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ARTICLE *in* CHEMISTRY - AN ASIAN JOURNAL · JUNE 2011

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Theoretical Investigation of 4,4',6,6'-Tetra(azido)azo-1,3,5-triazine-*N*-oxides and the Effects of N→O Bonding on Organic Azides

Cai Qi,^[a] Ru-Bo Zhang,^[b] Xue-Jiao Zhang,^[a] Yu-Chuan Li,^[a] Yuan Wang,^[a] and Si-Ping Pang^{*[a]}

Abstract: A family of 4,4',6,6'-tetra(azido)azo-1,3,5-triazine-*N*-oxides was designed and investigated by theoretical method. The effects of the N→O bond on the properties of TAAT-*N*-oxides, such as density, heat of formation, and detonation performance, were discussed. By comparison with the bond-dissociation energy of the weakest bond and the electrostatic po-

tentials, the effects of the N→O bond on the stability and impact sensitivity of organic azides were also discussed. The results show that the introduction

Keywords: azides • bond-dissociation energy • detonation performances • heat of formation • N→O bond

of N→O bonds at the appropriate positions increases the oxygen balance and density of the compounds, while it has little effect on the stability and impact sensitivity. Consequently, their introduction results in energetic compounds with improved detonation performances.

Introduction

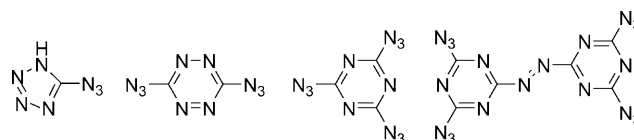
High-nitrogen-content compounds, based on C/N heteroaromatic rings such as tetrazine,^[1] triazole,^[2,3] and tetrazole,^[4] have attracted significant attention in the area of high-energy-density materials (HEDMs) research because of their novel properties, such as high density and a high positive heat of formation, which can be directly attributed to the large number of inherently energetic N–N and C–N bonds contained in the molecule.^[5] In contrast with traditional energetic compounds, their high energy is mainly derived from the high positive heat of formation rather than from the combustion of the carbon backbone or the cage strain. In addition, because of the high nitrogen content, the decomposition product of this kind of compound is mainly

N₂, which makes them promising candidates as environmentally friendly energetic materials.

Organic azido-substituted compound is an important class of high-nitrogen compounds.^[6–8] Since the preparation of the first organic azide, phenyl azide, by Peter Griess in 1864, these energy-rich and flexible intermediates have enjoyed considerable interests.^[9–15] Polyazido heteroaromatic compounds have relatively high heats of formation, as one azido group adds about 87 kcal mol^{−1} of endothermicity to a hydrocarbon compound;^[16] thus, despite many difficulties, many fascinating organic azides have been prepared and structurally characterized over the last few decades (Scheme 1).^[10,11,17–25]

In addition, the azo linkage is known to improve the properties of this kind of compounds; it not only increases the heat of formation of the compounds, but also desensitizes them.^[5]

4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT) is a typical example of polyazido-azo-heterocyclic systems, which possesses high nitrogen content (79.5 %) and the largest heat of formation (2171 kJ mol^{−1}) among all reported energetic ma-

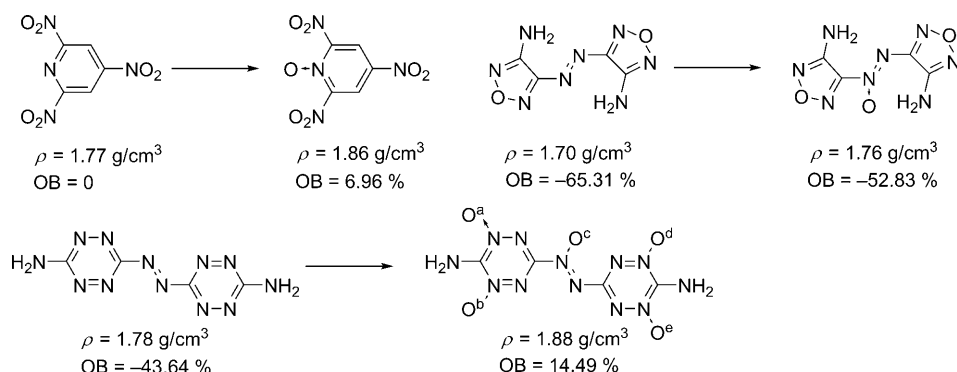


Scheme 1. Examples of organic azides.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/asia.201000897>.



Scheme 2. The effects of N→O bonding.

terials.^[5] As a natural consequence of its chemical structure, it will generate large amount of N_2 gas when it decomposes; this decomposition pathway is highly desirable for energetic materials in order to avoid environmental pollution, health risks, as well as untraceable signatures.^[26]

Besides heat of formation, high density and good oxygen balance are also required properties for a high-performing energetic compound. Compared with traditional energetic materials, like RDX and HMX, the detonation performance of TAAT is not so good, owing to its relatively low density (1.67 g cm^{-3}),^[5] and there is no oxygen contained in the molecule. The introduction of nitro groups could effectively increase the density and oxygen balance of the compounds. However, because all of the C atoms in the molecule are fully substituted, it is difficult to modify TAAT with nitro groups.

Pagoria et al.^[27] presented a method that would not only improve the oxygen balance, but also increase the density in heterocyclic systems, that is, through the conversion of tertiary amines into their corresponding N-oxides (Scheme 2). The feasibility of the method has been confirmed by a variety of experimental data.^[27,28] Meanwhile, theoretical studies have shown that the formation of an N-oxide can increase the stability of some polynitrogen systems, whilst the efficiency of the system as high energy density materials were not affected.^[29,30] To the best of our knowledge, most of the N→O bonds have previously been introduced into amino and nitro heterocycles;^[27,28,31] there is no report on the introduction of N-oxides into the polyazido heterocyclic compounds. If TAAT could be modified by N→O bonds, the density and oxygen balance could be further improved.

Abstract in Chinese:

本文以四叠氮偶氮三嗪化合物为母体，设计了一系列三嗪类氮氧化物。通过理论研究，讨论了氮氧键对于四叠氮偶氮三嗪氮氧化物密度、生成热、爆轰性能的影响。通过将系列氮氧化物的静电势以及最弱键的键解离能进行对比，探讨了氮氧键的引入对于有机多叠氮化合物的撞击感度和稳定性的影响。结果表明，在适当的位置引入氮氧键可以改善化合物的氧平衡、密度，进而得到性能更为优越的含能化合物。

However, it is not clear whether the introduction of N→O bonds will have a negative effect on the stability and sensitivity of this kind of compounds.

As part of our continual effort in the pursuit of novel high-nitrogen energetic compounds,^[3,32,33] TAAT derivatives containing tertiary N-oxides are investigated and the effects of the N→O bond on organic azides are discussed.

The optimized structures (Figure 1, 2) are obtained theoretically, and then properties including the density, heat of formation, detonation performance, bond dissociation energy, and electrostatic potential are predicted. In addition, the effect of the N→O bond on molecular properties is discussed. A TAAT derivative with two N→O bonds is thought to be a high-energy-density compound.

Results and Discussion

TAAT is polymorphous.^[5] The optimized structures of TAAT molecules with different conformations and their rel-

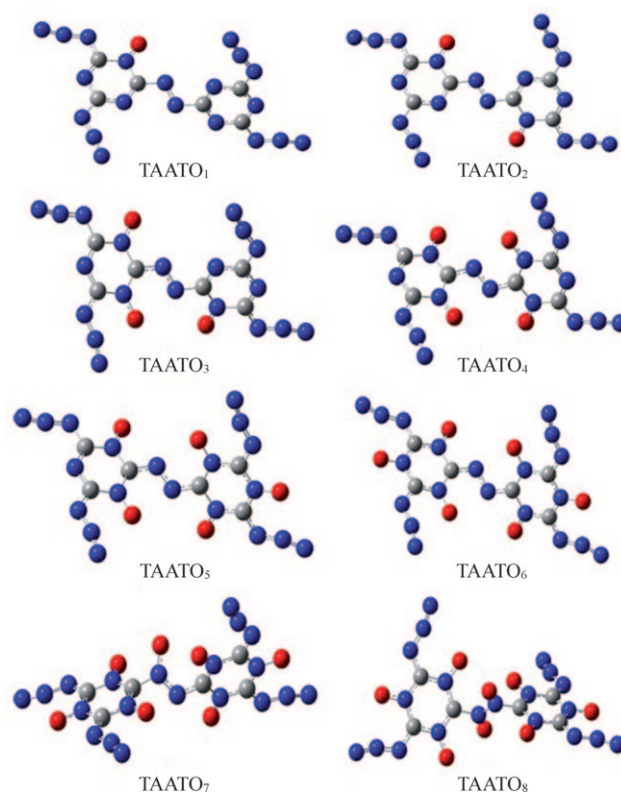


Figure 1. The optimized structures of TAAT-N-oxides with different numbers of N→O bonds (O red, N blue, C gray).

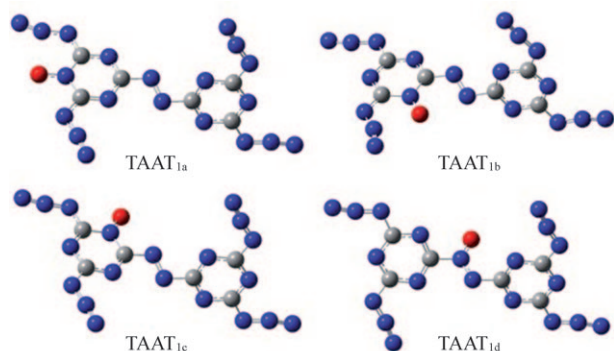


Figure 2. The optimized structures of TAAT with one N-oxide group (TAATO_{1c} is used as the representative of TAATO₁ in Figure 1).

ative energies are shown in Figure 3 and Table 1, respectively. Although the energy differences between the three conformers are very small, TAAT-β₂ has been selected as the parent compound for further investigation because it has the lowest energy.

Predicted Properties

In order to illustrate the effects of the N→O bond on the properties of TAAT-N-oxides, eight compounds with be-

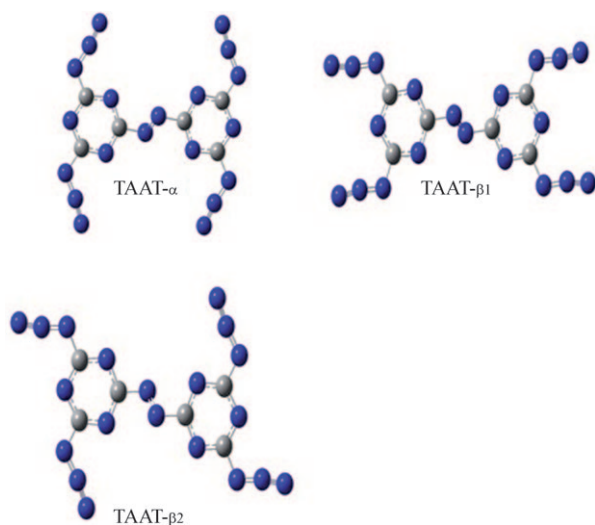


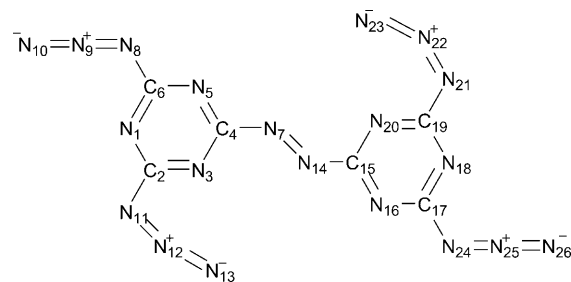
Figure 3. The optimized structures of TAAT molecules with different conformations.

Table 1. Relative energy of TAAT molecules with different conformations (kJ mol⁻¹).

	TAAT-α	TAAT-β ₁	TAAT-β ₂
Relative energy ^[a]	0	7.06	-3.77

[a] Single point energy was obtained using MP2/6-311++g(d,p).

tween one and eight N→O bonds were designed (Figure 1). The atomic number is shown in Scheme 3 and in the Supporting Information. Based on the optimized structures, properties like heat of formation (HOF), density, and detonation property were predicted (Table 2).



Scheme 3. Atom numbering for TAAT.

According to the Kamlet–Jacobs equations,^[34,35] density and heat of formation are two parameters in determining the detonation performances of an energetic compound, with density playing a more-prominent role as the detonation velocity is directly proportional to the square of density.

By comparison with the parent compound TAAT, oxidation of the tertiary amine affords a family of TAAT-N-oxides with higher densities. TAATO₅ and TAATO₆ have predicted densities larger than 2.0 g cm⁻³, whilst the value of TAAT is 1.70 g cm⁻³. The highest density was for TAATO₆. However, the influence of oxidation on the density is not simply linear. The density does not always increase with the number of oxygen atoms in TAAT-N-oxides. When the number of N→O bonds is larger than six, the density becomes smaller. This is probably due to the interaction between the oxygen atoms. Because oxygen atoms are likely to repel each other when they are placed close to one-another, it will have negative effects on molecular packing, which is in turn directly related to the densities of compounds. Although the introduction of N→O bonds could in-

Table 2. The predicted properties of TAAT-N-oxides.

	TAAT	TAATO ₁	TAATO ₂	TAATO ₃	TAATO ₄	TAATO ₅	TAATO ₆	TAATO ₇	TAATO ₈	TNT ^[b]	RDX ^[c]	HMX ^[c]	CL-20 ^[c]
ρ [g cm ⁻³]	1.70 ^[a]	1.73	1.78	1.79	1.83	2.02	2.03	1.91	1.92	1.65	1.82	1.91	2.04
HOF [kJ mol ⁻¹]	2171.0	2139.9	2105.7	2087.3	2066.2	2059.0	2052.1	1954.6	1930.9	-67.0	66.9	75.3	418.4
Q _v [kJ kg ⁻¹] ^[d]	6167.6	6349.6	6508.4	6694.0	6858.8	7043.5	7215.8	7180.9	7302.0	5401.8	6228.2	6181.2	6654.5
OB [%]	-27.3	-21.7	-16.7	-12	-7.7	-3.7	0	4.6	9.1	-74.0	-21.6	-21.6	-11.0
D [km s ⁻¹]	7.79	8.01	8.29	8.44	8.68	9.43	9.57	9.20	9.27	6.88	8.75	9.10	9.4
P [GPa]	26.0	27.8	30.3	31.5	33.8	42.1	43.5	38.8	39.6	19.5	34.0	39.0	42.0

[a] The experimental value is 1.67 g cm⁻³. [b] U. Teipel, *Energetic Materials*, Wiley-VCH, Weinheim, **2005**. [c] The data were obtained from ref. [17]. [d] Calculated heat of detonation. ρ = density, HOF = heat of formation, Q_v = heat of detonation, OB = oxygen balance, D = detonation velocity, P = detonation pressure.

crease the density of energetic compounds, attention should be paid to the choice of an appropriate number of N→O bonds. For example, the predicted density of TAAT and TAATO₆ is 1.70 and 2.03 g cm⁻³, respectively, whilst the value for TAATO₇ is 1.91 g cm⁻³.

Owing to the increase in density, the detonation performances of TAAT-*N*-oxides are much better than TAAT. For example, the predicted detonation velocity of TAATO₆ is 9.57 km s⁻¹ and the detonation pressure is 43.5 GPa, whereas the corresponding values of TAAT are 7.79 km s⁻¹ and 26.0 GPa, respectively.

On the other hand, oxidation of the tertiary nitrogen atoms tends to dilute the energy of the molecules, because the heat of formation (HOF) of the molecules is reduced. As the number of N→O bonds increases, the HOF of TAAT-*N*-oxides decreases. Such a downward trend becomes obvious when the seventh N→O bond is introduced. The largest difference between TAAT and its *N*-oxide derivatives is 240 kJ mol⁻¹.

On the contrary, the predicted heat of detonation (Q_v) increases as the number of N→O bonds increases, except TAATO₇. The value increases from 6167.6 kJ kg⁻¹ to 7215.8 kJ kg⁻¹, as the number of N→O bonds increases from one to six, whilst it is 7180.9 kJ kg⁻¹ for TAATO₇. Meanwhile, the values of *N*-oxide derivatives are generally larger than those of TNT, RDX, and HMX. When there are more than two N→O bonds attached to TAAT, their values are even larger than CL-20. Because of the introduction of N→O bonds, other detonation properties like detonation velocity and detonation pressure also improve. As shown in Table 2, the detonation parameters (Q_v , D , P) of TAATO₅ and TAATO₆ are better than those of traditional energetic compounds.

Structures

For further investigation, the simplest TAAT-*N*-oxides are discussed first. The optimized structures of TAATO₁ are shown in Figure 2 (for detailed information, see the Supporting Information). There are four kinds of positions that could be modified by the N→O bond in TAAT. When the oxygen atom is introduced into the system, the C–N bonds adjacent to the N→O bond are stretched (Table 3). For example, the bond length of N1–C2 is 1.335 Å in TAAT, whilst the same bond is 1.384 Å long in TAATO_{1a}. It is worthy of note that the bond length of C4–N7 in TAATO_{1d} is 1.487 Å, a little longer than the length of a standard C–N bond (1.47 Å).^[36] This observation is probably due to the

strongly electron-withdrawing nature of the oxygen atom. Meanwhile, the bond lengths of the remaining bonds in the molecule, especially the bonds in the other triazine ring, are not obviously affected by the N→O bond. All of the lengths of the C–N bonds in the triazine rings are still between the lengths of the standard C–N (1.47 Å) and C=N bonds (1.28 Å), which indicates that the aromaticity of the molecule still exists. It is also worthy of note that the bond length of the N→O bond on the triazine ring is a little longer than that of the N→O bond attached to the azo group. The average bond length is 1.27 Å for the former, whilst it is 1.239 Å for the latter.

As shown in Table 4, the two triazine rings in TAAT are planar, and the dihedral angle of N3–N5–N16–N20 indicates that they are parallel. In addition, no matter if there is a N→O bond or not, or which position the N→O bond is introduced at, the azido groups are always coplanar with the ring they are attached to. The oxygen atom of the N→O bond is also coplanar with respect to the triazine ring it is linked to. However, the introduction of the N→O bond has a great impact on the conformation of TAAT. When the N→O bond is attached to the triazine ring, the two triazine rings become almost axially vertical, whereas the dihedral angle is –158.3° when the azo group is modified by the oxygen atom.

Compared with the obvious impact of the N→O bond on the bond lengths and dihedral angles of the structure, it does not have much influence on the bond angles of the system, especially the values of the other triazine ring and the azido groups attached to it. The bond angle including the N→O bond is around 120°.

As mentioned above, based on the structural changes of TAAT with one N→O bond, it is reasonable to believe that the introduction of N→O bonds onto one triazine ring of TAAT would have little effect on the structure of the other ring. Therefore, when the effect of N→O bonds on the bond-dissociation energy is studied, only one triazine ring is discussed.

Bond-Dissociation Energy

Besides detonation performances, stability is also an important factor when determining whether an energetic compound merits investigation. Bond-dissociation energy (BDE) is an effective physical quantity for predicting the thermal stability of compounds, especially energetic compounds. Because dissociation of the bond with the lowest BDE value is supposed to be the first step in the molecule

Table 3. Selected bond lengths of the optimized TAAT-*N*-oxides (Å).

	N1-C2	N1-C6	C2-N11	C6-N8	N11-N12	N8-N9	C2-N3	N3-C4	C4-N5	N5-C6	C4-N7	N7-N14	N→O
TAAT	1.335	1.339	1.393	1.393	1.253	1.252	1.344	1.332	1.329	1.340	1.435	1.246	
TAATO _{1a}	1.384	1.391	1.382	1.367	1.252	1.261	1.318	1.337	1.33	1.323	1.425	1.252	1.276
TAATO _{1b}	1.317	1.341	1.364	1.395	1.263	1.25	1.404	1.383	1.324	1.329	1.408	1.253	1.279
TAATO _{1c}	1.344	1.312	1.395	1.38	1.250	1.252	1.329	1.328	1.383	1.402	1.402	1.255	1.264
TAATO _{1d}	1.334	1.339	1.388	1.389	1.255	1.254	1.348	1.320	1.316	1.344	1.487	1.273	1.239
TAATO ₂	1.347	1.311	1.396	1.381	1.250	1.252	1.325	1.332	1.390	1.404	1.387	1.270	1.262

Table 4. Selected dihedral angles [°] of the optimized TAAT-*N*-oxides.

	TAAT	TAATO _{1a}	TAATO _{1b}	TAATO _{1c}	TAATO _{1d}	TAATO ₂
N1–C2–N3–C4	–1.2	1.0	4.4	–0.6	–0.7	–0.73
N1–C2–N3–N11	179.7	–179.9	–178.6	179.5	–180.0	179.5
N1–C2–N11–N12	–179.8	179.5	179.8	180.0	–179.7	179.9
C2–N11–N12–N13	–180.0	179.9	–180	179.5	–180	179.6
N1–C6–N5–N8	179.4	–179.7	–179.1	179.4	–180	179.5
N1–C6–N8–N9	0	0	–0.2	0.7	0	0.5
C6–N8–N9–N10	179.9	–179.8	–179.7	–179.9	–179.8	–179.6
N3–N5–N16–N20	–180	–104.3	–90.9	–100.5	–158.3	–128.2
C2–N3–C4–N7	–176.1	178	170.8	172.1	–178.1	174.1
N3–C4–N7–N14	–47.3	23.0	40.2	31.3	–48.1	21.9
C4–N7–N14–C15	180.0	–176.4	–175.4	–173.0	–176.7	–171.1

decomposition, this value can indicate the stability of the corresponding compounds. The smaller the value is, the weaker the bond is, and the more unstable the compound is; that is to say, the compound should have relatively good thermal stability first, so that it is possible to be experimentally synthesized. Therefore, in order to predict the experi-

mental viability of the related TAAT-*N*-oxides, the bond dissociation energies of the C–N and N–N bonds were studied.

By comparison with the BDE value in Table 5, the most-stable bond was determined to be the C–N bond connecting the triazine ring to the azido group, with the BDE values ranging from 87–89 kcal mol^{–1}. Meanwhile, the N=N bond of the azido group, like N8–N9 and N11–N12, is the weakest bond. However, the BDE value of this N–N bond varied with the position of the N→O bond. When the N→O bond is on the N1 atom, both of the two azido groups are unstable. Their BDE values are negative, which indicates the instability of the molecule. When the oxygen atom is attached to N3, the bond dissociation energy of N11–N12 is –4.78 kcal mol^{–1}, whereas the value of N8–N9 remains basically unchanged. However, when the N→O bond is on N5, both of the two azido groups are thermally stable, because the BDE values of them are comparable to those of TAAT. If the oxygen atom is on N7 of the azo group, the stability of most of the bonds is not affected, except C4–N7, comparing with TAAT. The BDE value of C4–N7 is so negative that the corresponding compound may not be synthesized. Therefore, TAATO_{1c} is thought to be the most-stable one in TAATO₁ series. The conformation of the azido groups may contribute to this result. The terminal nitrogen atom of the azido group attached to C6 derives from the oxygen atom in TAATO_{1c}, whilst in TAATO_{1b}, the terminal nitrogen atom of the azido group adjacent to the N→O bond is pointed towards the oxygen atom, which may intensify the interaction between the oxygen atom and the azido group. Owing to the electron-withdrawing nature of the oxygen atom, such an intense interaction probably results in the dissociation of the compound.

Thus, because of the structure of TAAT, there is still one corresponding position in the other triazine ring that could be modified. However, it seems difficult to introduce more than two N→O bonds according to the BDE analysis above. By comparison with the BDE values of TAATO_{1c} and TAATO₂ in Table 5, it seems that the introduction of the second N→O bond into the corresponding position of the other triazine ring has little effect on the stability of the compound.

Electrostatic Potential

For further studies of the effect of the N→O bond on the stability of TAAT-*N*-oxides, the ESP of TAAT, TAATO₁, and TAATO₂ were computed based on the optimized structures at the B3LYP/6-31G(d) level. It has been confirmed that the electrostatic potential (ESP) is a useful guide in assessing the degree of sensitivity of a CHNO explosive to impact.^[37–39] Contrary to non-energetic organic molecules in which the positive regions are always larger but weaker in strength, wider regions with

Table 5. Bond-dissociation energies of TAAT-*N*-oxides (kcal mol^{–1}).

	TAAT	TAATO _{1a}	TAATO _{1b}	TAATO _{1c}	TAATO _{1d}	TAATO ₂
C2–N11	87.62	88.46	89.93	89.22	88.56	88.33
C6–N8	88.01	89.97	88.60	88.40	88.76	89.14
N8–N9	41.63	–0.54	38.94	39.07	42.83	39.05
N11–N12	42.22	–4.48	–4.78	40.17	44.88	39.56
C4–N7	63.47	66.53	63.78	67.14	–190.84	69.23
C15–N14					90.32	

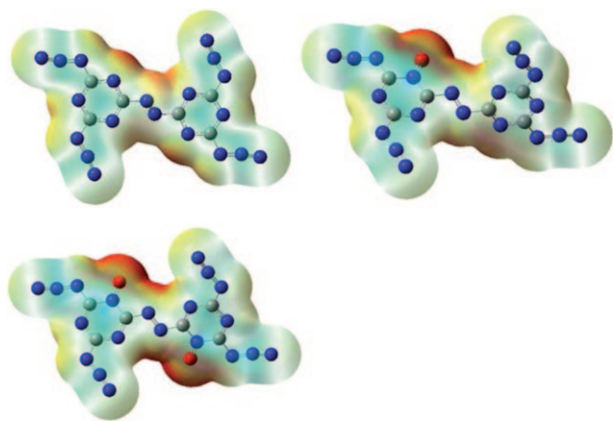


Figure 4. Electrostatic potentials (ESPs) of TAAT, TAATO₁, and TAATO₂ for the 0.001 electron/bohr³, ranging from −0.05 (red) to 0.075 hartrees (dark blue).

larger and stronger positive potentials are observed in energetic compounds, which can be related to the increased impact sensitivities. Figure 4 shows the electrostatic potentials for the 0.001 electron/bohr³ isosurfaces of electron density evaluated at the B3LYP level of theory. The colors range from −0.05 to +0.075 hartrees with dark blue denoting extremely electron-deficient regions ($V(r) \geq 0.075$) and red denoting electron-rich regions ($V(r) \leq -0.05$).

The compounds under investigation in this paper differ from TAAT only in the number of electron-withdrawing N→O bonds connected to the aromatic ring system. As shown in Figure 4, the magnitude of the positive region over the azide moieties is approximately similar for all three of the investigated molecules. Meanwhile, the introduction of the N→O bond into the aromatic ring makes the ring a little more positive. However, such a difference is not obvious, which means that the differences between TAAT and its *N*-oxide derivatives towards impact stimulus are subtle.

The N→O bond has little effect on the impact sensitivity of TAAT-*N*-oxides, which is in agreement with the result of the BDE prediction. The introduction of the N→O bond also does not have much influence on the BDE value of the bonds in TAAT-*N*-oxides.

According to the analysis above, TAATO₂ (Figure 5) is probably the most-promising candidate of TAAT-*N*-oxides, since the stability and sensitivity of TAATO₂ are not badly affected. The important parameters of the optimized structure of TAATO₂ are shown in Table 3 and 4. TAATO₂ has C₂ symmetry. The bond lengths and bond angles of the two

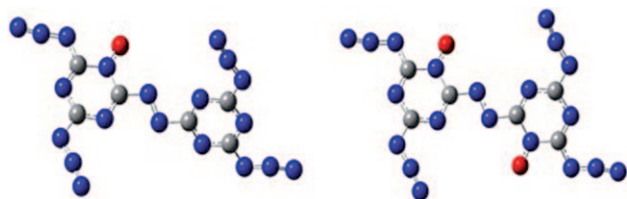


Figure 5. Promising candidates for TAAT-*N*-oxides.

triazine rings are similar to the triazine ring modified by the N→O bond in TAATO_{1c}, whilst the dihedral angle of the two triazine rings changes from −100.5° to −128.2°. Such a change is favorable for the packing of molecules, and results in density improvements. The difference in the heat of formation between TAAT and TAATO₂ is 66 kJ mol^{−1}, whilst the density increases from 1.70 g cm^{−3} to 1.78 g cm^{−3}. As a consequence, the detonation performance of TAATO₂ becomes much better. For example, the Q_v of TAATO₂ is 6508.4 kJ kg^{−1} which is comparable to RDX, whereas the value of TAAT is 6167.6 kJ kg^{−1}. More importantly, the main decomposition product of TAATO₂ is N₂ which is eco-friendly. Both of these will make it a promising energetic compound.

Conclusions

The effects of the N→O bond on the properties of TAAT-*N*-oxides were investigated. Although the heat of formation was lowered a little when the N→O bonds were introduced, energetic compounds with higher density and better oxygen balance were obtained. As a result, the detonation performances of TAAT-*N*-oxides were extremely satisfying. Moreover, the introduction of the N→O bonds had little effect on the ring structure, whilst conformation of the azido group played an important role in determining the positions of the N→O bonds. Attention should be paid to the choice of appropriate positions and numbers of N→O bonds. Finally, TAATO₂, which has shown good detonation performance and moderate sensitivity towards impact, is believed to be a candidate as a potential high energy density material. This work may have further implications for improving the performances of other organic azido compounds.

Experimental Section

Theoretical Study

All calculations were carried out using the Gaussian03 program.^[40] Geometries were optimized at the B3LYP/6-31g(d) level using the default convergence criteria and were conformed to be true local energy minima on the potential-energy surfaces without imaginary frequencies. Details of theoretical calculations were shown in the Supporting Information.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under Grant No. 20772011.

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Received: December 14, 2010

Published online: May 9, 2011