Polish J. Chem., **76**, 1113–1125 (2002)

Structure and Rearrangement of Ring Substituted *N*-Methyl-*N*-phenylnitramines

by Z. Daszkiewicz*, J. Zaleski, E.M. Nowakowska and J.B. Kyzioł

Institute of Chemistry, University of Opole, 45-052 Opole, ul. Oleska 48, Poland

(Received February 15th, 2002; revised manuscript May 6th, 2002)

The mechanism of the acid catalyzed nitramine rearrangement must account for the unusual sensitivity of the reaction of *N*-methyl-*N*-phenylnitramine derivatives to the ring substituents. Spectral analyses indicate the lack of interaction between the nitramino group and the second substituent through the aromatic ring. X-ray analyses confirm the spectral data: there is no conjugation between the aromatic and nitramine sextets of π-electrons. X-ray structural data also indicate that the nitramino group cannot behave as the basic centre. A reconsideration of the rearrangement rate constants of the series of ring substituted *N*-methyl-*N*-phenylnitramines lead to the conclusion that migration of the *N*-nitro group precedes protonation. The influence of the substituents on the reaction rates is determined by their influence on the basicity of the imino nitrogen in an intermediate. The CIDNP effect, observed in the rearrangement, results from the transformation of mobile nitrito group into the stable nitro substituent.

Key words: nitramines, rearrangement, reaction mechanism

The nitramine rearrangement belongs to the class of aromatic rearrangements involving migration of a substituent from heteroatom to the aromatic ring. Despite of their formal similarity, the mechanisms of the transformations are different. The benzidine and the Claisen rearrangements are intramolecular, while the Fischer-Hepp, Wallach and Bamberger rearrangements follow a dissociative path. The nature of the nitramine rearrangement remains unclear [1]. There are several derivatives of nitramide (NH_2NO_2) which are, less or more, susceptible to the rearrangement under influence of an acid or elevated temperature. Most of the primary and secondary aromatic (phenyl, naphthyl) or heteroaromatic (thiazolyl, pyridyl) nitramines can be isomerized under proper conditions [2]. In the mechanistic studies, the most frequently employed model compound is *N*-methyl-*N*-phenylnitramine and its ring substituted derivatives [3]. The kinetic experiments, carried out by White, demonstrated that the reaction is very sensitive to the character and position of a substituent bonded to the ring. White has established a linear relationship ($r = 0.99$) between the rate constants and the σ^+ substituent constants with the coefficient $\rho = -3.76$. His conclusion that "there must be strong interaction between the reaction centre and the substituent" seems to be obvious [4].

*Author for correspondence.

On the other hand, the studies of spectral properties of the ring substituted *N*-methyl-*N*-phenylnitramines have demonstrated that the interaction between the nitramino group and the second substituent across the ring is negligible. In the NMR spectra, the signals of *N*-methyl groups appear in narrow ranges and the chemical shifts of aromatic protons and carbons are predictable according to the increments additivity rule. In the FTIR spectra, the bands characteristic of the secondary nitramino group appear at 1517–1536, 1285–1299 and 755–759 cm^{-1} regions, irrespective of the substituent present [5]. Elucidation of the contradiction between the kinetic and spectral data should provide some information on the mechanism of the nitramine rearrangement.

RESULTS AND DISCUSSION

The chemical shift of the [^{15}N]-nitrogen atom is very sensitive to its environment. The ^{15}N-NMR spectra of selected *N*-methyl-*N*-phenylnitramines are collected in Table 1. The chemical shifts of the amide (from –201 to –203 ppm) and nitro (from –26 to –31 ppm) nitrogens indicate specific electronic structure of the nitramino group. The influence of the substituents is negligible considering that the chemical shift of the reference compound (CH_3NO_2) changes from –2 to +7 ppm depending on the solvent. Hence the differences of *ca*. 5 ppm in the nitramine series are meaningless. The nitramino group remains unaffected with the presence of another substituent irrespective of its character.

Table 1. ^{15}N-NMR and UV spectra of *para*-substituted *N*-methyl-*N*-phenylnitramines[a].

Substituent	Chemical shift/δ ppm		Electronic spectra		UV spectra of PhX	
σ_p^+	nitro group	amide nitrogen	λ_{max}	ε	λ_{max}	ε
$MeSO_2$	–29.6	–201.0			217	6700
+0.747			270	5400	264	977
			287	2800		
NO_2	–30.9	–201.3[b]	254	3070	252	10000
+0.740					280	1000
			303	9620	330	125
Cl	–27.5	–202.9	215	12000	210	7600
+0.025			259	7180	265	240
			284	3280		
H	–27.9	–202.1	258	2770	256	200
0.000			265	2070		
F	–26.6	–203.3			204	6200
–0.247			254	2840	254	900
			265	1920		
Me	–27.0	–202.8	259	7000	262	270
–0.256			309	1900		
t-Bu	–27.0	–202.5	256	17240	207	7800
–0.275			300	6190	257	170

Table 1 (continuation)

MeO	–26.4	–203.5	228	5870	217	6400
–0.648			260	1740	269	1480
			281	2230		
			316	420		

[a)]The substituent constants are taken from [7], the UV spectra of mono substituted benzenes come from [6]; [b)]From [8].

Conjugation between complementary substituents through the aromatic ring causes a strong bathochromic shift in the electronic spectra. The secondary aliphatic nitramines, as *N*,*N*-dimethylnitramine (λ_{max} = 238 nm, ε = 7900) and *N*,*N*-diisobutylnitramine (λ_{max} = 244 nm, ε = 8050), give in the near UV region one narrow band of medium intensity. The absorption bands of *para*-substituted *N*-methyl-*N*-phenylnitramines are broad, irregular in shape and shifted bathochromically to 246–262 nm. Resolution of the envelopes into gaussian curves by a computer program gave two or more maxima listed in Table 1. The short-wave absorption bands (254–274 nm) have their counterparts in the electronic spectra of monosubstituted benzenes [6]. Hence the bands in the 265–316 nm region can be assigned to the nitramine chromophore. Consideration of the nitramino group and aromatic ring as two independent chromophores is an oversimplification, but the results confirm our previous statement *viz*. there is no interaction between the substituents across the aromatic ring.

X-ray structural examination of *N*-methyl-*N*-phenylnitramine and its derivatives, containing electron releasing (OMe) and electron withdrawing (SO_2Me) groups, provided a simple explanation of the spectral properties of the nitramines. The relevant bond lengths and angles, completed with some literature data, are collected in Table 2. The diagram, showing numbering of atoms, is presented in Fig. 1.

Table 2. The geometry of the nitramine group in some *para*-substituted *N*-methyl-*N*-phenylnitramines.

Bond length (pm) an angles (degrees)	OMe	*Para*-substituent in the nitramine			
		H	Cl[a]	SO_2Me	NO_2[b]
N(7)–C(11)	143.8(3)	144.6(2)	144.6(2)	145.4(3)	144.8(4)
N(7)–C(1)	143.4(2)	142.8(2)	142.3(2)	142.9(3)	143.1(2)
N(7)–N(8)	134.1(2)	134.9(2)	134.6(2)	134.7(3)	134.6(3)
N(8)–O(9)	122.7(2)	123.0(2)	122.2(2)	122.7(3)	122.5(2)
N(8)–O(10)	122.8(2)	122.1(2)	122.9(2)	122.5(3)	123.8(3)
C(11)–N(7)–C(1)	122.6(2)	122.2(2)	122.4(2)	121.8(2)	122.0(2)
C(11)–N(7)–N(8)	118.4(2)	117.9(2)	118.3(2)	118.3(2)	119.1(2)
N(8)–N(7)–C(1)	119.0(2)	118.2(2)	118.4(2)	117.9(2)	118.8(2)
O(9)–N(8)–O(10)	124.2(2)	124.3(2)	125.0(2)	124.4(2)	125.1(2)
O(9)–N(8)–N(7)	118.5(2)	117.7(2)	118.3(2)	118.4(2)	117.1(3)
O(10)–N(8)–N(7)	117.3(2)	118.0(2)	116.6(2)	117.2(2)	117.8(2)
Torsion angle	85.2	69.4	65.6	70.9	72.3

[a)]From [10]; [b)]from [11].

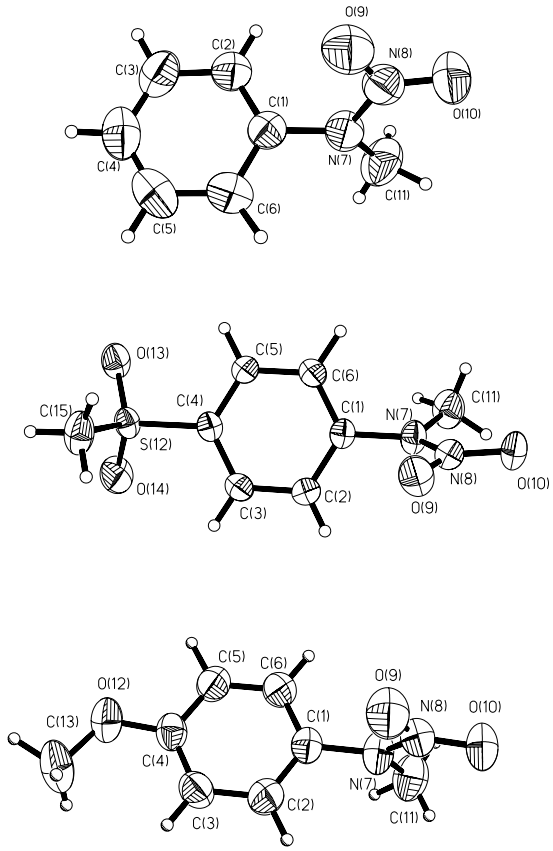
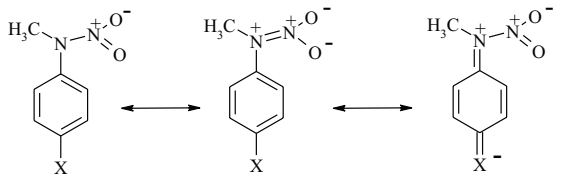


Figure 1. The ORTEP diagram of *N*-methyl-*N*-phenylnitramine, its *para*-methanesulphonyl and *para*-methoxy derivatives.

The nitramino group ($C_2N–NO_2$) is planar, both nitrogen atoms are sp^2 hybridized. There is usually a significant difference between the $N(sp^2)–C(sp^2)$ and $N(sp^2)–C(sp^3)$ bond lengths (*ca*. 136 pm *vs*. 146 pm) [9]. In the nitramines, the Ar–N bond is nearly as long as the $CH_3–N$ bond and its length is not influenced with the *para*-substituent. Moreover, the torsion angle between the aromatic ring and the plane of nitramino group amounts *ca*. 75±10° excluding conjugation among them. Consequently, the interaction of the nitramino group and another substituent, if it actually takes place, is of inductive character. The bond lengths (138±1 ppm) and angles (120±1°) within the aromatic ring confirm the lack of the mesomeric effect. Such a picture is consistent with the spectral data but complicates the problem of kinetics even further. The N(7)–N(8) bond length (134.5 pm) is invariable within two standard deviations, and intermediate between that of a typical single (145 pm) and double (125 pm) N–N bond [9]. The high N(7)–N(8) bond order corresponds to the planar arrangement of the nitramino group. Consequently, the mesomeric form in the centre of Scheme 1 is the best representation of its electronic structure. Contribution of the re-

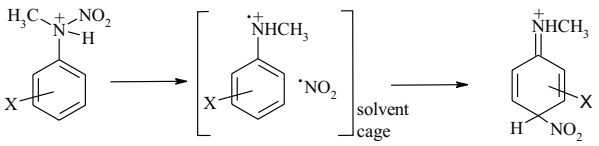
maining canonical forms to the resonance hybrid may be neglected. It means, that six π-electrons within the nitramino group occupy a four-centred orbital system.

Scheme 1



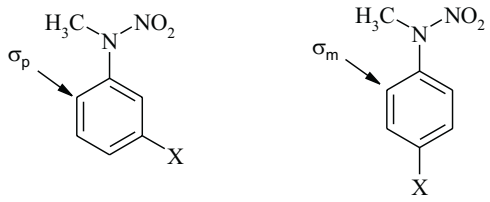
There is no unshared electron pair on the amide N(7) nitrogen. This atom bears a formal positive charge, hence it cannot behave as the basic centre. The results of our QM calculations are in agreement with this picture. In all compounds examined, independent of the method employed, both oxygen atoms bear a strong, negative partial charge. The N(8) nitro nitrogen atom is positively charged, while a partial negative charge appears on the N(7) amide nitrogen atom on the expense of the methyl and aryl substituents. Its magnitude is not influenced by the character and position of a substituent, indicating an inductive nature of the interaction across the ring. The theoretical approach confirms the spectral and structural data on the planar conformation of the *N*-methylnitramino group and high N(7)–N(8) bond order. It also indicates that addition of proton to the intact nitramino group must destroy a multicentre π-electron system [12,13,14,15]. The function of an acidic catalyst, the site and the moment of protonation will be discussed later. Now, let us consider some uses and misuses of the correlation analysis in chemistry. The σ^+ substituent scale is one of more than twenty analogous scales [7]. It was established using solvolysis of the ring substituted cumyl chlorides in 90% aqueous acetone as the model reaction. This is a nucleophilic substitution process following the S_N1 mechanism, *i.e.* formation of the ion pair, with the positive charge on the α-carbon, is the rate limiting step. White observed an excellent linear correlation between the logarithms of the rearrangement rate constants and the σ^+ substituent constants. He concluded that the influence of the ring substituents is of the same nature in the rearrangement as in the model reaction. Consequently, the intermediate with the electron deficient nitrogen atom must participate in the rate-limiting step of the rearrangement.

Scheme 2



In such a way White's *solvent-caged-pair* theory of the nitramine rearrangement came into being (Scheme 2) [4]. In fact, the substituent constant of any kind expresses the influence of a substituent on the reaction centre. However, the nitramine rearrangement is the rearrangement reaction, *i.e*. there is no reaction centre. Instead, we have the migration origin and the migration terminus. The spectral and structural data indicate that the ring substituents do not influence the migration origin (nitramino group) but it cannot be excluded that they interact with the migration termini, *i.e*. the aromatic ring. We have transformed White's kinetic data into ($\log k_X$) and plotted them *versus* the σ substituent constants in a slightly different way (*cf.* Scheme 3).

Scheme 3



The rate constants of the rearrangement of *para*-substituted *N*-methyl-*N*-phenylnitramines were plotted against σ_m substituent constants. A good straight-line correlation was observed (Fig. 2). The ($\log k_X$) of the *meta*-substituted nitramines were plotted against σ_p substituent constants, assuming that *N*-methyl-2-nitro-5-X-anilines were the main products of the rearrangement. In fact, in this series, the 2 position, pointed out with an arrow, is the main but not the only migration terminus. Probably, a better correlation could be obtained taking into account the isomer distribution, *i.e*. using the relative rate constants corrected with partial rate factors. However, even the best fit cannot provide any explanation of the influence of the ring substituents on the rate of the nitramine rearrangement. The aim of the above reasoning is to demonstrate that the correlation analysis can be used in various ways, but in no way it can be considered as the evidence of a reaction mechanism. This is of special importance in the case of the reaction, which follow a complex, multistep mechanism. On the other hand, some irregularities may be more informative than a linear relationship between two variables. Fig. 2 demonstrates that the *N*-methyl-*N*-(4-tolyl)-nitramine rearrangement is thousand times slower than it can be predicted from the diagram. The *para*-methyl substituent requires a special consideration.

Ipso-attack in the aromatic series is well known since early seventies; among several examples of the *ipso*-substitution, the methyl derivatives are the most frequently encountered [16]. The product of *ipso*-nitration of *N*,*N*-dimethyl-4-toluidine is stable enough to register its NMR spectra. It rearranges to *N*,*N*,4-trimethyl-2-nitroaniline under reaction conditions [17], but nitrated *N*,*N*,2,4,6-pentamethylaniline looses its amino group under the influence of water yielding 2,4,6-trimethyl-4-nitro-2,5-cyclohexadienone [18]. An analogous reaction path was observed in the rearrange-

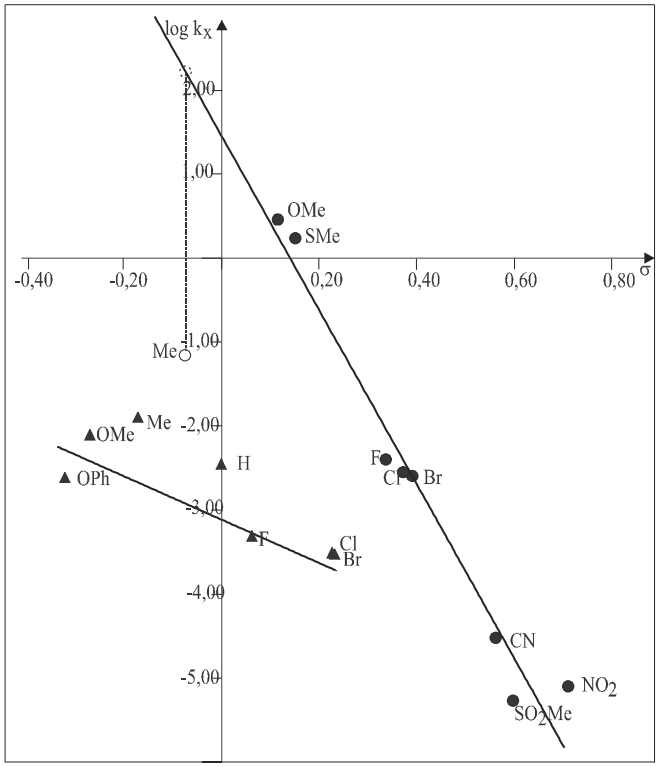
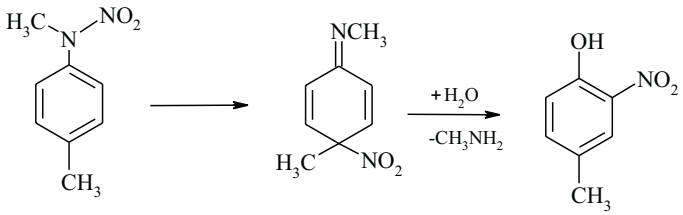


Figure 2. The influence of the ring substituents on the rate of rearrangement of *N*-methyl-*N*-phenyl-nitramine derivatives. • – reaction rate constants ($\log k_X$) of *para*-X-substituted nitramines in relation to *meta* (σ_m) substituent constants, ▲ – reaction rate constants ($\log k_X$) of *meta*-X-substituted nitramines in relation to *para* (σ_p) substituent constants.

ment of *N*-(9-anthracenyl)-*N*-methylnitramine under the influence of an acid; methylamine and 10-nitroanthrone were the only products isolated [19]. We have assumed that retardation of the *N*-methyl-*N*-(4-tolyl)-nitramine rearrangement results from the formation of the long-living σ-complex shown on the scheme below.

Scheme 4



According to [16], there are several possibilities of its further transformations but hydrolysis and rearrangement to 2-nitro-4-cresol seems to be one of the most probable side reactions. We have rearranged the nitramine under kinetic conditions described by White (*op. cit*.) and analysed the reaction mixture by the GCMS method. 2-Nitro-4-cresol, prepared by nitration of 4-cresol, was used as the standard. It was established that this compound was one of the by-products formed in a minute but detectable amount. Some other peaks could be assigned to *N*,4-dimethyl-*N*-nitrosoaniline and its 2-nitro derivative, the typical side products of the nitramine rearrangement [20]. The differences in the reaction rates of the nitramines can be understood if the driving force of the rearrangement is strongly dependent on the nature of ring substituents. We have no facilities to estimate the enthalpies of the reaction carried out in acidic solutions, hence we have analysed neat nitramines employing DSC/TGA method. Several acid catalyzed aromatic rearrangements have their thermally induced counterparts [21] and the nitramine rearrangement is not an exception [22]. Twenty *para* and *meta* substituted *N*-methyl-*N*-phenylnitramine derivatives were examined; some relevant results are collected in Table 3.

Table 3. The thermal nitramine rearrangement of some ring substituted *N*-methyl-*N*-phenylnitramines (DSC data).

Substituent	σ_p^+ or σ_m	Melting		Rearrangement		
		M.p. (°C)	ΔH_1 (kJ/mol)	Onset (°C)	Max. (°C)	$-\Delta H_2$ (kJ/mol)
p-$MeSO_2$	0.747	164.9	19.2	165	180.3	149.8
p-NO_2	0.740	143.7	25.0	148	167.4	140.6
m-NO_2	0.674	77.3	25.3	152	175.9	103.3
m-$MeSO_2$	0.522	104.6	26.1	162	178.8	107.4
p-Cl	0.035	50.2	19.5	141	162.1	68.7
p-Ph	–0.085	141.9	24.0	142	160.0	77.2
p-CH_2Ph		56.4	21.7	146	165.8	86.6
p-t-Bu	–0.275	78.0	23.4	141	162.4	49.7
p-MeO	–0.648	69.4	22.7	130	148.7	61.9

N-Methyl-*N*-phenylnitramine itself melts in the crucible at 39.4°C giving rise to the sharp endothermic peak on the thermal curve. The rearrangement is observed as an exothermic effect in the 139–162°C region. The enthalpy of the reaction (ΔH_2) cannot be measured, due to the distillation of *N*-methyl-2-nitroaniline. Generally speaking, the rearrangement is the exothermic process, which occurs in the molten state and begins at 130°C (MeO) to 165°C ($MeSO_2$), depending on the substrate. In the case of high melting (m.p. > 110°C) substrates, the onset of the reaction cannot be established precisely since the *endo* (melting) and *exo* (reaction) effects overlap to some extent. If we assume that the temperature of the rearrangement is the gauge of activation energy, we must conclude that the influence the of the ring substituents is negligible (*cf.* 148°C for NO_2 and 146°C for $PhCH_2$ groups). Comparison of the thermal effects ΔH_2

of the rearrangement leads to the conclusion that the substrates containing electron accepting substituents are more prone to the rearrangement than those with electron releasing groups. The enthalpies of the rearrangement are underestimated in the latter case, due to the volatility of the products *e.g*. the mass loss in the case of *p*-MeO derivative is nearly 20% at 150°C and exceeds 30% at 162°C in the case of *N*-(4-t-butylphenyl)-*N*-methylnitramine. Hence, the final conclusion is that there are no significant differences in the enthalpy of the rearrangement, which can be made responsible for the sizeable influence of the substituents on the reaction rates.

The kinetic experiments, described by White, were carried out in diluted (0.001 to 0.501 M.) aqueous solutions of perchloric acid, in which the products exist mainly as the free bases [4]. The basicity of 2,4-dinitroaniline ($pK_A = -4.26$ in perchloric acid) is very low, *i.e*. it is half protonated in 34.5% (4.3 M.) perchloric acid. The influence of the *N*-methyl group on the basicity of anilines is unpredictable but it usually does not exceed ±0.3 units on the pK_A scale [23]. Consequently, rearrangement of *N*-methyl-*N*-(4-nitrophenyl)-nitramine in 0.501 M perchloric acid must provide 2,4-dinitro-*N*-methylaniline and not its protonated form. Analogously, protonation of 4-chloro-2-nitro-*N*-methylaniline (*ca*. 0.4%) should not influence the reaction enthalpy. Obviously, the solvent effects and other intermolecular interactions may contribute to the total driving force of the rearrangement, but they must be of the same nature in both series of experiments. Our DSC/TGA results can be applied to the acid catalyzed rearrangement, leading to the conclusion that the reaction rate must be determined by some property of the transition state or a reactive intermediate.

To resolve the problem we considered White's kinetic data. The slope of the straight-line plot of $\log k_X$ *vs*. σ^+ is very high ($\rho = -3.7$), considering that the influence of a ring substitutent on the reaction centre, situated out of the ring, usually does not exceed ±4.0. Much higher ρ values, up to ±10.0, are observed in the ring substitution reactions [24]. Our recent investigations on the proton affinity of *N*-methyl-*N*-phenylnitramines revealed that the influence of ring substituents can be expressed with the coefficient ρ of *ca*. 1.0 [25]. The spectral and X-ray diffraction studies excluded the influence of the substituent on the migration origin, while the ρ value suggests that the rearrangement rate is not determined with the electronic properties of the migration terminus. Consequently, we must look for a property of a hypothetical intermediate, which is the rate-determining factor. The ring substituents change the reaction rate constants for six orders of magnitude. Their influence on the basicities (pK_A's) of anilines is nearly the same (we cannot find a reliable and consistent set of pK_A's for the corresponding *N*-methylanilines). On the other hand, it is well known that the protonation plays an important role in the nitramine rearrangement. We have transformed White's kinetic data into $\log k_X/k_H$ and plotted it *versus* the pK_A's of the analogously substituted primary anilines. This parallelism is demonstrated on the diagram in Fig. 3.

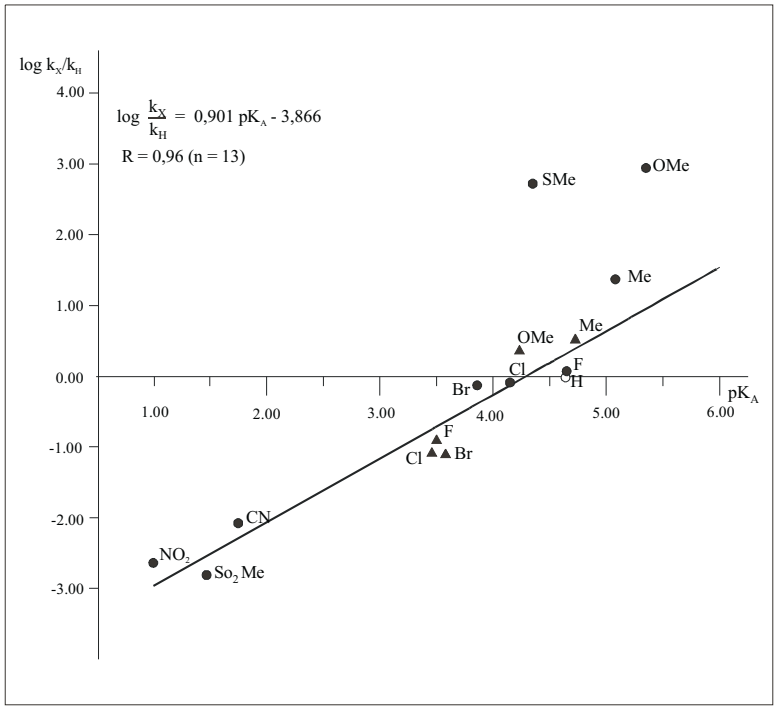
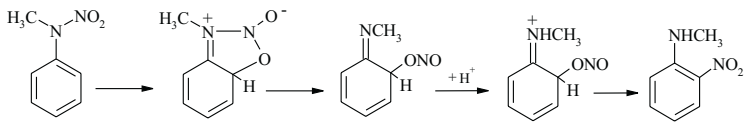


Figure 3. Correlation between the relative rate of the rearrangement and basicities of the parent primary anilines. • – *para*-X-substituted nitramines; ▲ – *meta*-X-substituted nitramines.

Twelve points are set up along the straight line indicating that the proton affinity of the nitrogen atom is the rate-determining factor in most cases. The pK_A's of 4-methanesulfonylaniline (1.47) and 4-anisidine (5.35) differ markedly, so do the logarithms of the relative rate constants (–2.81 *vs*. +2.94), but the geometry of the nitramino group (bond lengths and angles) is not affected with the ring substituents in the corresponding nitramines. It also militates in favour of the hypothesis that the nitramino group is not the basic centre. Considering that migration can occur without inference of proton, it is not necessary to assume that protonation of the intact substrate molecule is the preliminary step of the rearrangement. Several examples of the *N*-nitro group migrations, in a melt or in an inert solvent, were described [22]. In our opinion, the shift of *N*-NO_2 group to the *ortho* position, precedes protonation, hence the *N*-methylimino group in the intermediate (Scheme 5) is the protonation site. The presumption that its basicity is similar to that of the analogously substituted aniline seems to be reasonable.

Scheme 5



The *N*-nitro group migrates to the aromatic ring, through the cyclic transition state, forming the *ortho*-nitrito intermediate. Concerted transformation of the *N*-NO_2 into *N*-ONO form is prohibited by the symmetry conservation rules, moreover, it has been shown that the transformation requires assistance of an aromatic system [20]. Further migrations, to the amino nitrogen or other positions in the ring, occur *via* sigmatropic [3, 3] shift, as postulated in the *cartwheel theory* of the nitramine rearrangement [26]. Addition of proton in the next step prevents return of the NO_2 group to the migration origin and facilitates expulsion of the ring proton. As shown in Scheme 5, the nitrogen atom, bound to the ring, is electron deficient in the transition state, hence electron releasing substituents facilitate its formation, as established by White [4]. Deprotonation of the intermediate (σ-complex) is probably concerted with the transformation of the mobile nitrito (ONO) group into the nitro substituent, conjugated with the aromatic ring. The mechanism of the nitramine rearrangement, presented in Scheme 5, explains how the stable *N*-nitro group can be transformed into mobile *N*-nitrito group without breaking of the orbital symmetry conservation rule. It can be considered as the confirmation and accomplishment of Ingold's *cartwheel theory.*

The proton transfer from the intermediate (σ-complex) to the solvent molecule (H_2O) and re-transformation of the mobile nitrito (–ONO) group into the nitro substituent are two separate stages of the final step of the nitramine rearrangement. The second one cannot follow an analogous path as the first step of the reaction. The explanation was provided by Ridd *et al*., using the NMR technique. In the rearrangement of some [^{15}N-NO_2]-labelled nitramines, the CIDNP effect was observed in the ^{15}N-NMR spectrum of the product [27]. It must be emphasized that the CIDNP effect was observed in the spectrum of the final product and not in the spectrum of a σ-complex, as in the case of nitration product of *N*,*N*,2,4,6-pentamethylaniline [28]. The conclusion is obvious: the proton transfer occurs first, then a homolytic cleavage of the C–O bond generates radicals which recombine immediately with the formation of the C–N bond. The transformation proceeds rapidly in a solvent cage, which is responsible for the intramolecularity of the rearrangement and the non-Boltzmann spin population. Such an interpretation provides a resolution of some commonly known apparent contradictions in the experimental data *e.g*. CIDNP effect indicates that radicals are involved, but all attempts to detect radicals in the nitramine rearrangement have been unsuccessful.

EXPERIMENTAL

The electronic spectra were registered in methanolic solutions ($c = 0.4 \cdot 10^{-4}$ to $1.4 \cdot 10^{-4}$ mol L^{-1}) at 25°C using Beckman DU 640B Spectrometer. The ^{15}N-NMR spectra were recorded on a Bruker DPX spectrometer (250 MHz) in 0.3 M. solutions in acetone-d_6 in the presence of $Cr(acac)_3$; the chemical shifts are given with respect to nitromethane as the external standard.

Table 4. Experimental data on the rentgenostructural analyses of *N*-methyl-*N*-phenylnitramine (H) and its *para*-substituted (OMe, SO_2OMe) derivatives.

Parameter	OMe	H	SO_2Me
Crystal dimensions	0.25×0.3×0.6	0.8×1.0×0.8	0.65×0.45×0.7
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	Pbca	$P2_12_12_1$
Cell dimensions	10.918(2), 9.237(2) 9.265(2), 108.13(3)	8.806(1), 10.926(1) 15.925(2)	5.857(1), 13. 079(3) 13.312(3)
Cell volume	888.0(3)	1532.2(3)	1019.7(4)
$\rho_{calc.}$	1.363	1.319	1.500
$2\theta_{max}$	55.4°	60.1°	61.0°
Radiation wavelength		0.71073	
Scan mode		$\omega - \theta$	
Temp. of measurment		298	
No of ind. reflections	3642	2244	1673
No of reflections incl. in refinement	3642	2244	1673
σ limits		$F > 2\sigma(F)$	
Lorentzian polarization and absorption correction	Lorentzian and polarization correction applied, absorption correction not app		
Method of structure solution and program	Direct methods, SHELXS 97		
Method of refinement and program	Least squares, SHELXL 97		
No. of parameters	159	133	177
Treatment of H atoms		Freely refined	
R, wR refined against F^2	$R_1 = 3.54\%$	$R_1 = 3.71\%$	$R_1 = 3.09\%$
Residual electron density	+0.162/–0.135	+0.140/–0.150	+0.213/–0.257

The thermal behaviour was investigated using a TA-Instruments differential scanning calorimeter DSC-2010. Operational characteristics: heating rate –10°C/min., sample size – 4 to 9 mg, atmosphere – nitrogen, 40 ml min^{-1}, crucible – standard aluminium pans. The DTA thermograms were obtained with a TGA-2050 thermal balance (TA-Instruments) using 13–35 mg samples in open platinum crucibles, in a current (10 ml/min) of dry nitrogen. The chromatographic analyses were performed using Hewlett-Packard GC system HP 6890 with Mass Selective Detector 5973, equipped with the on-column inlet and the capillary HP-1 methyl siloxane column (30 m × 320 μm × 0.25 μm). The oven temperature program was: 30°C – 10°C min^{-1} – 280°C; auxiliary temperature program was: 130°C (isotherm, 10 min) – 10°C min^{-1} – 280°C. The X-ray data collection was carried out at 25°C on KM4 KUMA diffractometer with Mo Kα radiation. Some most relevant experimental parameters are given in Table 4.

CCDC No. 136896, 136897 and 136898 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Acknowledgment

This work was supported by the Polish State Committee for Scientific Research (grant No 3 T09A 156 18).

REFERENCES

1. Williams D.L.H., The Chemistry of the Amino, Nitroso and Nitro Compounds and Their Derivatives; Patai S. (Ed.), J. Wiley: London, 1975; vol. 2, p. 127.
2. a) Banthorpe D.V. and Thomas J.A., *J. Chem. Soc*., 7149 (1965); b) Banthorpe D.V., Thomas J.A. and Williams D.L.H., *ibid*., 6135 (1965); c) Tóth G., Nemes A., Tamás J. and Volford J., *Acta Chim. Sci. Hung*., **88**, 319 (1976).
3. White W.N., White H.S. and Fentiman A., *J. Org. Chem*., **41**, 3166 (1976) and references cited herein.
4. White W.N. and Klink J.R., *J. Org. Chem*., **35**, 965 (1970).
5. Daszkiewicz Z., Nowakowska E.M., Prezhdo V.V. and Kyzioł J.B., *Polish J. Chem*., **69**, 1437 (1995).

6. Gillam A.E. and Stern E.S., *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*; Edward Arnold Publ.; London, **1960**; p. 131.
7. Swain C.G. and Lupton E.C., *J. Am. Chem. Soc*., **90**, 4328 (1968).
8. Kolehmainen E., Laihia K., Kauppinen R., Gawinecki R. and Rasała D., *Magn. Reson. Chem*., **31**, 659 (1993).
9. Allen F.H., Kennard O., Watson D.G., Brammer L., Orpen A.G. and Taylor R., *International Tables for Crystallography*; Vol. C, Wilson A.J.C. (Ed.); Kluwer Academic Publ., Dordrecht; **1995**; pp. 685–706.
10. Ejsmont K., Kyzioł J.B., Daszkiewicz Z. and Bujak M., *Acta Cryst*., **C54**, 672 (1998).
11. Anulewicz R., Krygowski T.M., Gawinecki R. and Rasała D., *J. Phys. Org. Chem*., **6**, 257 (1993).
12. Prezhdo V.V., Bykova A.S., Głowiak T., Prezhdo O.V., Daszkiewicz Z. and Kyzioł J.B., *Polish J. Chem*., **75**, 707 (2001).
13. Prezhdo O.V., Bykova A.S., Prezhdo V.V., Koll A., Daszkiewicz Z. and Kyzioł J.B., *J. Mol. Struct*., **559**, 321 (2001).
14. Prezhdo V.V., Bykova A.S., Głowiak T., Daszkiewicz Z., Koll A., Kyzioł J.B. and Zhukhlistova N.E., *Kristallogr.*, **46**, 439 (2001).
15. Kyzioł J.B., Broda M.A., Zaleski J. and Daszkiewicz Z., *J. Mol. Struct*., **605**, 157 (2002).
16. Moodie R.B. and Schofield K., *Acc. Chem. Res*., **9**, 287 (1976).
17. Fujiwara K., Giffney J.C. and Ridd J.H., *J. Chem. Soc., Chem. Commun*., 301 (1977).
18. Helsby P. and Ridd J.H., *J. Chem. Soc., Chem. Commun*., 926 (1980).
19. Banthorpe D.V. and Winter J.G., *J. Chem. Soc., Perkin 2*, 1259 (1972).
20. Daszkiewicz Z., Nowakowska E.M. and Kyzioł J.B., *Tetrahedron*, **54**, 5991 (1998).
21. Shine H.J., *Aromatic Rearrangements*; Elsevier; Amsterdam, **1967**; pp. 89, 171, 205.
22. a) Daszkiewicz Z., Domański A. and Kyzioł J.B., *Chem. Papers*, **51**, 22 (1997); b) Naud D.L., *J. Chem. Soc., Perkin 2*, 1321 (1996); c) Janssen J.W.A.M. and Habraken C.L., *J. Org. Chem*., **36**, 3081 (1971).
23. Abrams W.R. and Kallen R.G., *J. Am. Chem. Soc*., **98**, 7777 (1976).
24. Shorter J., *Correlation Analysis in Organic Chemistry: An Introduction to Linear Free-Energy Relationships*; Oxford University Press, Oxford, 1973.
25. Daszkiewicz Z., Spaleniak G. and Kyzioł J.B., *J. Phys. Org. Chem*., **15**, 115 (2002).
26. a) Banthorpe D.V., Hughes E.D. and Williams D.L.H., *J. Chem. Soc*., 5349 (1964); b) Brownstein S., Bunton C.A. and Hughes E.D., *J. Chem. Soc*., 4354 (1958); c) Brownstein S., Bunton C.A. and Hughes E.D., *Chem. & Ind*., 981 (1956).
27. Abu-Namous A.M.A. and Ridd J.H., *Can. J. Chem*., **64**, 1124 (1986).
28. Helsby P., Ridd J.H. and Sandall J.P.B., *J. Chem. Soc., Chem. Commun*., 825 (1981).