Communication

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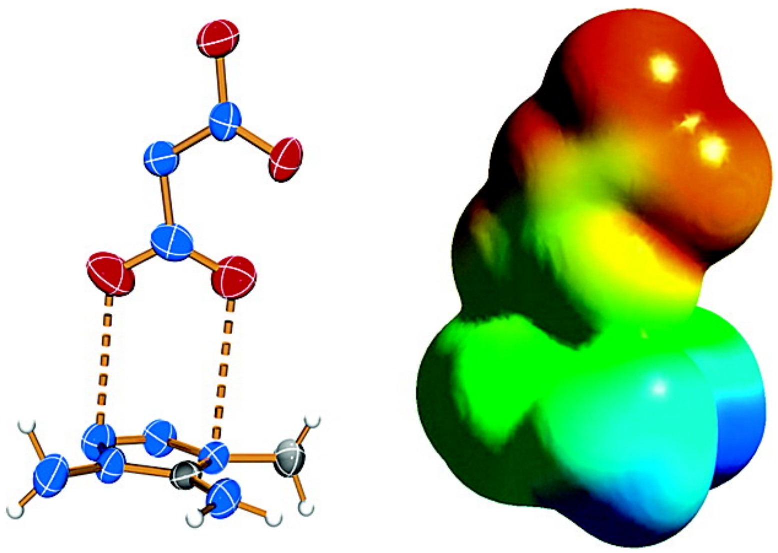

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1,5-Diamino-4-methyltetrazolium Dinitramide

Thomas M. Klapötke,* Peter Mayer, Axel Schulz,* and Jan J. Weigand

Department of Chemistry and Biochemistry, Ludwig-Maximilian University of Munich, Butenandtstrasse 5-13 (Haus D), 81377 Munich, Germany

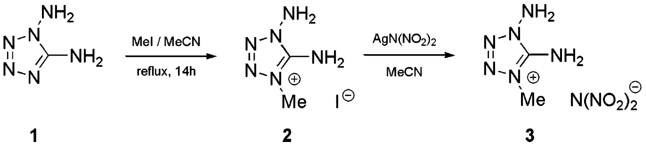
Received December 9, 2004; E-mail: tmk@cup.uni-muenchen.de

Since the generation of molecular nitrogen as an end-product of a propulsion or explosion is highly desired in order to avoid environmental pollution, health risks, as well as the reduction of detectable plume signatures, compounds containing a backbone of directly linked nitrogen atoms (nitrogen catenation) are of great interest.[1a−c] The ability of the dinitramide (DN) anion to form stable oxygen-rich salts with high densities with a variety of cations[2a−d] makes DN a promising candidate in the development of new tetrazole-based oxidizers. Such salts would be expected to possess both a high nitrogen *and* a high oxygen content. The combination of the oxygen-rich anion (DN) with a nitrogen-rich cation forms a class of energetic materials whose energy is derived from their very high positive heat of formation (directly attributed to the large number of inherently energetic N−N, N−O, and N−C bonds) as well as the combustion of the carbon atoms.

Here, we wish to report (i) the synthesis of the highly friction-sensitive 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide (**3**), (ii) the X-ray determination with respect to an intriguing interaction of one nitro group with the tetrazolium cation, and (iii) a discussion of the chemical bond utilizing the theory of atoms in molecules (AIM).[3]

The two-step synthesis of **3** starts from 1,5-diamino-1*H*-tetrazole (DAT, **1**)[4] via quaternization of **1** with MeI in acetonitrile (**2**, 86%). The metathetical reaction of **2** with a freshly prepared solution of AgDN[5] yields **3** as light-yellow crystals suitable for X-ray structure determination (85%) (Scheme 1).

Scheme 1



Pure **3** is stable up to ∼150 °C (starts to decompose) and shows a melting point of 85 °C. Product **3** belongs to the new class of energetic ionic liquids related to the low melting salts of 1,2,4- and 1,2,3-triazole systems introduced by Drake et al.[6a,b] Compared to the rather low impact sensitivity (7 J), **3** possesses a high friction sensitivity with a value of 24 N.[7,8]

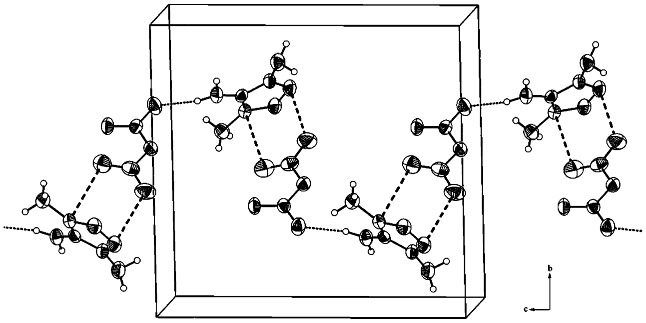


Figure 1. View of the strand formed by alternating cations (MeDAT) and anions (DN) displayed along the *a*-axis in **3**. Short contacts between the cations and anions are shown by dotted (····, N5−H5b····O2) and dashed (- - -, O(dinitramide) and tetrazole moiety) lines, respectively. (ORTEP plot, thermal ellipsoid represents 50% probability).

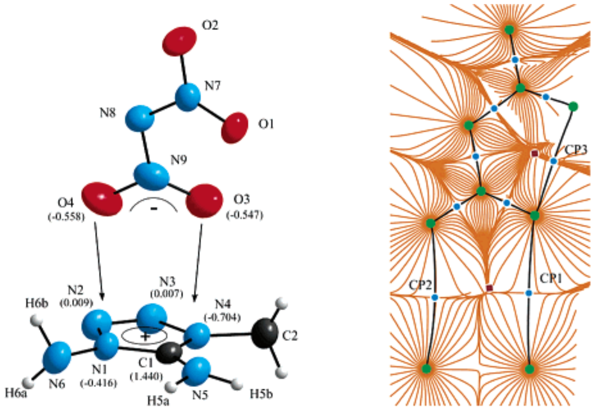


Figure 2. Left: Formula unit and labeling scheme used for **3** (ORTEP plot, thermal ellipsoid represents 50% probability; structural parameters are given in Table S2). Selected AIM charges are in parentheses. Right: Gradient lines of the electron density and the projection of the molecular graph onto the N2−N4−O3 plane. The bond CPs are shown as green circles, and the ring CPs are shown as brown rectangles.

Product **3** crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in the unit cell (numbering scheme of **3** is depicted in Figure 2) as racemic twin. The structure contains one crystallographically independent cation and one anion. As the methyl group hardly influences the molecular parameter of the tetrazole moiety (MeDAT), we abstain from a detailed discussion. (cf. X-ray data of 1,5-diamino-1*H*-tetrazolium cation; see ref 9). The overall geometry of the dinitramide ion is similar to that observed for other comparable dinitramide salts, such as guanidinium and biguanidinium salts.[2c,d] The two N−N bond lengths are asymmetric (N7−N8 1.350(3) Å; N8−N9 1.391(3) Å; cf. a typical N═N double bond (1.245 Å); N−N single bond (1.454 Å)),[10] and N−N−N angles of 115.4(2)° were observed. The nitro groups are twisted out of the central N−N−N plane (O3−N9−N7−O1, −24.5(2)°). Hence, the local symmetry of the anion is C_1. As known also from others, the metrical parameters of the DN ion are easily and strongly influenced by the environment.[2a−f]

In Figure 1, the view along the *a*-axis is displayed showing the zigzag strand composed of alternating MeDAT and DN ions. Each strand is further connected by strong hydrogen bonds (N5−H5a····O1^{i} and N5−H5a····O2^{i} [symmetry code: (i) $-1 + x, y, z$]) forming a three-dimensional network (Table S3 in Supporting Information). In turn, these strands are formed by two different types of interactions: (1) a strong hydrogen bond between N5−H5b····O2^{ii} (symmetry code: (ii) $-0.5 + x, 0.5 - y, 1 - z$), and (2) a closed-shell interaction between the O atoms of one nitro group (O3−N9−O4) with the tetrazole moiety (Table S3 in Supporting Information).

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Table 1. Bond Critical Points in **1**[a]

	$\rho(\mathbf{r}_b)$	$\nabla^2\rho(\mathbf{r}_b)$	λ_1	λ_2	λ_3	$\lvert\lambda_1\rvert/\lambda_3$	$G(\mathbf{r}_b)$	$V(\mathbf{r}_b)$	$G(\mathbf{r}_b)/\rho(\mathbf{r}_b)$
CP1	0.008338	0.0296	−0.00651	−0.00142	0.03758	0.173	0.00645	−0.00549	0.77
CP2	0.006762	0.0218	−0.00536	−0.00359	0.03077	0.174	0.00471	−0.00396	0.70
CP3	0.021239	0.0893	−0.01876	−0.01843	0.12651	0.148	0.02027	−0.01822	0.95

[a] All quantities are in atomic units; CP is a (3, −1) critical point; ρ is electron density; $\nabla^2\rho$ is the Laplacian of ρ; $\lambda_{1,2,3}$ are eigenvalues of Hessian of ρ; G is the kinetic and V the potential energy density; B3LYP/6-311+G(3d,2p) density; X-ray structural data used.

The interionic distances for the O4 and O3 contacts with the tetrazole ring are in the range of 3.020(3)−3.278(3) Å. For closed-shell interactions, there is a somewhat arbitrary dividing line between what is or is not an interaction when only the sum of the van der Waals radii is applied as criterion. Since the MeDAT is a nonspheric ion which is also able to form hydrogen bonds, it is hard to compare the anion−cation interactions with those in alkali DN salts which are observed in the range of 2.810(2) ($K^+[N_3O_4]^-$) to 3.534(6) Å ($Cs^+[N_3O_4]^-$).[2b]

What is the nature of bonding between the dinitramide anion and the tetrazolyl cation in **3**? Although further extensive hydrogen bonding could be possible, the anion and cation adopt an almost perpendicular arrangement ($\angle$(N2−N4−O3) = 91.64(9)°) with fairly short O3···N4 and O4···N2 contacts (d(O3−N4) = 3.18(3) Å and d(O4−N2) = 3.020(3) Å). Selected AIM[3] charges are given in Figure 2,[11] and we note that all oxygen atoms carry a negative charge as expected, whereas the nitrogen atoms of the tetrazole ring possess net charges which are also negative or close to zero (Figure 2, Table S4 in Supporting Information). The positive charge of the cation locates mainly at the two carbon and the hydrogen atoms of the amino groups. The negatively charged oxygen atoms of the dinitramide anion ($q_{O3} = -0.55e$ and $q_{O4} = -0.56e$), however, are directed toward N2 and N4 ($q_{N2} = 0.01e$ and $q_{N4} = -0.70e$). In agreement with the larger negative charge on N4, the O4···N2 distance is slightly longer (0.16 Å). Moreover, there is only a very small degree of charge transfer from the dinitramide anion to the tetrazolium cation ($q_{ct} = 0.02e$).[11]

The theory of atoms in molecules[3] was used to analyze the chemical bonding in **3**. This theory describes a molecule in terms of electron density, $\rho(\mathbf{r})$, its gradient vector field, $\nabla\rho(\mathbf{r})$, Laplacian, $\nabla^2\rho(\mathbf{r})$, and bond critical points, CP.[3,12] The type of interaction is characterized by the sign and magnitude of the Laplacian of $\rho(\mathbf{r}_b)$ at the bond critical point. If electronic charge is concentrated in the bond CP ($\nabla^2\rho(\mathbf{r}_b) < 0$)), this type of interaction is referred to as a shared interaction.[3] Interactions which are dominated by contraction of charge away from the interatomic surface toward each nuclei ($\nabla^2\rho(\mathbf{r}_b) > 0$) are called closed-shell interactions. For closed-shell interactions, $\rho(\mathbf{r}_b)$ is relatively low in value, and the value of the $\nabla^2\rho(\mathbf{r}_b)$ is positive. The sign of the Laplacian is determined by the positive curvature of $\rho(\mathbf{r}_b)$ along the interaction line, as the exclusion principle leads to relative depletion of charge in the interatomic surface. In **3**, every expected covalent bond has been characterized by a negative Laplacian at the bond CP (Supporting Information). In addition to the expected bond path network, three (3, −1)[13] unusual bond CPs have been found on the O3···N4 (CP1), O4···N2 (CP2), and O1···O3 (CP3) lines (Figure 2). The origin of the latter bond CP (CP3) has been described recently by Pinkerton et al. as a bonding closed-shell-type interaction between the negatively charged oxygen atoms belonging to different nitro groups.[14] CP1 and CP2 are associated with an interaction between the atoms which are linked by these bond CPs. A ring CP inside the O4−N2−N4−O3−N9 space was also found, thus the Poincaré−Hopf rule is satisfied.[3] The calculated positive Laplacian of the electron density ($\nabla^2\rho(\mathbf{r}_b)$) and the relatively low value of $\rho(\mathbf{r}_b)$ at both bond critical points (CP1 and CP2) indicate that the O3···N4 (CP1) and O4···N2 (CP2) contacts are dominated by bonding closed-shell interaction.[15] The high values of the ratio $G(\mathbf{r}_b)/\rho(\mathbf{r}_b)$ at the bond CPs (0.77 and 0.70) and the ratio of the eigenvalues $|\lambda_1|/\lambda_3 \ll 1$ support this conclusion (Table 1).[16] Additional information about chemical bond type is available from the total electronic energy density $E^e(\mathbf{r}_b) = G(\mathbf{r}_b) + V(\mathbf{r}_b)$. Closed-shell interactions are dominated by the kinetic energy density, $G(\mathbf{r}_b)$, in the region of the bond CP, with $G(\mathbf{r}_b)$ being slightly greater than potential energy density $|V(\mathbf{r}_b)|$ and with the energy density ($E^e(\mathbf{r}_b) > 0$) close to zero (Table 1).

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Supporting Information Available: Crystallographic data of **3** (cif files, Tables S1−S3); experimental and computational details (Tables S4 and S5). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Dixon, D. A.; Feller, D.; Christe, K. O.; Wilson, W. W.; Vij, A.; Vij, V.; Brooke, H. D. B.; Olson, R. M.; Gordon, M. S. *J. Am. Chem. Soc.* **2004**, *126* (3), 834−843. (b) Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Vij, V.; Christe, K. O. *Angew. Chem., Int. Ed.* **2002**, *41* (16), 3051−3054. (c) Huynh, M.-H. V.; Hiskey, M. A.; Hartline, E. L.; Montoya, D. P.; Gilardi, R. *Angew. Chem., Int. Ed.* **2004**, *43* (37), 4924−4928.

(2) (a) Bottaro, J. C.; Penwell, P. E.; Schmitt, R. J. *J. Am. Chem. Soc.* **1997**, *119* (40), 9405−9410. (b) Gilardi, R.; Flippen-Anderson, J.; Georg, C.; Butcher, R. J. *J. Am. Chem. Soc.* **1997**, *119* (40), 9411−9416. (c) Sitzmann, M. E.; Gilardi, R.; Butcher, R. J.; Koppes, W. M.; Stern, A. G.; Trasher, J. S.; Trivedi, N. J.; Yang, Z.-Y. *Inorg. Chem.* **2000**, *39* (4), 843−850. (d) Martin, A.; Pinkerton, A. A.; Gilardi, R. D.; Bottaro, J. C. *Acta Crystallogr.* **1997**, *B53*, 504−512. (e) Christe, K. O.; Wilson, W. W.; Petrie, M. A.; Michels, H. H.; Bottaro, J. C.; Gilardi, R. *Inorg. Chem.* **1996**, *35*, 5068−5071. (f) Pinkerton, A. A.; Ritchie, J. P. *J. Mol. Struct.* **2003**, *657*, 57−74.

(3) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; The International Series of Monographs of Chemistry; Oxford University Press: Oxford, 1990.

(4) Gaponik, P. N.; Karavai, V. P. *Khim. Geterotsikl. Soedin.* **1984**, 1388−1391.

(5) How-Ghee, A.; Fraenk, W.; Karaghiosoff, K.; Klapötke, T. M.; Mayer, P.; Nöth, H.; Sprott, J.; Warchhold, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2894.

(6) (a) Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; Mckay, M. *Propellants, Explos., Pyrotech.* **2003**, *28* (4), 174−180. (b) Xue, H.; Arritt, S. W.; Twamely, B.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43* (25), 7972−7977.

(7) *Recommendation on the Transport of Dangerous Goods: Manual of Tests and Criteria*; ST/SG/AC.10/11 Rev. 2, United Nations, New York, and Geneva, 1995; pp 74 and 105.

(8) For experimental and crystallographic (Table S1) details, see the Supporting Information.

(9) Matulis, V. E.; Lyakhov, A. S.; Gaponik, P. N.; Voitekhovich, S. V.; Ivashkevich, O. A. *J. Mol. Struct.* **2003**, *649*, 309−312.

(10) N−N values and N═N values from: *International Tables for X-ray Crystallography*; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. C.

(11) For NPA charges, see the Supporting Information. NPA charges give a similar picture and exactly the same amount of charge transfer.

(12) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893−928.

(13) For nomenclature definitions of critical points, see ref 3.

(14) Zhurova, E. A.; Tsirelson, V. G.; Stash, A. I.; Pinkerton, A. *J. Am. Chem. Soc.* **2002**, *124*, 4574−4575 and references therein.

(15) Bianchi, R.; Gervasio, G.; Marabello, D. *Inorg. Chem.* **2000**, *39*, 2360−2366.

(16) Bader, R. F. W.; Essen, H. *J. Chem. Phys.* **1984**, *80*, 1943−1960.

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