The intermolecular interactions in the aminonitromethylbenzenes

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Abstract: The intermolecular non-covalent interactions in aminonitromethylbenzenes namely 2-methyl-4-nitroaniline, 4-methyl-3-nitroaniline, 2-methyl-6-nitroaniline, 4-amino-2,6-dinitrotoluene, 2-methyl-5-nitroaniline, 4-methyl-2-nitroaniline, 2,3-dimethyl-6-nitroaniline, 4,5-dimethyl-2-nitroaniline and 2-methyl-3,5-dinitroaniline were studied by quantum mechanical calculations at RHF/311++G(3df,2p) and B3LYP/311++G(3df,2p) level of theory. The calculations prove that solely geometrical study of hydrogen bonding can be very misleading because not all short distances (classified as hydrogen bonds on the basis of interaction geometry) are bonding in character. For studied compounds interaction energy ranges from 0.23 kcal mol\(^{-1}\) to 5.59 kcal mol\(^{-1}\). The creation of intermolecular hydrogen bonds leads to charge redistribution in donors and acceptors. The Natural Bonding Orbitals analysis shows that hydrogen bonds are created by transfer of electron density from the lone pair orbitals of the H-bond acceptor to the antibonding molecular orbitals of the H-bond donor and Rydberg orbitals of the hydrogen atom. The stacking interactions are the interactions of delocalized molecular \(\pi\)-orbitals of the one molecule with delocalized antibonding molecular \(\pi\)-orbitals and the antibonding molecular \(\sigma\)-orbital created between the carbon atoms of the second aromatic ring and vice versa.

Keywords: Intermolecular interactions • Ab initio • Hydrogen bonding • NBO

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selected aminonitromethylbenzenes were made [23], but, due to limitation of the work to the only geometrical considerations, the formerly presented results are misleading and lead to some improper interpretations of real hydrogen bonding schemes.

The best and unambiguous way to describe hydrogen-bond patterns in crystal structures is graph-set methods as developed by Etter and followers [24,25]. Usage of the graph-set approach to the study of hydrogen-bond networks leads to simplifications of even very complicated intermolecular interactions networks to combination of three basic patterns: chains, rings and finite intermolecular patterns (described by C, R and D letters, respectively). Specification of a pattern is followed by a subscript designating the number of intermolecular interaction donors - d (in the most common case of hydrogen bond this refers to covalently bonded hydrogen atoms), a superscript that gives the number of intermolecular interaction acceptors - a, and next the number of atoms (n) involved in the pattern (also called the pattern degree) is specified in parentheses. Thus, the graph set descriptor is given as G_{a,d}^{n-}(n), where G is one of the three possible designators. When a hydrogen-bond pattern contains only one type of a hydrogen bond it is called a motif. A listing of the descriptors for all of the motifs in a crystal structure defines the unitary (or first level) graph set – \textit{N}_1. A higher graph-set level appears when more than one type of a hydrogen bond is included in a pattern. Referring to a structure containing two distinct hydrogen bonds (designated a and b) it is possible to find a pattern which is described by these two H-bonds, \textit{N}_2(ab), and that is a binary (or second level) graph set (Scheme 1). Such a description of hydrogen bonds in a crystal structure is tremendously useful in providing a soundly based taxonomy for describing the diversity of hydrogen bonding patterns [26] and can lead to considerable insights regarding the patterns of recognition between both like and unlike molecules [24].

2. Methodology Of Theoretical Calculations

The molecular electronic properties have been calculated in a single point for X-ray determined coordinates as well as for optimised geometries of structurally characterised aminonitromethylbenzenes, namely 4-methyl-3-nitroaniline [22] - C₇H₈N₂O₂, 2-methyl-4-nitroaniline - C₇H₉N₂O₂ [27], 2-methyl-6-nitroaniline [28] - C₇H₈N₂O₂, 4-amino-2,6-dinitrotoluene [29] - C₇H₉N₂O₃, 2-methyl-5-nitroaniline [30] - C₇H₈N₂O₂, 4-methyl-2-nitroaniline [31] - C₉H₉N₂O₃, 2,3-dimethyl-6-nitroaniline [32] - C₇H₈N₂O₃, 4,5-dimethyl-2-nitroaniline [33] – C₈H₁₀N₂O₄, 2-methyl-3,5-dinitroaniline [28] - C₇H₈N₂O₄. The structural parameters obtained from crystalographic determinations were a starting model in each calculation. In general, the optimised geometrical parameters of non-hydrogen atoms were in agreement with those found from X-ray measurements. The bonds involving hydrogen atoms show typical elongation (from 0.11 to 0.38 Å) in comparison with those ones found from X-ray structural investigations based on H-atom deriving from difference Fourier syntheses. The intermolecular interactions were calculated for sets containing from 2 to 8 molecules (with hydrogen atoms positions optimised in all cases). The sets were constructed using a molecule occupying an asymmetric unit as a starting point and adding one by one molecules along intermolecular interactions in a semispherical mode [34]. The energies of non-interacting molecules were calculated for subsets created from dividing of above mentioned sets into two parts. Each of the subsets contains from 1 to 7 molecules. Both RHF and DFT methods (B3LYP density functional) with 6-311++G(3df,2p) basis set were used as implemented in Gaussian03 [35]. B3LYP density functional has been shown to be effective at accurate predicting of intermolecular interaction energies and properties for various systems [36,37]. Additionally, since the dispersion energy does not contribute in noticeable amount (or does not contribute at all) into hydrogen bonding, the Møller-Plesset correlation energy correction truncated at second or higher order was unnecessary in the current study. The highest possible to calculate basis set was used (6-311++G(3df,2p)), because generally with enlarging the number of basis set functions, the intermolecular interactions have more reasonable energies [38]. However the f-type polarisation functions might be considered as unnecessary, the NBO analysis shows that some Rydberg f orbitals have a significant electron population, thus 3df polarisation functions were applied to all non-hydrogen atoms. The polarisation functions on hydrogen atoms were limited to 2p due to restrictions of NBO subroutine. The differences in electronic properties and energies originating from different number of molecules used in calculations and differences between used methods are given in parentheses as standard deviations of the average value. If no deviation is given the values were the same in the range of reported precision. The energies of hydrogen bonds were also calculated in terms of Natural Bond Orbital (NBO) energetic analysis [39-41]. The contributions of separate orbitals to the intermolecular bonding energy were calculated on the basis of second order perturbation theory confirmed by
NBO energetic analysis with deleted specific elements (corresponding to the orbital-orbital interactions) from the Fock matrix of the RHF calculation. All intermolecular interactions energies values were corrected for basis set superposition error by usage of the counterpoise method [42].

3. Results and Discussion

Molecules of the studied compounds interact with themselves mostly by hydrogen bonds, but in the structures that they create, the different patterns [25] can be found (Figs. 1-7). Taking into consideration N,C patterns the following ones were found: C(6), C(7) and C(8). On the basis of geometrical considerations the interacting molecules are linked by N-H···O or C-H···O hydrogen bonds. N,C(6) patterns exist in 2,3-dimethyl-6-nitroanniline (Fig. 8) and 4,5-dimethyl-2-nitroaniline (Fig. 9). In the first mentioned compound only one such a pattern was found and it involves N-H···O hydrogen bonds, and in the second one four such patterns exist. It must be mentioned that the presence of the C(6) pattern in 2,3-dimethyl-6-nitroanniline structure was confirmed by the performed computations (the N2-H4···O2 hydrogen bond), while in the case of 4,5-dimethyl-2-nitroaniline

Table 1. The hydrogen-bond motifs found in the analysed compounds. Number of specific patterns are indicated by Arabic numeral before the pattern descriptor

| Compound | Patterns based on the geometrical considerations | Patterns based on the quantum-mechanical computations |
|----------|--------------------------------------------------|-----------------------------------------------------|
|          | C R D                                             | C R D                                               |
| 2-Methyl-4-nitroaniline | N1C(7)2C(8) N1C(6)C(16) C(15) | N1R1(8) (13) N2C(8) (6)C(16) C(15) |
| 4-Methyl-3-nitroaniline | N1C(7) N4C(4) (14) | N2R1(4)3(8) (12) N3(8) |
| 2-Methyl-6-nitroaniline | N2C(12) (12) N2R1(4) (12) N3D | N2C(12) (12) |
| 4-Amino-2,6-dinitrotoluene | N1C(7) N5C(12)C(10)C(14) | N2R1(4)3(20) (12)2 C(10) |
| 2-Methyl-5-nitroaniline | N1C(7) N2R1(10) (6) N2R4 (24) | N1C(7) N2R1(10) (6) N2R4 (24) |
| 4-Methyl-2-nitroaniline | N1C(12) N2R1(14)4(8) N2D | N1C(12) N2R1(14) (8) |
| 2,3-dimethyl-6-nitroaniline | N1C(6) | N1C(6) |
| 4,5-dimethyl-2-nitroaniline | N1C(6) N2C(12) (12) N2R1(16)4(12) | N1C(6) N2C(12) (12) N2R1(16)4(12) |
| 2-methyl-3,5-dinitroaniline | N2C(7) N1C(15) N1R1(24) | N2C(7) N1C(15) N1R1(24) |

Scheme 1. The example of motifs designators of unitary and binary graph set. The dashed lines indicate intermolecular hydrogen bonds. The a and b letters designate two distinct hydrogen bonds.
the presence of only two of four geometrically allowed C(6) patterns were confirmed in that way: N1-H2•••O2 and C16-H20•••O4 hydrogen bonds. C(7) turned out to be the most common pattern (Table 1). An example of this pattern – involving the N-H···O hydrogen bond - is shown in Fig. 1. N1C(8) patterns were found only in the 2-methyl-4-nitroaniline structure (Fig. 10).

Considering N2 level the following hydrogen bond C patterns were found: C2(6), C2(8), C2(10), C2(12), C2(14), C2(15) and the C2(16). The C2(6) pattern is presented in the Fig. 2. Most of the C patterns connected with this graph level exist in the 4-amino-2,6-dinitrotoluene structure (Fig. 11). Referring to higher graph set levels another C patterns can be found. This can be for example an N4C4(11) pattern existing in the 2-methyl-6-nitroaniline (Fig. 12).

In the structures of the analysed compounds, R and D patterns are common as well for non-unitary graphs sets. In 2-methyl-4-nitroaniline an N3R3(13) pattern exists, but in other compounds smaller and larger ring

### Table 2. The hydrogen bonds of 2-methyl-4-nitroaniline. The atom numbering scheme as in Fig. 10.

| Hydrogen bond D—H•••A | Interaction energy [kcal mol⁻¹] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy | D···A distance [Å] | H···A distance [Å] | D—H···A angle [°] |
|------------------------|-------------------------------|---------------------------------------------------------------------------------|----------------|----------------|----------------|
| N1-H2-O2               | 5.59                         | 24.67% 75.33%                                                                 | 3.081          | 2.213          | 168.94         |
| N1-H1-O1               | 1.83                         | 32.65% 20.41% 46.94%                                                         | 3.186          | 2.500          | 135.24         |
| C7-H6-O1               | 0.00(3)                      | - - -                                                                       | 3.383          | 2.626          | 134.28         |

**Figure 1.** The N1C(7) hydrogen-bond pattern in 4-methyl-3-nitroaniline structure (a part of molecular packing used in calculated molecules sets).

**Figure 2.** The N2C4(6) hydrogen-bond pattern in 2-methyl-4-nitroaniline structure (a part of molecular packing used in calculated molecules sets).
patterns can be also found. In the 2-methyl-6-nitroaniline \( \text{N}_2\text{R}_4 \) and \( \text{N}_2\text{R}_6 \) patterns appear while in 2-methyl-3,5-dinitroaniline (Fig. 13) the \( \text{N}_2\text{R}_4 \) and in 2-methyl-5-nitroaniline (Fig. 14) the \( \text{N}_2\text{R}_6 \) pattern can be observed. The 4-Methyl-3-nitroaniline (Fig. 15) forms D motifs. All patterns found on the basis of geometrical considerations, as well as motifs confirmed by quantum mechanical calculations, are presented in the Table 1.

The studied molecules interact in different geometrical arrangements. These interactions - appearing in the chosen geometrical packing - were analysed (Tables 2-9). The intermolecular interactions were mostly hydrogen bonds between the amine groups and oxygen atoms of nitro groups, but other ones also can be found, e.g. stacking interactions, hydrogen bonds between the methyl and oxygen atoms and others. It was detected that when the hydrogen bond between the amine groups and oxygen atoms is created, the electron density from the oxygen atom is transferred to antibonding molecular orbital/orbitals created between the nitrogen and the hydrogen atoms of the amine group.

In case of the 2-methyl-4-nitroaniline (Fig. 10) - \( \text{C}_7\text{H}_8\text{N}_2\text{O}_2 \) – the intermolecular interactions between molecules exist in two geometrical arrangements. In the

### Table 3. The hydrogen bonds of 4-methyl-3-nitroaniline. The atom numbering scheme as in Fig. 15.

| Hydrogen bond D—H···A | Interaction energy [kcal mol\(^{-1}\)] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy | \( \text{D}····\text{A} \) distance [Å] | \( \text{D}—\text{H}····\text{A} \) angle [°] | \( \text{H}····\text{A} \) distance [Å] |
|-----------------------|----------------------------------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| N1—H2···O1            | 3.93                                  | 17.42% 78.03% 4.55%                            | 3.235                           | 163.08                           | 2.383                           |
| N5—H17···O1           | 4.41                                  | 100% - -                                         | 3.491                           | 151.37                           | 2.692                           |
| C16—H19···O1          | 0.74(1)                               | - 100% -                                         | 3.483                           | 151.45                           | 2.618                           |
| N6—H3···O6            | 0.00(2)                               | - - -                                            | 3.316                           | 126.20                           | 2.666                           |
| N3—H10···O3           | 3.24                                  | 14.24% 78.03% 6.73%                            | 3.256                           | 158.12                           | 2.422                           |
| N3—H10···O4           | 0.65                                  | - 100% -                                         | 3.432                           | 142.53                           | 2.691                           |
| N3—H9···O8            | 1.73                                  | 48.15% 51.85%                                   | 3.259                           | 128.43                           | 2.638                           |
| N7—H25···O3           | 2.95                                  | 69.57% 30.43%                                   | 3.308                           | 154.30                           | 2.494                           |
| C23—H27···O3          | 0.00                                  | - - -                                            | 3.455                           | 145.89                           | 2.627                           |
| N5—H18···O5           | 2.60                                  | 45.03% 37.58% 17.39%                           | 3.099                           | 148.39                           | 2.315                           |
| N7—H26···O8           | 0.23                                  | - 100% -                                         | 3.425                           | 144.59                           | 2.669                           |
| N7—H26···O7           | 1.31                                  | 15.60% 72.48% 11.93%                           | 3.174                           | 149.07                           | 2.387                           |
| C28—H32···O7          | 0.00(1)                               | - - -                                            | 3.422                           | 136.64                           | 2.668                           |

### Table 4. The hydrogen bonds of 2-methyl-6-nitroaniline. The atom numbering scheme as in Fig. 12.

| Hydrogen bond D—H···A | Interaction energy [kcal mol\(^{-1}\)] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy | \( \text{D}····\text{A} \) distance [Å] | \( \text{D}—\text{H}····\text{A} \) angle [°] | \( \text{H}····\text{A} \) distance [Å] |
|-----------------------|----------------------------------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| N2—H2···O4            | 2.59                                  | 12.08% 69.13% 18.79%                           | 3.151                           | 152.59                           | 2.383                           |
| N4—H4···O2            | 2.45(3)                               | 8.92% 35.13% 55.95%                           | 3.014                           | 101.52                           | 2.701                           |
| N4—H4···O1            | 1.39(1)                               | 30.83% 69.17%                                  | 3.161                           | 151.23                           | 2.340                           |

### Table 5. The hydrogen bonds of 4-amino-2,6-dinitrotoluene. The atom numbering scheme as in Fig. 11.

| Hydrogen bond D—H···A | Interaction energy [kcal mol\(^{-1}\)] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy | \( \text{D}····\text{A} \) distance [Å] | \( \text{D}—\text{H}····\text{A} \) angle [°] | \( \text{H}····\text{A} \) distance [Å] |
|-----------------------|----------------------------------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| N2—H1···O2            | 3.29                                  | 18.72% 81.28%                                  | 3.152                           | 2.276                           | 161.11                           |
| C5—H6···O1            | 0.78                                  | 56.60% 43.40%                                  | 3.333                           | 2.497                           | 146.77                           |
| N2—H5···O4            | 1.66                                  | 26.47% 73.53%                                  | 3.381                           | 2.498                           | 154.71                           |
| C3—H2···O3            | 2.00                                  | 23.02% 76.98%                                  | 3.218                           | 2.353                           | 160.56                           |
| C10—H10···O7          | 2.05                                  | 50.69% 49.31%                                  | 3.203                           | 2.304                           | 157.55                           |
| N5—H3···O8            | 1.39                                  | 17.35% 82.65%                                  | 3.265                           | 2.435                           | 171.75                           |
| N5—H4···O6            | 1.72                                  | 22.62% 73.81% 3.87%                           | 3.319                           | 2.403                           | 165.71                           |
| C12—H11···O5          | 1.55                                  | 64.90% 35.10%                                  | 3.214                           | 2.300                           | 161.09                           |
first one the total energy of the interactions between two molecules is equal to 1.84 kcal mol\(^{-1}\) and the \(\text{N1-H1}\cdots\text{O1}\) hydrogen bond created between them is responsible for almost all energy of the interactions. Electron density from the H-bond acceptor (the oxygen atom) is transferred to the antibonding molecular orbital created between the hydrogen atom and the nitrogen atom of the amine group of H-bond donor molecule. This bond is composed of three separate interorbital interactions and for each of them, the one of three H-bond acceptor lone electron pair orbitals (LPs) is utilised (the contributions of the particular lone pair orbitals are given in the Table 2). In the second kind of arrangement the energy of the interactions between two molecules of this compound is equal to 5.61 kcal mol\(^{-1}\). As it was described in the first case, the \(\text{N1-H2}\cdots\text{O2}\) hydrogen bond between molecules is created and the bonding energy originates mainly from it. Similarly to previous interaction, the electron density is transferred from the oxygen atom to an antibonding molecular orbital created between the hydrogen and the nitrogen atoms of the amine group, but only two orbital-orbital interactions are responsible for current bond creation. Nevertheless of that fact the H-bond acceptor orbitals are still LPs (the contributions both LPs are given in the Table 2). In this case of hydrogen bond the interactions between lone electron pair orbitals of the oxygen atom and Rydberg orbitals of the hydrogen atom also appear, but their contributions are smaller than 0.01% thus they can be considered as

**Table 6.** The hydrogen bonds of 2-methyl-5-nitroaniline. The atom numbering scheme as in Fig. 14.

| Hydrogen bond D—H\cdots\text{A} | Interaction energy [kcal mol\(^{-1}\)] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy LP1 | LP2 | LP3 | D\cdots\text{A} distance [Å] | H\cdots\text{A} distance [Å] | D—H\cdots\text{A} angle [°] |
|-------------------------------|---------------------------------------|-------------------------------------------------|-----|-----|--------------------------|-----------------------------|-----------------------------|
| N1-H4-O1                      | 3.28                                  | 18.99%                                          | 81.01% | -   | 3.151                    | 2.340                       | 146.95                      |
| N1-H5-O2                      | 2.91                                  | 58.97%                                          | 41.03% | -   | 3.239                    | 2.441                       | 152.99                      |
| C6-H3-O2                      | 4.37                                  | 65.38%                                          | 34.62% | -   | 3.365                    | 2.627                       | 136.24                      |

**Table 7.** The hydrogen bonds of 4-methyl-2-nitroaniline. The atom numbering scheme as in Fig. 16.

| Hydrogen bond D—H\cdots\text{A} | Interaction energy [kcal mol\(^{-1}\)] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy LP1 | LP2 | LP3 | D\cdots\text{A} distance [Å] | H\cdots\text{A} distance [Å] | D—H\cdots\text{A} angle [°] |
|-------------------------------|---------------------------------------|-------------------------------------------------|-----|-----|--------------------------|-----------------------------|-----------------------------|
| C7-H3-O1                      | 0.57                                  | —                                                | —   | —   | —                        | 3.483                       | 149.79                      |
| C3-H8-O2                      | 1.02                                  | 59.57%                                          | 40.43% | -   | 3.592                    | 2.703                       | 161.46                      |
| N2-H7-O1                      | 2.74                                  | 17.46%                                          | 82.54% | -   | 3.034                    | 2.285                       | 150.26                      |
unimportant. The hydrogen-bonding patterns in both arrangements can be described as N1C(8).

A hydrogen bond can be composed of one kind of the interactions as happens in one of the geometrical arrangements of 4,5-dimethyl-2-nitroaniline (Fig. 9) – C9H10N2O2. The interactions energy between two molecules in this case is 0.70 kcal mol⁻¹. The second (with higher energy) lone electron pair orbital interacts with the antibonding molecular orbital created between the nitrogen and hydrogen atoms of the amine group.

In the structure of 4-methyl-3-nitroaniline four symmetrically independent molecules exist (Fig. 15) and two of them are joined by two hydrogen bonds and create the N2R2(14) motif (Fig. 3). The energy of the interactions between these molecules is equal to 5.15 kcal mol⁻¹ and there are two hydrogen bond donors and two acceptors in that system. The N5-H17•••O1 hydrogen bond grants 81.48% of the total intermolecular interactions energy of the system and it is composed only of one NBO interaction - the first (with lower energy) lone electron pair orbital of the oxygen atom donating electrons to the antibonding molecular orbital created between the hydrogen and the nitrogen atom. The N1-H1•••O6 intermolecular interaction of the N2R2(14) system is much weaker and it is composed of two NBO interactions: the first (60% energy of this intermolecular bond) and the second (40% energy of this intermolecular bond) lone electron pair orbital of the

Table 8. The hydrogen bonds of 2,3-dimethyl-6-nitroaniline. The atom numbering scheme as in Fig. 8.

| Hydrogen bond D–H•••A | Interaction energy [kcal mol⁻¹] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy | D•••A distance [Å] | H•••A distance [Å] | D–H•••A angle [°] |
|-----------------------|--------------------------------|--------------------------------------------------------------------------------|--------------------|--------------------|------------------|
| N2-H4•••O2            | 3.19(2)                        | 100% - - - - - 3.035 2.249 149.48                                              |

Table 9. The hydrogen bonds of 4,5-dimethyl-2-nitroaniline. The atom numbering scheme as in Fig. 9.

| Hydrogen bond D–H•••A | Interaction energy [kcal mol⁻¹] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy | D•••A distance [Å] | D–H•••A angle [°] | H•••A distance [Å] |
|-----------------------|--------------------------------|--------------------------------------------------------------------------------|--------------------|--------------------|------------------|
| N3-H11•••O4           | 0.69                           | 0.03% 43.62% 56.35% 3.078 155.45 2.256                                             |
| C16-H20•••O4          | 1.45                           | 1.66% 23.62% 74.73% 3.393 140.30 2.607                                             |
| C15-H18•••O4          | 0.00                           | - - - - - 3.436 138.61 2.639                                               |
| N1-H1•••O3            | 0.00(2)                        | - - - - - 3.015 104.39 2.674                                               |
| N1-H2•••O3            | 0.00                           | - - - - - 3.015 102.63 2.698                                               |
| N3-H12 –O1            | 0.00                           | - - - - - 2.920 114.40 2.444                                               |
| N1-H2•••O2            | 2.93                           | 50.00% 40.77% 9.23% 3.102 153.15 2.291                                             |
| C8-H10•••O2           | 0.00(1)                        | - - - - - 3.325 142.23 2.522                                               |

Figure 6. The N2R2(8) pattern created between 4-methyl-2-nitroaniline molecules (a part of molecular packing used in calculated molecules sets).

Figure 7. The O•••O bonding interaction between two nitro groups of the 4-methyl-2-nitroaniline (a part of molecular packing used in calculated molecules sets).

Figure 8. The 2,3-dimethyl-6-nitroaniline molecule (experimental-geometry) with atom-labelling scheme used in tables and discussion.
oxygen atom interacts with the antibonding molecular orbital involving the hydrogen and the nitrogen atoms. Other set of two interacting molecules creates the $N_2R_1^2(4)$ pattern (Fig. 4) and the lone pairs of both oxygen atoms of the nitro group interact with the antibonding molecular orbital created between the hydrogen and the nitrogen atoms of the second molecule amine group. The total interactions energy between the molecules is 3.89 kcal mol$^{-1}$. The interaction of the N-H moiety with the O$_3$ atom is stronger than the interaction with O$_4$ atom and it is responsible for about 83% of the total interactions energy. The three lone electron pair orbitals of the O$_3$ atom are involved into intermolecular interaction at different fraction (Table 3) and O$_4$ atom donates only one lone electron pair orbital to the intermolecular bond.

In the 2,3-dimethyl-6-nitroaniline (Fig. 8) structure the intermolecular interactions creating hydrogen bond are different in character, because the lone pair donates electron density only to Rydberg orbital (Table 8) and does not interact with the antibonding

Table 10. The hydrogen bonds of 2-methyl-3,5-dinitroaniline. The atom numbering scheme as in Fig. 13.

| Hydrogen bond | Interaction energy [kcal mol$^{-1}$] | Contribution of free lone electron pair orbitals (LP) of the oxygen atom to hydrogen bond energy | D⋯A | H⋯A | D—H⋯A angle |
|---------------|--------------------------------------|------------------------------------------------------------------------------------------------|-----|-----|-------------|
| D—H•••A       |                                      |                                                                                                   |     |     |             |
| N1-H2•••O1    | 4.36                                 | 24.87%                                                                                           | 75.13% | -  | 3.102       |
| N1-H1•••O4    | 2.73(1)                              | 86.83%                                                                                           | 13.17% | -  | 3.154       |
| C7-H7•••O4    | 1.05                                 | 100%                                                                                             | -    | -   | 3.593       |

Table 11. The selected charges of 2-methyl-4-nitroaniline in separate (non-interacting) molecule and in the molecule involve into intermolecular interactions. The atom numbering scheme as in Fig. 10.

| group             | atom | non interacting molecule | interacting molecule* |
|-------------------|------|--------------------------|-----------------------|
| nitro group       | N2   | 0.672                    | 0.633                 |
|                   | O1   | -0.438                   | -0.429                |
|                   | O2   | -0.448                   | -0.433                |
| amine group       | N1   | -0.955                   | -1.022                |
|                   | H1   | 0.419                    | 0.438                 |
|                   | H2   | 0.422                    | 0.470                 |

*Interaction by N1-H2•••O2 and N1-H1•••O1 hydrogen bonds.
orbital created between atoms of the hydrogen bond donor. Apart from hydrogen bonding in this compound the stacking interactions of aromatic rings also appear (Fig. 5). This interaction is very weak and its energy is 0.59 kcal mol\(^{-1}\). The NBO analysis shows that the origins of the intermolecular interaction are the interactions of delocalized molecular π-orbitals of the one molecule with delocalized antibonding molecular π-orbitals and antibonding molecular σ-orbital created between the carbon atoms of the second aromatic ring and vice versa. The interactions with antibonding molecular σ-orbitals contribute significantly more (73%) to the total intermolecular binding energy than the interactions with the delocalized antibonding molecular π-orbitals. This confirms the generally accepted model of stacking interactions, which postulates that the interactions appear when the attractive interactions between π-electrons and the σ-framework outweigh unfavourable contributions such as π-electron repulsion [17]. Because such kind of interactions was observed only in this compound it can be assumed that for remaining compounds the stacking interactions are energetically unfavourable.

In the structure of the hydrogen bonds in 4-methyl-2-nitroaniline (Fig. 16) weak hydrogen bonds are created between the nitro group and the hydrogen atom bonded directly to the aromatic carbon atom. Beside these, the stronger hydrogen bonds are created between nitro and amine groups. In one of the geometrical arrangements these two types of hydrogen bonds form the N\(_2\)R\(_2\)2(8) pattern (Fig. 6). The total intermolecular interaction energy is equal to 3.76 kcal mol\(^{-1}\). As expected, the strongest is the N-H•••O hydrogen bond and it participates at 72.87% in total binding energy. Both these hydrogen bonds are composed from two interactions: the interactions of the first (LP1) and the second (LP2) lone electron pair orbitals of the oxygen atoms (O1, O2) with respect antibonding molecular orbital created between atoms of the hydrogen bond donor group (N2-H7, C3-H8, respectively). It must be noted that in the case of the C-H•••O bond the lower energy lone electron pair orbital (LP1) predominates in the intermolecular bond, and for the N-H•••O bond the higher energy lone electron pair orbital (LP2) predominates (Table 7). This compound shows also uncommon intermolecular interaction between the nitro groups of two molecules (Fig. 7) with binding energy of 1.43 kcal mol\(^{-1}\). This interaction is composed from two components: the third (most energetic) lone electron pair orbital of the oxygen atom (O2) of the first molecule interacts with N—O antibonding molecular orbital of the second molecule and vice versa the third lone electron pair orbital of the oxygen atom (O2) of the second molecule interacts with N—O antibonding molecular orbital of the first molecule.

In general, the type of hydrogen bond donor and acceptor does not depend on the type of the created pattern. C and R schemes are observed in both hydrogen bonds created between nitrogen and amine groups and between nitrogen and methyl groups.

The interaction energies between atoms that are engaged in the intermolecular bonding differ and the strongest hydrogen bond is found in 2-methyl-4-nitroaniline (bonding energy 5.59 kcal mol\(^{-1}\)) while the energy of the weakest hydrogen bond (in 4-methyl-3-nitroaniline), is equal to 0.23 kcal mol\(^{-1}\). Thus all intermolecular interactions can be classified as medium strong and weak ones. It can be stated that hydrogen bonds that involve amine groups as a hydrogen bond donor are, in general, stronger and a little bit shorter than those that involve methyl groups. The interaction energies in the case of amine groups range from 0.23 kcal mol\(^{-1}\) to 5.59 kcal mol\(^{-1}\) but the mean value is 2.67 kcal mol\(^{-1}\). In the case of methyl groups this range is tighter (0.57 - 4.37 kcal mol\(^{-1}\)) but the average value is distinctly smaller (1.61 kcal mol\(^{-1}\)). The mean hydrogen bond D•••A length in the case of amine groups is
3.187 Å, and for the methyl groups it is 3.404 Å. The average angles between the atoms engaged in hydrogen bonds both in the case of amine and methyl groups are similar (mean angles are 149.45° and 151.12°, respectively). The most different and the largest number of hydrogen bonds exist in 4-methyl-3-nitroaniline structure (Fig. 15) because of the number of the symmetry-independent molecules. The second most intermolecular interactions populated compound is 4-amino-2,6-dinitrotoluene (Fig. 11) due to the same reason - two molecules in the asymmetric unit. It must be outlined that some of the intermolecular short contacts classified on the basis of geometrical considerations as hydrogen bonds have no real bonding energy, thus they are forced by packing effects and other “real” intermolecular interactions. That fact confirms that solely geometrical study of hydrogen bonding can be very misleading and may lead to serious mistakes reflecting in wrong interactions patterns. For example, for 4,5-dimethyl-2-nitroaniline only three (of supposed eight) hydrogen bonds exist (Table 2 and Table 10). In general, the non-bonding interactions have smaller D—H•••A angles ranging from 102.63° to 145.89°, with the average value of 127.25°. The mean H•••A distance of these short contacts is 2.618 Å (distances range from 2.444 Å to 2.698 Å) and this value is about 0.2 Å longer than respect distance of 2.450 Å for “real” hydrogen bonds. The intermolecular binding distances limits (2.213 Å - 2.718 Å) cover the range observed for non-bonding interactions but the angles of the longest interactions are distinctly larger for bonding interactions.

Analyses of the both NBO charges and those derived from electrostatic properties with usage of Breneman radii [43] show that the positive charges are located on the nitrogen atoms of nitro substituents and on hydrogen atoms of amine and methyl groups. The negative charges exist on oxygen atoms of nitro groups, carbon atoms of methyl substituents and nitrogen atoms of amine groups. Comparison of these groups charge distribution between the interacting molecules and separate (non-interacting) molecules shows that the charges differ slightly but obviously (Table 11). The creation of intermolecular interactions leads to depolarisation of nitro groups as a result of electron density donation to the hydrogen bond donor, and, in consequence, larger polarisation of the amine groups (Table 11).

4. Conclusions

This study provides structural insights into supramolecular bonding properties of a series aminonitromethylbenzenes and describes interplaying of different interactions in supramolecular bonding. As it was shown, not all short intermolecular contacts are bonding in character, and some geometrically similar interactions can have distinctly different bonding strength. Thus taking into account only the crystal packing can be very misleading and all considerations of biological activity and similar effects based on docking of molecules must be conducted very carefully and should be accompanied by an energetic analysis. It must be outlined that not only typical intermolecular interactions should be considered, but some rare intermolecular bonding (like bonding interactions between the nitro groups) may also occur. Because the benzene substituted by amino, nitro, and/or methyl groups often coparticipates in binding of biologically active molecules into macromolecular sites, the presented results are relevant to the biochemical activity of compounds containing such substituents.
bonded to the aromatic ring as well as can be useful in designing of new drugs and targeting molecules.

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