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Characterizing the Oxygen−Oxygen Interaction in the Dinitramide Anion

Elizabeth A. Zhurova,[†] Vladimir G. Tsirelson,[‡] Adam I. Stash,[§] and A. Alan Pinkerton*,[†]

Department of Chemistry, University of Toledo, Toledo, Ohio 43606, Mendeleev University of Chemical Technology, Moscow 125047, Russia, and Karpov Institute of Physical Chemistry, Moscow 103064, Russia

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In the past decade, the Theory of Atoms in Molecules[1] became widely recognized for it's utility in the analysis of chemical bonding. This theory is rooted in quantum mechanics;[2] it describes a molecule or crystal in terms of the electron density [ED, $\rho(\mathbf{r})$], its gradient vector field, $\nabla\rho(\mathbf{r})$, ED curvature, critical point positions, and their characteristics.[3] Atoms in this theory are considered to be connected by a network of atomic interaction lines or bond paths: lines along which the ED decreases for any lateral displacement. The bond path network is an intrinsic property of each compound. The type of pairwise atomic interactions is characterized by the sign of the Laplacian of the ED at the bond critical point (CP).[1] If electrons are locally concentrated in the bond CP ($\nabla^2\rho(\mathbf{r_b}) < 0$), then ED is shared by both nuclei (shared interactions). Otherwise, electrons are concentrated in each of the atomic basins separately ($\nabla^2\rho(\mathbf{r_b}) > 0$) and the interaction belongs to the closed-shell type. At the same time, a more detailed description of bonding is often necessary, especially in the nonstandard cases of atomic interactions, when the bond path network differs from the classical picture. Earlier[4] we reported an extensive topological analysis of atomic interactions in biguanidinium dinitramide (BIGH)(DN)[5] and biguanidinium bis-dinitramide $(BIGH_2)(DN)_2$[6] based on the experimental ED. These two compounds consist of isolated cations and anions linked by extensive hydrogen bonding. The twist angles describing the mutual arrangement of the two nitro groups in the (DN) anion are 7.1 and 28.8° for the (BIGH)(DN) and $(BIGH_2)(DN)_2$ crystals, respectively. The dinitramide anion with Bader's atomic charges obtained from integration over the atomic basins[7] is shown in Figure 1, and we note that all oxygen atoms carry a negative charge as expected. In both crystals, every expected covalent bond has been characterized by a negative Laplacian at the bond CP: relatively high ED value, ED curvature, and bond ellipticity. The interpretation of these results has been reported along with the analysis for the hydrogen bonds.[4]

On closer examination, in addition to the expected bond path network, unusual bond CP's have been found on the O(1)···O(4) lines in both crystals (Table 1). It is worth noting that the O(1)···O(4) interatomic distance is very close to twice the atomic radius of the oxygen atom.[8] No such CP's have been found in the atomic procrystals in which no chemical bonding is expected. The positive sign of the Laplacians and relatively low values of the electron density at O(1)···O(4) bond CP's indicate the closed-shell type of this interaction. A ring CP inside the O(1)-N(2)-N(1)-N(3)-O(4) space was also found, thus the Poincaré-Hopf rule[1] is satisfied.

The observation of interactions between atoms classically considered as nonbonding or repulsive (in the point-atom model) is not new. Though unusual, this kind of interaction has been found, for example, between oxygens in trinitromethane;[9] between anions in some rock-salt type crystals;[10−12] between Li and the closest methylenic carbon in 1,3-dilithiocyclobutane;[13] between hydrogens in benzenoid hydrocarbons;[14] between carbons in propellanes[15] and bridged annulenes;[16−17] and between halogen atoms in some perovskites,[18] perhalogenated cyclohexanes, dodecahedranes, and [60]fulleranes.[19] With the exception of the rock-salt type crystals[11] and *syn*-1,6:8,13-biscarbonyl[14]annulene,[17] all the above cited works are theoretical, and all of them were based only on the analysis of the ED. Difference in languages used for the ED treatment in the cited works led to polemics in the literature[10] concerning the identification of the interactions mentioned. Resolving the controversies resulting from these discussions; Bader[10] has stressed the role of the analysis of the potential energy density and showed that no repulsive potential energy exists in a system at equilibrium. For every atomic interaction type, each bond path is homeomorphically mirrored by a virial path, a line of maximally negative potential energy density linking the same nuclei.[20] Thus, the presence of a virial path between two atoms yields a bond path between them. The corresponding electron accumulation leads to the balancing of the Hellmann−Feynman forces and results in the equilibrium of the system. Therefore, the presence of a bond path and its associated virial path provide a "universal indicator of bonding between atoms".[10]

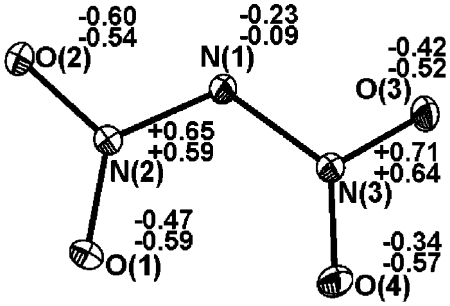

Figure 1. Dinitramide anion with 50% atomic probability ellipsoids as in (BIGH)(DN) at 90 K. The atomic charges integrated over the atomic basins are shown: the first number is for the (BIGH)(DN) and second is for the $(BIGH_2)(DN)_2$ crystals.

We applied the potential energy density analysis to identify the O−O interactions in the dinitramide anion. Our approach was as follows:

The Laplacian of the ED connects the (quasi-classical) kinetic energy density $g(\mathbf{r})$ and potential energy density $v(\mathbf{r})$ through the local form of the virial theorem[21]

$$2g(\mathbf{r}) + v(\mathbf{r}) = (1/4)\nabla^2\rho(\mathbf{r}) \qquad (1)$$

The potential energy density is negative everywhere,[10] while the kinetic energy is positive. Whether kinetic or potential energy plays the dominant role in the interaction depends on the latter specificity.

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* Corresponding author. E-mail: apinker@uoft02.utoledo.edu.
[†] University of Toledo.
[‡] Mendeleev University of Chemical Technology.
[§] Karpov Institute of Physical Chemistry.

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Table 1. O(1)···O(4) Bond Critical Points in Biguanidium Dinitramides[a]

compd	CP in	R, Å	CP: x	CP: y	CP: z	ρ, eÅ^{-3}, or v, au	$\nabla^2\rho$, eÅ^{-5} or $\nabla^2 v$, au	λ_1, eÅ^{-5} or au	λ_2, eÅ^{-5} or au	λ_3, eÅ^{-5} or au
(BIGH)(DN)	$\rho(\mathbf{r})$	2.531	0.348	−0.281	0.351	0.123	2.39	−0.50	−0.47	3.36
	$-v(\mathbf{r})$	2.531	0.344	−0.279	0.350	0.016	0.61	−0.07	−0.06	0.74
$(BIGH_2)(DN)_2$	$\rho(\mathbf{r})$	2.562	0.153	0.640	0.026	0.118	2.35	−0.43	−0.40	3.19
	$-v(\mathbf{r})$	2.562	0.149	0.644	0.022	0.015	0.59	−0.07	−0.04	0.69

[a] R is the bond/virial path length, ρ is electron density, and v is potential energy density; $\lambda_{1,2,3}$ are principle curvatures of the electron density and potential energy density at the bond critical point. CP's positions are fractional crystallographic coordinates. CP's positions are not shifted from the O(1)···O(4) interatomic line. Standard deviations are less than 0.001 for the interatomic distances, 0.01 for the electron density, and 0.02 for the Laplacian.

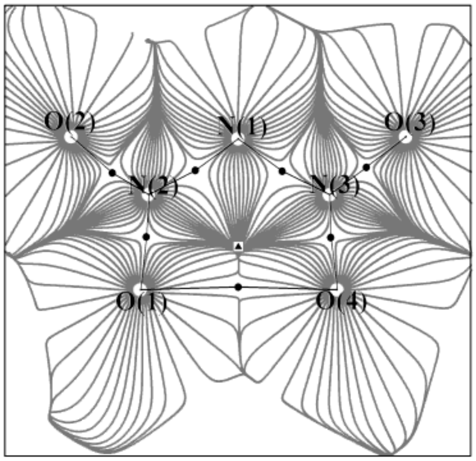

Figure 2. (BIGH)(DN): the gradient lines of the electron density and the projection of the (DN) molecular graph onto the O(1)−N(1)−O(4) plane. The bond critical points are shown as black circles and the ring critical point is shown as a triangle.

The potential energy density distribution is usually calculated with quantum chemical methods. It also can be be obtained using the virial theorem (eq 1). The latter approach allows us to use the Laplacian of the ED and kinetic energy density derived from the experimental ED.[22,23] For this purpose the kinetic energy density can be calculated using the gradient-expansion formula from density functional theory[24]:

$$g(\mathbf{r}) = (3/10)(3\pi^2)^{2/3}\rho(\mathbf{r})^{5/3} + (1/72)[\nabla\rho(\mathbf{r})]^2/\rho(\mathbf{r}) + (1/6)\nabla^2\rho(\mathbf{r}) \quad (2)$$

As it has been recently demonstrated,[23] this approach leads to results which are quantitatively close to Hartree−Fock values.

Our analysis showed that the negative potential energy density, $-v(\mathbf{r})$, in (BIGH)(DN) and $(BIGH_2)(DN)_2$ carries the same set of critical points (Table 1) as the ED.[25] The proximity of bond paths and virial paths experimentally proves the existence of homeomorphism between the electron density gradient and virial fields. The molecular graph reflecting the bond and virial path network forms a five-membered ring in this case (Figure 2). The positive electronic energy values $h_e(\mathbf{r}) = g(\mathbf{r}) + v(\mathbf{r}) = 0.005$ au at the bond CP's for both crystals also show that the O(1)···O(4) interaction does not belong to the standard covalent type. The high value of the ratio $g(\mathbf{r})/\rho(\mathbf{r})$ at the CP [1.11 for (BIGH)(DN) and 1.13 for $(BIGH_2)(DN)_2$] corresponds to a closed-shell type interaction.[26]

The topological analysis of theoretically calculated dinitramide anion[27] (twist angle 26.1°) also reveals a bond CP between the oxygen atoms belonging to different nitro groups. The ED and the Laplacian values at this CP ($\rho = 0.11$ eÅ^{-3} and $\nabla^2\rho = 2.0$ eÅ^{-5}) are in a good agreement with our experimental values (Table 1).

Therefore, we conclude that the interactions between the closest negatively charged oxygen atoms found in dinitramides can be characterized as **bonding** closed-shell type interactions.

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Note Added in Proof. Similar O−O and O−F interactions have also been recently reported for coesite,[28] dimanganese decacarbonyl,[29] and pentafluorobenzoic acid.[30]

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