Theoretical study on the *trans–cis* isomerization and initial decomposition of energetic azofurazan and azoxyfurazan

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ABSTRACT

In this work, we carried out the hybrid density functional theory (DFT) calculations in order to understand the thermal *trans–cis* isomerization and initial thermal decomposition of 3,3′-diamino-4,4′-azofurazan (DAAzF), 3,3′-diamino-4,4′-azoxyfurazan (DAAF), 3,3′-dinitro-4,4′-azofurazan (DAAF) and 3,3′-dinitro-4,4′-azoxyfurazan (DAAzF). The relative energy between the *trans-* and *cis*-isomer was also calculated at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory. We found that a negative correlation existed between the relative energy and the sensitivity for these energetic azofurazan and azoxyfurazan compounds, where the higher relative energy means the lower the sensitivity. It was also found that the oxidation of azo-group could cause the decreasing in the relative energy between the *trans-* and *cis*-isomer, as well as the alteration of the isomerization mechanism. An inversion mechanism operates for azofurazan compounds (DAAzF and DNAF) while a rotation mechanism works for azoxyfurazan compounds (DAAF and DNOAF). Compared with the thermal *trans–cis* isomerization, the homolytic cleavage of C–N bond needs to overcome a much higher energy barrier, which indicates that the energy of the external stimulus should firstly trigger the *trans–cis* isomerization, rather than the breakage of C–N bond. A self-desensitization effect caused by the reversible thermal *trans–cis* isomerization process was firstly proposed to explain that the azofurazan and azoxyfurazan compounds are class of energetic materials with lower sensitivity. This new concept (self-desensitization effect) is expected to be useful to design the novel high density, insensitive energetic material.

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1. Introduction

Energetic azofurazan and azoxyfurazan compounds are very important class of furazan-based energetic materials, which have received much attention due to their favorable properties such as high energy density, low sensitivity, good heat stability, and high percentage of nitrogen content. Energetic azofurazan and azoxyfurazan compounds have found great application as an insensitive explosive [1], as well as an energetic additive to modify the properties of rocket propellant and explosive formulations [2,3]. Unlike conventional high energy materials (e.g. nitroamine, nitroester, etc.), energetic azofurazan and azoxyfurazan compounds originate their energy from the positive heat of formation and generation of large volume of N_2. A large quantity of C–N and N–N bonds and low percentage of carbon and hydrogen also endow these compounds with higher density and need of lesser amount of oxygen for combustion.

Azofurazan and azoxyfurazan compounds are made up of two aromatic furazan rings linked by an azo- or azoxy-group, which are generally produced by the oxidation of 3,4-diaminofurazan (DAF) with oxidizing agents (e.g. hydrogen peroxide, sulfuric acid, etc.). Since the 3,3′-diamino-4,4′-azoxyfurazan (DAAF) and 3,3′-diamino-4,4′-azofurazan (DAAzF) were firstly synthesized by Russian scientists in 1981 [4], some works have been focused on the properties of these energetic azofurazan and azoxyfurazan compounds, including thermal stability [1,5], thermal decomposition [6,7], heat of formation [8], detonation [1], sensitivity [8], and so on. Some explosive and propellant formulations containing DAAzF, 3,3′-dinitro-4,4′-azofurazan (DNAF), or 3,3′-dinitro-4,4′-azoxyfurazan (DNOAF) have also been designed and it has found that the addition of these azofurazan or azoxyfurazan compounds can evidently decrease the sensitivity of the explosive formulation [9] or improve the specific impulse of solid propellant [10,11].

Energetic azofurazan and azoxyfurazan compounds with different substituent groups exhibit different sensitivity. For example, Lei et al. [12] have found that, measured under the same conditions, the friction sensitivity (probability of initiating an explosion) of DAAzF, DAAF, and DNOAF are 4%, 36%, and 100%, respectively. In addition, Li et al. [13] also compared the impact sensitivity (H_{50}, the height in centimeters in which a given weight falling upon the compound gives a 50% probability of initiating an explosion) of DAAzF and DAAF. They found that the H_{50} value of DAAzF with 5 kg drop hammer is greater than 140 cm while the value of DAAF is 112 cm. In another paper [14], the H_{50} value of DNOAF was found to be only 7 cm. Clearly, the difference in the molecular structure has effect on the sensitivity for the azofurazan and azoxyfurazan compounds.

It is well known that azobenzene has two isomers: the thermally stable *trans*-form and metastable *cis*-form. These two forms can be converted reversibly into each other by heat or light irradiation [15]. Similar to azobenzene, energetic azofurazan and azoxyfurazan compounds also have the characteristic of the reversible *trans*–*cis* isomerization. In our previous work [16], we have found that a correlation exists between the sensitivity and the relative energy of *trans*- and *cis*-isomers of the energetic azo-compounds. The higher the relative energy, the lower the sensitivity. The relative energy can be regarded as one of the parameters that evaluate the sensitivity of energetic azo-compounds. However, it is still not clear that how the thermal isomerization mechanism and activation energy affect the sensitivity of these energetic azo-compounds. In addition, the initial thermal decomposition reaction is usually considered to be essential for the sensitivity of energetic compound. In the case of energetic azofurazan and azoxyfurazan compounds, the thermal *trans*–*cis* isomerization and initial decomposition belong to a pair of competing reactions. Which process dominates in the initial stage of stimulation will be determined by the activation energies of these reactions. However, little attention has been paid on the competitive relationship of initial decomposition and *trans*–*cis* isomerization.

In this work, four azofurazan derivatives were studied by using ab initio calculation based on a hybrid density functional theory. The initial decomposition and isomerization process were analyzed to explore the possible reason that energetic azofurazan and azoxyfurazan compounds have different sensitivity. Moreover, a self-desensitization effect was proposed to understand the general characteristic that most energetic azofurazan and azoxyfurazan compounds belong to insensitive energetic material.

2. Computational details

Density functional theory (DFT) has been utilized to study the energetic materials [17–20]. The calculations on azobenzene, whose structure is very similar to that of azofurazan, have shown that the hybrid B3LYP/6-31G* method can accurately reproduce the experimental geometries [21,22]. Accordingly, the geometrical parameters of DAAzF, DAAF, DNAF, and DNOAF were optimized at the B3LYP/6-31G(d) level of theory in this work. The transition state (TS) of the thermal *trans*–*cis* isomerization was also obtained with the same method. Harmonic vibrational frequencies were calculated to confirm the stable configurations and transition states. To confirm that the TS is the correct saddle point connecting the *trans*- and *cis*-isomer, intrinsic reaction coordinate (IRC) calculation was further performed. In order to improve the energy accuracy, single-point energy was recalculated at the B3LYP/6-311++G(d,p) level of theory, using the geometries obtained at the B3LYP/6-31G(d) level of theory. The B3LYP/6-31G(d) calculated zero-point vibrational energy (ZPE) was included in the calculation of the relative energy for the isomer and transition state.

Thermal decomposition experiments of DAAzF [6] and DNOAF [7] have suggested that the mechanism of thermolysis and combustion includes the initial rupture of C–N bond connecting the furazan ring and azo- or azoxy-group with subsequent nitrogen evolution and decomposition of the heterocyclic ring. In this study, therefore, the C–N bond homolytic cleavages of these azofurazan and azoxyfurazan compounds were taken into account and the corresponding bond dissociation energies (BDEs) were computed. These thermolysis reactions concerned are given in Scheme 1. For brevity, some of the species are denoted by symbols as shown in Scheme 1. The BDE was calculated at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory. All the calculations were carried out using a Gaussian 03 program package [23]. In addition, natural bond orbitals (NBOs) were investigated using the NBO 3.1 [24] embedded in the Gaussian 03 package.

3. Results and discussion

3.1. Molecular structure and relative energy of trans- and cis-isomer

The B3LYP/6-31G* optimized geometrical parameters of *trans*-DAAzF are given in Fig. 1, where the experimental values (in italics) obtained by the X-ray crystallography are also provided [25]. It can be seen that the theoretical calculation result and the experimental observation indicate that the *trans*-DAAzF has C_2 symmetry. The molecular backbone of *trans*-DAAzF is approximately a planar structure, whereas the two hydrogen atoms of the –NH$_2$ group are out of the molecular plane because of the existence of the lone-pair electrons on the nitrogen of –NH$_2$. For the structural parameters of furazan rings, the theoretical and experimental results are very similar to each other. The calculated N=N bond lengths is 1.274 Å, only about 0.008 Å shorter than the experimental value, although for the C–N bond connecting the azo-group and furazan ring, the difference in length between the calculation and experimental value is about 0.015 Å. The discrepancy of the CNN angle is found to be only 4°. In view of the difference in the molecular environment between the theoretical calculation and experiment (gas-phase vs. condensed-phase), these small discrepancies in the structural parameters are acceptable. Therefore, it is reasonable to optimize the structural parameters of azofurazan compounds at the B3LYP/6-31G* level of theory.

Similar to the case of azobenzene, energetic azofurazan and azoxyfurazan compounds also have two relatively stable configurations. On the basis of the geometry obtained at the B3LYP/6-31G(d) level of theory, the single-point energies of these azofurazan compounds were recalculated at the B3LYP/6-311++G(d,p) level of theory. The total energies and relative energies of the isomers for DAAzF, DAAF, DNAF, and DNOAF are listed in Table 1. It is found that the *trans*-isomer has a lower energy than the *cis*-isomer. The energies of *cis*-isomers are 22.4, 11.5, 9.5, and 5.6 kcal/mol higher than those of *trans*-isomers for DAAzF, DAAF, DNAF, and DNOAF, respectively. The energy difference between the *trans*- and *cis*-isomer of azoxyfurazan (DAAF and DNOAF) is only about half of that of azofurazan (DAAzF and DNAF). The oxidation of azo-group has significantly effect on the relative energy between the *trans*- and *cis*-isomer of azofurazan compounds.

As mentioned above, the sensitivities (e.g. friction and impact sensitivity) are ordered as follows: DNOAF > DAAF > DAAzF [12–14]. A significant negative correlation can be found between the sensitivity and the energy difference of *trans*- and *cis*-isomer. In other words, a larger energy difference means a lower sensitivity. To analyze the reason for this negative correlation, we suggest that, for energetic azofurazan and azoxyfurazan compounds, the *trans*-to-*cis* isomerization process can firstly convert the energy of the external stimulus (e.g. heating, impact, and friction, etc.) into the
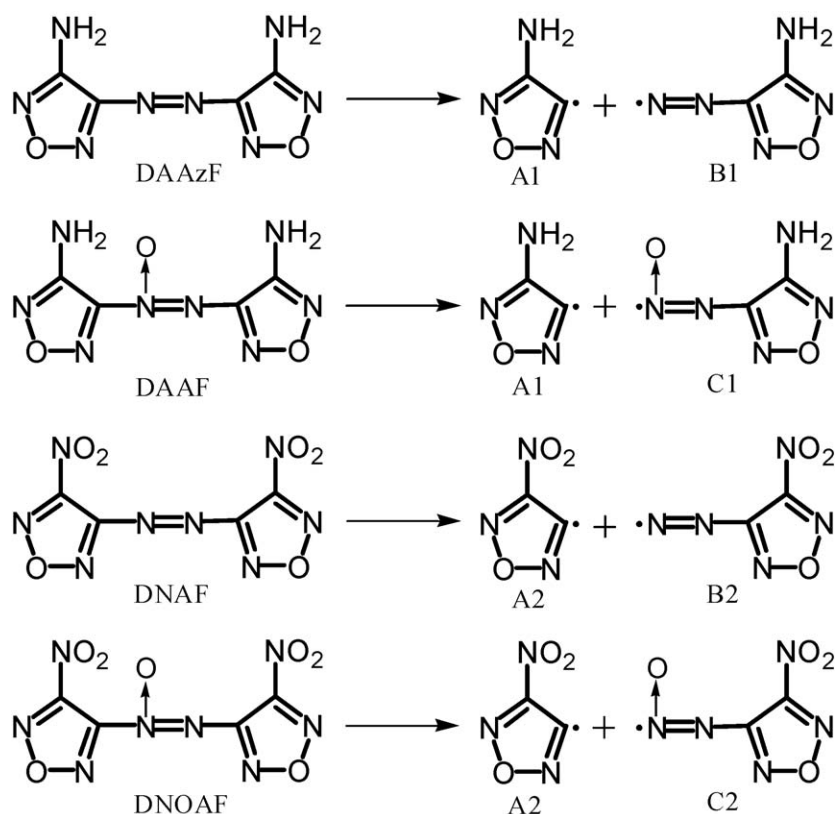
Scheme 1. Initial thermal decomposition (C–N bond homolytic cleavage) of energetic azofurazan and azoxyfurazan compounds.

inner energy of *cis*-isomer, and then the subsequent *cis*-to-*trans* recovery process can gradually dissipate the inner energy. The greater energy difference between the *trans*- and *cis*-isomer means that more external stimuli energy can be converted into the inner energy of *cis*-isomer. That is, once stimulated by heat, impact or friction, etc., DAAzF can dissipate more energy of the external stimulus and may be more likely to inhibit the initial decomposition in comparison with DAAF and DNOAF. This indicates that DAAzF has the higher safety and lower sensitivity than DAAF and DNOAF. The reversible isomerization process, which is expected to be one of the reasons that energetic azofurazan and azoxyfurazan compounds are generally insensitive, is an intrinsic characteristic of this kind of compounds, hence it can be suggested that the azofurazan and azoxyfurazan compounds are class of energetic materials with a property of self-desensitization

A precondition for the reversible *trans–cis* isomerization process inhibiting the initial decomposition of these azofurazan and azoxyfurazan compounds is that the activation energy of isomerization is lower than that of initial decomposition. Accordingly, the isomerization mechanism and initial decomposition should be considered intensively. The corresponding discussions are presented in the next sections.

3.2. Thermal isomerization

The *trans–cis* isomerization of azobenzene has been extensively investigated from both the experimental and theoretical points of view in the past few years [26–31], but little attention has been paid on the thermal isomerization of the energetic azofurazan and azoxyfurazan compounds. The thermal *trans–cis* isomerization mechanism of DAAzF, DAAF, DNAF, and DNOAF are now examined. Fig. 2 gives the transition states that were optimized at the B3LYP/6-31G* level of theory. These transition states were verified by the calculation of the harmonic vibrational frequencies (only one imaginary frequency). IRC calculations were further carried out to confirm that the transition state connects the *trans*- and *cis*-isomer, which can be seen in Fig. 3.

In view of the structure, it can be found that the thermal isomerization processes of the azofurazan and azoxyfurazan compounds mainly involve the CNN angle bending or the CNNC dihedral rotation.

For DAAzF and DNAF in which the two furazan rings are connected by an azo-group, both TS_{DAAzF} and TS_{DNAF} have a semi-linear characteristic with one CNN angle of $\sim177°$ and another of $\sim115°$. During the thermal isomerization process, the most typical change in molecular structure of DAAzF and DNAF is the bending of one of the CNN angles, leading to the formation of a semi-linear transition state. Evidently, the inversion mechanism based on the inversion of CNN angle plays an important role in the thermal isomerization process of DAAzF and DNAF. Nevertheless, the two transition states also show some differences in structure. For example, the two furazan rings of TS_{DAAzF} approximately keep in a plane, but the plane of two furazan rings of TS_{DNAF} are almost perpendicular to each other. This dissimilarity indicates that *trans*-DAAzF firstly occurs the inversion of CNN angle in the molecular plane and the furazan rings sequentially rotate out of the plane when DAAzF is isomerized from *trans*- to *cis*-form via the TS_{DAAzF}. In the case of DNAF, however, the inversion of CNN angle can occur concomitantly with the rotation of furazan ring. The approximate plane structure of TS_{DAAzF} is likely to result from the substitution of NH_2 group which forms the hydrogen bond with the N atom of furazan ring. The length of NH···N hydrogen bond is found to be 2.162 Å.

As for DAAF and DNOAF, the transition states show a twist configuration with the CNNC dihedral of about 90°, which can be seen in Fig. 2. This structural characteristic of TS_{DAAF} and TS_{DNOAF} indicates that a rotation mechanism operates in the *trans–cis* isomerization process of DAAF and DNOAF, which is very different
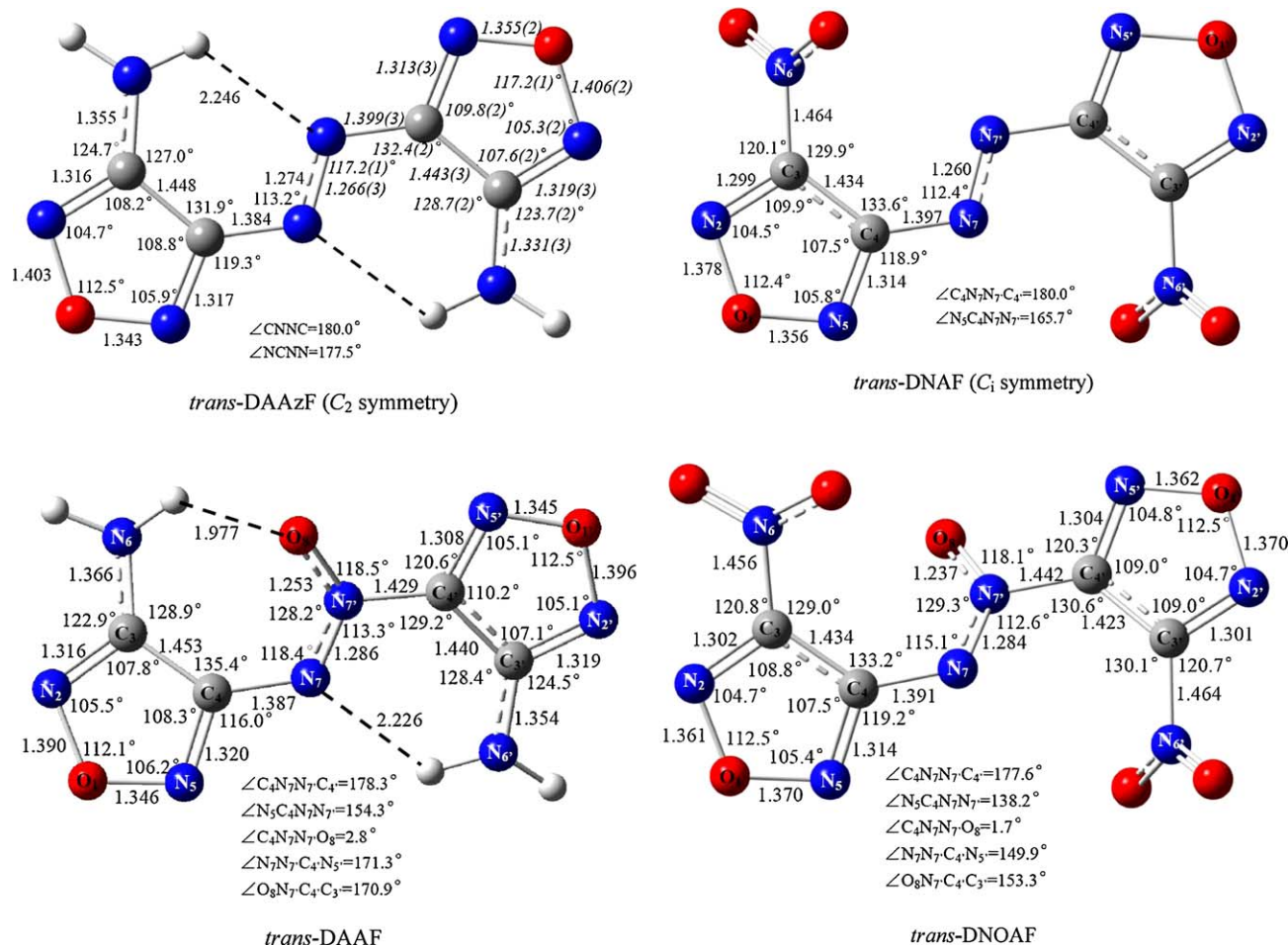
Fig. 1. Structures of *trans*-isomers for DAAzF, DAAF, DNAF, and DNOAF, optimized at the B3LYP/6-31G(d) level of theory. The geometrical parameters obtained by the X-ray crystallography are given in italics [25]. All bond lengths are in angstroms, and bond angles and dihedral angles are in degree.

from the cases of DAAzF and DNAF. Evidently, the oxidation of azo-group has significant effect on the isomerization mechanism of azofurazan compounds.

The energies of the transition state are presented in Table 2. With respect to the *trans*-isomer, the TS_{DAAzF}, TS_{DAAF}, TS_{DNAF}, and TS_{DNOAF} have the energies of 42.6, 32.0, 33.8, 26.9 kcal/mol, respectively. A lower activation energy barrier to be overcome means that the *trans*-isomer can be easily converted to *cis*-isomer. Interestingly, compared to the energies of *cis*-isomers, the relative energies of TS_{DAAzF}, TS_{DAAF}, TS_{DNAF}, and TS_{DNOAF} are close to each other (20.2, 20.5, 24.3, and 21.3 kcal/mol, respectively). The *cis*-to-*trans* isomerization rates are expected to be quite similar for these

azofurazan and azoxyfurazan compounds due to their very close activation energy barriers.

3.3. C–N bond dissociation energy

On the basis of the thermal analysis experiment [6], it has been proposed that the homolytic cleavage of C–N bond connecting the furazan ring and azo-group is the most probable initial step of DAAzF decomposition as N_2 is the only gaseous product formed in the early stage of thermal decomposition. In another work [7], the thermal decomposition characteristic of DNOAF also suggests that the possible thermal decomposition mechanism of DNOAF involves the initial rupture of C–N bond between the furazan ring and azoxy-group with subsequent decomposition of the furazan ring. These experimental results indicate that the homolytic cleavage of C–N bond is very likely to be responsible for the thermal stability and safety (e.g. sensitivity) of the azofurazan and azoxyfurazan compounds. Thus, we stressed the C–N bond dissociation energy in this work.

In view of the molecular structure of DAAzF and DNAF, the two C–N bonds connecting furazan ring and azo-group are identical as *trans*-DAAzF has the C_2 symmetry and *trans*-DNAF has the C_i symmetry. However, this is not the case for *trans*-DAAF and *trans*-DNOAF. Due to the oxidation of azo-group, these two C–N bonds are no longer equal. As an example of *trans*-DAAF shown in Fig. 1, the C_4N_7 and $C_{4'}N_{7'}$ bond lengths are 1.387 and 1.429 Å, respectively. In addition, the natural bond orbital (NBO) theory analysis shows that the C_4N_7 and $C_{4'}N_{7'}$ bond orders are 1.12 and 0.966, respectively.

Table 1
Total energies and relative energies of DAAzF, DAAF, DNAF, and DNOAF.

	Total energy (a.u.)[a]	ZPE (kcal/mol)[b]	Relative energy (kcal/mol)[c]
Trans-DAAzF	−743.28135	72.6	0.0
Cis-DAAzF	−743.24504	72.2	22.4
Trans-DAAF	−818.47630	75.9	0.0
Cis-DAAF	−818.45747	75.6	11.5
Trans-DNAF	−1041.57285	53.7	0.0
Cis-DNAF	−1041.55739	53.5	9.5
Trans-DNOAF	−1116.77059	57.0	0.0
Cis-DNOAF	−1116.76115	56.7	5.6

[a] Calculated at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory.
[b] Obtained at the B3LYP/6-31G(d) level of theory.
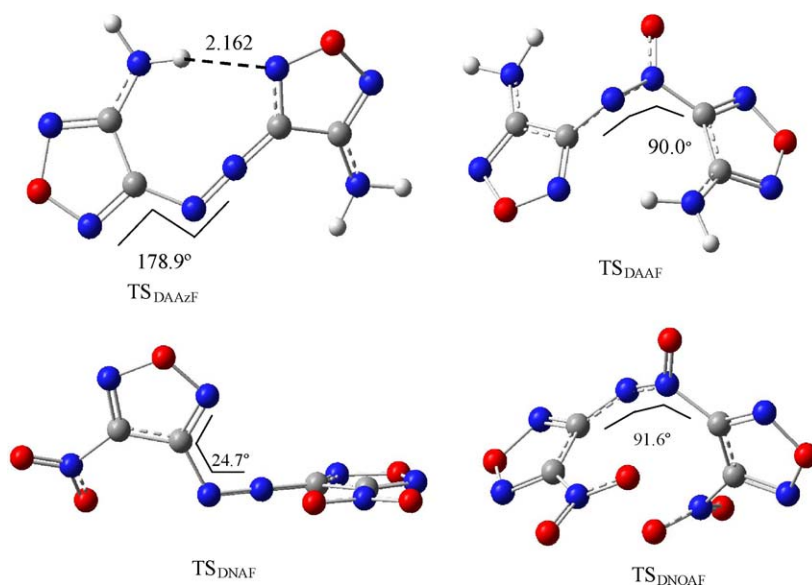[c] Relative to the energy of *trans*-isomer with the ZPE correction.

Fig. 2. Transition states in the thermal *trans–cis* isomerization of DAAzF, DAAF, DNAF, and DNOAF, optimized at the B3LYP/6-31G(d) level of theory.

The calculations on the C–N bond lengths and bond orders of *trans*-DNOAF also give the same trend. From the point of view of geometrical parameter and bond order, the C–N bond on the side of O-atom of azoxy-group should be weaker than the one on the other side, hence it is reasonable to consider the C–N bond homolytic cleavages that are illustrated in Scheme 1 as the initial thermolysis reactions of *trans*-DAAzF, DAAF, DNAF, and DNOAF. The C–N BDEs of these *trans*-isomers were calculated to evaluate the competitive

relationship between the initial thermal decomposition and *trans–cis* isomerization.

The energies of the species originated from the C–N bond homolytic cleavages of DAAzF, DAAF, DNAF, and DNOAF are provided in Table 3. The corresponding C–N BDEs are also given in Table 3. It can be found that the C–N BDE of DAAzF is very close to that of DAAF and the value of DNAF is also very similar to that of DNOAF. This means that the oxidation of azo-group does not result
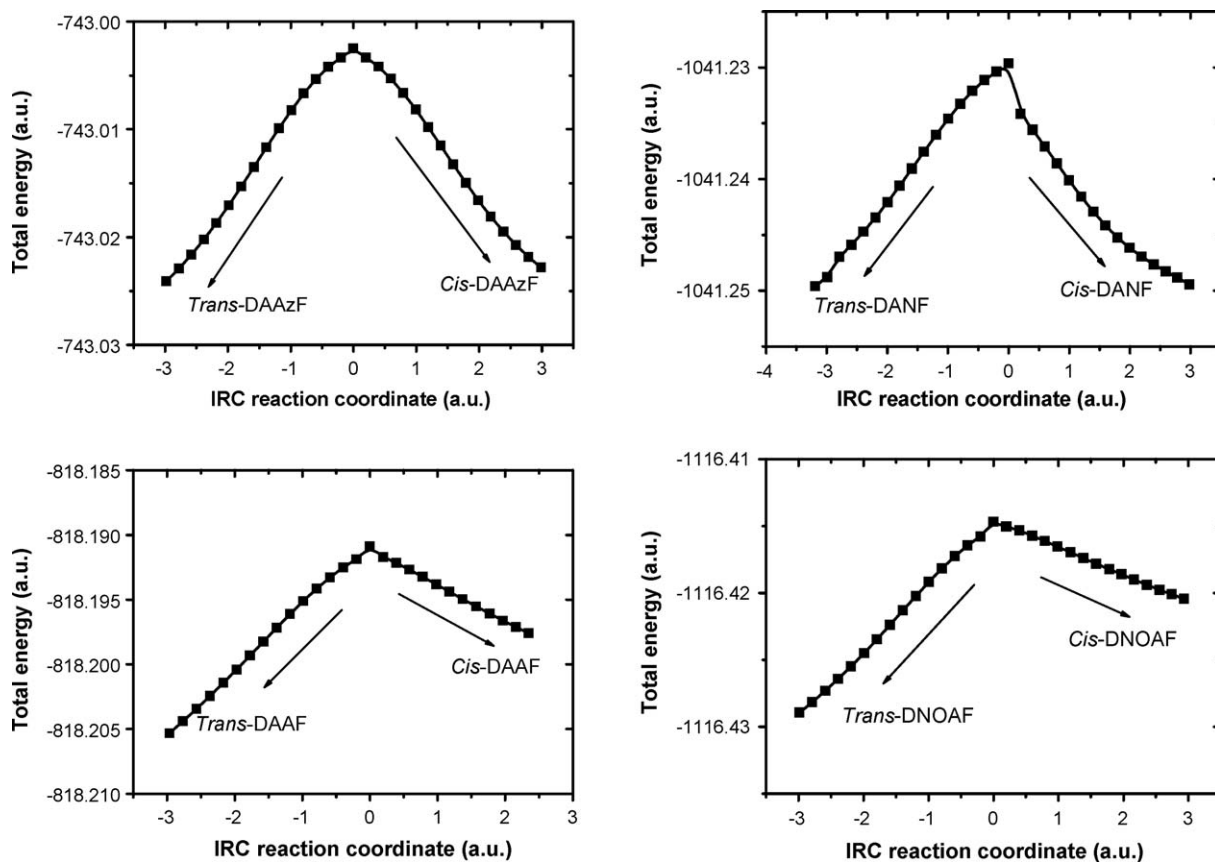

Fig. 3. IRC curves of TS$_{DAAzF}$, TS$_{DAAF}$, TS$_{DNAF}$, and TS$_{DNOAF}$ obtained at the B3LYP/6-31G(d) level of theory.

Table 2
Energies of transition states in the thermal *trans–cis* isomerization of DAAzF, DAAF, DNAF, and DNOAF.

	Total energy (a.u.)[a]	ZPE (kcal/mol)[b]	Relative energy (kcal/mol)[c]	Imaginary frequency (cm^{-1})[b]
TS$_{DAAzF}$	−743.21158	71.4	42.6	467.4
TS$_{DAAF}$	−818.42375	74.9	32.0	330.8
TS$_{DNAF}$	−1041.51701	52.5	33.8	430.3
TS$_{DNOAF}$	−1116.72642	56.2	26.9	310.9

[a] Calculated at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory.
[b] Obtained at the B3LYP/6-31G(d) level of theory.
[c] Relative to the energy of *trans*-isomer with the ZPE correction.

Table 3
Energies of the species and the BDEs in the C–N bond homolytic cleavage of *trans*-isomers for DAAzF, DAAF, DNAF, and DNOAF.

	Total energy (a.u.)[a]	ZPE (kcal/mol)[b]	BDE (kcal/mol)[c]
A1	−316.79762	31.2	–
A2	−465.95547	21.9	–
B1	−426.35658	37.5	–
B2	−575.50453	28.0	–
C1	−501.55071	40.7	–
C2	−650.70423	31.3	–
Trans-DAAzF	–	–	75.9
Trans-DAAF	–	–	76.3
Trans-DNAF	–	–	67.0
Trans-DNOAF	–	–	65.9

[a] Calculated at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory.
[b] Obtained at the B3LYP/6-31G(d) level of theory.
[c] As an example of *trans*-DAAzF, BDE = E_{A1} + ZPE$_{A1}$ + E_{B1} + ZPE$_{B1}$ − ($E_{trans-DAAzF}$ + ZPE$_{trans-DAAzF}$), calculated at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory.

in the remarkable change in the C–N BDE of azofurazan compounds, although the molecular structure is clearly affected by the oxidation of azo-group. On the other hand, amino-substituted azofurazan derivatives (DAAzF and DAAF) have a larger C–N BDE than the nitro-substituted azofurazan derivatives (DNAF and DNOAF), which could be used to explain the reason that the DAAzF and DAAF are more insensitive to friction and impact than DNOAF. Only in view of the BDE, the very similar C–N BDEs of DAAzF and DAAF indicate that the two azofurazan compounds should have the similar sensitivity. However, this prediction is inconsistent with the experimental observation [12–14]. That is, there are some other factors that determine the difference in the sensitivity of DAAzF and DAAF.

Comparing the energies shown in Tables 2 and 3, it can be found that the energy required for the C–N homolytic cleavage is much higher than the activation energy barrier of *trans–cis* isomerization for DAAzF, DAAF, DNAF, and DNOAF. Therefore, the energy of the external stimulus (e.g. heat, impact or friction) should firstly trigger the *trans–cis* isomerization, rather than the breakage of C–N bond for these azofurazan and azoxyfurazan compounds. As discussed before, the energy of the external stimulus can be dissipated by the reversible *trans–cis* isomerization process and the relative energy between *trans*- and *cis*-isomers is directly related to the ability to inhibit the initial thermal decomposition. The difference in the sensitivity of the azofurazan and azoxyfurazan compounds may be attributed to the different relative energy between the *trans*- and *cis*-isomers.

4. Conclusion

In the present study, the thermal *trans–cis* isomerization and initial decomposition of DAAzF, DAAF, DNAF, and DNOAF were studied using B3LYP hybrid DFT method. Our calculation results

show that, for the azofurazan and azoxyfurazan compounds, the relative energies between *trans*- and *cis*-isomer are in the following order: DAAzF > DAAF > DNAF > DNOAF. This order is reverse to the ordering of the sensitivity of these energetic compounds. In addition, it is found that the thermal *trans–cis* isomerization of azofurazan and azoxyfurazan compounds follows a different mechanism: an inversion mechanism operates for DAAzF and DNAF while a rotation mechanism works for DAAF and DNOAF. The oxidation of azo-group has significantly effect on the isomerization mechanism, as well as the relative energy between the *trans*- and *cis*-isomer. In comparison with the thermal *trans–cis* isomerization, the homolytic cleavage of C–N bond involves the overcoming of a much higher energy barrier, which indicates that the energy of the external stimulus should firstly trigger the *trans–cis* isomerization, rather than the breakage of C–N bond. On the basis of the analysis of the *trans–cis* isomerization, we firstly proposed that a self-desensitization effect resulting from the reversible *trans–cis* isomerization process could be responsible for the low sensitivity of the azofurazan and azoxyfurazan compounds. This new desensitization mechanism may be useful to design the novel high density, insensitive energetic material.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmgm.2009.04.007.

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