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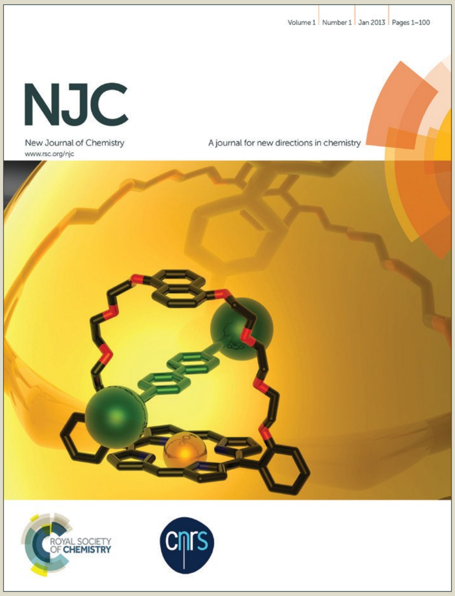

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Studies on the synthesis and properties of polynitro compounds based on esteryl backbones

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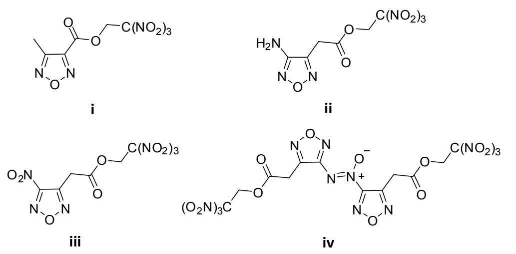
Zhen Xu, Hongwei Yang and Guangbin Cheng*[a]

Four esteryl-bridged energetic compounds were derived from 2,2,2-trinitroethanol with polynitro benzoic acids and characterized by IR, multinuclear NMR spectroscopy, elemental analysis as well as differential scanning calorimetry (DSC). The structures of 2,2,2-trinitroethyl 2,4,6-trinitrobenzoate(**5**), bis(2,2,2-trinitroethyl) 4,6-dinitroisophthalate(**6**), bis(2,2,2-trinitroethyl) 2,5-dinitroterephthalate(**7**) and bis(2,2,2-trinitroethyl) 2,4,6-trinitroisophthalate (**8**) were further confirmed by X-ray diffraction studies, which show favorable densities (1.804-1.850 g cm^{-3}). Interestingly, most of the polynitro esters decompose at temperatures over 180 °C (expect for **6 :** 171.6 °C), exhibit good thermal stability. In addition, the performance calculations gave detonation pressures and velocities for the ester derivatives in a range of 30.4-32.9 GPa and 8267-8559 m s^{-1}, respectively. The esteryl-bridged compounds possess acceptable impact sensitivities (14-22 J), friction sensitivities (240–360 N), and electrostatic sensitivities (0.20-0.32 J). These values indicate that polynitro esters can be candidates as promising energetic materials.

Introduction

Over the past decades, research on the energetic materials that combine high performance and low sensitivities is ongoing in many research groups worldwide.[1] However, these requirements are somewhat mutually exclusive. Materials with higher stability and lower sensitivity often exhibit poorer energetic performance and vice versa. The goal is often to discover an optimum balance between them. Driven by increasing demands from both military and civilian applications,[2] structural design of energetic molecules has to meet diverse standards, such as performance properties, environmental compatibility, as well as safety concerns.[3] Given these backgrounds, rational introduction of polynitro groups requires not only pursuing the highest detonation velocity and pressure, but also addressing the problems of thermal stability and impact insensitivity in order to obtain final products with acceptable properties. Polynitro functionalized compounds are one of the most significant structural motifs in High-energy density materials (HEDMs) since most of them have positive oxygen balance values and high densities, which are positively correlated with their energetic performances.[4-12]

Molecules which contain polynitro groups are one of the important classes of useful high energetic materials, such as triaminotrinitro benzene (TATB), 1,3,5-trinitrotriazacyclohexane (RDX), 1,3,5,7-tetranitrotetraazacyclooctane (HMX), and octanitrocubane (ONC) are well-known. Of the nitro-based functional groups, the trinitroethyl group is a fascinating energetic unit in a lot of high-energy, high-density compounds. The incorporation of the trinitroethyl group into nitro-rich parent compounds is helpful to enhance the oxygen balance and density of the energetic materials, which improves the detonation performances.[13-15] Additionally, 2,2,2-trinitroethanol has long been recognized as a useful building block for such materials.[16] In the past few years, many efforts have been undertaken in the chemistry of trinitroethyl esters to evaluate



Scheme 1 Trinitroethyl esters derivatives based on furazan rings.

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[a] School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing, P. R. China. E-mail: hyang@mail.njust.edu.cn, gcheng@mail.njust.ed.cn

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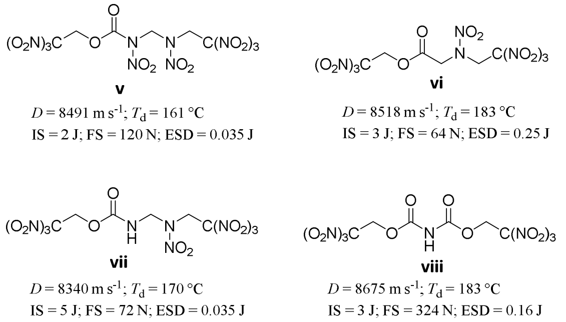


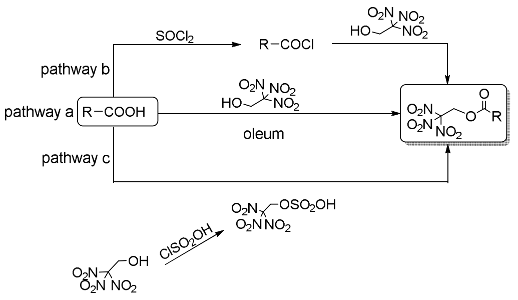
Scheme 2 Trinitroethyl esters derivatives based on modified aliphatic acids.

their potential as energetic materials.[16-21] The esterification of 1,2,5-oxadiazolylacetic acids with 2,2,2-trinitroethanol was reported.[16, 17] Nevertheless, their detonation performances have not been described (scheme 1). Recently, a series of energetic polynitro esters were derived from amino acid glycine and oxalyl chloride (scheme 2).[20] The effective method is remarkable to improve the pressure and velocity of explosives. However, their thermal and energetic performance are not quite satisfying because of relatively low decomposition temperatures and high sensitivity towards impact and friction, as well as electrical discharge. To address these issues, the multi-nitrophenyl structures were introduced into the polynitro esters. As known, phenyl-containing energetic compound is more stable toward thermal and external stimuli.

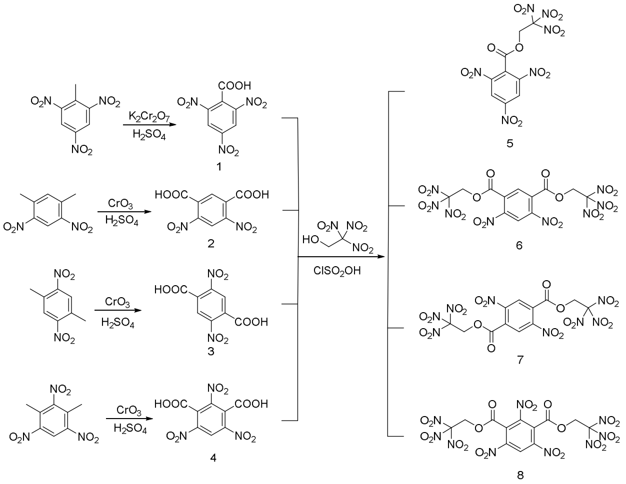
Herein, a new family of trinitroethyl esters based on polynitro benzoic acids were synthesized. The combination of polynitro benzoic acid and trinitroethyl moieties into one molecule is expected to increase the oxygen balance so as to improve the detonation performance. All the energetic compounds were well characterized by IR and multinuclear NMR spectroscopy, differential scanning calorimetry (DSC), elemental analysis and further supported by single crystal X-ray diffraction. Their key detonation properties and sensitivity towards impact, friction and electrical discharge were determined by experimental and theoretical methods.

Results and discussion

Synthesis



Scheme 3 Three pathways for esterification of 2,2,2-trinitroethanol



Scheme 4 synthesis of compounds **5**-**8**

In general, trinitroethyl esters were synthesized from the esterification of carboxylic acids and 2,2,2-trinitroethanol in three pathways (scheme 3). The primitive way is to adopt the so-called sulfuric acid catalyzed esterification, such as the direct reaction of benzoic acids with the easily available 2,2,2-trinitroethanol in the sulfuric acid medium at high temperatures (scheme 3, pathway a). An alternative to this is the nucleophilic substitution of chlorine atoms in active benzoic acid chlorides with 2,2,2-trinitroethanol (scheme 3, pathway b). The third and effective route, is by transesterification of trinitroethylsulfuric acid with aromatic acids (scheme 3, pathway c). However, the low reactivity of polynitro alcohol requires the use of a strong condensing agent or a reactive carboxylic acid derivative to effect reaction. Initially, we did not succeed in isolating the desired polynitro benzoic acid chlorides to following pathway a, owing to the chlorides are unstable compounds and decompose in the attempt of isolating them in the individual state. While pathway b was used in this trial, polynitro benzoic acids decomposed at high temperatures by sulfuric acid catalyzed esterification. Hence, to afford trinitroethyl derivatives of polynitro benzoic acids, we turn to try the transesterification reaction in pathway c. The polynitro benzoic acids were dissolved in 2,2,2-trinitroethylsulfuric acid prepared from 2,2,2-trinitroethanol and chlorosulfonic acid led to polynitro esters in good yields. The synthetic pathway to all of the new energetic materials **5**-**8** is illustrated in Scheme 4, the starting compounds such as 2,4,6-trinitrobenzoic acid (**1**), 4,6-dinitroisophthalic acid (**2**), 2,5-dinitroterephthalic acid (**3**) 2,4,6-trinitroisophthalic acid (**4**) and 2,2,2-trinitroethanol were synthesized according to the literatures. The 2,4,6-trinitrobenzoic acid (**1**) was dissolved in 2,2,2-trinitroethylsulfuric acid led to 2,2,2-trinitroethyl 2,4,6-trinitrobenzoate (**5**). When reaction temperature is below 60 °C, the reaction of **1** with 2,2,2-trinitroethylsulfuric acid affords a low yield of **5** (<40%). Enhancing of temperature from 60 °C to 80 °C is favorable to improve yield of **5** to 86 %. Further increase of temperature resulted in yield decline, which could be attributed to the decomposition of **1** by the decarboxylation at 90-100 °C. In addition, excess of 2,2,2-trinitroethanol (2-fold) and chlorosulfonic acid (3-fold) were used to increase the reaction rate and they are easily removed by washed with cold water. Bis(2,2,2-trinitroethyl) 4,6-dinitroisophthalate (**6**), bis(2,2,2-trinitroethyl) 2,5-

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dinitroterephthalate (**7**) and bis(2,2,2-trinitroethyl) 2,4,6-trinitroisophthalate (**8**) can also be obtained from the reaction of aromatic acids **2**, **3** or **4** with 2,2,2-trinitroethylsulfuric acid in the similar way.

Spectroscopy

The structures of the new polynitro derivatives **5-8** are supported by IR, ^{1}H and ^{13}C NMR spectroscopic data as well as elemental analysis. In the IR spectra of **5**-**8**, the characteristic asymmetric stretching vibrations ν_{as} NO_2 are found in the range of 1638–1539 cm^{-1} and the symmetric stretching vibrations ν_s NO_2 at 1310-1295 cm^{-1}. The signals lie in the range of 1678–1600 cm^{-1} representing the stretching vibrations of C=O, strong absorption peaks at 1350-1010 cm^{-1} are attributed to the C-O bond of the ester groups. The vibration around 3100 cm^{-1} and 1400 cm^{-1} can be interpreted as the stretching vibrations of methylene groups as well as signals for valence vibrations of C–H in the polynitro benzene ring around 2900 cm^{-1}.

For compounds **5**-**8**, in the ^{1}H NMR spectra, the hydrogen signals of the methylene groups, which are attached to the ester side chains appeared between δ = 6.23 and 6.30 ppm. For compounds **5** and **8**, the proton signals of polynitro benzene rings are located in the range of δ = 9.43 to 9.49 ppm, which are at a little lower field than that of compounds **6** (δ = 8.89, 8.82 ppm) and **7** (δ = 8.66 ppm) owing to the electron-withdrawing property of the additional nitro groups. In the ^{13}C NMR spectra of all compounds, the carbon resonance signals of the trinitromethyl moieties can be found as weak peaks around the chemical shifts of 125 ppm, which is in good agreement with previously recorded shifts for similar compounds. Moreover, the carbon atoms of the methylene moiety are identified at δ = 63.46 (**7**) to 64.58 ppm (**8**) at the highest field while the carbon signals of carbonyl groups are observed in a range from δ = 159.34 (**8**) to 161.25 ppm (**6**). Four distinct peaks are observed in the polynitroaryl moiety belong to compounds **5** and **8** in the ^{13}C NMR spectra, the resonances of two carbon atoms appear around 149 ppm, and another two nearly 127 ppm. However, for compounds **6** and **7**, only one carbon signal of the polynitroaryl group locates in the lower field around 150 ppm and another two (**7**) or three (**6**) can be detected between δ = 122 and 134 ppm. It can be attributed to the fact that the electron-withdrawing inductive effect of trinitroaryl moiety is stronger than dinitroaryl moiety.

X-ray crystallography

Single crystals of **5**, **6**, **7** and **8**, suitable for single-crystal X-ray diffraction, were obtained by slow solvent evaporation method at room temperature and normal pressure. Selected crystallographic data are summarized in Table 1. Their structures are shown in Fig. 1-8.

Crystals of **5** suitable for crystal-structure analysis were obtained by recrystallization from the component solvent of dichloromethane and n-hexane. It crystallizes in the monoclinic space group $P2_1/c$, with a cell volume of 1508.4(2) Å^3 and four molecules per unit cell. A calculated density of 1.850 g cm^{-3} was determined from the X-ray crystal structure at 173 K. The torsion angle of O3-C7-C2-C1 is equal to 98.028(208)°, this shows that a very distorted system is formed by the benzene ring and the branch appendage. The length of the C8-O3 bond is 1.435 Å, shows typical C-O single bond value, which is longer than that of C7-O3 (1.337(2) Å) due to the strong electron-withdrawing influence of the carbonyl group. As shown in Fig. 2, crystal packing of **5** shows that the 3D network is criss-crossed. It can be clearly seen that intermolecular hydrogen bonds between the CH_2 group and the oxygen atoms of nitro group, C8−H8A ··· O5 and C8−H8B ··· O4. Additional information about crystal **5** can be found in the Electronic Supplementary Information (ESI).

An appropriate crystal of **6** for X-ray analysis was obtained from dichloromethane, and the structure was determined by low-temperature X-ray diffraction (Fig. 3). It crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell (Z= 4) and the calculated density is 1.815 g cm^{-3} (173 K). The esteryl groups are twisted out of the benzene ring plane with torsion angles of C5–C4–C7–O5, 71.074(231)°; C1–C6–C10–O13, -38.722(260)°. It is seen that the molecule is asymmetric due to the hydrogen bonds and distinction between C1-*NO_2* group and C3-*NO_2* group in the benzene ring. Therefore, there are small differences in the parameters of the bond lengths, the N–O bonds in C1-*NO_2* moiety are in the range of 1.218(2)-1.222(2) Å and are significantly longer than that of C3-*NO_2* moiety (1.179(11)-1.197(11)), because of the C3-*NO_2* has a unstable structure and a spatial range of oscillation. In the packing diagram of **6**, intra-molecular hydrogen bond (C8−H8B···O6) and intermolecular hydrogen bonds (C2−H2···O7, C5−H5···O17, C8−H8B···O6, C11−H11A···O14, C11−H11B···O16) are observed. These extensive hydrogen-bonding interactions form a complex 3D network within the structure of **6**.

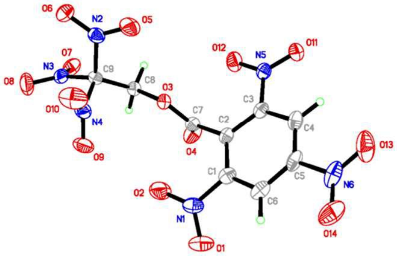

Fig. 1 Molecular structure of **5**. Hydrogen atoms are shown, but are unlabeled for clarity.

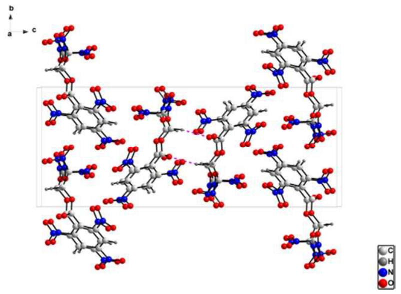

Fig. 2 Ball and stick packing diagram of **5** viewed down the b axis. Dashed lines indicate strong hydrogen bonding.

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Table 1 Crystallographic data for **5**, **6**, **7** and **8**

Crystals	**5**	**6**	**7**	**8**
Formula	$C_9H_4N_6O_{14}$	$C_{12}H_6N_8O_{20}$	$C_{12}H_6N_8O_{20}$	$C_{12}H_5N_9O_{22}$
Formula weight	420.18	582.25	582.25	627.25
Temperature	173(2) K	173(2) K	173(2) K	173(2) K
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
***a*(Å)**	5.8335(4)	14.3744(16)	12.9246(18)	13.8583(10)
***b*(Å)**	10.1818(8)	8.2651(10)	10.0302(15)	16.6279(13)
***c*(Å)**	25.563(2)	19.305(2)	8.6402(12)	10．0771(6)
***α*(°)**	90	90	90	90
***β*(°)**	96.540(3)	111.692(3)	106.913(3)	103.879(2)
***γ*(°)**	90	90	90	90
V (Å^3)	1508.4(2)	2131.2(4)	1071.6(3)	2254.3(3)
Z	4	4	2	4
ρ_{calc} (g·cm^{-3})	1.850	1.815	1.804	1.848
GOF on F^2	1.026	1.027	1.043	1.041
FinalR indexes [I>2σ(I)]	R_1 = 0.0362, wR_2 = 0.0752	R_1 = 0.0380, wR_2 = 0.0657	R_1 = 0.0426, wR_2 = 0.0872	R_1 = 0.0398, wR_2 = 0.0724
Final R indexes	R_1 =0.0680, wR_2 =0.0866	R_1 = 0.0799, wR_2 = 0.0759	R_1 =0.0619, wR_2 = 0.0955	R_1 =0.0816, wR_2 = 0.0847
CCDC	1447319	1447314	1447110	1447316

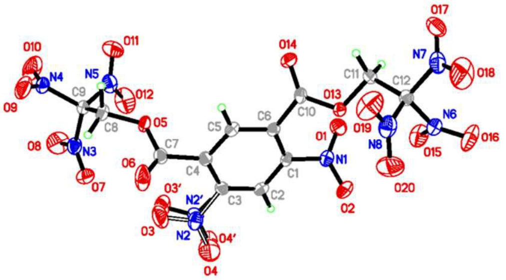

Fig. 3 Molecular structure of **6**. Hydrogen atoms are shown, but are unlabeled for clarity.

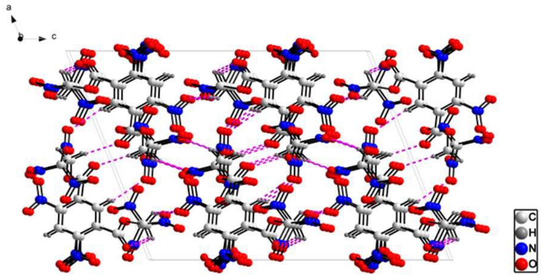

Fig. 4 Ball and stick packing diagram of **6** viewed down the b axis. Dashed lines indicate strong hydrogen bonding.

Single crystals of **7** were obtained from acetonitrile solution. It crystallizes in the monoclinic space group $P2_1/c$ with a higher than that of **6**, means the molecule packing of **7** is less compact. Intuitively, the density of **7** is lower than that of **6**. As shown in Fig. 6, the hydrogen bonds are observed in the packing diagram. The oxygen atoms (O4, O7 and O10) in the trinitromethyl groups are involved into the formation of the non-classical hydrogen bonds with the CH_2 fragments (C3−H3⋯O10, C3−H3⋯O7 and C5−H5B⋯O4) formed a complex 3D network.

Compound **8** crystallizes from dichloromethane in a monoclinic space group $P2_1/c$ with four molecules per unit cell. The calculated density is 1.848 gcm^{-3} (173 K), higher than that of **6** owing to the addition of a nitro group. The C-C bonds of the benzene ring in **8** are slightly longer than the corresponding bonds in **6** due to the strong

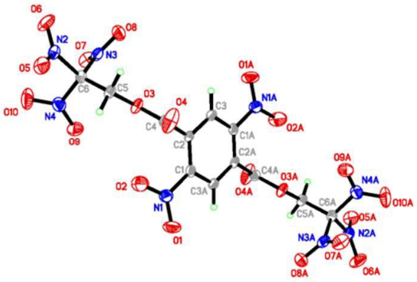

Fig. 5 Molecular structure of **7**. Hydrogen atoms are shown, but are unlabeled for clarity.

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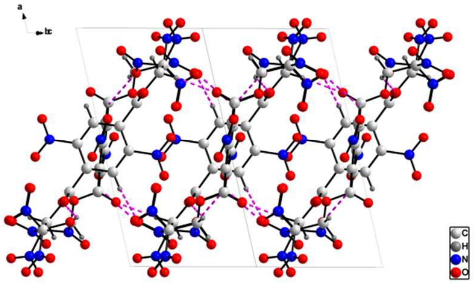

Fig. 6 Ball and stick packing diagram of **7**. Dashed lines indicate strong hydrogen bonding.

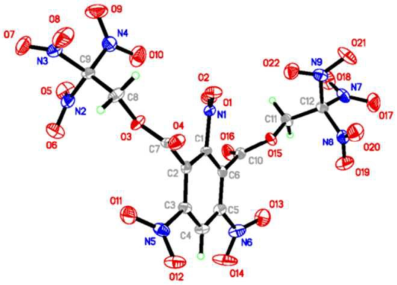

Fig. 7 Molecular structure of **8**. Hydrogen atoms are shown, but are unlabeled for clarity.

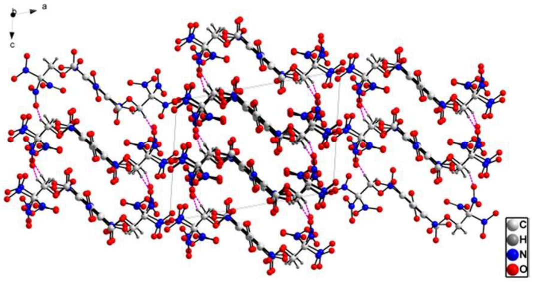

Fig. 8 Ball and stick packing diagram of **8** viewed down the b axis. Dashed lines indicate strong hydrogen bonding.

electron-withdrawing influence of the additional nitro group. The geometry of the trinitromethyl moiety is consistent with that of the similar moiety in the literature.[22] The C-N bond lengths of the trinitromethyl groups are in the range of 1.515-1.525 Å, longer than that of normal C-N single bond (1.469(3)-1.480(3) Å), located on both sides of the benzene ring. A similar difference is also observed in other compounds. As illustrated in Fig. 8, non-classical intermolecular hydrogen bonds C8–H8B⋯O5 and C11–H11⋯O19 were observed within the structure of **8** owing to the acidity of the methylene protons.

Energetic materials properties

Thermal stability is one of the most important physicochemical properties of energetic materials. The thermal behavior of all products was investigated by differential scanning calorimetry (DSC) at a heating rate of 5 °C min^{-1} in Al pans. The plots were shown in the ESI. As summarized in Table 2, while **5**, **7** and **8** were melting at 134.3 °C, 185.1 °C and 133.3 °C, and **6** do not melt prior to decomposition. In particular, the decomposition process of **6** and **7** possess two steps with the peak temperatures. However, the other energetic esters exhibit one exothermic process. Most of these compounds show broad exothermic peaks, which indicate extremely slow decomposition. Except for compound **6**, which decompose at 171.6 °C, the decomposition onset temperatures of the other energetic compounds are observed in a range from 187.3 (**8**) to 193.2 °C (**5**), higher than that of trinitroethyl esters reported (as showing in scheme 2).[20] As known, a thermal stability above 180 °C is an essential requirement for energetic compounds to adaptation for practical use.[23-24] Compared to TNT and TATB, compounds **5**-**8** have lower decomposition temperatures, the undesirable thermal behavior maybe due to the introduction of trinitromethyl moieties and esteryl structures.

The sensitivities of the resulting compounds **5**-**8** toward impact and friction were tested by using standard BAM method.[25] As depicted in Table 2, the impact sensitivity (IS) values of trinitroaryl derivatives (**5**: 17.4 J, **8**: 14 J) are lower than that of dinitroaryl derivatives (**6**: 20 J, **7**: 22 J), because of the presence of additional nitro moiety within their structures. All compounds are less sensitive than RDX (7.5 J), and except for the compound **8**, the IS values of other polynitro compounds are much higher than that of TNT (15 J). Moreover, similar trends can be found at the friction sensitivity (FS) values, the FS values of **5**-**8** are 280 N, 320 N, 360 N and 240 N, respectively. Additional, all new compounds were tested for sensitivity toward electrical discharge by an ESD JGY-50 III electric spark tester.[26] As illustrated in Table 2, the electrostatic sensitivities (ESD) of polynitro derivatives **5** (0.28 J), **6** (0.30 J) and **7** (0.32 J) were lower than that of RDX (0.10-0.20 J). The ESD value of compound **8** (0.20 J) is comparable to that of RDX. Compared with the trinitroethyl esters have been described (as depicted in scheme 2), compounds **5**-**8** exhibit good sensitivities.

The heat of formation (HOF) plays an important role in evaluating the performance of energetic materials. The heats of formation of the resulting compounds **5**-**8** were calculated based on appropriate isodesmic reactions. Calculations were carried out using the Gaussian 09 program suite. The geometry optimization of the structures and frequency analyses were carried out using the B3LYPn functional with the 6-311 + G** basis set. All of the optimized structures were characterized by true local energy minima on the potential energy surface without imaginary frequencies. As summarized in Table 2, the resulting compounds **5**-**8** exhibit unsatisfactory heats of formation. The calculated values fall in the range from -534.9 (**7**) to -243.9 kJ mol^{-1} (**5**) , which are extremely negative due to the feature of esteryl backbones.

By using the calculated values of the heats of formation and density from gas pycnometer experiments, the detonation velocities (*D*) and pressures (*P*) of compounds were calculated based on the empirical Kamlet-Jacobs (K-J) equations. The detonation performance data are summarized in Table 2, the detonation velocities of compounds **5**-**8** range from 8267 (**7**) to 8559 m s^{-1} (**8**), which indicates that the detonation velocities of all are comparable to that of TATB (8114 m s^{-1}, 31.2 GPa). Their detonation pressures are found in the range between 30.4 (**7**) and 32.9 GPa (**8**), in which the highest detonation pressure value of **8** (32.9 GPa) is slightly lower than that of RDX (34.9 GPa).

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Table 2 The physicochemical properties of **5**-**8** compared with trinitrotoluene (TNT), triaminotrinitrobenzene (TATB) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX)

Compounds	T_m [a] [°C]	T_d [b] [°C]	Ω_{CO} [c] [100%]	Ω_{CO2} [d] [100%]	ρ [e] [g cm^{-3}]	D [f] [m s^{-1}]	P [g] GPa	$\triangle H_f$ [h] [kJ mol^{-1}]/[kJ g^{-1}]	IS [i] [J]	FS [j] [N]	ESD [k] [J]
5	134.3	193.2	11.43	-22.86	1.839	8389	31.7	-243.9/-0.58	17.4	280	0.28
6	-	171.6	13.75	-19.24	1.807	8320	30.9	-504.2/-0.87	20	320	0.30
7	185.1	192.7	13.75	-19.24	1.792	8267	30.4	-534.9/-0.92	22	360	0.32
8	133.3	187.3	19.14	-11.48	1.832	8559	32.9	-500.3/-0.80	14	240	0.20
TNT[l]	80.4	295	-24.7	-73.8	1.654	6881	19.5	-295/-1.30	15	-	-
TATB[l]	-	324	-18.6	-55.8	1.94	8114	31.2	-154.2/-0.60	50	-	-
RDX[m]	-	204	0	-21.6	1.80	8795	34.9	70.3/0.32	7.5	120	0.10-0.20[n]

[a] Melting point. [b] Thermal decomposition temperature under nitrogen gas (determined by the DSC exothermal peak, 5 °C min^{-1}). [c] Oxygen balance, assuming the formation of CO; the oxygen balance of ammonium perchlorate is 34.0 %. [d] Oxygen balance (%) for CaHbNcOd: OB (%) = 1600 * (d-2a-b/2)/Mw (based on carbon dioxide). [e] Density measured by gas pycnometer at 25°C. [f] Detonation velocity. [g] Detonation pressure. [h] Calculated molar enthalpy of formation in solid state. [i] Impact sensitivity. [j] Friction sensitivity. [k] Sensitivity against electrostatic discharge. [l] Data from ref. 27. [m] Data from ref. 28. [n] Data from ref. 29.

Conclusion

A family of esteryl-bridged energetic compounds was synthesized by polynitro benzoic acids and the 2,2,2-trinitrorthanol. All of the new compounds were well characterized. Additionally, the structures of them were confirmed by single-crystal X-ray diffraction analysis. According to the DSC results, except for the compound **6** ($T_{d,onset}$ = 171.6 °C), the decomposition onset temperatures of other compounds are higher than 180 °C, which indicates that these new energetic compounds possess good thermal stabilities. In particular, compared with these esters have been reported, compounds **5**, **7** and **8** are potential candidates for energetic materials with good thermal stabilities owing to the existence of multi-nitrophenyl structures. As known, oxygen balance (OB) is an important parameter to classify energetic materials, trinitroethyl group introduced into materials is helpful to enhance the oxygen balance. Assuming the formation of CO_2, OB values of the polynitro esters in the range from -22.86 % to -11.48 %, which are comparable to RDX (-21.6 %). Nevertheless, based on CO, OB values of the polynitro esters are rising to the range from 11.43 % to 19.14 %, much higher than that of RDX (0 %). The calculated detonation velocities lie in the range between 8267 and 8559 m s^{-1}. The detonation pressures range from 30.4 to 32.9 GPa. Particularly, compounds **5** (31.7 GPa and 8389 m s^{-1}) and **8** (32.9 GPa and 8559 m s^{-1}) also exhibit moderate detonation properties, which are significantly higher than those of TATB (31.15 GPa and 8114 m s^{-1}). Additionally, for all energetic polynitro esters, their impact sensitivity values are found in the range between 14 (**8**) and 22 J (**7**). The friction sensitivity values range from 240 (**8**) to 360 N (**7**), which shows that they are significantly less sensitive than RDX (7.5 J, 120 N). The simple synthetic route and the good detonation properties of these compounds suggest potential application as energetic materials.

Experimental

General methods

^1H and ^{13}C NMR spectra were recorded on 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometers operating at 300 and 75 MHz, respectively, by using acetone-d_6 as the solvent and locking solvent unless otherwise stated. Chemical shifts in ^1H and ^{13}C NMR spectra are reported relative to acetone. The decomposition temperatures were determined by a differential scanning calorimeter (DSC823e instruments) at a heat rate of 5 °C min^{-1}. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Analyses of C/H/N were performed with a Vario EL III Analyzer. The electrostatic sensitivity tests were carried out with an Electric Spark Tester ESD JGY-50 III. The sensitivities towards impact and friction were determined by using a HGZ-1 drophammer and a BAM friction tester.

X-ray crystallography

The data for **5**, **6**, **7** and **8** were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 173(2) K during the data collection. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data Reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogenatoms were located and refined.

Syntheses

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Caution: Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged.

2,4,6-trinitrobenzoic acid (**1**),[30] 4,6-dinitroisophthalic acid (**2**),[31] 2,5-dinitroterephthalic acid (**3**),[32] 2,4,6-trinitroisophthalic acid (**4**)[33] and 2,2,2-trinitroethanol[34] were synthesized according to the literatures procedures.

Synthesis of 2,2,2-trinitroethyl 2,4,6-trinitrobenzoate (5)

2,2,2-trinitroethanol (0.9 g, 5.0 mmol) was added slowly to chlorosulfonic acid (0.5 mL, 7.5 mmol) at -10 °C. The reaction mixture was gradually warmed to 50 °C and stirred for 1 h, then 2,4,6-trinitrobenzoic acid (**1**: 0.64 g, 2.5 mmol) was added, keeping the temperature at 80 °C for 2 h, the reaction mixture was cooled to room temperature and poured on ice. The precipitate was filtered off, washed with water and dried *in vacuo* to afford 0.903 g yellow powder in a yield of 86 %. DSC: $T_{\mathrm{d,onset}}$ = 193.2 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ = 9.43 (s, 2H, -C*H*-), 6.29 (s, 2H, -CH_2-) ppm. ^{13}C NMR (75 MHz, Acetone-d_6) δ = 160.42 (-*C*OO-), 150.08 (-*C*(NO$_2$)(C(COO-))), 148.20 (-*C*NO$_2$), 127.52 (-*C*(COO-)), 126.61 (-*C*H-), 125.00 (-*C*(NO$_3$)$_3$), 64.37 (-*C*H$_2$-) ppm. IR (KBr): 3547(s), 3011(w), 2964(w), 2893(w), 1764(s), 1613(s), 1550(s), 1459(m), 1438(m), 1344(s), 1304(s), 1258(s), 1178(m), 1117(s), 1088(s), 1067(s), 926(m), 881(w), 850(w), 800(m), 781(m), 732(m). Elemental analysis calcd (%) for $C_9H_4N_6O_{14}$ (420.16): C 25.73, H 0.96, N 20.00; found C 25.12, H 1.02, N 19.84 .

Synthesis of bis(2,2,2-trinitroethyl) 4,6-dinitroisophthalate (6)

2,2,2-trinitroethanol (0.9 g, 5.0 mmol) was added slowly to chlorosulfonic acid (0.5 mL, 7.5 mmol) at -10 °C. The reaction mixture was gradually warmed to 50 °C and stirred for 1 h, then 4,6-dinitroisophthalic acid (**2**: 0.32 g, 1.25 mmol) was added, keeping the temperature at 80 °C for 2 h, the reaction mixture was cooled to room temperature and poured on ice. The precipitate was filtered off, washed with water and dried *in vacuo* to afford 0.582 g yellowish powder in a yield of 80 %. DSC: $T_{\mathrm{d,onset}}$ = 171.6 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ = 8.89 (s, 1H, -C*H*(C-NO$_2$)), 8.84 (s, 1H, -C*H*(C-COO)), 6.23 (s, 4H, -CH_2-) ppm. ^{13}C NMR (75 MHz, Acetone-d_6) δ = 161.25 (-*C*OO-), 150.95 (-*C*NO$_2$), 133.56 (-*C*(COO-)), 129.08 (-*C*H-C(NO$_2$)), 124.77 (-*C*H-C(COO-)), 122.46 (-*C*(NO$_3$)$_3$), 62.42 (-*C*H$_2$-) ppm. IR (KBr): 3503(w), 3112(m), 3056(m), 3018(m), 2968(m), 2892(m), 1763(s), 1598(s), 1549(s), 1437(m), 1387(m), 1350(s), 1296(s), 1235(s), 1183(m), 1153(m), 1116(m), 852(w), 832(w), 799(s), 778(s). Elemental analysis calcd (%) for $C_{12}H_6N_8O_{20}$ (582.22): C 24.76, H 1.04, N 19.25; found C 24.12, H 0.98, N 19.04 .

Synthesis of bis(2,2,2-trinitroethyl) 2,5-dinitroterephthalate (7)

A similar procedure was followed as that described above for **6**, 2,5-dinitroterephthalic acid (**3**: 0.32 g, 1.25 mmol) was subjected to the same method to obtain 0.604 g **7** as yellowish solid in a yield of 83 %. DSC: $T_{\mathrm{d,onset}}$ = 171.6 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ = 8.89 (s, 1H, -C*H*(C-NO$_2$)), 8.84 (s, 1H, -C*H*(C-COO)), 6.23 (s, 4H, -CH_2-) ppm. ^{13}C NMR (75 MHz, Acetone-d_6) δ = 161.25 (-*C*OO-), 150.95 (-*C*NO$_2$), 133.56 (-*C*(COO-)), 129.08 (-*C*H-C(NO$_2$)), 124.77 (-*C*H-C(COO-)), 122.46 (-*C*(NO$_3$)$_3$), 62.42 (-*C*H$_2$-) ppm. IR (KBr): 3503(w), 3112(m), 3056(m), 3018(m), 2968(m), 2892(m), 1763(s), 1598(s), 1549(s), 1437(m), 1387(m), 1350(s), 1296(s), 1235(s), 1183(m), 1153(m), 1116(m), 852(w), 832(w), 799(s), 778(s). Elemental analysis calcd (%) for $C_{12}H_6N_8O_{20}$ (582.22): C 24.76, H 1.04, N 19.25; found C 24.12, H 0.98, N 19.04 .

Synthesis of bis(2,2,2-trinitroethyl) 2,4,6-trinitroisophthalate (8)

A similar procedure was followed as that described above for **6**, 2,4,6-trinitroisophthalic acid (**4**: 0.38 g, 1.25 mmol) was subjected to the same method to obtain 0.596 g **8** as brown solid in a yield of 83 %. DSC: $T_{\mathrm{d,onset}}$ = 187.3 °C. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 9.46 (s, 1H, -C*H*-), 6.28 (s, 4H, -CH_2-) ppm. ^{13}C NMR (75 MHz, Acetone-d_6) δ = 159.34 (-*C*OO-), 149.10 (-*C*(NO$_2$)(C(COO-))), 147.61 (-*C*(NO$_2$)(C(COO-))(-CH-)), 127.88 (-*C*-C(COO-)), 127.75 (-*C*H-), 123.64 (-*C*(NO$_3$)$_3$), 63.49 (-*C*H$_2$-) ppm. IR (KBr): 3439(w), 3106(w), 3015(w), 2964(w), 2895(w), 1777(s), 1604(s), 1550(s), 1439(m), 1390(m), 1343(s), 1298(s), 1219(s), 1149(s), 1089(m), 1041(w), 924(w), 854(w), 795(m), 736(m). Elemental analysis calcd (%) for $C_{12}H_5N_9O_{22}$ (626.95): C 22.98, H 0.80, N 20.10; found C 22.19, H 0.83, N 19.51 .

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Four polynitro esters were derived from 2,2,2-trinitroethanol with multi-nitrobenzoic acids by transesterification.

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