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Acidity and basicity of primary *N*-phenylnitramines: catalytic effect of protons on the nitramine rearrangement

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ABSTRACT: *Para*-substituted *N*-phenylnitramines were prepared either by oxidation of diazonium salts or by nitration under alkaline or acidic conditions. Isotopic [^{15}N-NO_2] labelling indicated that the bands characteristic of the *N*-nitro group appear in the 1318–1323 and 1585–1607 cm^{-1} regions. In the nitrogen NMR spectra, the nitramino group gives two resonances at -193 ± 3 (NH) and -32 ± 3 ppm (NO_2). The chemical shifts in proton and carbon NMR spectra are predictable, based on increments and the additivity rule. The spectral data indicate the lack of conjugation between the nitramino group and another substituent bound to the ring. It seems to contradict the well-known fact that substituents strongly ($\rho = 4$) influence the rate of nitramine rearrangement. The acidities of primary *N*-phenylnitramines ($3.77 < pK_A < 5.62$) are similar to those of benzoic acids and weakly dependent ($\rho = 1$) on the electronic character of a substituent. Based on the analogy with benzoic acids, it has been calculated that basicities of nitramines ($pK_B \approx 21$) are extremely low. Consequently, addition of protons to an intact nitramine molecule, as the preliminary step of the rearrangement, seems to be improbable. Migration of the *N*-nitro group precedes protonation; the latter process facilitates transformation of intermediates into stable final products. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: nitramines; amphiprotic compounds; NMR spectroscopy; rearrangement; reaction mechanism

INTRODUCTION

Primary and secondary nitramines are susceptible to rearrangement under the influence of an acid (Scheme 1). The nitramine rearrangement involves migration of the *N*-nitro group to the *ortho* or *para* position of an aromatic ring. There are at least three theories explaining the mechanism of the nitro group migration:

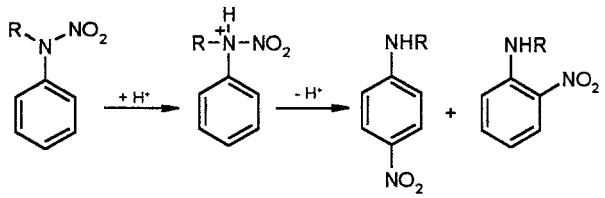
- the nitro group remains covalently bonded to the aromatic ring during migration, three or five nodes from the migration origin;[1]
- the nitro group migrates as the NO_2 radical; the process occurs in the solvent cage, which is responsible for its intramolecularity;[2]
- heterolytic cleavage of the N—N bond provides nitronium cations, forming a π-complex with an aromatic moiety, which is subsequently transformed into final products.[3]

The nature of the rearrangement remains controversial; however, there is a common agreement in two aspects:

- rearrangement is intramolecular;
- protonation on the amide nitrogen is a preliminary step of the reaction.

The first assumption seems to be experimentally confirmed;[4] the second one will be discussed in this paper.

N-Methyl-*N*-phenyl nitramine and its ring-substituted derivatives are the most frequently used as model compounds in the investigations on the mechanism of nitramine rearrangement. The acid–base equilibria cannot be established because in acidic solutions the rearrangement occurs immediately. Acidity requirements are strongly dependent on the substituents bound to the ring. *N*-Methyl-*N*-phenylnitramine can be rearranged in 0.01 M perchloric acid, its 4-nitro derivative rearranges in 0.5 M $HClO_4$,[5] whereas *N*-methyl-*N*,2,4-trinitroaniline requires concentrated sulfuric acid.[6] The most simple explanation is that electron-withdrawing substituents on



Scheme 1

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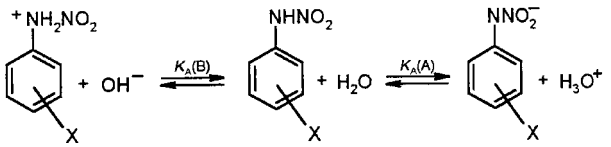

Scheme 2

the ring decrease the proton affinity of the nitramine group. In fact, the problem is more complex.

X-ray diffraction studies have indicated that the nitramino group in *N*-(4-chlorophenyl)-*N*-methylnitramine is planar with a short N—N bond.[7] Its geometry is nearly the same as in *N,N*-dimethylnitramine.[8] The latter compound was studied with the use of photoelectron spectroscopy. The results, supported with quantum-mechanical calculations, revealed that the outer valence shell consists of three π-orbitals, spread all over the NNO_2 group.[9] This means that there is no unshared electron pair on the amide nitrogen; consequently, protonation at this site must completely rearrange the charge distribution within the nitramino group. Moreover, our recent studies on the nitro derivatives of *N*-phenyl-*N*-methylnitramine demonstrated that the electron-acceptor substituents do not influence the geometry of the *N*-methylnitramino group.[10] It is inferred that we cannot see a basic centre and its interaction with a ring substituent; consequently, a catalytic effect of an acid on the nitramine rearrangement cannot be explained in a simple way.

The aim of this work is to evaluate the proton-donating properties of nitramines, *i.e.* the right-hand equilibrium given in Scheme 2, and calculate a hypothetical equilibrium of the basic dissociation of primary phenylnitramines.

Two presumptions were made:

- the mechanism of rearrangement is the same in the primary and secondary nitramine series;
- the acidic and basic properties of amphiprotic compounds are interrelated.

The latter requires some comment. The problem has been investigated by Arnett with the final conclusion that there is no correlation between acidity, expressed as $pK_A(A)$, and basicity, given as $pK_A(B)$, of the conjugated acid.[11] There is, however, a linear correlation between $pK_A(A)$ and $pK_A(B)$ provided that the same functional group is the basic and acidic centre. Arnett's plot, completed with some other data, is presented on Fig. 1.

The correlation is surprisingly good, considering that the pK_A values are defined in three acidity–basicity scales, *i.e.* Hammett's H_o acidity scale, the Sørensen pH scale and the H_- scale for strongly basic solutions. On the other hand, several species do not obey the simple relation given in Fig. 1. Monocations of aminopyridines, monoanions of phthalic acids and several heterocyclic compounds, such as imidazole, pyrazole and indazole,

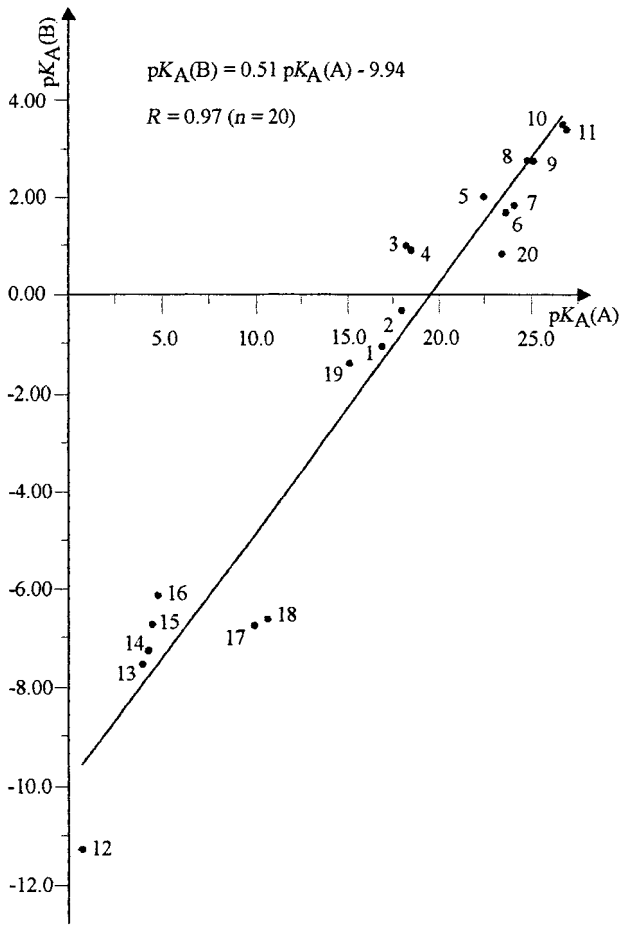

Figure 1. Arnett's plot, correlation between the acidity $pK_A(A)$ and basicity $pK_A(B)$ of some amphiprotic compounds

were excluded for obvious reasons. In these amphiprotic ions or molecules, a protonation site and an acidic centre are separated. In *N*-phenylnitramine, protons are added or abstracted from the same amide nitrogen atom, hence estimation of its acidity may provide some information on its proton affinity.

EXPERIMENTAL

The proton and carbon NMR spectra were obtained using a Tesla BS 567A (100 MHz) spectrometer. For the registration of ^{15}N NMR spectra a Bruker DPX instrument (250 MHz) was used. The FTIR spectra were recorded on a Philips PU 9804 apparatus. A Hewlett-Packard GC system HP 6890 with mass selective detector 5973, equipped with a direct inlet and on-column inlet, was used for registration of the mass spectra and chromatographic control of the reactions. An HP-1 methyl siloxane capillary column (30 m × 320 μm × 0.25 μm) was employed. A Beckman DU 640B spectrometer was used for registration of the UV–VIS spectra.

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The pK_A values were measured using CI-316 pH-meter (Elmetron). The aqueous solutions of nitramines ($1.377 \times 10^{-3} < c < 0.015$ M) were triturated with 0.0542 M sodium hydroxide.

(4′-Methanesulfonyl)-*N*-phenylnitramine (procedure A, 2b)

4-(Methanesulfonyl)-aniline (3.42 g, 0.02 mol) was dissolved in nitromethane (35 ml). Absolute nitric acid (1.05 ml, 25 mmol) was added to cold acetic anhydride (10 ml), the solution was maintained for 15 min at room temperature and combined with the substrate solution. The mixture was left for 0.5 h at room temperature and cooled to −20 °C. The crude product was collected by filtration and crystallized twice from toluene, yielding (4′-methanesulfonyl)-*N*-phenylnitramine (2.20 g, 51%) as colourless prisms, m.p. 179–181 °C. Calc. for $C_7H_8N_2O_4S$ (216.21): 38.88% C, 3.73% H. Found: 39.11% C, 3.70% H. MS, *m/z* (int.): 216 ($M^{\cdot+}$, 26), 201 (2), 170 (69), 156 (26), 108 (100), 91 (40), 81 (53), 63 (72). IR (KBr): 1613, 1597, 1581, 1502, 1467, 1385, 1311, 1287.

N-(4-Fluorophenyl)-nitramine (procedure B, 2d)

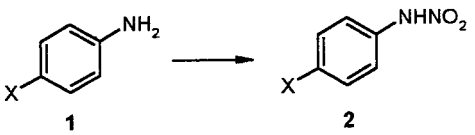
4-Fluoroaniline (3.33 g, 0.03 mol) was dissolved in dry toluene (150 ml); methylmagnesium iodide in isoamyl ether (3.5 ml of 1 M solution, 35 mmol) was added and the mixture was stirred intensely at the boiling point for 3 h. It was cooled to room temperature and *n*-butyl nitrate (4.00 g, 33 mmol) in toluene (4 ml) was added. The mixture was stirred for 3 h at room temperature. Water (30 ml) acidified with acetic acid (3 ml) was added dropwise and the layers were separated. A toluene solution was extracted (3 × 30 ml) with 1 M aqueous potassium hydroxide. The extract was neutralized with 4 M hydrochloric acid at 0 °C; the crude product was collected with methylene chloride. The solution was dried over anhydrous sodium sulfate, filtered, diluted with *n*-hexane and cooled. The crude product was collected by filtration and crystallized from a mixture of methylene chloride and *n*-hexane. *N*-(4-Fluorophenyl)-nitramine (2.11 g, 45%) was obtained as white leaflets, m.p. 100–101 °C. Calc. for $C_6H_5FN_2O_4$ (156.12): 46.16% C, 3.23% H. Found: 46.25% C, 3.33% H. MS, *m/z* (int.): 156 ($M^{\cdot+}$, 14), 110 (100), 90 (6), 83 (92), 63 (14), 57 (34). IR (KBr): 1621, 1598, 1513, 1433, 1381, 1335, 1294, 1250, 1207.

N-(4-Methoxyphenyl)-nitramine (procedure C, 2g)

4-Anisidine (24.63 g, 0.20 mol) was dissolved in a mixture of concentrated hydrochloric acid (50 ml) and water (50 ml). The solution was cooled to +5 °C and diazotized with an excess of sodium nitrite (29.35 g, 0.28 mol) dissolved in a minimum amount of water (30 ml). Ammonium tetrafluoroborate (29.35 g, 0.28 mol), as a saturated aqueous solution, was added and the precipitate of diazonium tetrafluoroborate was collected by filtration. It was added to the cold (−5 °C) aqueous potassium hydroxide (60.0 g of 50% aq. KOH) and the suspension was poured into potassium cyanoferrate(III) (200.0 g, 0.60 mol) dissolved in water (1200 ml) containing potassium hydroxide (60.0 g). The solution was stirred for 18 h at room temperature. A yellow precipitate was collected by filtration, purified and identified as 4,4′-azoxybenzene. The filtrate was cooled in an ice bath and neutralized with 30% sulfuric acid. Extraction with methylene chloride (3 × 100 ml) gave a multicomponent mixture, which was re-extracted with 1 M aq. KOH. The alkaline solution was neutralized as before; the precipitate was collected by filtration, dried in vacuum and crystallized from *n*-hexane. *N*-(4-Methoxyphenyl)-nitramine (13.45 g, 40%) was obtained as colourless crystals melting at 77–79 °C. MS, *m/z* (int.): 168 ($M^{\cdot+}$, 17), 153 (4), 122 (100), 107 (15), 95 (69), 80 (23), 79 (25), 65 (19), 52 (35). IR (KBr): 1592, 1581, 1512, 1466, 1436, 1396, 1327, 1306, 1252, 1220.

RESULTS AND DISCUSSION

We have prepared a series of *para*-substituted *N*-phenylnitramines by nitration of corresponding anilines; standard procedures were slightly modified to facilitate isolation of the products in the pure state (scheme 3). The derivatives containing electron-withdrawing substituents were obtained in sulfolane or nitromethane solutions by the action of acetyl nitrate (procedure A). The acetyl group, as the electron acceptor, is not strong enough, hence 4-aminoacetophenone cannot be *N*-nitrated in this way. More basic anilines were nitrated with *n*-butyl nitrate after pretreatment with a strong base (procedure B); sodium hydride and Grignard reagents were alternatively employed. We could not find reaction conditions (solvent, strong base) that were applicable in the preparation of any primary nitramine. *N*-Phenylnitramine was prepared from aniline by diazotation and oxidation



1 2

X = NO_2, SO_2CH_3 - procedure A
X = F, Br, CH_3 - procedure B
X = H, OCH_3 - procedure C

Scheme 3

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Table 1. Para-substituted *N*-phenylnitramines

No.	Substituent X	Procedure	Yield (%)	M.p. (°C), (solvent)	Lit. m.p.
2a	NO_2	A	54	112–113 (CH_2Cl_2)	111–112[12]
2b	SO_2Me	A	51	179–181 (PhMe)	–
2c	Br	B	25	92–100 (Et_2O–*n*-hexane)	101–102[12]
2d	F	B	45[a]	100–101 (CH_2Cl_2–*n*-hexane)	–
2e	H	C	26[b]	41.5–42 (Et_2O–*n*-hexane)	46–47[13]
2f	Me	B	28[c]	51–52 (CH_2Cl_2–*n*-hexane)	52[12]
2g	OMe	C	40	77–79 (*n*-hexane)	79[14]

[a] With the use of sodium hydride, the reaction does not occur.
[b] Procedure B, using the $MeMgI/BuONO_2$ system gives 6% yield.
[c] Sodium hydride was used as a strong base; the labelled compound was prepared analogously.

(procedure C). The compound details are collected in Table 1.

Example procedures are given in the experimental section. The diversity of the procedures reflects the different susceptibilities of nitramines to rearrangement; those containing electron-acceptor groups are more resistant to diluted acids and elevated temperature, whereas electron-releasing substituents facilitate isomerization.

The compounds **2a–2g** were characterized using spectroscopic methods, and the results were compared with previously published data on analogous *N*-methyl-*N*-phenylnitramines.[15]

The spectra of primary and secondary phenylnitramines, with the same substituents on the ring, differ in some aspects. The FTIR spectra will be considered first; in those of *N*-methyl-*N*-phenylnitramines the bands characteristic of the *N*-nitro group (1285–1299 and 1517–1536 cm^{-1}) were recognized using [^{15}N-NO_2] labelling.[15] However, their primary counterparts give no peaks in this region. Among the strong bands at 1585, 1596 cm^{-1} and 1305, 1322 cm^{-1}, in the spectrum of **2f**, two of them can be assigned to the *N*-nitro group. Isotopic labelling [^{15}N-NO_2] shifts the asymmetric stretch to 1562 cm^{-1} and symmetric stretching vibrations to 1293 cm^{-1}. The bands at 1585 and 1305 cm^{-1} remain unchanged, so they must be skeletal vibrations. The result was extrapolated for other nitramines, which give very similar spectra; some relevant data are collected in Table 2.

Asymmetric stretching vibrations of the *N*-nitro group and the N—H stretch give rise to strong bands that appear in narrow regions; the influence of substituents is negligible. On the other hand, the frequencies vary in a regular way; hence, we cannot conclude whether the nitramino group interacts with the second substituent or not.

All the aforementioned spectra were registered in diluted (*ca* 0.2 M) solutions, using deuterated methylene chloride as the solvent, because it is transparent in the regions of interest. In the solid-state spectra, two strong bands at *ca* 3250 and 3160 cm^{-1} were observed, accompanied by a broad absorption with several submaxima up to *ca* 2900 cm^{-1}. This indicates the presence of hydrogen bonds. Such specific interactions also usually evolve some additional bands in the IR spectra in the lower wavenumbers regions. To our surprise, the nitramines **2a–2g** give identical spectra in solutions and in potassium bromide pellets; the bands characteristic of the *N*-nitro group appear at the same wavenumbers. The nature of the intermolecular interactions in crystal lattices seems to be obscure.

The carbon NMR spectra of the primary nitramines do not differ significantly from those of corresponding *N*-methyl-*N*-phenylnitramines,[15] although the chemical shifts of ring carbon atoms are lower in the former, usually by 1–5 ppm. The substituent-induced chemical shift differences (SCSD, increments) of the nitramino group derived from the spectrum of the parent compound and the average values from all the spectra are nearly the same. The result indicates that there is no electronic interaction between the nitramino group and another substituent in a conjugated position.[16] Despite the diversity of the substituents investigated (from NO_2 to OMe), the additivity rule is obeyed in all the spectra. The *ipso* increment of the nitramino group ($S_{ipso} = +7.6$) differs markedly from that of the nitro ($S_{ipso} = +19.9$) and amino ($S_{ipso} = +20.7$) groups, and resembles that of the methyl group ($S_{ipso} = +9.3$).[17] Consequently, the interaction between the nitramino group and the aromatic

Table 2. The IR spectra of *para*-substituted *N*-phenylnitramines (in CD_2Cl_2)

No.	Substituent	σ^+	$\nu(NO_2)$ asym.	$\nu(NO_2)$ symm.	N—H region
2a	NO_2	0.720	1607	1318	3367
2b	SO_2Me	0.778	1607	1319	3370
2c	Br	0.232	1601	1320	3373
2d	F	0.062	1591	1320	3374
2e	H	0.000	1587	1323	3375
2f	Me	−0.170	1596	1322	3376
2g	OMe	−0.268	1585	1322	3376

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Table 3. The carbon (^{13}C) and nitrogen (^{15}N) NMR spectra of *para*-substituted primary *N*-phenylnitramines in DMSO-d_6; chemical shifts δ are given in ppm *versus* tetramethylsilane as the internal standard, and *versus* nitromethane as the external standard

Substituent	C-1	C-2	C-3	C-4	NH	NO_2
NO_2	141.6	119.9	124.9	144.2	−190.3	−32.2[a]
SO_2Me[b]	140.1	123.5	128.3	137.8	−191.2	−34.4
Br	135.2	123.5	132.0	119.0	Not observed	−35.2
F	132.2	125.1	116.0	160.5	−194.9	−30.6
H	135.1	122.0	128.1	126.8	Not observed	−31.1
Me[c]	133.4	122.2	129.5	136.5	−193.7	−30.4
OMe[d]	128.6	125.0	114.2	158.2	−195.5	−29.4

[a] −11.6 (*C*-NO_2).
[b] 43.5 (SO_2Me).
[c] 20.5 (ArMe).
[d] 55.4 (OMe).

ring must be of an inductive nature. Structural data confirm this conclusion: the substituent (NNO_2) is nearly perpendicular to the plane of the aromatic ring.[7,18] Such twisted conformations exclude mesomeric interaction of the aromatic sextet and the π-electron system of the nitramino group. Theoretical calculations by Anulewicz *et al.*,[18] although based on false (mesomeric) premises, gave a result ($\sigma = +0.36$) very close to the experimental characteristics of the secondary nitramino group ($\sigma = +0.57$).[19] We believe that the nitramino group is an electron-demanding substituent, but its mesomeric interaction with the ring is not possible. The resonances in ^{15}N NMR spectra of the amide (193.1 ± 3 ppm) and nitro (32.4 ± 3 ppm) nitrogen atoms appear within a narrow range, indicating that the intramolecular interaction across the ring can be neglected (see Table 3).

The proton NMR spectra confirm the observation—the lack of conjugation between the nitramino group and another substituent on the ring may be considered as a fact. The data collected in Table 4 indicate that the nitramine proton is strongly deshielded; hence, it must display some acidic properties.

Another interesting feature of the spectra reported is the strong dependence of chemical shifts on the solvent used. It is not limited to the N—H proton; its interaction with the solvent molecules influences significantly the absorption of ring protons, especially those in the *ortho* positions.

The first attempts to measure pK_A values of primary phenylnitramines, using the spectrophotometric method, were unsuccessful. The spectra registered in Britton–Robinson buffer solutions, at $2 < pH < 10$, demonstrated that the UV–VIS spectra of dissociated and undissociated nitramines are too similar to enable the measurements of concentrations of both forms in the equilibrium. The exceptions were the nitramines containing a strong,

Table 4. Proton NMR spectra of primary *para*-substituted *N*-phenylnitramines in DMSO-d_6; chemical shifts δ are given in ppm *versus* tetramethylsilane as the internal standard

	Primary nitramines				Secondary nitramines[15]	
Substituent	H-2,6[a]	H-3,5[a]	N—H	Others	H-2,6	H-3,5
NO_2	7.70	8.25	Not observed	–	7.47	8.25
NO_2[b]	7.80	8.34	13.06	–		
SO_2Me	7.70	8.06	Not observed	3.22	7.57	8.06
SO_2Me[b]	7.78	8.05	12.91	3.15		
Br	7.66	7.40	Not observed	–	7.20	7.59
Br	6.39	7.59	8.81[c]	–		
F	7.29	7.44[d]	13.79	–	7.26	7.09
H	7.42–7.46[e]		Not observed	–	7.27–7.54	
Me	7.34	7.24	13.70	2.32	7.26	7.16
OMe	7.33	7.00	13.45	3.77	7.23	6.95

[a] Doublets with the coupling constants 8.9–9.4 Hz.
[b] In acetone-d_6.
[c] The spectrum registered in deuterated benzene.
[d] Two multiplets, due to the coupling with the fluorine atom.
[e] Proton on C-4 gives a multiplet centred at 7.29 ppm.

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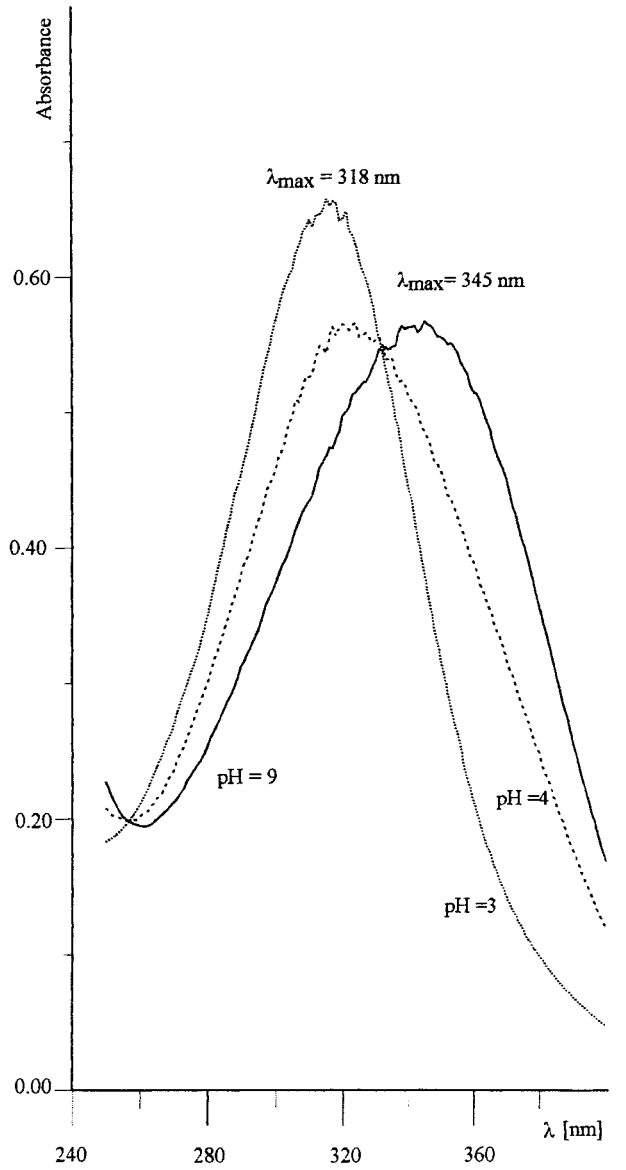

Figure 2. The UV spectra of *N*,4-dinitroaniline in aqueous solutions of various acidities (pH)

electron-demanding substituent; the spectra of *N*,4-dinitroaniline are presented in Fig. 2.

Acidities of primary phenylnitramines were measured by the standard potentiometric method.[20] Saturated, aqueous solutions of the nitramines were titrated with diluted aqueous solution of sodium hydroxide at room temperature. The results, collected in Table 5, are the average numbers from six pH measurements.

As is to be expected, the electron-withdrawing substituents facilitate ionization of nitramines due to the stabilization of anionic species. Acidities vary within nearly two units on the logarithmic scale and resemble closely those of ring-substituted benzoic acids. Their acidities, *i.e.* $pK_A(A)$ values, were estimated in diluted aqueous solutions,[21] and their basicities, expressed as

Table 5. Acidic $pK_A(A)$ and basic $pK_A(B)$ dissociation constants of *para*-substituted *N*-phenylnitramines (at 24 °C) estimated in aqueous solutions by the potentiometric method

Para-substituent	K_A	$pK_A(A)$	$pK_A(B)$
NO_2	1.70×10^{-4}	3.77[a]	−7.69
SO_2Me	1.62×10^{-4}	3.79[b]	−7.67
Br	5.37×10^{-5}	4.27	−7.05
Cl	3.16×10^{-5}	4.50[c]	−6.76
F	4.07×10^{-5}	4.39	−6.90
H	2.34×10^{-5}	4.63[d]	−6.59
Me	2.19×10^{-5}	4.66	−6.55
OMe	2.40×10^{-6}	5.62	−5.33

[a] $pK_A(A) = 3.91$ by spectrophotometric method.
[b] $pK_A(A) = 3.80$ by spectrophotometric method.
[c] At 15 °C, from Ref. 23.
[d] $4.75 < pK_A(A) < 4.91$, depending on the temperature in the region of 1 to 18 °C; measured by the conductometric method.[24]

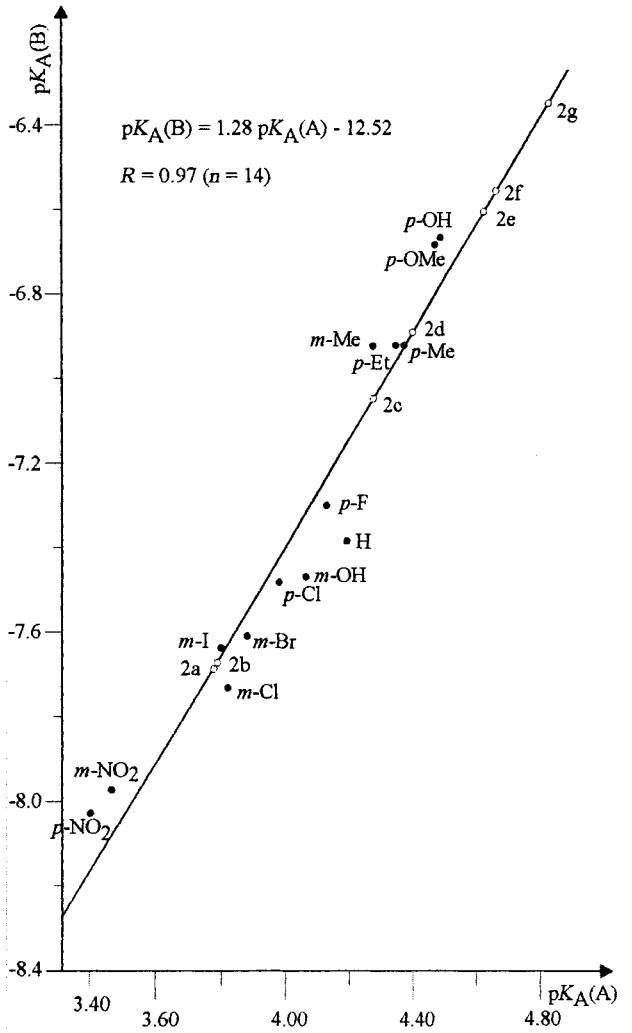

Figure 3. Arnett's plot, correlation between the acidic and basic dissociation constants of the ring-substituted benzoic acids, extrapolated to the phenylnitramine region

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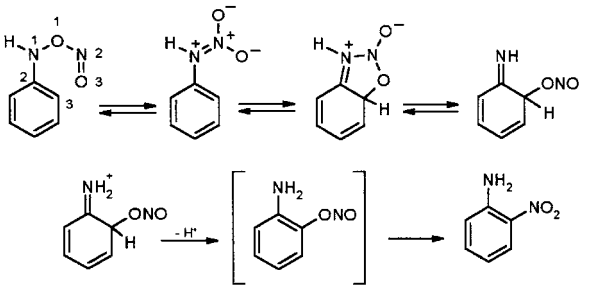


Scheme 4

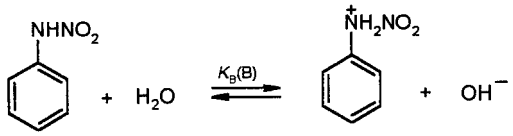
$pK_A(B)$ values, were also measured in the water–sulfuric acid binary mixtures.[22] There is a simple relationship between the proton-releasing and proton-demanding properties of benzoic acids, as shown in Fig. 3.

The same correlation can be used for the prediction of 'basicities' of primary *N*-phenylnitramines; some relevant data in the last column of Table 5 indicate that protonation of these species can be expected in moderately concentrated sulfuric acid but not in diluted aqueous solutions. Half protonation requires concentrations between 67 and 82% of sulfuric acid; in such solutions the decomposition of a nitramine prevails over its rearrangement. Consequently, protonation of the nitramine, as the preliminary step of the rearrangement, seems to be impossible.

The same conclusion can be reached in another way, considering that the Sørensen (pH) and Hammett (H_o) acidity scales are compatible. If so, the relationship $pK_A(B) + pK_B(B) = 14$ should be obeyed, and, consequently, the basicities of *N*-phenylnitramines in aqueous solutions will be expressed with dissociation constants of $2.0 \times 10^{-22} < K_B\,(B) < 4.7 \times 10^{-20}$ (Scheme 5). The basicities of nitramines are too low to explain the catalytic effect of an acid. Moreover, the reaction constant ρ of the basic dissociation of nitramines exceeds unity negligibly, whereas the kinetic ρ constant of the rearrangement is close to the maximum value ($\rho = 4$).[5] If migration of the *N*-nitro group occurs within a protonated molecule, the influence of ring substituents on the proton affinity and the rate of rearrangement should be parallel.

The spectral properties of *para*-substituted *N*-phenylnitramines, as well as their acidic properties (pK_A), indicate that the substituents do not influence significantly the electronic structure and chemical properties of the nitramino group. The proton affinity of the nitramino group seems to be insufficient to explain the catalytic effect of an acid. The conclusions are well confirmed with the data reported above, but they seem to contradict some theories of the nitramine rearrangement. Now we wish to demonstrate that our results are in agreement with commonly known facts and that the apparent discrepancies emerge from misinterpretations.

The catalytic effect of an acid used to be interpreted as the result of protonation of the intact substrate molecule, in



Scheme 5

the preliminary step of the rearrangement. Such a presumption is acceptable if we ignore two well-known facts:

- the *N*-nitro group can migrate to an aromatic ring without intervention of protons;[25,26]
- there is no basic centre within the nitramino group.[7–9]

Otherwise, we can rationalize these facts assuming that reversible shift of the *N*-nitro group precedes protonation. There are two possible routes of transformation of the substituent into its mobile nitrito form (Scheme 4). Homolytic cleavage of the N—N bond and recombination within the solvent cage provides *N*-nitrite. Migration to the *ortho* position, *via* cyclic transition-state, gives *C*-nitrite. Further migrations occur rapidly as the [3, 3] sigmatropic shifts in accordance with Woodward–Hoffmann rules.

It should be pointed out that the shift of the *N*-nitro group to the ring forms a basic centre, which is absent in the intact molecule, *viz*. the imino group. Its protonation prevents retro-migration of the nitro group, facilitates expulsion of ring protons and restitution of the aromatic system. The influence of ring substituents on the basicity of anilines is strong ($\rho = 3$) and corresponds well to the Hammett equation applied to the kinetics of the nitramine rearrangement. Transformation of a labile nitrito form into the stable final product follows a probable dissociation–recombination pathway, as indicated by the chemically induced dynamic nuclear polarization (CIDNP) effect observed during rearrangement of some primary nitramines.[27]

[^{15}N-NO_2]-*N*-(2,6-Dibromophenyl)-nitramine and its 2,6-dichloro analogue were rearranged in a strongly acidic solution.[27,28] The ^{15}N NMR spectra, registered during the rearrangement, indicated the enhancement of the absorption of the 4-nitro group in the products. The results with [^{15}N-NO_2]-*N*-methyl-*N*-phenylnitramine were similar, except that the product composition was much more complex. According to Kaptein's rules, the nuclear polarization is the evidence that 2,6-dibromo-4-nitroaniline is formed through recombination of free radicals.[27,28] This confirms our hypothesis, that the expulsion of a *C*-proton precedes transformation of the ONO group into the stable nitro group, conjugated with the amino substituent across the ring. The ONO to NO_2 rearrangement may occur in the *solvent cage*, since it does not require distant migrations. Obviously, the whole transformation cannot be entirely intramolecular, otherwise the CIDNP effect would not have been observed.[29] However, the escape from the *cage* is

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responsible for some side reaction accompanying the rearrangement, whereas migration of the nitro group is strictly intramolecular.

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