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# FEATURES OF THE PNICTOGEN BONDS FORMED BY NEIGHBORING NITRO GROUPS IN CRYSTALS

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Features of pnictogen O…N bonds were considered from the point of view of analyzing various geometric orientations of the neighboring nitro groups $NO_2$…$NO_2$ observed in molecular crystals. The “idealized” orientation for a pnictogen bond, where the nucleophilic fragment of the atom O of one nitro group was directed to the electrophilic site of the atom N of the other one, and the “stacking” orientation, which was characterized by the parallel stacking of nitro groups, differ in the features of the electron density and electrostatic potential distribution between O and N atoms. The applied electronic criterion, obtained with the use of quantum chemical calculations with periodic boundary conditions, confirmed that for the considered O…N interactions the necessary condition for their classification as pnictogen bonds was met.

*Keywords: pnictogen bond, nitro group, electrostatic potential, electron density, Laplacian of the electron density.*

## Introduction

Non-covalent bonds play an important role in formation of the physicochemical properties of a substance, and their study is important for predicting the properties of new multicomponent compounds with useful applications. The interest in organic nitro compounds containing a large number of interacting nitro groups in crystals is due to the opportunity to look at the role of these non-covalent interactions in formation of the properties of high-energy materials. A new approach is being formed to systematize non-covalent bonds according to the principle based on the involvement of the electrophilic sites of atoms of groups 14–17 of Mendeleev's Periodic Table in intermolecular interactions with a pronounced electrostatic component [1, 2]. Such systematization makes it possible to distinguish halogen, chalcogen, pnictogen, tetrel, *etc.* bonds into separate types of non-covalent bonds [3]. If we define a pnictogen bond by analogy with the IUPAC formulation of a halogen bond [3], we obtain the following: the pnictogen bond is a directed non-covalent interaction of electrostatic nature in which the electrophilic site of a covalently bound atom of group 15 interacts with the nucleophilic fragment in a molecular system.

Among the theoretical methods and tools suitable for describing the properties of pnictogen bonds, examples of use are known for NBO analysis [4], QTAIM [5], extrema of the electrostatic potential [6] on electron density isosurfaces, electron localization function ELF [7, 8], electron density shift EDS [9], the NCI method [10], developed on the basis of the reduced density gradient (RDG) analysis. One can distinguish such works in which the main attention is paid to the σ-holes formed by elements of group 15 on the continuations of their covalent bonds. A σ-hole is understood as a region of increased values of the electrostatic potential located on the extension of a covalent bond [11].

Such studies include the analysis of intramolecular pnictogen bonds Pn…Pn, where Pn = N or P, in naphthalene derivatives [12–14]. Among the conclusions made by the authors, one can note the exponential dependences between the second-order disturbance energy and topological characteristics of the electron density (ED) or interatomic distance. The critical point in electron density is the point at which the electron density gradient $\nabla\rho(\mathbf{r})$ is equal to zero. The main components of the electron density curvature at the point determine the rank $p$ and the signature $q$ of the critical point. The rank is equal to the number of nonzero eigenvalues of the Hessian of electron density, and the signature is the algebraic sum of these values. Only four non-degenerate critical points in electron density are possible: (3, –3), (3, –1), (3, 1), (3, 3). In the case of a bond critical point (3, –1) the electron density falls down in two perpendicular directions of space and rises in the third direction. This is a saddle point with a maximum of electron density in two directions of space and a minimum in the third one. This point is between two neighboring atoms defining a bond between them and also called a bond critical point (bcp) [15–21]. It is important that in spite of the absence of a bcp between interacting atoms of pnictogens, the conclusions based on the NCI method has shown the presence of attractive interactions between the Pn…Pn atoms.

We can also note the works [22, 23] aimed at studying the complexes of pyrazine, as well as phosphoborane crystals, with the $PnX_5$ molecules, where Pn = P, As or Sb and X = F, Cl or Br. The authors considered the significant contribution of the electrostatic component to the energy of relatively strong pnictogen bonds B…P and its key role in the formation of crystalline packing [22]. The B…P bond length was significantly lower than the sum of the van der Waals radii, and the energy value exceeded 10 kcal/mol. In study [24] the presence of a non-covalent O…P bond in the $CH_3$–HO…$PCl_3$ adducts was confirmed using infrared spectroscopy. The formation of a bound adduct was evidenced by displacements of stretching vibrations of the P–Cl, O–C, and O–H bonds into the long-wavelength region. Calculations showed that the adduct with a pnictogen bond was more stable than the adduct with a hydrogen bond. Using QTAIM, it was shown that the electron density at the critical point of the pnictogen bond was higher than in the case of hydrogen bonding. The NBO analysis showed that the conjugation effect in the adduct with a pnictogen bond is stronger than in the adduct with a hydrogen bond. The authors [25] concluded that the high electronegativity of fluorine plays an important role in ensuring that the elements of group 15 associated with it acted as effective donors of the pnictogen bond. In addition, fluorine was able to increase the electrophilicity of pnictogens to such an extent that the formation of pnictogen bonds becomes the determining factor in formation of the crystalline structure [25].

There are studies in which the authors' attention is focused on the concept of a π-hole and the electron properties determined by it. By analogy with a σ-hole, a π-hole is the region of increased values of the electrostatic potential, but at the same time it is formed due to the vacancy in the π*-orbital. In the nitro group, the π-hole is located above and below the planes of the conjugated system [11]. In studies [26–29] the relative strength and directivity of the O…N pnictogen bonds in crystals of nitro compounds and nitrates were discussed, as well as their structure-forming role in crystals. The authors revealed a shift of the π-hole to the center of the C–N covalent bond from the nitrogen atom of the nitro group [26]. In study [30], three-membered $Pn_3X_3$ cycles (X = H, F or Cl, Pn = P or As) were considered and their complexes with HCN were described. The authors correlated the interaction energy in the corresponding complexes with the maximum values of the electrostatic potential in the region of a π-hole. It was shown that the calculated interaction energy of molecules in the complexes depended on the atomic radius of the pnictogen atom and the electronegativity of the halogen atom. In [31], devoted to the $XNO_2$ homodimers, where X = F, Cl, Br or I, the exponential dependence of the Laplacian of the electron density values at the critical point on the X…N bond length, as well as relatively low delocalization of the charge between the lone pair electrons of the O atoms and antibonding orbital of the N–O bond. We can also note the works [32–33] devoted to the O…N bonds in crystals of nitro compounds at various temperatures and pressures. Based on X-ray analysis [33], a phase transition of 4-amino-4'-nitrobiphenyl at the pressure above 1 GPa was observed; the interactions $NO_2$…$NO_2$ could be less repulsive than $NH_2$…$NO_2$, as indicated by the observed compressibility of such non-covalent bonds under applied external pressure.

It can be stated that to date the greater part of the encountered examples describing the electronic properties of pnictogen bonds has been performed for molecules or structural models of molecular complexes. Nevertheless, pnictogen bonds formed by neighboring nitro groups occur under conditions of multiple non-covalent interactions and are observed in molecular crystals.

Thus, reliable modeling of crystalline structures and analysis of electronic properties of pnictogen bonds in crystals, as well as the identification of their attributes, remains an urgent task. In our research the crystal structures of nitro compounds have been chosen as objects, in which two types of mutual orientation of neighboring nitro groups are found: an “idealized” pnictogen O…N bond, in which the electron pair of the O atom of one nitro group is directed to the π-hole of the N atom of the other nitro group, and “stacking” is the O…N interaction in which atoms of neighboring nitro groups remain close due to their parallel arrangement. The functions under study, for which calculations have been performed in the crystalline approximation, have been chosen: the electrostatic potential φ(**r**), electron density $\rho(\mathbf{r})$, and Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$. The behavior of these functions has been compared for different geometric orientations of nitro groups in crystals and in isolated molecules.

### Experimental

Quantum chemical calculations with periodic boundary conditions were performed using the CRYSTAL14 program (v.1.0.4) [34] at the B3LYP/6-31G** level. Localization of the equilibrium geometry of the crystal structure was carried out with the optimization of atomic coordinates, with fixed unit cell parameters in order to maximize compliance with experimental data. The following convergence parameters have been used for all calculations: TOLDEG (root-mean-square on gradient) is less than 0.0001 a.u., TOLDEX (root-mean-square on estimated displacement) is less than 0.0003 a.u., TOLDEE (energy change between optimization steps threshold) is less than $10^{-10}$ a.u., TOLINTEG (truncation criteria for bi-electronic integrals) are 14 14 14 14 and 24, respectively. The SHRINK parameter, which determines the number of k-points in reciprocal space in the Pak-Monkhorst scheme, at which the Kohn-Sham matrix is diagonalized, has been set to 8. The calculations were performed on the TORNADO LSM supercomputer of South Ural State University [35]. The structure of isolated molecules was optimized at the B3LYP / 6-31G** level in the GAMESS R2 program [36] with a gradient convergence of 0.000009.

The QTAIM analyses of electron density in crystals were carried out in the TOPOND program [37]. At the critical points of electron density ($\mathbf{r}_{\text{bcp}}$), the values of $\rho(\mathbf{r}_{\text{bcp}})$, the Laplacian $\nabla^2\rho(\mathbf{r}_{\text{bcp}})$, $g(\mathbf{r}_{\text{bcp}})$, and $v(\mathbf{r}_{\text{bcp}})$, the kinetic and potential energy densities, were calculated. In addition, the values and relative positions of the minima of Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ in the outer electron shell of the O and N atoms, which were found along the O…N bond line, were analyzed. Along the same line, the disposition of the minima of the electrostatic potential $\varphi(\mathbf{r})_{\min}$ and electron density $\rho(\mathbf{r})_{\min}$ was analyzed.

The features and differences for the characteristics obtained in the crystal and in the isolated molecule were analyzed. We analyzed the differences between the minima of Laplacian of the electron density $\Delta(\nabla^2\rho(\mathbf{r}_\text{O}))$ corresponding to the outer O and N electron shells, calculated for a crystal and for an isolated molecule.

### Results and Discussion

As the objects of study, we selected 15 compounds from the Cambridge base of crystal structures CSD version 5.39 [38], in which twelve O…N interactions were observed that fitted the description of the “idealized” orientation of nitro groups (Fig. 1a) and eight O…N interactions of the “stacking” type (Fig. 1b). With the “idealized” orientation, the region of concentration of the electron density of the O atom, which corresponds to a lower value of the molecular electrostatic potential, is directed to the region of the increased value of the molecular electrostatic potential (π-hole) (Fig. 2) of the N atom of the neighboring nitro group.

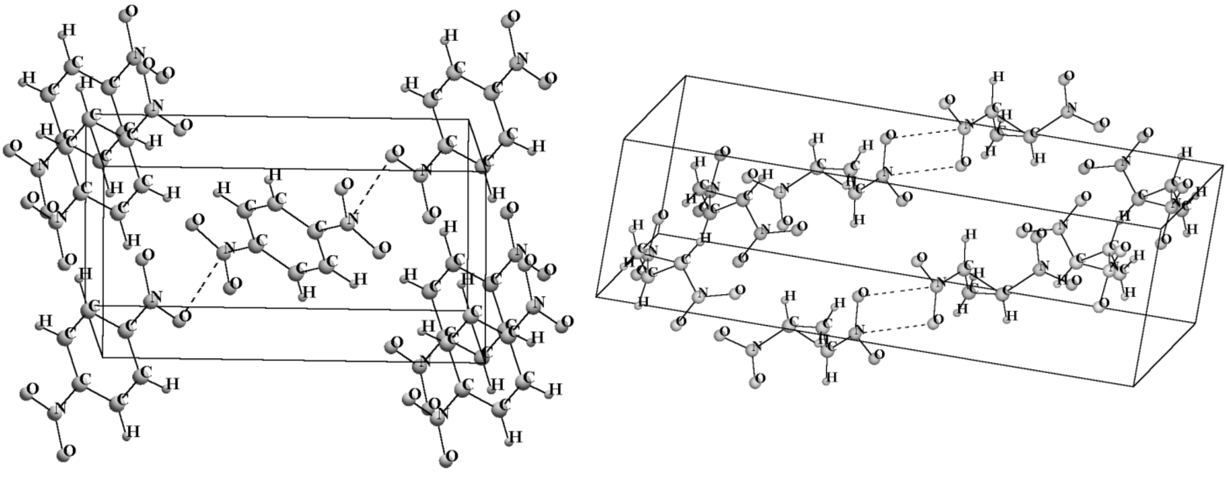

a) b)

**Fig. 1. Orientation of nitro groups in case of a) the “idealized” type using para-dinitrobenzene as an example (DNITBZ02) and b) “stacking” type using trans-1,2-dinitrocyclopropane as an example (FOHMUK)**

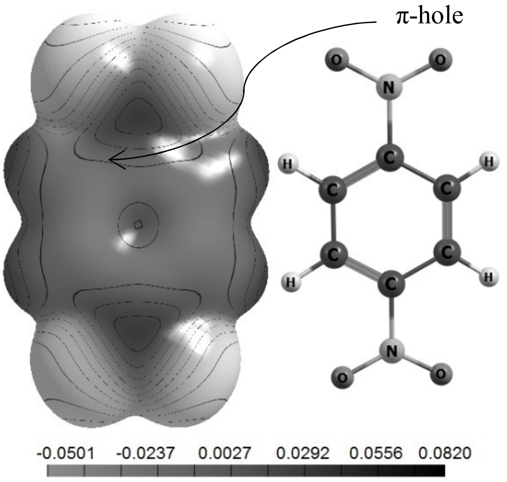


**Fig. 2. Molecular electrostatic potential built on the electron density isosurface (0.001 a.u.) for a 1,4-dinitrobenzene molecule**

As a result of topological analysis of the electron density for 11 from twelve O…N interactions with the “idealized” orientation, the critical points of the electron density (3, –1) have been found, signifying atoms between which there is a chemical bond. For “stacking” orientation, bond critical points have been found only for three O…N interactions out of eight. Table 1 shows the obtained local characteristics of such bonds.

**Table 1**

**Topological characteristics of electron density at the bond critical points of O…N interactions in crystals**

| Refcode | $\rho(\mathbf{r}_{bcp})$ | $\nabla^2\rho(\mathbf{r}_{bcp})$ | $g(\mathbf{r}_{bcp})$ | $k(\mathbf{r}_{bcp})$ | $v(\mathbf{r}_{bcp})$ | $\eta(\mathbf{r}_{bcp})$ |
|---|---|---|---|---|---|---|
| “Idealized” O…N interactions | | | | | | |
| CEDMUV | 0.00941 | 0.03763 | 0.00807 | –0.00134 | –0.00673 | 0.02179 |
| DNITBZ02 | 0.00911 | 0.03588 | 0.00769 | –0.00129 | –0.00640 | 0.02159 |
| PELMOJ | 0.00937 | 0.03672 | 0.00810 | –0.00109 | –0.00701 | 0.02136 |
| PUGQOY | 0.01001 | 0.04185 | 0.00896 | –0.00150 | –0.00746 | 0.02542 |
| PUGQOY | 0.01001 | 0.04347 | 0.00928 | –0.00159 | –0.00769 | 0.02635 |
| PUGQOY | 0.01001 | 0.04364 | 0.00935 | –0.00156 | –0.00779 | 0.02571 |
| TACGIN | 0.00762 | 0.03088 | 0.00659 | –0.00113 | –0.00546 | 0.01624 |
| TENTUE | 0.00771 | 0.03094 | 0.00665 | –0.00109 | –0.00556 | 0.01664 |
| WIKCIE | 0.00801 | 0.03237 | 0.00692 | –0.00118 | –0.00574 | 0.01742 |
| INEZIM | 0.00988 | 0.03966 | 0.00850 | –0.00142 | –0.00708 | 0.02306 |
| RUBSUD | 0.00452 | 0.01896 | 0.00393 | –0.00081 | –0.00313 | 0.00806 |
| “Stacking” O…N interactions | | | | | | |
| BAZQAV | 0.00584 | 0.02388 | 0.00512 | –0.00085 | –0.00426 | 0.01115 |
| RODLOM | 0.00832 | 0.03293 | 0.00705 | –0.00118 | –0.00586 | 0.01901 |
| FOHMUK | 0.00594 | 0.02382 | 0.00503 | –0.00092 | –0.00411 | 0.01221 |

Positive values of Laplacian of the electron density at bond critical points (3, –1) indicate that the electron density is concentrated not in the bond itself, but in atomic basins. Such interactions as closed shells belong to non-covalent bonds. This is also evidenced by the fact that the values of the potential energy density, $v(\mathbf{r}_{bcp})$, are smaller in absolute value than those of the kinetic energy density, $g(\mathbf{r}_{bcp})$.

To identify the pnictogen bond as a non-covalent interaction with a pronounced electrostatic component, it is necessary to confirm that the pnictogen atom, in this case, the N atom of one of the nitro groups, provides its electrophilic site for interaction with the nucleophilic fragment. To confirm this fact, we analyzed the disposition of the electron density and electrostatic potential minima [39, 40] along the line connecting the pair of considered O and N atoms. Our analysis has shown that the electron density minimum, $\rho(\mathbf{r})_{min}$, for all the studied O…N interactions is closer to the N atom, and the electrostatic potential minimum, $\varphi(\mathbf{r})_{min}$, is located closer to the O atom (Fig. 3). This means that for all considered orientations of nitro groups, the O atom acts as the nucleophilic fragment, and the N atom in these interactions of electrostatic nature provides its electrophilic site. Thus, the obtained result reveals a necessary, although not sufficient, condition for the interactions under consideration to be called pnictogen bonds.

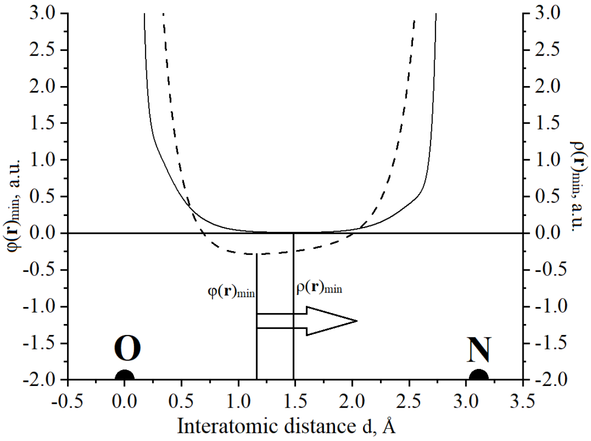
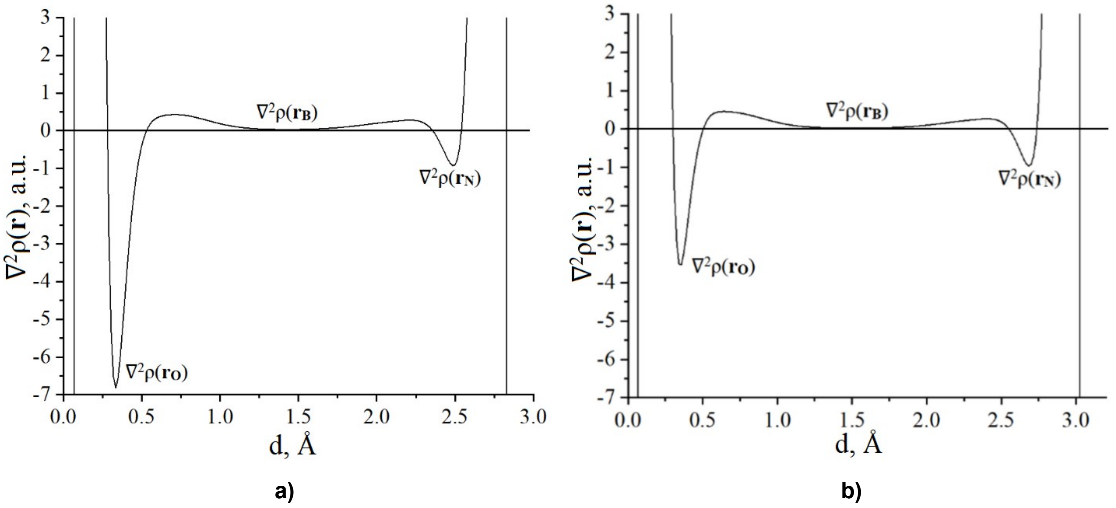


**Fig. 3. Disposition of the minima of electrostatic potential, $\varphi(\mathbf{r})_{\min}$, and electron density, $\rho(\mathbf{r})_{\min}$ along O…N line for a typical pnictogen bond**

The analysis of Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ along the O…N bond line has shown that the minimum of this function, corresponding to the outer electron shell of the O atom, $\nabla^2\rho(\mathbf{r}_O)_{\min}$, is deeper for all O…N interactions than the minimum, $\nabla^2\rho(\mathbf{r}_N)_{\min}$, corresponding to the outer electron shell of the N atom. This indicates the accumulation of electrons in the outer electron shell of the O atom along the line of this bond. For the “idealized” orientation of nitro groups, the values of $\nabla^2\rho(\mathbf{r}_O)_{\min}$ are much more negative than those for the orientation of neighboring nitro groups of the stacking type (Fig. 4).



a)

b)

**Fig. 4. Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ along the O…N line; a) “idealized” orientation in the p-dinitrobenzene crystal (DNITBZ02); b) “stacking” orientation in the crystal of 4-(N,N-dimethylamino)-2-methylnitrobenzene (BAZQAV)**

Figure 5 show the distribution diagrams of the minimum positions of Laplacian of the electron density of the O atoms, $d_O(\nabla^2\rho_{\min})$, and electrostatic potential, $d(\varphi_{\min})$, along the line of pnictogen O…N bonds, which are suitable for identifying the “idealized” and “stacking” orientations of interacting nitro groups.

In pnictogen bonds, corresponding to the “idealized” orientation of nitro groups, the line connecting the centers of the O…N atoms passes through the region of electron concentration belonging to one of the lone pairs of the O atom. In this case, the minimum position $\nabla^2\rho(\mathbf{r}_O)_{\min}$ corresponding to its outer electron shell, is always located closer to the O atom precisely in the case of an “idealized” orientation of nitro groups (Fig. 4a).

Thus, on the basis of such factors as $\nabla^2\rho(\mathbf{r}_O)_{\min}$, $d_O(\nabla^2\rho_{\min})$, and $d(\varphi_{\min})$ on the O…N bond line we can identify the “idealized” orientation of neighboring nitro groups and, accordingly, a stronger pnictogen O…N bond, relying only on the properties of electron density.

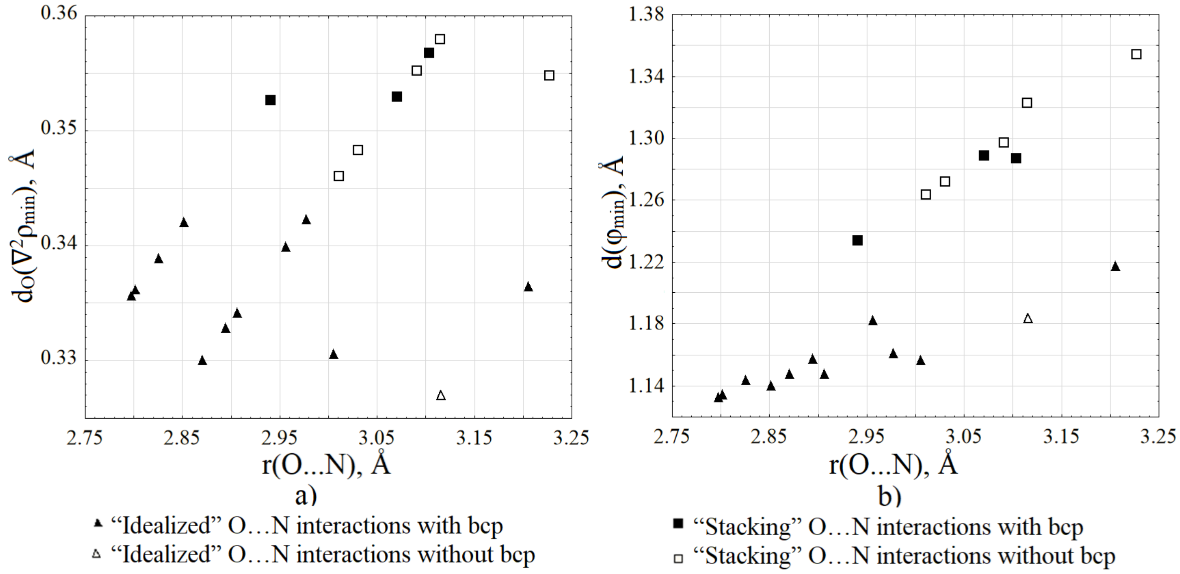


**Fig. 5. Scatterplots for the positions of minima of a) the Laplacian of electron density and b) the electrostatic potential along the O…N bond lines in relation to the interatomic distances**

To assess the influence of the crystalline environment on the properties of pnictogen bonds between the O and N atoms, the O=N and C–N bond lengths have been compared for the equilibrium crystal geometry and for isolated molecules, the geometry of which has been optimized in the gas phase. Crystals in which all molecules are symmetrically equivalent are taken as objects of study from the samples.

For all pnictogen O…N bonds, the $O_{(1)}$=N and $O_{(2)}$=N lengths are longer in the crystal than in the gas phase. In this case, the C–N bond in a crystal is, as a rule, shorter than in an isolated molecule. An exception is the WIKCIE compound, in which the C–N bond values are shorter in the crystal.

The values of $\nabla^2\rho(\mathbf{r_O})_{min}$ in the isolated molecule are more negative than in the crystal for all structures (Table 2). In addition, relying on analysis of the positions of the minima $d_{\mathbf{O}}(\nabla^2\rho_{min})$ (Table 3), we can conclude that in the crystal the regions of concentration of the electron density of O atoms are shifted toward neighboring atoms. In the gas phase, on the contrary, they are located closer to the nuclei.

Table 2

**The values of minima of the Laplacian of electron density along O…N bonds in crystals and along the preferred potential bonding directions in isolated molecules**

| Refcode | Crystal | | Isolated molecule | | $\Delta(\nabla^2\rho(\mathbf{r}_O)_{min})$ | $\Delta(\nabla^2\rho(\mathbf{r}_N)_{min})$ |
|---|---|---|---|---|---|---|
| | $\nabla^2\rho(\mathbf{r}_O)_{min}$ | $\nabla^2\rho(\mathbf{r}_N)_{min}$ | $\nabla^2\rho(\mathbf{r}_O)_{min}$ | $\nabla^2\rho(\mathbf{r}_N)_{min}$ | | |
| “Idealized” O…N interactions | | | | | | |
| BABRIF | –6.6728 | –0.9494 | –7.1626 | –0.9446 | –0.4898 | 0.0048 |
| CEDMUV | –6.3932 | –0.9031 | –6.7839 | –0.9014 | –0.3907 | 0.0017 |
| DNITBZ02 | –6.8217 | –0.9234 | –7.1867 | –0.9201 | –0.3650 | 0.0033 |
| INEZIM | –5.9144 | –1.0046 | –6.3372 | –0.9700 | –0.4228 | 0.0346 |
| PELMOJ | –6.3911 | –0.9057 | –6.7715 | –0.9078 | –0.3804 | –0.0021 |
| RUBSUD | –6.1796 | –1.0494 | –6.4762 | –0.9872 | –0.2966 | 0.0622 |
| TACGIN | –6.6128 | –0.9276 | –7.1277 | –0.9190 | –0.5149 | 0.0091 |
| WIKCIE | –6.8215 | –1.0619 | –7.2548 | –0.9835 | –0.4333 | 0.0784 |
| “Stacking” O…N interactions | | | | | | |
| BAZQAV | –3.5397 | –0.9579 | –3.7234 | –0.9985 | –0.4898 | 0.0048 |
| TACGIN | –3.6970 | –0.9095 | –3.8008 | –0.9295 | –0.3907 | 0.0017 |
| TEVHEH | –3.4166 | –0.9377 | –3.4895 | –0.9487 | –0.3650 | 0.0033 |
| RODLOM | –3.2444 | –0.9527 | –3.5567 | –0.9418 | –0.4228 | 0.0346 |
| RODLOM | –3.6764 | –0.9377 | –3.9018 | –0.9340 | –0.3804 | –0.0021 |
| FOHMUK | –3.2194 | –0.9193 | –3.4542 | –0.9151 | –0.2966 | 0.0622 |
| FOHMUK | –2.9682 | –0.9007 | –3.1601 | –0.9131 | –0.5149 | 0.0091 |

This suggests that in the crystalline environment, atom O is a nucleophilic fragment, it consumes its electron density to participate in pnictogen bonds or the other non-covalent interactions. The values of $\nabla^2\rho(\mathbf{r}_N)_{min}$ along the O…N line, on the contrary, are more negative in the crystalline environment than in the isolated molecule. This means that the properties of N as the electrophilic site provider in a crystal are less pronounced than in nitro group of an isolated molecule. This is in good agreement with the fact that for the electrophilic site of N atom involved in the pnictogen bond, redistribution of electron density has already occurred, and in this bond, N is the acceptor of electron density. For structures with the "stacking" orientation of nitro groups, a decrease in $\nabla^2\rho(\mathbf{r}_N)_{min}$ upon transition to the crystalline state is less frequent than for a stronger pnictogen bond with an "idealized" orientation of nitro groups.

**Table 3**

**The positions of minima of the Laplacian of electron density along the O…N bonds in the crystals and in isolated molecules**

| Refcode | Crystal | | Isolated molecule | | $\Delta(d_O(\nabla^2\rho_{min}))$ | $\Delta(d_N(\nabla^2\rho_{min}))$ |
|---|---|---|---|---|---|---|
| | $d_O(\nabla^2\rho_{min})$ | $d_N(\nabla^2\rho_{min})$ | $d_O(\nabla^2\rho_{min})$ | $d_N(\nabla^2\rho_{min})$ | | |
| "Idealized" O…N interactions | | | | | | |
| BABRIF | 0.6180 | 0.7946 | 0.6311 | 0.7809 | 0.0131 | –0.0137 |
| CEDMUV | 0.6237 | 0.7864 | 0.6332 | 0.7864 | 0.0095 | 0.0000 |
| DNITBZ02 | 0.6315 | 0.7963 | 0.6304 | 0.7853 | –0.0011 | –0.0110 |
| INEZIM | 0.6465 | 0.7812 | 0.6357 | 0.7828 | –0.0108 | 0.0016 |
| PELMOJ | 0.6290 | 0.7930 | 0.6338 | 0.7856 | 0.0048 | –0.0074 |
| RUBSUD | 0.6359 | 0.7873 | 0.6346 | 0.7812 | –0.0013 | –0.0061 |
| TACGIN | 0.6247 | 0.7950 | 0.6316 | 0.7856 | 0.0069 | –0.0094 |
| WIKCIE | 0.6424 | 0.7821 | 0.6299 | 0.7821 | –0.0125 | 0.0000 |
| "Stacking" O…N interactions | | | | | | |
| BAZQAV | 0.6743 | 0.7916 | 0.6609 | 0.7838 | –0.0134 | –0.0078 |
| TACGIN | 0.6584 | 0.8015 | 0.6606 | 0.7843 | 0.0022 | –0.0172 |
| TEVHEH | 0.6714 | 0.7882 | 0.6640 | 0.7843 | –0.0074 | –0.0039 |
| RODLOM | 0.6541 | 0.7963 | 0.6634 | 0.7850 | 0.0093 | –0.0113 |
| RODLOM | 0.6666 | 0.7777 | 0.6584 | 0.7851 | –0.0082 | 0.0074 |
| FOHMUK | 0.6671 | 0.7831 | 0.6643 | 0.7851 | –0.0028 | 0.0020 |
| FOHMUK | 0.6706 | 0.7925 | 0.6687 | 0.7864 | –0.0019 | –0.0061 |

As a result, the deeper minima of Laplacian of the electron density $\nabla^2\rho(\mathbf{r}_O)$ corresponding to the outer electron shell of oxygen are observed in an isolated molecule, which suggests that in a crystal with the "idealized" orientation of nitro groups this O atom consumes its electron density to participate in non-covalent interactions. For the N atom, more negative minima $\nabla^2\rho(\mathbf{r}_N)$ in a crystal are observed. For structures with the orientation of nitro groups of the "stacking" type, the minimum values of $\nabla^2\rho(\mathbf{r}_N)$ are deeper in an isolated molecule, which indicates strong delocalization of the electron density in the region of the π-hole of the nitrogen atom.

## Conclusions

In this research, we have studied the electron characteristics of non-covalent O…N interactions in crystals of nitro compounds for two types of orientation of nitro groups: the "idealized" orientation and "stacking" orientation. As a result of the study, the following conclusions have been made.

1. The minimum electron density, $\rho(\mathbf{r})_{min}$, for all studied short O…N contacts along the bond line is closer to the N atom, and the minimum electrostatic potential, $\varphi(\mathbf{r})_{min}$, is closer to the O atom. This means that the N atom provides its electrophilic site and the necessary, but insufficient condition is met that this interaction can be attributed to pnictogen bonds.

2. Deeper minima of the Laplacian of the electron density $\nabla^2\rho(\mathbf{r}_O)$ corresponding to the outer electron shell of the O atom are observed in an isolated molecule, which suggests that in a crystal with the "idealized" orientation of nitro groups this O atom consumes its electron density to participate in non-covalent interactions. For the N atom, the reversed situation is observed: more negative minima $\nabla^2\rho(\mathbf{r}_N)$ are in a crystal. For structures with the orientation of nitro groups of the "stacking" type, the minimum values of $\nabla^2\rho(\mathbf{r}_N)$, on the contrary, are deeper in an isolated molecule. This suggests that, in the "stacking" orientation, the electron density of the π-hole of the N atom is relatively strongly delocalized.

3. The interactions of the “idealized” orientation and “stacking” orientation are recommended to be identified on the basis of the following criteria found by us: the value and relative position of the minimum $\nabla^2\rho(\mathbf{r}_O)_{min}$ corresponding to the outer electron shell, as well as the relative position of the minimum electrostatic potential $\varphi(\mathbf{r}\ )_{min}$ along the line connecting the nuclei of the O…N atoms.

It can be concluded that the pnictogen O…N bond can be formed both in the case of the attractive “idealized” orientation of nitro groups and in the case of “stacking”, in which the region of the π-hole is removed from the concentration of the O atom electron density. In this case, the bonds formed with different orientations of nitro groups can be distinguished on the basis of anisotropy of electron density and electrostatic potential between the interacting atoms.

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# ОСОБЕННОСТИ ПНИКТОГЕННЫХ СВЯЗЕЙ, СФОРМИРОВАННЫХ СОСЕДНИМИ НИТРОГРУППАМИ В КРИСТАЛЛАХ

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Особенности пниктогенных связей O…N рассмотрены с позиций анализа различных геометрических ориентаций соседних нитрогрупп $NO_2$…$NO_2$, наблюдаемых в молекулярных кристаллах. «Идеализированная» для пниктогенной связи ориентация, когда неподеленная пара электронов атома O одной нитрогруппы направлена на электрофильный сайт атома N другой, и «стэкинг»-взаимодействие, для которого характерна параллельная укладка нитрогрупп, отличаются особенностями распределения электронной плотности и электростатического потенциала. Примененный электронный критерий, полученный с помощью квантово-химических расчетов с периодическими граничными условиями, подтвердил, что для рассмотренных O…N взаимодействий выполняется необходимое условие их отнесения к пниктогенным связям.

*Ключевые слова: пниктогенная связь, нитрогруппа, электростатический потенциал, электронная плотность, лапласиан электронной плотности.*

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