the amino group structure and enhance the p-character of LEP and, on the other hand, decrease the population of the p-orbital.

It follows from the data in Fig. 1 that the basicity constants of amines with the polar substituents correlate well with the H—N—H (α) and C—N—H (β) bond angles (straight lines *a* and *b*, respectively), and their changes are described by the equations

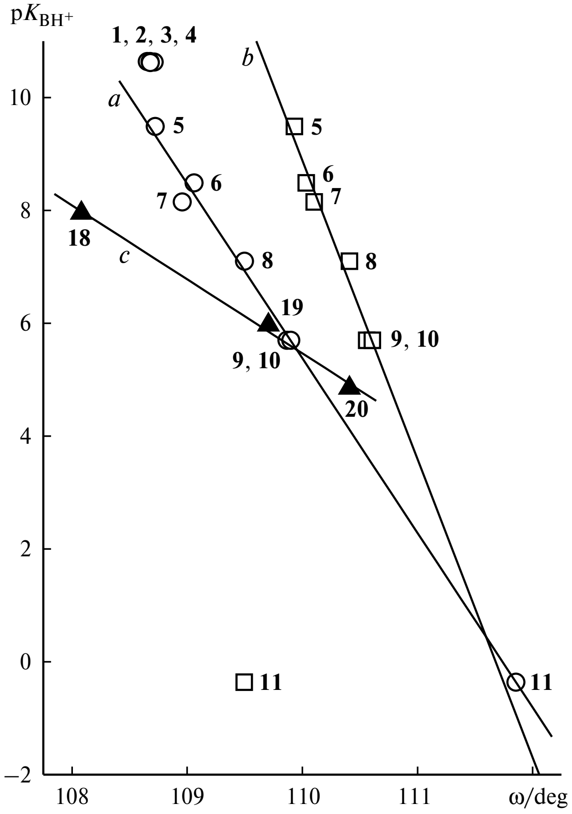

Fig. 1. Plots of the pK_{BH^+} values of aliphatic amines **1—11** and **18—20** *vs.* bond angles (ω/deg) H—N—H (straight lines *a* and *c*) and C—N—H (straight line *b*).

$$pK_{BH^+} = (346.66\pm10.42) - (3.10\pm0.09)\alpha,$$

$$S_0 = 0.25, \qquad r = 0.997, \tag{1}$$

$$pK_{BH^+} = (548.86\pm24.62) - (4.91\pm0.22)\beta,$$

$$S_0 = 0.14, \qquad r = 0.996. \tag{2}$$

The point for cyanamide, which deviates substantially (see Fig. 1) from line *b*, although excellently obeys the correlation $pK_{BH^+} = f(\alpha)$, was ignored in the calculaltion of the $pK_{BH^+} = f(\beta)$ plot. The influences of the CN substituent on the change in the bond angles (β < α, while in other amines β > α, see Table 1) are different, likely, because this substituent is directly bound to the N atom of the amino group (in other amines it is bound through the methylene unit), due to which the n→π-conjugation $\overset{\curvearrowleft}{N{\equiv}C{-}\ddot{N}}H_2$ becomes possible. Therefore, the β angle, unlike α, determines both the state of LEP and the character of interaction of the substituents with the amino group.

It is noteworthy that cyanamide demonstrates the difference in changes in the p-character of LEP (p) and pK_{BH^+}. Therefore, the point for this compound was ignored in the correlation

$$pK_{BH^+} = (132.85\pm6.97) - (164.34\pm9.11)p,$$
$$S_0 = 0.21, \qquad r = 0.992. \qquad (3)$$

The different correlation (3) indicates the key role of the p-character of LEP in the formation of the basic properties of amines with the electron-withdrawing substituents.

The data in Fig. 1 show that the point for hydrazine deviates substantially from the straight line $pK_{BH^+} = f(\alpha)$. This is caused, most likely, by the LEP-containing heteroatom (Het), which is a part of the NH_2 group. The points for hydroxylamine and *O*-methylhydroxylamine, which also contain heteroatoms with LEP, satisfactorily obey the correlation *a*.

Note that analysis of the values of the bond angles at the N atom in hydrazine, hydroxylamine, and *O*-methylhydroxylamine (see Table 1) indicates that their changes are identical (in all compounds the H—N—H angle are greater than H—N—Het), but the regularities of the changes differ for amines with the polar substituents of the other nature ($\alpha < \beta$). In this connection, we can assume that hydrazine and hydroxyl- and *O*-methylhydroxylamines represent a particular series (α-nucleophiles[13]) because, according to the bond angles, they are inherent in their own order of changing the p-character and, correspondingly, the basicity constants. Then correlation (1) for hydroxyl- and *O*-methylhydroxylamines is random.

Comparison of the parameters in the correlations, which relate the basicity constants of these compounds to the H—N—H (α) and H—N—Het (γ) bond angle values and the p-character of LEP (p)

$$pK_{BH^+} = (152.28\pm8.58) - (1.34\pm0.08)\alpha,$$
$$S_0 = 0.13, \qquad r = 0.998, \qquad (4)$$

$$pK_{BH^+} = (-100.14\pm10.57) + (1.02\pm0.10)\gamma,$$
$$S_0 = 0.23, \qquad r = 0.996, \qquad (5)$$

$$pK_{BH^+} = (-44.80\pm4.16) + (77.75\pm6.33)p,$$
$$S_0 = 0.18, \qquad r = 0.997, \qquad (6)$$

to the parameters of correlations (1)—(3), indicates substantial differences between them (in the series of amines, the angular coefficients are higher by several times and have opposite signs), confirming the above assumption. The earlier attempts (see Ref. 8 and literature cited therein) to include these compounds into the correlations $pK_{BH^+} = f(\sigma^*)$, which are common for aliphatic amines, were successful only when the selected appropriate σ^* constants of the series of magnitudes for each substituent were used for the NH_2, OH, and OMe substituents. The differences in the character of the influence of the polar substituents reflect both the basicity constants and rate constants of other reactions of the compounds under study (for example, the α-effect of hydrazines and hydroxylamines in acylation[13]).

It follows from the correlations for the series of primary amines with the polar substituents, which relate the H—N—H (α) and C—N—H (β) bond angles and the p-character of LEP (p) to the σ^* constants of the substituents,

$$\alpha = (108.75\pm0.14) + (0.94\pm0.11)\sigma^*,$$
$$S_0 = 0.28, \qquad r = 0.964, \qquad (7)$$

$$\beta = (109.89\pm0.03) + (0.75\pm0.09)\sigma^*,$$
$$S_0 = 0.04, \qquad r = 0.995, \qquad (8)$$

$$p = (0.751\pm0.0004) + (0.025\pm0.0007)\sigma^*,$$
$$S_0 = 0.0002, \qquad r = 0.997, \qquad (9)$$

that in primary amines the differences in the bond angles and, correspondingly, in the fraction of the p-character of LEP are caused by the electron-acceptor substituents only. Therefore, the recommendations[9,13—15] to consider only polar substituents in plotting the $K_{BH^+} = f(\sigma^*)$ correlation for aliphatic amines are not surprising. This can be understood because, according to the above data, the influence of the alkyl radicals cannot be characterized by the inductive constants σ^*.

The results considered show that the character of changing the bond angles at the N atom of amines with the electron-withdrawing substituents depends substantially on the nature of these substituents and, hence, the p-character of LEP and basicity constants would also depend on it. Therefore, it is not correct to plot the single (for all and even for primary amines) correlation $pK_{BH^+} = f(\sigma^*)$. Each series of amines containing substituents of the same type is characterized by its particular correlation. All these data should be kept in mind (along with the recommendations[9,13—15]) for plotting the correlations $pK_{BH^+} = f(\sigma^*)$ in the reaction series of aliphatic amines.

As can be seen from the data in Table 1, the decrease in the basicity, on going from primary to secondary and tertiary amines, is parallel to the change in the p-character of LEP. Since in secondary and tertiary amines the steric effect of the polar substituents on the change in the bond angles at the N atom, as in the case of the saturated hydrocarbon radicals,[24] is more complicated due to the "superposition" of the electron-acceptor effects, the correlation relating the basicity constants to the p-character of LEP for the series primary—secondary—tertiary amine is valid only for one-type substituents. For example, for amines containing the $CH_2=CH-CH_2$ and $CH\equiv C-CH_2$ substituents, these correlations, respectively, take the form

$$pK_{BH^+} = (22.5\pm5.2) - (17.1\pm6.6)p, \quad S_0 = 0.32, \quad r = 0.932, \tag{10}$$

$$pK_{BH^+} = (63.7\pm9.5) - (73.1\pm12.0)p, \quad S_0 = 0.38, \quad r = 0.987. \tag{11}$$

Comparison of Eqs. (10) and (11) shows that the angular coefficient increases substantially with an enhancement of the electron-acceptor properties of the substituents (the σ^* constants of the $CH_2=CH-CH_2$ and $CH\equiv C-CH_2$ groups are equal[13] to 0.02 and 0.56, respectively), *i.e.*, the enhancement of the p-character of LEP is accompanied by an increase in the sensitivity of the latter to the influence of the electron-acceptor properties of the substituents.

Therefore, when the series of amines containing electron-withdrawing substituents different in nature is extended, more points do not obey the correlation $pK_{BH^+} = f(\sigma^*)$ or these points are grouped to form particular correlations. This can be confirmed by the results,[25] which show that the tertiary amines containing functional substituents different in nature in the hydrocarbon radicals form particular correlations $pK_{BH^+} = f(\sigma^*)$.

We have already mentioned that, contrary to the traditional concepts on the electron-acceptor effect of polar substituents, their introduction into the ammonia molecule results in the enhancement, instead of decreasing, of the basic properties of amines in the gas phase. It is important to note that in water the basicity constants decrease greatly with an increase in the electron-acceptor properties of the substituents (*cf.* in the series of amines with the $HC\equiv C-CH_2$ substituent, pK_{BH^+} decrease in a ratio of 2.64 : 1.97 : 1, while in the series with the $H_2C=CH-CH_2$ substituent, this ratio is 1.14 : 1.12 : 1), whereas the enhancement of the basicity of these amines in the gas phase is almost independent (although some tendency is observed) of the electron-acceptor properties of the substituent (the ΔG_B ratios for the same series are 1 : 1.75 : 2.24 and 1 : 1.71 : 2.19, respectively).

Thus, we can conclude that the order of changing the basicity observed for amines with the polar substituents in the gas phase is a result of the influence of the opposite factors: increasing the basicity (the polarizability, steric and electron-acceptor effects of the polar substituents, favoring the $sp^3\rightarrow sp^2$-rehybridization of the atomic orbitals of the N atoms and enhancement of the p-character of LEP) and decreasing the basicity (the electron-acceptor effect of the polar substituents).

Thus, the changes in the hybrid state of the atomic orbitals of the N atom and the p-character of LEP, which determine the main properties of amines and occur under the steric effect of the saturated hydrocarbon radicals, differ in nature from the changes under the steric and electron-acceptor effects of the polar substituents. Therefore, the influence of substituents of these two types on the basicity constants of the substituents cannot be described by the single formal type of interaction. The permanently discussed "anomalous" changes in basicity in the series of primary, secondary, and tertiary alkylamines and the correlations $pK_{BH^+} = f(\Sigma\sigma^*)$ and $\Delta G_B = f(\Sigma\sigma^*)$ are, in fact, imaginary, because the alkyl radicals at the N atom manifest the electron-donor inductive effect in neither solutions nor the gas phase.

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