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Structure-based evaluation of the resonance interactions and effectiveness of the charge transfer in nitroamines

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Abstract Structural data for five nitroamines of general formula $\text{Me}_2\text{N-G-NO}_2$ show effectiveness of the ground-state charge transfer to be most and least efficient in *N,N*-dimethylnitramine and in 4-*N,N*-dimethylamino- β -nitrostyrene, respectively. Electron-donor power of the amino nitrogen atom in the latter compound is less than that in 4-nitro- β -*N,N*-dimethylaminostyrene (these two compounds are isomers). Natural population analysis shows that the charge transfer from the amino to the nitro oxygen atoms is most effective in *N,N*-dimethylnitramine, $\text{Me}_2\text{N-NO}_2$. The nitro oxygen atoms are not the only acceptors of the negative charge lost by the amino nitrogen atom. The nitro group in two substituted nitrobenzenes studied was found to be independent on substituent (nitro group attached to the benzene ring withdraws a constant electron density regardless the substitution).

Keywords Nitroamines · Resonance interaction · Charge transfer · Molecular structure · Quantum-chemical calculations

Introduction

Numerous properties of the conjugated push–pull systems, e.g. basicities, dipole moments, and spectral parameters, are significantly affected by the intramolecular charge

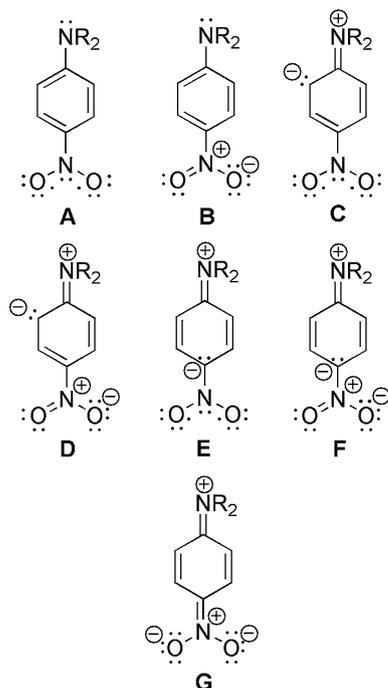
transfer [1]. A series of such compounds has been recently studied by us [2]. Since nitro and amino groups are among the most common acceptors and donors known, nitramines $\text{R}_2\text{N-NO}_2$ are subjected to extremely effective electron transfer. For this reason, intramolecular interactions in these compounds have often been studied [3–7]. *p*-Nitroanilines also contain these two strongly interacting groups where they are separated by the *p*-phenylene moiety. There is a question about the effect of conjugated spacers on the charge transfer in compounds of general formula $\text{R}_2\text{N-G-NO}_2$. This problem has been studied only occasionally. Thus, comparison of the dipole moments and spectral (IR and UV–vis) parameters for $\text{Me}_2\text{N-NO}_2$ and *p*- $\text{Me}_2\text{N-C}_6\text{H}_4\text{-NO}_2$ was found helpful to prove that the said interaction is really weaker when the NMe_2 and NO_2 groups are separated with the system of conjugated π bonds [8, 9]. Effective intramolecular charge transfer in the molecules of 4-*N,N*-dimethylamino- β -nitrostyrene is responsible for their stacking in dimers and tetramers with antiparallel dipoles [10].

The very basic concept of intramolecular charge transfer from the amino to the nitro groups in nitroamines [11, 12] has been criticized [13, 14]. Relatively low values of the net π -electron population in the molecule [15, 16] and unexpectedly low contribution (12.7% for *N,N*-diethyl-*p*-nitroaniline, based on X-ray data) of the full through-resonance structure **G** (Scheme 1) [13] are in line with this criticism. On the other hand, it was shown for $R = Et$ that, at least in the crystalline state, other structures presented in Scheme 1 were found to be more important [13]. Valence bond description gives some support to this idea: negative charge from the amino group in *p*-nitroaniline is transferred to the benzene ring but not to the nitro group [14].

Although structural (X-ray and electron diffraction) data for nitroamines of general formula $\text{R}_2\text{N-G-NO}_2$ are available for G being none, *trans*-CH=CH–,

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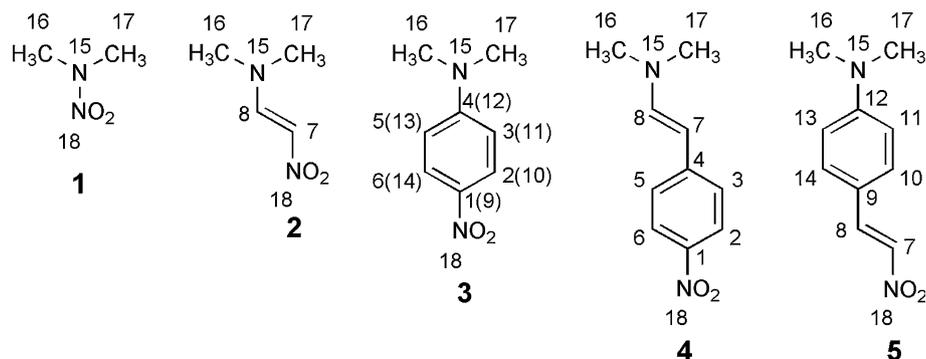
Scheme 1 Resonance structures of *p*-nitroanilines

p-C₆H₄⁻, *p*-C₆H₄-CH=CH-*trans*, and *trans*-CH=CH-C₆H₄-*p* [8, 10, 17–25, 9], these parameters have not practically been used to study the ground-state charge transfer in their molecules. Thus, we found it reasonable to examine usefulness of these data in learning the effect of the conjugated spacer on nature and effectiveness of the interaction between the amino and nitro groups. This effect will be additionally evaluated from the point of view of natural population analysis. Present studies are expected to help to understand the properties of nitroamines. For the sake of convenience, numbers of atoms present in the common molecular fragments of **1–5** were always the same (Scheme 2).

Results and discussion

The literature data show that *N,N*-dimethylnitramine, **1**, is planar both in the crystal and gas states [17, 18]. Length of

Scheme 2 Formulas of the compounds studied and numbering of heavy atoms in their molecules



the N–N bond (126 pm) proves that it has significantly double-bond character [8, 17, 9]. In the crystal state, the C2–C3 and C5–C6 bonds in the molecule of *N,N*-dimethyl-*p*-nitroaniline, **3**, are significantly shorter than other bonds in the ring [19, 20]. The C1–N18 and C4–N15 bonds in the compounds studied are shorter as compared with the average values for C_{Ar}–NO₂ and C_{Ar}–NMe₂ distances [21]. Thus, there is a significant quinoid contribution to the electronic structure of *N,N*-dimethyl-*p*-nitroaniline.

C7–C8 bond lengths in **2** and **4** (Table 1) are comparable. On the other hand, that bond in **5** is much shorter. This proves that charge transfer in **5** is less effective than in **2** and **4**. Although the bonds between the amino nitrogen and alkene or aromatic carbon atoms, i.e. C4–N15, C8–N15, C12–N15, in **3**, **4**, and **5** are comparable, this bond in **2** is visibly shorter. Thus, the charge transfer in **2** is more effective than in **3**, **4**, and **5**. This conclusion is supported by longer bonds between the nitro nitrogen and alkene or aromatic carbon atoms (C1–N18, C7–N18) in **3**, **4**, and **5** as compared to this in **2**.

Delocalization of the lone electron pair of N15 shortens the N15–C8 bond in **4** and **5** (crystalline state) to 135.9 pm (it is much shorter than the standard single N–C bond) [10, 21, 23]. The molecule of 4-*N,N*-dimethylamino-β-nitrostyrene, **5**, is almost planar, indicating significant conjugation between the amino and nitro groups [10]. Analysis of the bond lengths supports significant quinoid character of the six-membered ring in this compound. The C13–C14 (139.0 pm) and C10–C11 (137.3 pm) bonds in **5** are significantly shorter than C12–C13 (141.8 pm), C12–C11 (142.3 pm), C14–C9 (140.45 pm), and C9–C10 (140.57 pm). For the above mentioned reason, C9–C8 bond in this compound (144.8 pm) is shorter than the standard single C–C bond [10]. One should pay attention to asymmetry of the benzene rings in compounds **4** and **5** (the lines passing by C1 and C4 and by C9 and C12 are not their symmetry axes) which is a result of the asymmetry of the CH=CH–NMe₂ and CH=CH–NO₂ moieties.

Analysis of the bond alternation [24, 26] in compounds **4** [23] and **5** [10] (crystalline state) shows that although the sum of differences between the longest bond and residual

Table 1 X-ray bond lengths [pm] in 2–5

Bond	2 [22]	3	4 [23] ^a	5 [10]
C7–C8	134.5	–	134.8 135.4	133.6
C4–N15, C8–N15 or C12–N15	133.4	135.8 [19] 135 [20]	135.9 135.1	135.95
C1–N18 or C7–N18	139.4	143.6 [19] 140 [20]	143.6 144.6	143.13
C1–C2 or C9–C10	–	138.9 [19] 140 [20]	138.9 138.3	140.57
C2–C3 or C10–C11	–	137.1 [19] 137 [20]	137.8 129.5	137.3
C3–C4 or C11–C12	–	141.9 [19] 143 [20]	139.3 141.7	142.3
C4–C5 or C12–C13	–	141.2 [19] 143 [20]	141.2 141.1	141.8
C5–C6 or C13–C14	–	137.8 [19] 137 [20]	139.2 139.5	139.0
C6–C1 or C14–C9	–	139.3 [19] 140 [20]	139.2 144.7	140.45

^a Data for different molecules present in the unit cell

bonds in the benzene ring are comparable (12.6 pm for **4** and 12.3 pm for **5**), differences between the C_{Ar}–C_{exo} and C7=C8 bond lengths are much more differentiated (0.3 pm for **4** and 11.2 pm for **5**). This clearly shows that charge transfer in **4** is much more effective than in **5**.

As this can be seen in Table 2, C16N15C17 valence angles in **2**, **3**, **4**, and **5** are comparable. On the other hand, this angle in **1** is significantly larger. The O18N18O18 valence angle in **1** is also visibly larger than these in **2**, **3**, **4**, and **5**.

Sums of the bond angles around the amine nitrogens in **2** (359.8° [22]), **3** (359.9° [19]), **4** (359.7° [23]), and **5** (359.2° [10]) reveal that these atoms are not fully *sp*² hybridized. The nitro groups in the molecules of compounds **1** [24, 25], **2** [22], and **4** [23] (crystal state) are always planar (sum of the bond angles around the nitro nitrogen is equal to 360.0°). Analysis of the bond lengths confirms that the charge transfer in **4** is much more

Table 2 X-ray bond angles [°] in 1–5

Angle	1	2 [22]	3	4 [23]	5 [10]
C16N15C17	124.6 [25] 125.3 [24] 127.6 ^a [18]	117.0	118.7 [19] 118.2 [20]	117.2	118.7
ON18O	124.0 [25] 124.0 [24] 130.4 ^a [18]	120.8	121.4 [20]	122.7	122.5

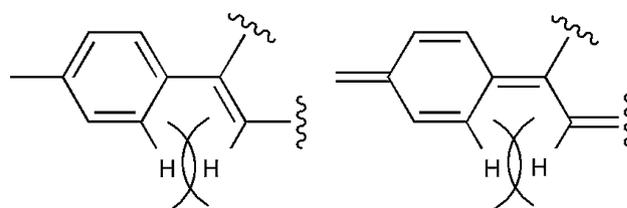
^a Electron diffraction data (gas state)

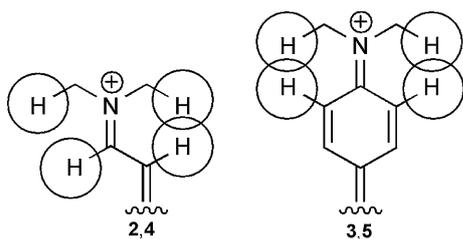
effective than in **5**. It is also proved by sum of the angles around the amino nitrogen being equal to 359.7° in the molecule of **4** [23] and 359.2° in the molecule of **5** [10] (sums of the angles around the nitro nitrogen atoms in these molecules are equal to 360.0° [10, 23]).

The *ortho* hydrogen atoms are known to interact sterically with these present at the α position in styrene and stilbene or with those at the *ortho* positions of another benzene ring in biphenyl [27–32]. Such an interaction is expected to be insensitive to the charge transfer (Scheme 3). On the other hand, number of steric interactions between hydrogen atoms in the charge-transfer resonance forms of the compounds studied seems to be responsible for differences between them. Thus, crowding in **2** resembles this in **4**. On the other hand, compounds **3** and **5** are of different type (Scheme 4). In consequence, loss of the charge by N15 in **2** is more easy than that in **4** and **5**.

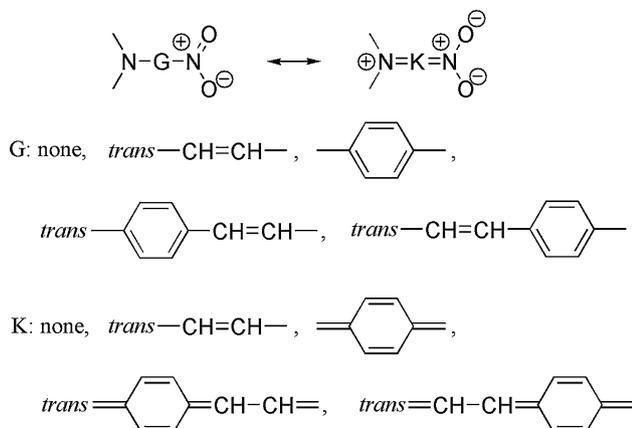
Increased multiplicity of the Me₂N–C bond in the compounds studied indicated also by its length (see X-ray and electron diffraction in Table 1) is a result of the intramolecular charge transfer (Scheme 5). Hindering of free rotation of the dimethylamino group in **2**, **4**, and **5** may result in non-equivalency of two *N*-methyl groups. ¹H and ¹³C NMR spectral data [33] show that it is the case in compound **2** only. Thus, charge transfer in its molecule is much more effective than this in **4** and **5**. The literature X-ray data show that Me₂N–C bond in **2** [22] is really much shorter than this in **3** [19, 20], **4** [23], and **5** [10] (the lengths of this bond in **3**, **4**, and **5** are comparable). Non-equivalent *N*-methyl groups were also found in some related compounds. Thus, due to increased contribution of the *p*-⁻O₂N=C₆H₄=N–CH=N⁺Me₂ quinoid form, two different ¹H signals of the *N*-methyl protons are seen in the NMR spectrum of *N,N*-dimethyl-*N*-(4-nitrophenyl)formamidinium below the coalescence temperature [34].

Natural population analysis (NPA) [35, 36] seems useful to show the character and effectiveness of the intramolecular charge transfer in the compounds studied. The calculated NPA charges at the nitrogen atoms (Table 3) show that amount of the charge at N15 in compound **1** is much lower than in other compounds studied (it is almost constant in compounds **2–5**). Notwithstanding two positively

**Scheme 3** Steric interactions in styrenes



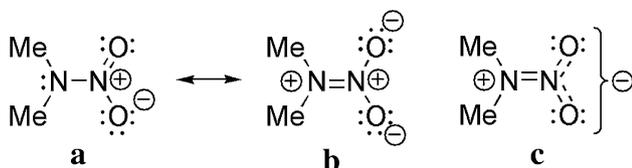
Scheme 4 Steric interactions in the molecules of compounds 2–5



Scheme 5 Charge transfer in different *N*-nitroamines

charged nitrogen atoms in **1b** (Scheme 6) are bound to each other, contribution of that resonance structure seems to be higher than that of **1c**. Non-equivalency of the nitro oxygen atoms (see NPA charges in Table 3) being a result of the restricted rotation around selected bonds in the molecules of some compounds studied seems noteworthy. As this can be seen in Table 3, except O18 and N15 other atoms that accept the negative charge lost by N15 in the molecules of compounds 2–5 are C3, C5, C7, C9, C10, C11, C13, and C14. Relatively high NPA values for the methyl carbon atoms, C16 and C17, are also noteworthy.

Electron-withdrawing ability of the nitro group in a series of nitrobenzenes seems to be independent on substituent. Mulliken population analysis of the total and π electron densities at the nitro oxygen and nitrogen atoms in such compounds was really found independent on substitution [35, 37]. The calculated NPA charges at N18 and O18 (Table 3) show this to be the rule also for compounds



Scheme 6 Charge transfer in the molecule of *N,N*-dimethylnitroamine

Table 3 NPA charges at the heavy atoms in compounds 1–5 (in vacuum)

Atom	1	2	3	4	5
C1	–	–	–0.026	0.003	–
C2	–	–	–0.134	–0.161	–
C3	–	–	–0.323	–0.252	–
C4	–	–	0.282	0.016	–
C5	–	–	–0.323	–0.257	–
C6	–	–	–0.134	–0.162	–
C7	–	–0.286	–	–0.388	–0.163
C8	–	0.167	–	0.122	–0.087
C9	–	–	–	–	–0.189
C10	–	–	–	–	–0.129
C11	–	–	–	–	–0.310
C12	–	–	–	–	0.269
C13	–	–	–	–	–0.319
C14	–	–	–	–	–0.128
N15	–0.351	–0.531	–0.537	–0.543	–0.538
C16	–0.431	–0.404	–0.413	–0.406	–0.413
C17	–0.431	–0.423	–0.413	–0.421	–0.413
N18	0.765	0.611	0.626	0.624	0.604
O18	–0.473	–0.471, –0.504 ^a	–0.467	–0.463	–0.461, –0.479 ^a

NPA natural population analysis

^a Nitro oxygen atoms are not equivalent due to restricted rotation around some bonds in the molecule

3 and **4** (these compounds are substituted nitrobenzenes). The nitro group attached to the benzene ring seems to withdraw a constant electron density regardless the ring is electron rich or electron deficient [37]. Shortening of the C1–N18 bonds in the molecules of compounds **3** and **4** (Table 1), as compared with the averaged C_{Ar} –NO₂ distances [21], supports the nitro group in nitroarenes to be really conjugated with the aromatic moiety.

Conclusions

X-ray and electron diffraction structural data show that significant amount of the charge from the amino nitrogen atom in *N,N*-dimethylnitramine (**1**), *N,N*-dimethyl-2-nitroethanamine (**2**), *N,N*-dimethyl-*p*-nitroaniline (**3**), 4-nitro- β -*N,N*-dimethylaminostyrene (**4**), and 4-*N,N*-dimethylamino- β -nitrostyrene (**5**) was transferred to the nitro group. In general, effectiveness of the charge transfer changes in the following order: **1** > **2** > **3** > **4** > **5**. Evaluation of this effect is based mainly on the bond lengths (bond angles are less useful). More severe steric interactions between the *ortho* and α hydrogen atoms in **5**, with respect to these in **4**, are responsible for more effective charge transfer in the later

compound. The calculated NPA charges (Natural Population Analysis) at the amino and nitro nitrogen atoms show that amount of the charge at the former in compound **1** is much lower than in other compounds studied (it is almost constant in compounds **2–5**). Except the nitro oxygens, other atoms that accept the negative charge lost by the amino nitrogen in the molecules of compounds **2–5** are the vinylene, benzene as well as methyl carbons. The calculated NPA charges at the nitro nitrogen and oxygen atoms in compounds **3** and **4** show electron-withdrawing ability of the nitro group in substituted nitrobenzenes to be independent on substituent (nitro group attached to the benzene ring seems to withdraw a constant electron density regardless the substitution). Shortening of the $C_{Ar}-N_{nitro}$ bonds in compounds **3** and **4** (as compared with the averaged $C_{Ar}-NO_2$ distances) supports the nitro group in these nitroarenes to be really conjugated with the aromatic moiety.

Computational details

Natural population analysis [35, 36] was performed with Gaussian 03 [38] with use of MP2/6-31G(2d,p) method. Molecular geometries were optimized at the B3LYP/6-31G(2d,p) level (no intermolecular interactions were considered). The frequencies were calculated to make sure that geometry is in the energy minimum (no imaginary frequencies).

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