

## Phenylhydrazines. Structure and Basicity

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**Abstract**—The main properties of phenylhydrazines are governed by the  $p$ -character of the unshared electron pair of the nitrogen of imino group changing in keeping with  $sp^3 \rightarrow sp^2$ -regbridization of its atomic orbitals under the steric and electronic ( $-I$  effect of amino group) effect of substituents.

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A large amount of research is dedicated to investigation of the relations between the structure and reactivity of hydrazines and their derivatives ([1–5] and references cited therein). This high interest to the study of these compounds is evidently due both to the theoretical (abnormally high nucleophilic reactivity, excellent reducing qualities) and practical (missile propellants, polymers of a wide range of versatile properties, dyes etc.) aspects.

At the same time the results of the studies of physico-chemical characteristics of hydrazine and its derivatives are not always understandable from the viewpoint of traditional concepts on the effect of certain factors on the reactivity. For instance, there is still no unambiguous explanation why introducing alkyl radicals into the position  $I$  of phenylhydrazine reduces its basic properties and not increases as should have been according to the existing concept on the action of the electron-donor effect of these substituents. The reason is unknown why the replacement of a hydrogen in the imino group by methyl or ethyl increases the sensitivity of the reaction center to the effect of substituents in the benzene ring: in the phenylhydrazines series the  $\rho$  value in the correlation  $pK_{BH^+} = f(\sigma_{m,p})$  is  $-1.17$  [4], in 1-methyl-1-phenylhydrazines  $-1.86$  [5], and in 1-ethyl-1-phenylhydrazines the value of the reactivity constant is considerably higher:  $-4.61$  [6]. No reliable explanation exists why the correlation  $pK_{BH^+} = f(\sigma_{m,p})$  for the phenylhydrazines substituted in the ring is valid only for derivatives with *meta*-substituents, whereas the *para*-substituted compounds do not fit the correlation [5]. Up till now the reasons are unknown of the lack of correlation  $pK_{BH^+} = f(\sigma^*)$  for the

series of 1-alkyl-1-phenylhydrazines [2]. The problem of the protonation site in phenylhydrazine is also open to discussion (alternative points are amine and imine nitrogen atoms). Traditionally the nitrogen of amino group is regarded as the protonation center in the phenylhydrazine and its derivatives [4, 5], but no experimental proofs of this statement exist.

The goal of this study is to reveal the reason of decreasing the basicity and increasing the sensitivity of the reaction center to the effect of substituents in the benzene ring at replacement of the hydrogen of the imino group of phenylhydrazine by alkyl radicals, and also to refine and substantiate the protonation direction and to analyze the correlations  $pK_{BH^+} = f(\sigma_{m,p})$  and  $pK_{BH^+} = f(\sigma^*)$ .

A Fischer et al. [4] in the study on relation of basicity to the structure of phenylhydrazines in drawing the dependence  $pK_{BH^+} = f(\sigma_{m,p})$  evaluated the effect of substituents in the *meta*- and *para*-positions of the benzene ring by the Hammett inductive  $\sigma$ -constants. The application for the *para*-substituents of the  $\sigma$ -constants characterizing the inductive effect was substantiated by the consist that the protonation of phenylhydrazine occurred at the nitrogen of the amino group [4, 5] which was not linked directly to the phenyl ring and consequently could not be in conjugation with it. In the analysis of the correlation  $pK_{BH^+} = f(\sigma)$  it was established that the points for phenylhydrazines containing *para*-substituents considerably deviated from this correlation. Using the values  $pK_{BH^+}$  of the *para*-substituted phenylhydrazines and applying the obtained equation the desired  $\sigma$ -constants for the substituents in the *para*-position

were calculated. It turned out that the calculated value completely coincided with the standard  $\sigma_p^-$ -constants.

The effect of *para*-substituents in the benzene ring of phenylhydrazines may be characterized by the polar  $\sigma_p^-$ -constants in event when the protonation center would be the nitrogen of the imino group that according to UV spectral data [2] is in the conjugation with the phenyl ring. Therefore it is expectable that the basicity of phenylhydrazines should vary by the laws observed for the basicity of anilines. If so, the protonation of the nitrogen of the imino group may be even predicted using the concepts on the factors governing the anilines basicity described in [7–11].

The basic characteristics of nitrogen-containing organic compounds are known to be governed by the presence on the nitrogen atom of an unshared electron pair. The value of the basicity constant depends on the hybridized state of the unshared electron pair, namely, with the growing *p*-character of the pair the constant increases.

Due to the action of the steric and electron-acceptor effects of the amino group and of the phenyl ring the *p*-character of the unshared electron pair on the nitrogen of the imino group compared to that of amino group would be higher and consequently its basic qualities would be higher and the protonation should first occur at the nitrogen of the imino group.

The protonation of the nitrogen from the imino group may be also suggested on the following reasons. On substituting the hydrogens of the amino group by alkyls or other substituents its electron-acceptor effect grows, for example:  $\sigma^*(\text{NH}_2)$  0.72,  $\sigma^*(\text{NMe}_2)$  1.10 [12]. Consequently, in phenylhydrazine the electron density on the nitrogen of the amino group would decrease under the effect of phenylamino group, a substituent with higher electron-acceptor properties. Finally the electron density on the nitrogen of the imino group would be higher than on the nitrogen of the amino group and therefore the proton addition to the former would be preferable.

The protonation of phenylhydrazine at the nitrogen of the imino group can be also proved experimentally. It is known [13] that in the UV spectra of aromatic amines the band caused by the involvement of the phenyl ring in the delocalization of the unshared electron pairs of nitrogen ( $n \rightarrow \pi^*$  electron transition) disappeared at their protonation. The comparison of UV spectra of the neutral and protonated forms of phenylhydrazine shows that the band at  $\lambda_{\text{max}}$ , 287 nm corresponding to the  $n \rightarrow \pi^*$  electron transition [2] disappears on protonation. At the same time at the protonation of amino group nitrogen the changes

in the UV spectrum of the protonated form should be insignificant, like in the acyl derivatives of phenylhydrazine [2]: on replacement of a hydrogen of amino group by an acyl the spectrum changes insignificantly, but it alters very sharply when the acyl group is located contiguous to the imino group nitrogen. This sharp change in the UV spectrum in the last event, as also the spectral changes of the protonated form of phenylhydrazine occurred because of distortion of the conjugation between the imino group and phenyl ring.

Besides if the protonation of the phenylhydrazine occurs at the imino group nitrogen it should be expected at the first glance that its basicity would be lower than that of aniline for aside from the involvement of the phenyl ring in the delocalization of unshared electron pairs the amino group should also produce considerable influence since it is a substituent with a fairly strong ( $\sigma^*$  0.72 [12]) electron-acceptor effect. The experimental data show the opposite: the basic properties of the phenylhydrazine are stronger. This effect can be understood based on the results of studies on the relation between the structure and basicity of *N*-alkylanilines [9, 15]. According to these investigations the basicity of *N*-alkylanilines compared to aniline grows not under the influence of the electron-donor inductive effect of alkyl radicals (in this case the action of the latter does not operate [10, 11]), but because of the growing *p*-character of the unshared electron pairs of nitrogen in keeping with  $sp^3 \rightarrow sp^2$ -rehybridization of its atomic orbitals under the steric effect of the alkyl groups.

In phenylhydrazine  $sp^3 \rightarrow sp^2$ -rehybridization of the atomic orbitals of nitrogen occurs under the influence of the steric and electron-acceptor effects of the amino group, therefore the *p*-character of the unshared electron pair should grow stronger than, for instance, in the *N*-methylaniline.

It was established [11] that with growing *p*-character of the unshared electron pair grows the sensitivity of the pair to the influence of electron-acceptor substituents, on the one hand, and on the other hand gets stronger the ability of the phenyl ring in the delocalization of the unshared electron pair. Both factors operate in the phenylhydrazine, and they act in the same direction, reducing the basicity. Therewith the conjugation of the unshared electron pairs with the  $\pi$ -system of the phenyl ring much stronger (by several orders of magnitude) decreases the basic properties of amines. Thus in going from methylamine ( $\text{p}K_{\text{BH}^+}$  10.63 [12]) to aniline ( $\text{p}K_{\text{BH}^+}$  4.60 [12]) the basicity constant diminishes by 6 orders of magnitude.

The sufficiently high basicity of *N,N*-diisopropylaniline ( $pK_{\text{BH}^+}$  8.20 [9]) demonstrates that even insignificant distortion of the conjugation of the amino group with the phenyl ring considerably increases the basic properties of anilines.

In the phenylhydrazine the benzene ring is less involved into the delocalization of the unshared electron pair (it is apparently due to the action of the electron-acceptor effect of the amino group) not only compared with *N*-methylaniline whose nitrogen also possesses a high degree of *p*-character and hence the conjugation of the methylamino group with the phenyl ring is enhanced [9], but also compared with aniline where the atomic orbitals of nitrogen and its unshared electron pairs are in the state close to  $sp^3$ -hybrid and therefore the conjugation of the amino group is somewhat smaller. This conclusion follows from the comparison of the reaction constants values  $\bar{n}$  in the correlation equations  $pK_{\text{BH}^+} = pK_{\text{BH}^+}^0 + \rho\sigma_{m,p}$  for series of phenylhydrazine ( $\rho$  -1.17 [4]), *N*-methylaniline ( $\rho$  -3.56 [9]), and aniline ( $\rho$  -2.89 [9]). As seen, the least transfer of the electronic effects of substituents in the ring is observed in the substituted phenylhydrazines. Inasmuch as the growth of  $\rho$  values, on the one hand, and the delocalization of the unshared electron pairs of the amino group nitrogen, on the other hand, goes in parallel [9, 10], the decrease in the reaction constant  $\rho$  evidences the lesser involvement of the phenyl ring in the delocalization of unshared electron pair.

The above information permits a conclusion that higher basicity of the phenylhydrazine compared to aniline is caused by the weakening of the imino group conjugation with the phenyl ring.

The above reasoning can be also applied to the understanding of the decrease in the basicity at the substitution of the hydrogen in the imino group of phenylhydrazine by alkyls and the simultaneous increase in the sensitivity of the reaction center to the effect of substituents in the ring. In the study of the relation between the structure and basicity of 1-alkyl-1-phenylhydrazine it is feasible to draw an analogy with *N,N*-dialkylanilines. According to results of the studies [9, 10, 14] in *N,N*-dialkylanilines the steric effect of two alkyl groups causes the change in the hybridization of the atomic orbitals of nitrogen making it still closer to  $sp^2$  (in *N,N*-dimethylaniline the angle CNC equals  $116^\circ$  [14]). Consequently the degree of unshared electron pairs *p*-character grows stronger than in *N*-alkylanilines and hence the delocalization involving the benzene ring also gets stronger. As a result the transfer of electronic effects of the sub-

stituents in the ring grows (in the series of *N,N*-dimethylanilines  $\bar{n}$  -3.64 [9]). Therewith the growth of the degree of unshared electron pairs *p*-character is greater than the involvement of the benzene ring in their delocalization [10]. The latter fact is the reason of the growing basicity of *N,N*-dialkylanilines notwithstanding the higher conjugation of the dialkylamino group.

In the 1-alkyl-1-phenylhydrazines also occurs the  $sp^3 \rightarrow sp^2$ -rehybridization of the atomic orbitals of nitrogen under the steric effect of two substituents: methyl and amino group. Therewith the electron-acceptor effect of the amino group also assists the  $sp^3 \rightarrow sp^2$ -rehybridization. However the considerable increase in the *p*-character of unshared electron pairs in this case does not favor growth of basicity evidently, firstly, because of the enhanced influence of the electron-acceptor effect of the amino group: according to the data of [11, 15, 16] with the growing *p*-character the sensitivity of unshared electron pairs to the influence of electron-acceptor substituents increases. Secondly, the role of the benzene ring in the delocalization of unshared electron pairs grows, and consequently the conjugation of imino group with benzene ring increases, like in the case of *N,N*-dimethylanilines [10].

According to [9–11] the ethyl radical affects the  $sp^3 \rightarrow sp^2$ -rehybridization of the nitrogen atomic orbitals and the growth of the *p*-character of unshared electron pairs significantly stronger, than methyl. Hence a stronger basicity enhancement compared to aniline is observed (by 1.97 log.u.; in *N,N*-dimethylaniline only by 0.47 log.u.). This phenomenon is clearly seen by comparison of  $pK_{\text{BH}^+}$  of aniline, *N,N*-dimethyl- and *N,N*-diethyl-aniline (Table 1). The conjugation of diethylamino group with benzene ring ( $\sigma_R^0$  -0.61 [10]) is also stronger than that of amino ( $\sigma_R^0$  -0.47 [10]) and dimethylamino groups ( $\sigma_R^0$  -0.54 [10]) and consequently the sensitivity of basicity constants to the electronic effect of the substituents in the benzene ring is also higher ( $\rho$  -3.71 [10]).

By analogy with *N,N*-diethylaniline in the 1-ethyl-1-phenylhydrazine the hybrid state of the atomic orbitals of the imino group nitrogen would be close to  $sp^2$  (this is also favored by the electron-acceptor effect of the amino group) and therefore the *p*-character of unshared electron pairs will be sufficiently high. The latter favors the growth of the conjugation of the ethylimino group with the benzene ring as shows the high value of the reaction constant ( $\bar{n}$  -4.61 [2]). Therewith if in the 1-methyl-1-phenylhydrazine the action of electron-acceptor effect of amino group dominates and even affects the

conjugation of the methylimino group, in contrast the ethyl and amino groups caused flattening of the ethylamino group to such an extent and the *p*-character of unshared electron pairs grows so much that the influence of the electron-acceptor effect of amino group weakly affects both the basicity constants and the involvement of the benzene ring in the delocalization of unshared electron pair. As a result the basicity constant of the 1-ethyl-1-phenylhydrazine remains on the level of phenylhydrazine (Table 1), and the transfer of electronic effects of substituents in the phenyl ring in the series of 1-ethyl-1-phenylhydrazines is considerably higher than in the series of *N,N*-diethyl-anilines.

In the correlation  $pK_{BH^+} = f(\sigma^*)$  for the series of 1-alkyl-1-phenylhydrazines a considerable deviation of points from the straight line was observed [2]. This lack of correlation is natural, since it has been demonstrated in [7–10] that the electron-donor effect of alkyl groups at nitrogen does not operate.

The above statements can be additionally confirmed by applying to the analysis the approach we have formerly used in the study of relations between the structure and basicity of alkyl- and arylamines [7–10] based on establishing quantitative relationships between the basicity constants and the *p*-character of unshared electron pairs or the bond angles of the protonated nitrogen.

To obtain this information for a series of phenylhydrazines substituted in the ring and their 1-methyl and 1-ethyl derivatives we calculated by ab initio method in the basis B3LYP/6-31G(d) using quantum-chemical software GAMESS (US) [17] the bond angles of the imino group nitrogen carrying out complete optimization of geometry of molecules under study (Table 2). The comparison of the calculated values of the bond angles shows that the trends in their variation in going from phenylhydrazine to its 1-methyl and 1-ethyl derivatives are different. For instance, angle  $\alpha_2$ , the largest in

**Table 1.** Basicity constants of aniline, phenylhydrazine, and their *N*-alkyl derivatives

Compound	$pK_{BH^+}$	Compound	$pK_{BH^+}$
Aniline	4.60	Phenylhydrazine	5.27
<i>N</i> -Methylaniline	4.85	1-Methyl-1-phenylhydrazine	4.99
<i>N,N</i> -Dimethylaniline	5.07	1-Phenyl-1-ethylhydrazine	5.20
<i>N,N</i> -Diethylaniline	6.57		

phenylhydrazine, decreases in going to its 1-methyl and 1-ethyl derivatives, whereas the values of angles  $\alpha_1$  and  $\alpha_3$  increase.

Therewith the diminishing of angle  $\alpha_2$  and increasing of angle  $\alpha_3$  occurs in 1-methyl-1-phenylhydrazine to somewhat greater extent than in the 1-ethyl-substituted analog. These differences in the trends in variation of bond angles indicate existence of specific features in the nature of the hybrid state of atomic orbitals and hence in the *p*-character of unshared electron pairs of the nitrogen in these compounds. The latter evidently is reflected also in the conjugation of the imino group with phenyl ring, and in the basic properties.

As seen from Table 2, in going from phenylhydrazine to 1-methyl- and 1-ethyl-1-phenylhydrazines the degree of *p*-character (calculated as in [7]) of the unshared electron pair of the imino group nitrogen continuously grows assisting the enhancement of the involvement of the phenyl ring in delocalization of unshared electron pairs. The latter results in decreasing the basicity constants of 1-alkyl-1-phenylhydrazines compared with phenylhydrazine (Table 2).

The correlation equations relating the basicity constants to the *p*-character of the unshared electron pair of the imino group nitrogen for some derivatives of phenylhydrazine, 1-methyl- and 1-ethyl-1-phenylhydrazines (equations 1, 2, and 3 respectively) are as follows:

$$pK_{BH^+} = (25.4 + 0.9) - (22.8 + 1.0)p, \quad (1)$$

$$r 0.997, s_0 0.06, n 5;$$

$$pK_{BH^+} = (48.8 + 2.0) - (47.4 + 2.2)p, \quad (2)$$

$$r 0.997, s_0 0.06, n 5;$$

$$pK_{BH^+} = (85.4 + 28.6) - (85.1 + 30.4)p, \quad (3)$$

$$r 0.893, s_0 0.51, n 4;$$

The quality of correlations (2) and (3) improves at exclusion of the point *p*-CH<sub>3</sub>O that considerably deviates [especially in equation (3)] from the straight line. This is clearly seen in the correlation equations (4) and (5).

$$pK_{BH^+} = (50.2 + 1.2) - (49.5 + 1.3)p, \quad (4)$$

$$r 0.999, s_0 0.05, n 4;$$

$$pK_{BH^+} = (163.0 + 13.0) - (167.0 + 13.8)p, \quad (5)$$

$$r 0.997, s_0 0.11, n 3.$$

It is known [15] that the electron-acceptor substituents in the ring favor the  $sp^3 \rightarrow sp^2$ -rehybridization of the atomic orbitals of nitrogen from amino group in aniline, and the electron-donor ones, on the contrary,  $sp^2 \rightarrow sp^3$ -

rehybridization. Therewith, the higher the degree of the  $p$ -character of unshared electron pairs which changes under the steric effect of alkyl groups attached to nitrogen, the larger is the difference in the effect of electron-donor and electron-acceptor substituents.

It is presumable that analogous processes occur also with the imino group nitrogen in phenylhydrazines at replacement therein of a hydrogen by an alkyl.

In the series of phenylhydrazines substituted in the ring the transfer of the electronic effects of substituents is relatively low, therefore the derivatives with electron-donor and electron-acceptor substituents well fit to a single straight line. At replacement of the hydrogen imino group by a methyl and especially by an ethyl the degree of  $p$ -character of unshared electron pair increased favoring enhancement of the conjugation of the imino group with the phenyl ring and consequently increasing the transfer of the electronic effect of substituents. Under the effect of the electron-donor substituents in the ring ( $sp^2 \rightarrow sp^3$ -rehybridization) the degree of the  $p$ -character of unshared electron pairs is reduced resulting in weakening of the conjugation between the imino group and phenyl ring, on the one hand, and on the other hand, in decreasing basicity constant value. This is the most obvious by an example of the *para*-methoxy-substituted 1-ethyl-1-phenylhydrazine. In this compound under the action of the methoxy group considerably grows the  $s$ -character of the unshared electron pair and therefore decreases the involvement of the benzene ring in its delocalization; the latter essentially influences the transfer of the electronic effects of substituents. The above reasoning is confirmed by comparison of the reaction constants in equations (3) and (5). Thus when the point  $p$ -CH<sub>3</sub>O is excluded from the correlation, the reaction constant value doubled. The effect of  $p$ -CH<sub>3</sub>O group on the change in the  $p$ -character of unshared electron pair in the series of 1-methyl-1-phenylhydrazines is considerably weaker: the difference in the reaction constants in equations (2) and (4) is insignificant, although here also some improvement of the correlation parameters is observed. Unlike case of substituent  $p$ -CH<sub>3</sub>O the influence of the electron-donor effect of  $p$ -CH<sub>3</sub> group practically fits to the general rules for all other substituents.

The validity of the above arguments is indicated by expression (6) relating the reaction constants of the correlation equations  $pK_{\text{BH}^+} = pK_{\text{BH}^+}^0 + \rho p$  and  $pK_{\text{BH}^+} = pK_{\text{BH}^+}^0 + \rho_1 \sigma_{m,p}$  for series of phenylhydrazines, 1-methyl-

**Table 2.** Basicity constants ( $pK_{\text{BH}^+}$ ), bond angles of imine group nitrogen ( $\alpha_1, \alpha_2, \alpha_3$ ), and degree of  $p$ -character ( $p$ ) of unshared electron pair of imine nitrogen for some derivatives of phenylhydrazine, 1-methyl- and 1-ethyl-1-phenylhydrazines

R, R' in $p$ -R'C <sub>6</sub> H <sub>4</sub> NRNH <sub>2</sub>		$pK_{\text{BH}^+}$	Bond angles, deg			$p$
R'	R		$\alpha_1$	$\alpha_2$	$\alpha_3$	
CH <sub>3</sub> O	H	5.59	112.82	119.67	109.32	0.866
CH <sub>3</sub>	H	5.32	113.31	120.21	109.70	0.877
H	H	5.27	113.61	120.60	109.94	0.885
Cl	H	5.10	113.88	120.80	110.17	0.890
NO <sub>2</sub>	H	3.94	116.29	123.00	111.99	0.939
CH <sub>3</sub> O	CH <sub>3</sub>	5.60	118.67	117.29	111.33	0.909
CH <sub>3</sub>	CH <sub>3</sub>	5.30	119.10	117.80	111.74	0.919
H	CH <sub>3</sub>	4.99	119.53	118.13	111.98	0.927
Cl	CH <sub>3</sub>	4.65	119.62	118.43	112.27	0.932
NO <sub>2</sub>	CH <sub>3</sub>	2.65	121.57	120.47	114.08	0.973
CH <sub>3</sub> O	C <sub>2</sub> H <sub>5</sub>	6.15	120.75	117.87	111.22	0.928
CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	5.90	121.38	118.47	111.62	0.940
H	C <sub>2</sub> H <sub>5</sub>	5.20	121.69	118.77	111.73	0.945
Cl	C <sub>2</sub> H <sub>5</sub>	4.07	121.95	118.99	111.99	0.951

and 1-ethyl-1-phenylhydrazines containing in the ring substituents of different electronic character.

$$\rho = (27.6 + 2.0) - (42.2 + 0.7)\rho_1, \quad (6)$$

$$r 0.999, s_0 1.73, n 3.$$

Thus the basic properties of phenylhydrazines are governed by the  $p$ -character of the unshared electron pair of the imino group nitrogen varying according to  $sp^3 \rightarrow sp^2$ -rehybridization of its atomic orbitals under the influence of the steric and electronic ( $-I$ -effect of amino group) effects of the substituents attached to this atom. The increase in the degree of the  $p$ -character of the unshared electron pair of the imino group nitrogen enhances the involvement of the benzene ring in its delocalization favoring the transfer of the electronic effects of substituents in the ring and affects the basicity constant for the proton adds to the imine nitrogen. Therefore in drawing correlations  $pK_{\text{BH}^+} = f(\sigma_{m,p})$  for the quantitative evaluation of substituents effect for the *para*-substituents it is necessary to use the polar  $\sigma_p$ -constants. The lack of correlation  $pK_{\text{BH}^+} = f(\sigma^*)$  for the series of 1-alkyl-1-phenylhydrazines is due to the fact that the inductive effect of alkyl groups attached to

nitrogen does not show up. The main role plays the steric effect of alkyls strengthening the  $sp^3 \rightarrow sp^2$ -rehybridization of the imine nitrogen and thus even more increasing the degree of the  $p$ -character of the unshared electron pair and enhancing the involvement of the benzene ring in its delocalization. This is the reason why at introducing alkyl groups the basic properties of phenylhydrazine decrease and the electronic effect of substituents in the ring on the reaction center increases.

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