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Effect of Fluoro Substituents on Polynitroarylenes: Design, Synthesis and Theoretical Studies of Fluorinated Nitrotoluenes

Junlin Zhang,[a,b] Yingzhe Liu,[a] Jing Zhou,[a] Fuqiang Bi,[a] and Bozhou Wang*[a]

Abstract: The replacement of traditional polynitroarylenes by their fluorinated derivatives have attracted great attention due to the improvements on detonation performances caused by fluorinated effect. A straightforward synthesis of three novel fluorinated nitrotoluenes with different degree of nitration were achieved under selected high temperatures. The existence of fluorine exerted remarkable influence on the nitration process through electron-withdrawing effect and possible mechanism of the transformation was proposed according to the experimental results. Thermal decomposition behaviors of the fluorinated nitrotoluenes were investigated by differential scanning calorimetry and all the compounds showed ideal low melt points for melt-cast process. X-ray analysis of the molecules were carried out with electronic density and electrostatic potential on molecular surface of the optimized structures calculated by density functional theory. The good thermal and detonation properties make the newly developed fluorinated nitrotoluenes possible to replace trinitrotoluene (TNT) and dinitrotoluene (DNT) in the formation of melt-cast energetic materials.

Introduction

Fluorinated energetic materials are subject of intensive research due to the excellent detonation properties.[1] Calculation studies demonstrate that high fluorine content along with the presence of hydrogen leads to the formation of hydrogen fluoride (HF) upon detonation, generating a large amount of energy, and the existence of fluorine could also improve the densities of the molecules.[2] During recent decades, strategies for the preparation of fluorinated energetic materials focused on the introduction of fluorine-rich groups as pentafluorosulfanyl (–SF$_5$)[3], difluoramino (–NF$_2$)[4], fluorodinitromethyl[5] and fluoronitromethyl-ONN-azoxy[6] group, which have been widely applied in the design and synthesis of new energetic structures with great success. (Figure 1) However, intrinsic relationship between the promotion of energy-density level and introduction of fluorine is still unclear, which severely hampers the development of new high-performing energetic materials.
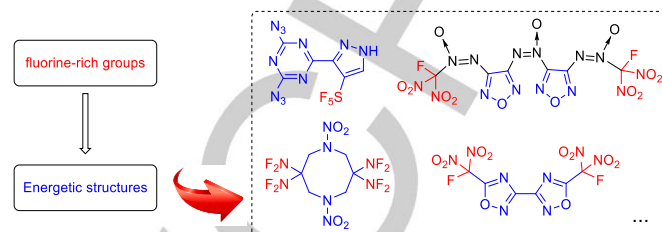
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Figure 1. FLUORINE-rich groups in energetic materials

Polynitroarylenes have contributed enormously to the progress and prosperity of mankind and are still applied as one of the most important class of explosives[7]. Although the detonation performances are not outstanding, some polynitroarylenes as 2,4,6-trinitrotoluene (TNT) and dinitrotoluene (DNT) exhibit ideal melting point (80~110℃) which permits melt casting of charges and make them highly important energetic binder for cast compositions.[8] From synthetic point of view, TNT and DNT were obtained by nitration treatment of toluene, meanwhile, DNT was usually obtained as annoying mixtures of 2,6-dinitrotoluene and 2,4-dinitrotoluene. (Figure 2)
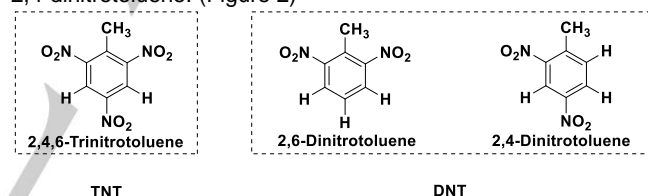

Figure 2. TNT and DNT structures

Nitration by mixed acid is the most widely used method for direct nitration of aromatic molecules and any increase or decrease in electron density will significantly influence the nitration effect.[9] Compared with the nitration of electron-deficient aromatic substrates, nitration of electron-rich aromatic substrates are much easier.[10] In aromatic structures, the newly formed nitro groups are generally located at the *o*- and *p*-positions of the activate substituents, whereas at the *m*-positions of the deactivate substituents.[11] (Figure 3) For the aromatic substrates with some highly strong deactivating substituents, direct nitration will be extremely difficult.[12] Therefore, direct nitration of fluorinated aromatic substrates has long been regarded as a formidable task due to the strong deactivating effect caused by the existence of fluorine.
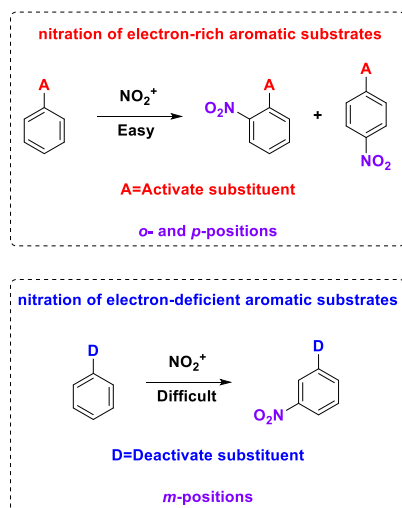
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Figure 3. Direct nitration of aromatic substrates

Here, we reported a straightforward synthesis of three novel fluorinated nitrotoluene molecules, 3,5-difluoro-2,4,6-trinitrotoluene (DFTNT), 3,5-difluoro-2,4-dinitrotoluene (DFDNT) and α,α,α,3,5-pentafluoro-2,4-dinitrotoluene (PFDNT). All the molecules were synthesized through nitration reactions under selected temperatures from electron deficient aromatics with high fluorine content. Thermal decomposition behaviors were investigated by differential scanning calorimetry and further compared with TNT and DNT, whereas densities, heats of formation, detonation velocities and pressures were calculated through computational methods. In addition, the optimized structure, electronic density and electrostatic potential on surface of the molecules were calculated with density functional theory for better understanding the fluorinated effect on energetic structures[13]. The deep research on the fluorinated nitrotoluenes will promote the studies of fluorinated energetic materials as well as the intrinsic mechanism of nitration process under high temperatures.

Results and Discussion

Synthetic studies and structure analysis

Replacement of traditional polynitroarylenes by their fluorinated derivatives have attracted great attention for the improvements on detonation performances caused by fluorinated effect, however, synthesis of fluorinated polynitroarylenes is highly difficult due to the limited synthetic approaches. All-fluorinated TNT, for instance, is supposed to be a super energetic molecule, but its preparation has never been achieved. Generally, there are two strategies to introduce fluorine into energetic structures. The most commonly used approach is modification of the existing molecules through fluorination reactions. In contrast, introduction of fluorine through direct nitration of fluorinated structures are rarely applied. During recent application research on TNT and DNT, it occurred to us that direct nitration of fluorinated aromatic hydrocarbons might provide a shortcut access to new fluorinated nitrotoluenes. To

investigate the chemical reactivity of the direct nitration strategies, 3,5-difluorotoluene and α,α,α,3,5-pentafluorotoluene were chosen and treated with HNO_3-H_2SO_4 mixture, the most widely used condition for the preparation of polynitroarylenes. To our disappointment, no desired products were detected. Obviously, the electron-deficient character of the substrates hampered the transformations and more strenuous conditions or reagents were required. After screening various nitration conditions and reagents, we finally arrived at conditions for the successful direct nitration transformation by using Oleum-$NaNO_3$ mixture as NO_2^+ source under selected high temperatures. (Scheme 1)

TNT and DNT were synthesized through direct nitration of toluene, but the products were usually obtained as mixtures with different degree of nitration. To our delight, single product was successfully achieved under our newly developed nitration process. By using Oleum-$NaNO_3$ mixture as the source of NO_2^+, 3,5-difluoro-2,4,6-trinitrotoluene (DFTNT) was obtained at the heating temperature of 160℃ while 3,5-difluoro-2,4-dinitrotoluene (DFDNT) was achieved as the only product at the heating temperature of 70℃. Obviously, temperature should be one of most important factors for the nitration process. When α,α,α,3,5-pentafluorotoluene was chosen as the substrate, α,α,α,3,5-pentafluoro-2,4-dinitrotoluene (PFDNT) was also achieved as the only product. No all-fluorinated TNT was observed during the heating process and the compound began to decompose when the heating temperature was further raised. From the synthetic point of view, it seemed that the newly formed nitro groups in PFDNT prevented the introduction of the third nitro group, leading to the failure in the preparation of all-fluorinated TNT (PFTNT), however, it is also possible caused by the decomposition of all-fluorinated TNT under high temperature.
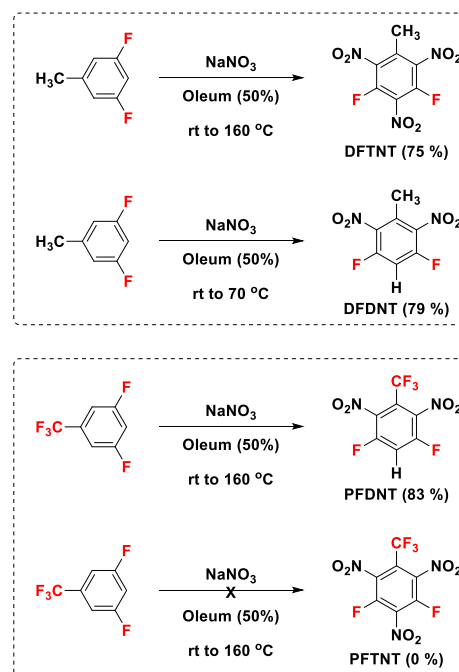
Scheme 1. Synthetic studies towards fluorinated nitrotoluenes.

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Suitable crystals of DFTNT, DFDNT and PFDNT for X-ray analysis were obtained by dissolving the compounds in a minimum amount of ethyl acetate held at room temperature, followed by filtration of the crystals after the volume of ethyl acetate had been reduced. The crystal structures of DFTNT, DFDNT and PFDNT were illustrated in Figure 4. Interestingly, strong hydrogen-bonding interaction was found between the fluoride in the aromatic ring and the hydrogen in the methyl group while no similar hydrogen-bonding interaction observed in the crystal structures of DFTNT or PFDNT, indicating that the hydrogen-bonding interaction of the fluorinated nitrotoluenes mainly existed between aromatic hydrogen and fluorine atom.
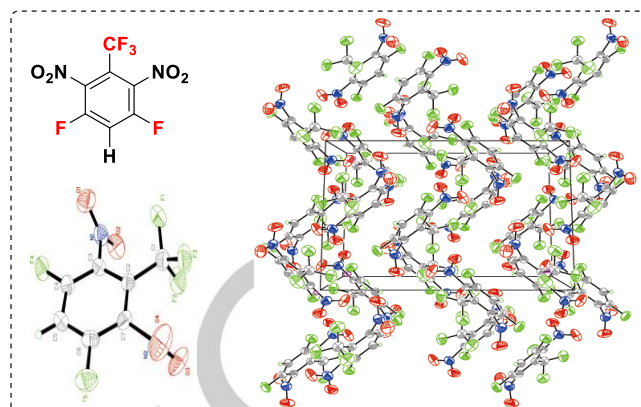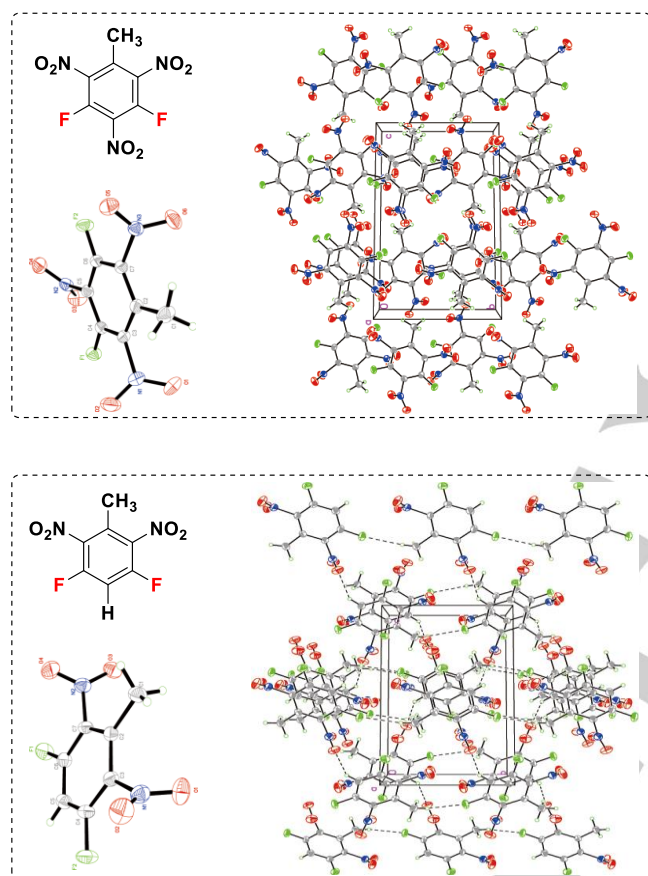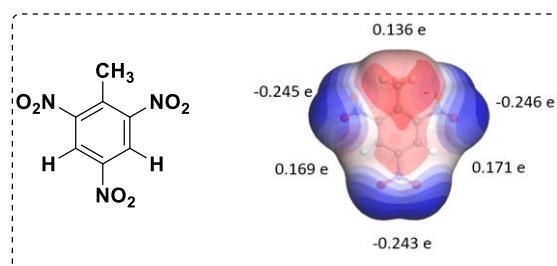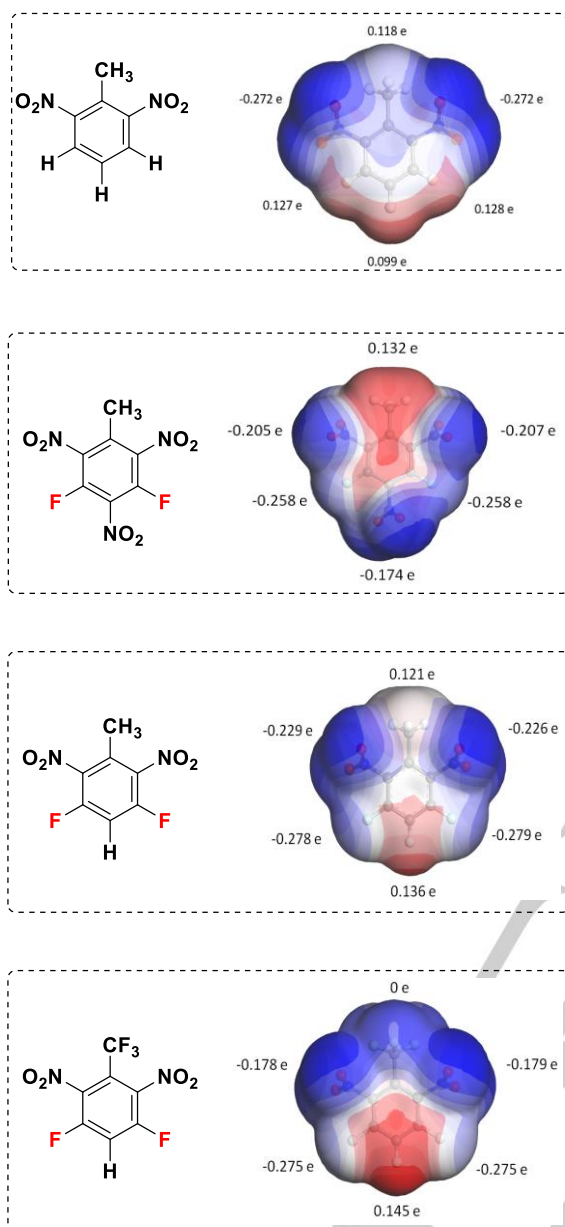

Figure 4. ORTEP diagram (50% probability) of DFTNT, DFDNT and PFDNT.

Eelectrostatic potentials (ESPs) on 0.001 au (electrons/Bohr^3) isosurfaces of electron density of the molecular structures DFTNT, DFDNT and PFDNT were studied by density functional theory and the general gradient approximation method in Dmol^3 module of Material Studio 8.0 software with the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional and the DNP basis set to further clarify the experimental results and mechanism of the transformations[13]. According to theoretical investigation of the relationship between stabilities and the charges of the nitro group in organic nitro compounds, nitro group Mulliken charges can be regarded as a structural parameter to estimate the stabilities of the nitro compounds. The compound with more negative Mulliken Charges of the nitro group will be more insensitive and usually gives a larger value of impact sensitivity H_{50}[14]. Calculations of DFTNT, DFDNT and PFDNT including optimizations, Mulliken population and frequency analyses were performed and the results were demonstrated in Figure 5. Compared with DFDNT, the Mulliken charges of nitro group in PFDNT is much more positive, which indicated that PFDNT is much less stable; therefore, the failure in the preparation of all-fluorinated TNT was more likely caused by the decomposition of PFDNT under high temperature.

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influenced the packing form of crystals remarkably. After the introduction of fluorine into DNT and TNT, the densities of molecules increased noticeably.

Table 1. Hirshfeldsurfaces[a] of crystal stacking[b] of TNT, DFTNT, DNT, DFDNT and PFDNT

TNT	O…H	O…C	O…O		
	46.0%	18.5%	17.9%		
DFTNT	O…H	F…O	O…C	O…O	
	27.0%	24.5%	16.5%	16.2%	
DNT	O…H	H…H	O…O		
	48.8%	19.4%	10.4%		
DFDNT	O…H	F…O	F…H	O…O	
	32.0%	17.1%	16.3%	10.8%	
PFDNT	F…O	F…F	O…C	O…H	O…O
	25.5%	25.2%	13.7%	10.8%	10.7%

[a] Only attributes of the Hirshfeld surface larger than 10% were displayed.
[b] Hirshfeld surface analyses were achieved through CrystalExplorer 3.0 program.

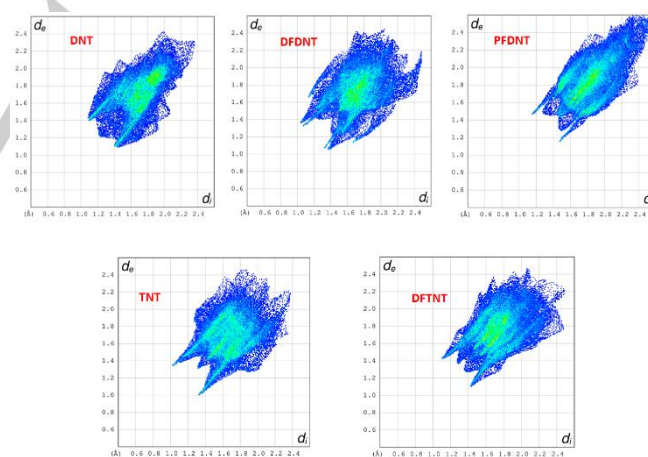**Figure 5.** ESPs on isosurfaces of electron density of TNT, DNT, DFTNT, DFDNT and PFDNT's crystal structures.

Hirshfeld surfaces are widely used to identify and quantify the interaction nature and proportion in crystals.[15] Hirshfeld surface analyses of DFTNT, DFDNT and PFDNT were achieved through CrystalExplorer 3.0 program[16] and further compared with DNT and TNT to study their intermolecular interactions. (Table 1 and Figure 6) After the fluorine was introduced into DNT and TNT, the interactions between fluorine and other atoms appeared. Interestingly, extra interactions of F…O and F…H increased significantly in DFDNT while extra interactions of F…O and F…F increased sharply in PFDNT. In contrast, compared with TNT, only extra interaction between fluorine and oxygen emerged apparently in DFTNT. Different intermolecular interactions

Figure 6. Hirshfeldsurfaces of crystal stacking of nitrotoluenes and their derivatives.

Studies on energetic properties and thermal decomposition behaviors of the fluorinated nitrotoluenes

TNT and DNT were widely applied as ideal organic solvents in the preparation of melt-cast explosives for their capability in the dissolution of numerous energetic materials resulting in acceptable processing viscosities. After the introduction of

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fluorine into these nitrotoluenes, most of the performances of the energetic molecules were improved obviously except for the sensitivities, which were higher than TNT and DNT due to the weaker hydrogen-bonding interactions. (Table 2)

Table 2. Physical and energetic properties of newly developed fluorinated nitrotoluenes compared with TNT and DNT

Compd	DFTNT	TNT	DFDNT	PFDNT	DNT
M [g·mol^{-1}]	263	227	218	272	182
Ω[a] [%]	-51.7	-73.9	-80.7	-47.0	-114.3
ρ[b] [g·cm^{-3}]	1.82	1.65	1.73	1.82	1.54
$\Delta_f H$[c] [kJ·mol^{-1}]	-273.8	18.4	-326.6	-917.3	12.9
IS[d] (H$_{50}$) [cm]	53	102	62	29	125
P[e] [Gpa]	27.2	19.5	17.9	17.1	16.4
V$_D$[f] [m·s^{-1}]	7435	6909	6642	6077	6263

[a] Oxygen balance assuming the formation of CO_2. [b] Gas pycnometer (25°C). [c] Calculated molar enthalpy of formation. [d] Impact sensitivity. [e] Detonation pressure. [f] Detonation velocity.

As potential ideal energetic materials for melt-cast explosives, researches on thermal behaviors of DFTNT, DFDNT and PFDNT are crucial for their further applications. Therefore, the research on thermal behaviors of DFTNT, DFDNT and PFDNT were carried out through DSC method. (Figure 7) Under heating, continuous endothermic curves could be observed from the DSC experiment, indicating the sustained volatilizations of these molecules. DFTNT and PFDNT melted at the temperature of 78.0℃ and 80.1℃, which are close to the melt point of TNT and DNT. However, DFDNT melted at a much higher temperature (101.8℃). The higher melt temperature is very likely caused by the strong hydrogen-bonding interaction in DFDNT. (Figure 4) With the further rise of heating temperature, a spontaneous endothermic volatilization process of DFTNT, DFDNT and PFDNT were also observed clearly, which means large amount of vapor was generated after the melt process. When the heating temperature was up to 220℃, the decomposition process of DFDNT and PFDNT started. DFTNT showed even better thermal stability and the decomposition of DFTNT started only when the heating temperature was higher than 290℃. DSC studies showed that the thermal decomposition processes of DFTNT, DFDNT and PFDNT were complex, which was caused by secondary decomposition reactions of the pyrolysis products. The low melting points and good thermal stabilities of the molecules rendered them excellent application prospect in the preparations of melt-cast energetic materials.
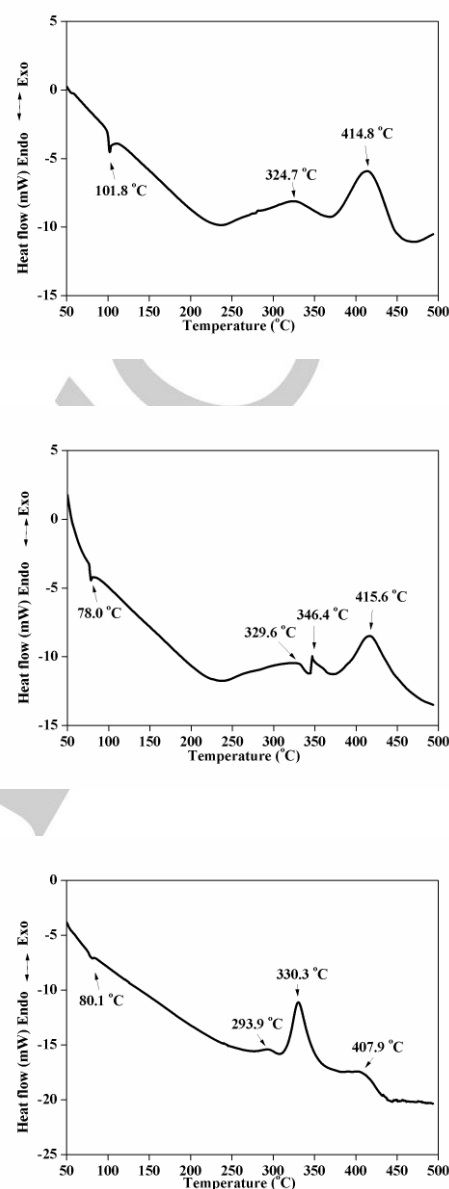
Figure 7. DSC curve of DFDNT, PFDNT and DFTNT.

Conclusions

Three novel fluorinated nitrotoluenes were obtained via nitration processes under selected high temperatures and their structure studies were achieved through quantum calculation and crystals analysis. The amount of the nitro groups induced to the highly electron deficient aromatics was dependent on the reaction conditions and single dinitration products could be successfully obtained without their isomers under the newly developed nitration method. The Mulliken Charges of nitro group in PFDNT is much more positive than DFDNT, indicating molecule structure can easily decompose in the preparation of all-fluorinated TNT

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under high temperature. Hirshfeld surface analyses showed that different intermolecular interactions influenced the packing form of crystals remarkably and the introduction of fluorine into DNT and TNT led to obvious increase of molecule densities. Furthermore, the good energetic properties, low melting points and good thermal stabilities of the molecules rendered them excellent application prospect in the formation of melt-cast energetic materials.

Experimental Section

Reagents and sample preparation

TNT (99.0%), DNT (99.0%) and Oleum (50%) were supplied by Xi'an Modern Chemistry Research Institute. 3,5-Difluorotolune, 3,5-difluorobenzotrifluoride and sodium nitrate were purchased from Accela Chem Bio Co., Ltd (Shanghai, China) without further purification.

General Procedure for the synthesis of DFTNT and PFDNT:

Oleum (50%, 75 mL) was placed in a three-neck flask, to which NaNO$_3$ (4.25 g, 50 mmol) was added in several potions and the temperature was kept below 50℃ during the addition. After the addition, fluorinated toluene (10 mmol) was added carefully. The mixture was heated to 80℃ and allowed to stir for 10 min at this temperature. The reaction was then further heated to 160℃ and stirred for another 3 h before cooled to room temperature. The mixture was poured into ice (200 g) and stirred for 1 h. The formed solid was filtered and washed by H$_2$O (20 mL) for three times to give a white solid product.

Apparatus and measurements

The thermal analysis experiments were performed with a model TG-DSC STA 449C instrument (NETZSCH, Germany). Operation conditions: sample mass, 0.6 mg; dynamic nitrogen; stainless steel seal cell; heating rate, 10℃·min-1; temperature range, 20℃~500℃. Single crystal X-ray experiment was carried out on a Bruker Apex II CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) using ω and φ scan mode. Structures were solved by the direct method using SHELXTL and refined by means of full-matrix least-squares procedures on F^2 with the programs SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters.

CCDC 1873174 (DFTNT), 1873178 (PFDNT) and 1873177 (DFDNT) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgements

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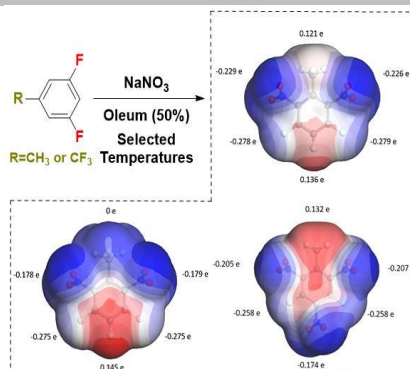
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