

## Inorganic Chemistry

## Energetic Materials - Nitrated Phenyl Peroxy Anhydrides as Peroxide Based Explosives with Relatively High Densities and Thermal Stabilities

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Nine different nitrated phenyl peroxy anhydrides were synthesized using two different strategies and crystal structures of two compounds were determined. Sensitivities of the compounds toward impact, friction and electrostatic discharge were measured and the thermal stability was determined.

Some of the compounds are remarkable insensitive and they show relatively high thermal decomposition points for organic peroxides. Detonation parameters and performance data were calculated using the EXPLO5 program yielding performance values in the range of trinitrotoluene (TNT).

## Introduction

Peroxy anhydrides are an interesting class of molecules which features the characteristic CO(OO)CO-moiety. The most prominent example is dibenzoyl peroxide which finds excessive application as initiator for radical polymerizations, since it is known to decompose in radicals.<sup>[1]</sup> However, detailed studies about the decomposition products of different, mostly polar substituted peroxy anhydrides revealed, that the compounds can decompose homolytically as well as heterolytically depending on the polarity of the environment.<sup>[2-3]</sup> Another application of dibenzoyl peroxide is the treatment of acne.<sup>[4]</sup> Peroxy anhydrides can also be used for the formation of C-C-bonds by exposing them to light, electric current or heat.<sup>[5]</sup> A very recent paper reports on the use of peroxyanhydrides as reagents for the synthesis of unsaturated esters starting from 1,3-dienes.<sup>[6]</sup> However there are a lot of other molecules which feature this moiety. Even cyclic derivatives are known, for example in the form of diphenoyl peroxide.<sup>[7]</sup> In this study, the compound was used for the production of electronically excited states. Another peroxy anhydride that is particularly interesting with respect to energetic materials is peroxy trifluoroacetic acid anhydride, which can be prepared by the reaction of trifluoroacetic acid and sodium peroxide at low temperatures.<sup>[8]</sup> This molecule has a positive oxygen balance which means it carries more oxygen in it as is needed for its complete combustion and could therefore be used as an oxidizer. However it is extremely sensitive toward outer stimuli and hydrolyses at ambient temperature into trifluoroacetic acid and peroxy trifluoroacetic acid.<sup>[8]</sup> The synthesis of organic peroxy anhydrides very often is performed by reacting the corresponding acyl chloride with aqueous hy-

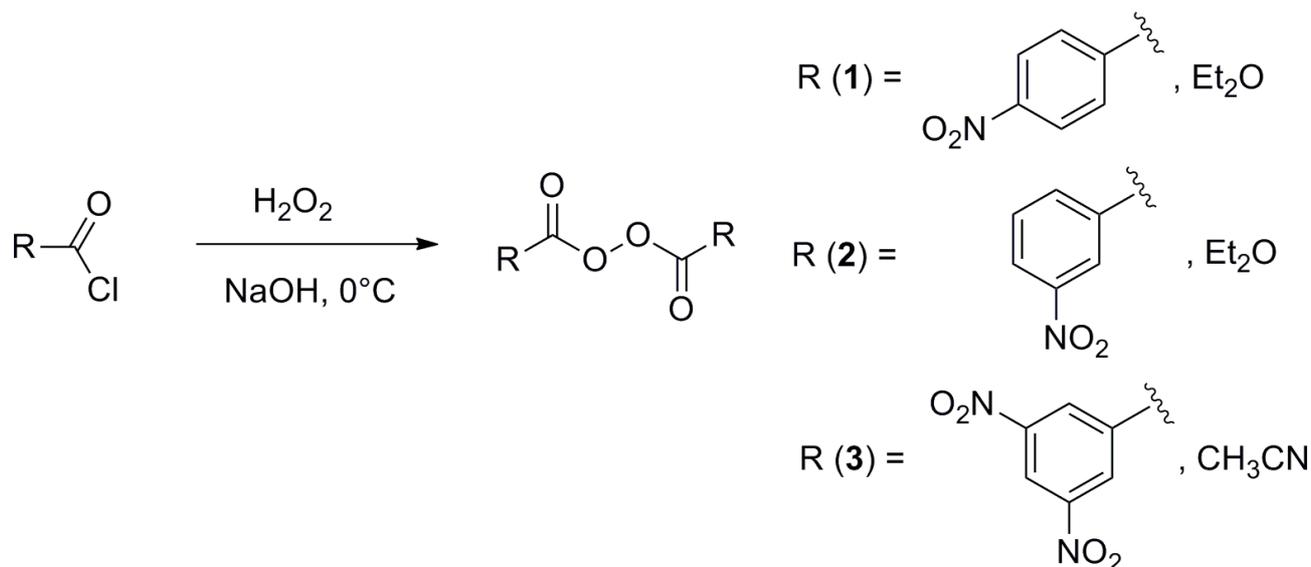
drogen peroxide solution and an aqueous solution of sodium hydroxide<sup>[9-10]</sup> in situ ( $S_N2t$ -mechanism) forming sodium peroxide. This reacts via nucleophilic substitution with the acyl chlorides. The sodium peroxide can also be used directly, but this and the reaction conditions mentioned before only lead to symmetrically substituted molecules.<sup>[11]</sup> If dissymmetric substituted molecules are desired, the peroxy acids have to be reacted with the corresponding acyl chloride.<sup>[9]</sup> The organic residue in this reactions can be varied over a large scale of different aliphatic and aromatic backbones<sup>[6,10,12-13]</sup> but with respect to energetic materials, nitrated aromatic compounds are the most promising ones since they are relatively easy to prepare and stable at ambient conditions. An example for those compounds is synthesized by the reaction of a cyclic acid anhydride with *p*-nitro perbenzoic acid.<sup>[14]</sup> However this molecule cannot be considered as energetic since the alkyl content is too high. In addition to the before mentioned advantages the nitro group delivers a high density, which is beneficial for a potential application as an energetic material. Therefore, nitro aryl substituted molecules with as less as possible not energetic C, H content might form suitable energetic materials. One existing example for such nitrated molecules is the peroxy anhydride derived from 4-nitrobenzoic acid. This compound is also commercially available and was investigated for use as initiation reagent for radical polymerization processes.<sup>[15]</sup> In this paper we would like to give an insight in the synthesis and characterization of this and some other potentially energetic nitroaryl peroxy anhydrides and investigate them comparatively concerning their performances as energetic materials as well as their sensitivities toward outer stimuli namely impact, friction, electrostatic discharge and heat.

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## Results and Discussion

Since this study was started with the intention to investigate peroxy anhydrides as possible energetic materials, we choose to limit the synthesis and determination of the different properties to compounds, which have at least slightly energetic ar-



**Scheme 1.** Synthetic pathway for the preparation of **1**, **2** and **3**.

omatic residues and did not investigate compounds like di-benzoyl peroxide.

### Synthesis

Eight new peroxy anhydrides and one literature known molecule for comparison were prepared using two different strategies. Bis-4-nitrobenzoyl peroxide (**1**),<sup>[15]</sup> bis-3-nitrobenzoyl peroxide (**2**) and bis-3,5-dinitrobenzoyl peroxide (**3**) were prepared by reacting the aqueous corresponding acyl chlorides with excessive amounts of 30% H<sub>2</sub>O<sub>2</sub> solution in diethyl ether, respectively acetonitrile under the addition of a slightly excess of aqueous NaOH solution at 0°C. The synthetic pathway is displayed in Scheme 1.

The reaction products precipitated instantly and were filtered off. After washing the solid residues with water and subsequently diethyl ether, the compounds were air dried and colorless solids were obtained in yields between 13% (**3**) and 37% (**1**). In the case of compound **3** a concurrent decomposition reaction takes place resulting in the formation of a red oil, what explains the poorer yield compared to compounds **1** and **2**.

The mixed binuclear peroxy anhydrides 3-nitrobenzoyl-4-nitrobenzoyl peroxide (**4**), 3,5-dinitrobenzoyl-3-nitrobenzoyl peroxide (**5**) and 3,5-dinitrobenzoyl-4-nitrobenzoyl peroxide (**6**) were prepared by reacting acyl chlorides with the corresponding peroxy acids in diethyl ether at 0°C. The synthetic pathway is displayed in Scheme 2. The peroxy acids were prepared according to a literature procedure.<sup>[16]</sup> A base is still needed to catch the HCl formed during the condensation reaction. Since pyridine turned out to be too weak for this task, an aqueous NaOH solution in slight excess was applied. The reaction products again precipitated instantly. The yields obtained are between 53% (**5**) and 61% (**6**).

It is also possible to exchange the functionalities, but with the peroxy acid respectively acyl chloride combination displayed in Scheme 2 the higher yields were obtained.

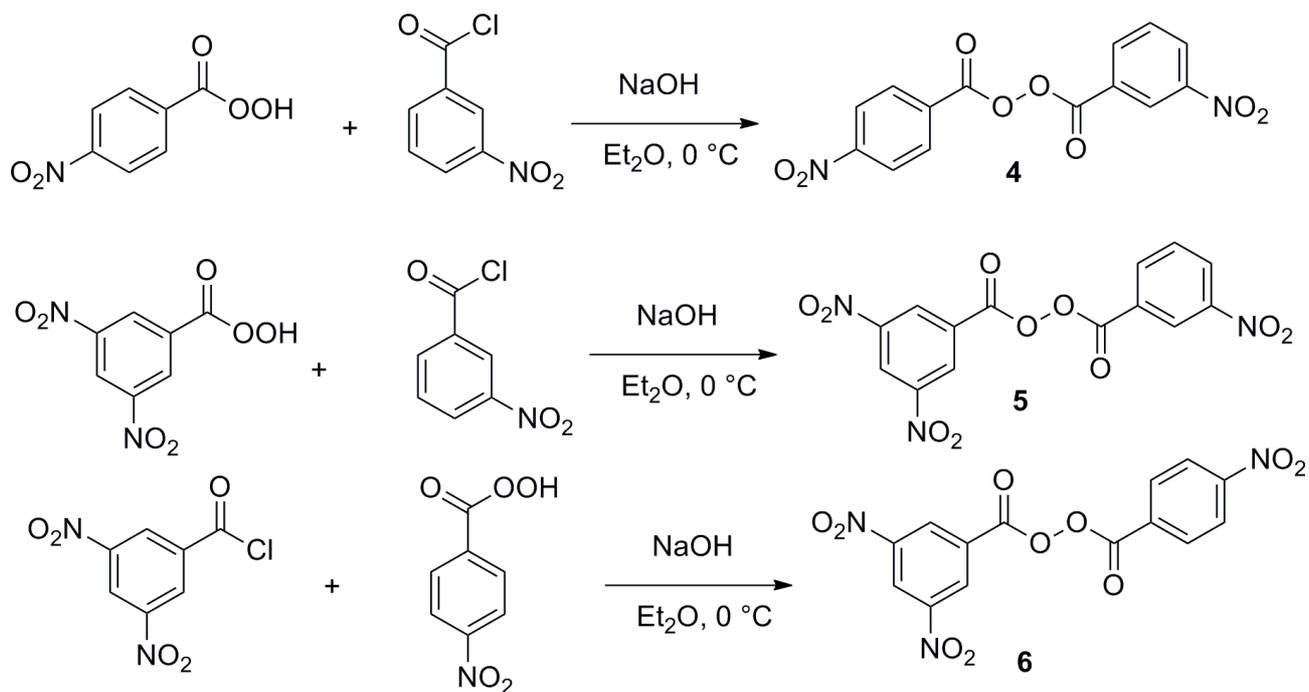
The third topic examined in this paper is the preparation of peroxy anhydrides derived from terephthalic acid. For this reactions, terephthaloyl chloride was reacted with 4-nitroperbenzoic acid, 3,5-dinitroperbenzoic acid and 3-nitroperbenzoic acid in diethyl ether at 0°C under the addition of slightly excessive aqueous NaOH solution resulting in the formation of bis-4-nitrobenzoyl-terephthaloyl peroxide (**7**), bis-3,5-dinitrobenzoyl-terephthaloyl peroxide (**8**) and bis-3-nitrobenzoyl-terephthaloyl peroxide (**9**). Scheme 3 displays the synthetic pathway. The products again precipitated instantly from the reaction mixture as colorless solids, were filtered off and air dried after washing with water and diethyl ether. The obtained yields are between 14% (**8**) and 40% (**9**).

Since the starting materials and the products all behave very similar toward standard analytical methods, the best way to prove product formation is to light a small sample on the spatula tip. A test has to be considered as positive, when the compound intensively decomposes under the formation of smoke.

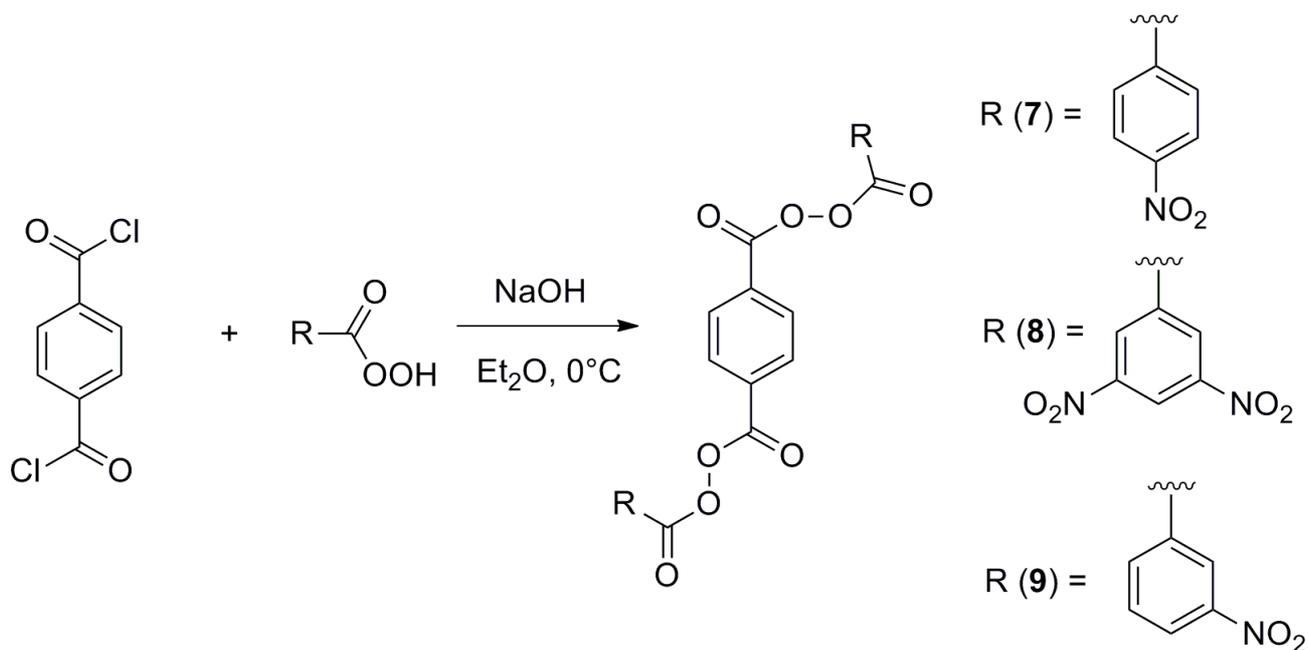
### Crystal structures

Single crystals for compounds **2** and **3** were grown from acetone and acetonitrile, respectively, at room temperature. Details of the low temperature (123 K) X-ray measurements and refinements are given in the SI. Figure 1 shows the molecular structures of the respective compounds.

The compounds crystallize in the common space groups *P*-1 (**2**) and *C2/c* (**3**). The observed densities are 1.65 g cm<sup>-3</sup> (**2**) and 1.75 g cm<sup>-3</sup>, respectively, (**3**) and therefore significantly higher than that of commonly known organic peroxides like TATP (1.22 g cm<sup>-3</sup>)<sup>[17]</sup> which is beneficial for their use as en-



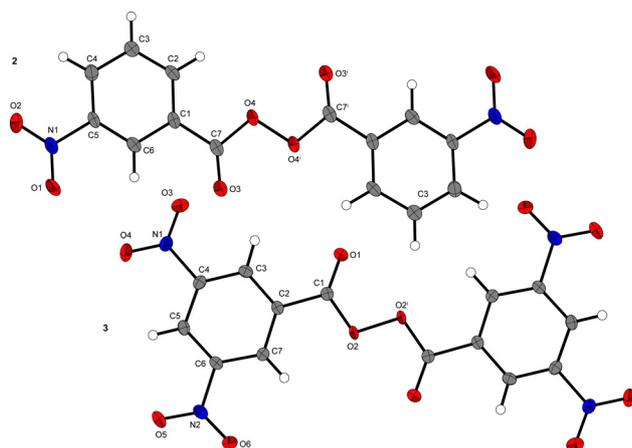
Scheme 2. Synthetic pathway for the preparation of 4, 5 and 6.



Scheme 3. Synthetic pathway for the preparation of 7, 8 and 9.

ergetic materials. They even are in the range or higher than the density of the commonly known and widely used secondary explosive trinitrotoluene (TNT) ( $1.654 \text{ g cm}^{-3}$ )<sup>[18]</sup> and close to the more potent RDX ( $1.82 \text{ g cm}^{-3}$ ).<sup>[12]</sup> The O–O bond distance is in the range between 144.1 and 145.3 pm. These values are in accurate accordance with values for other organic peroxy anhydrides published in the literature<sup>[19]</sup> and are also in the same

range as the O–O bond distance of hydrogen peroxide ( $145.3 \text{ pm}$ )<sup>[20]</sup>. The O–O–C bond angles have values between  $107.2^\circ$  and  $108.0^\circ$  which is slightly lower than literature values ( $110.1^\circ$  for the *m*-chloro substituted analogue).<sup>[19]</sup> The bond distances for the nitro group are in the range of 147 pm for C–N and 122 pm for N–O which are normal values for aromatic nitro compounds.<sup>[21–22]</sup> The same is true for the bond angles which



**Figure 1.** Molecular structures for compounds **2** and **3** and their labeling schemes. Thermal ellipsoids represent the 50% probability level. Both compounds do have a centre of inversion at the middle of the O–O bond. Symmetry codes: **2**: (i):  $-x, 1-y, -z$ ; **3**: (i):  $-x, 2-y, -z$ .

properties of the compounds. Impact sensitivities are in the range between 1 and 5 J. Conspicuously, the biperoxides are more sensitive (1 J) in comparison to the monoperoxides (1.5–4 J), which is a direct result of the increased peroxide percentage. But according to BAM (Bundesanstalt für Materialforschung und -prüfung) these compounds all have to be classified as extremely sensitive toward impact. However in contrast to commonly used primary explosives and most peroxides they only show decomposition and do not explode/fulminate which makes them safer. Friction sensitivities for compounds **1–6** are in the range of 240 N to 360 N. According to the BAM regulations they have to be classified as slightly sensitive to insensitive. For compounds **7, 8** and **9**, the friction sensitivities are between 8 and 18 N. This means the compounds must be classified as very sensitive (**8**) to extremely sensitive (**7**, **9**). This obvious difference can again most likely be explained with the additional peroxy group of the latter compounds. The ESD value for all compounds is much higher than

**Table 1.** Energetic properties of compounds **1** to **9**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>
Formula	$C_{14}H_8N_2O_8$	$C_{14}H_8N_2O_8$	$C_{14}H_6N_4O_{12}$	$C_{14}H_8N_2O_8$	$C_{14}H_7N_3O_{10}$	$C_{14}H_7N_3O_{10}$	$C_{22}H_{12}N_2O_{12}$	$C_{22}H_{10}N_4O_{16}$	$C_{22}H_{12}N_2O_{12}$
$F_w$ [g mol <sup>-1</sup> ]	332.22	332.22	422.20	332.22	377.21	377.21	496.34	586.32	496.34
$IS$ [J] <sup>[a]</sup>	3	3	1.5	5	4	4	1	1	1
$FS$ [N] <sup>[b]</sup>	240	≥ 360	240	≥ 360	≥ 360	≥ 360	8	18	9
$ESD$ [J] <sup>[c]</sup>	0.300	0.108	0.300	0.15	0.150	0.100	0.056	0.064	0.050
$\Omega_{CO_2}$ [%] <sup>[d]</sup>	-115.6	-115.5	-72.0	-115.6	-91.2	-91.2	-122.5	-90.1	-122.5
$T_{dec}$ [°C] <sup>[e]</sup>	158	140	164	125	143	141	164	163	149
$\rho$ [g cm <sup>-3</sup> ] <sup>[f]</sup>	1.61/psc.	1.608/X-ray	1.718/X-ray	1.67/psc.	1.70/psc.	1.69/psc.	1.46/psc.	1.51/psc.	1.45/psc.
$\Delta_f H_m^\circ$ [kJ mol <sup>-1</sup> ] <sup>[g]</sup>	-415	-406	-410	-404	-405	-405	-761	-752	-752
$\Delta_f U$ [kJ kg <sup>-1</sup> ] <sup>[h]</sup>	-1182	-1155	-906	-1149	-1008	-1009	-1468	-1219	-1449
EXPLO 5 6.02 values									
$\Delta_{ex} U^\circ$ [kJ kg <sup>-1</sup> ] <sup>[i]</sup>	-3810	-3832	-4555	-3870	-4259	-4253	-3485	-4010	-3492
$T_{det}$ [K] <sup>[j]</sup>	2686	2697	3311	2693	3024	3025	2545	3015	2552
$P_{CJ}$ [GPa] <sup>[k]</sup>	13	13	20	9	18	17	9	13	9
$V_{det}$ [ms <sup>-1</sup> ] <sup>[l]</sup>	6129	6130	7087	6395	6796	6757	5315	6007	5284
$V^0$ [L kg <sup>-1</sup> ] <sup>[m]</sup>	536	536	566	528	547	549	531	572	533

[a] Impact sensitivity according to BAM drophammer (method 1 of 6). [b] Friction sensitivity according to BAM friction tester (method 1 of 6). [c] Electrostatic discharge sensitivity (OZM ESD tester). [d] Oxygen balance. [e] Melting point resp. Temperature of decomposition according to DTA (onset temperatures at a heating rate of 5 °C/min). [f] Room temperature X-ray densities. Those were calculated by the low temperature X-ray values using the equation  $\{\rho_{298 K} = \rho T / [1 + \alpha_v(298 - T^0)]; \alpha_v = 1.5 \cdot 10^{-4} K^{-1}\}$ . [g] Calculated heat of formation using the atomization method and CBS-4 M electronic enthalpies. [h] Energy of formation [i] Heat of detonation. [j] Detonation temperature. [k] Detonation pressure. [l] Detonation velocity. [m] Volume of gas after detonation

have values around 118° (C–N–O) and 125° (O–N–O).<sup>[21–22]</sup> The CO(OO)CO moiety is almost planar for both compounds **2** and **3** with torsion angles between 0 and 1°. In compound **2** the nitro groups are twisted with a torsion angle of -7.00°. For compound **3** again all nitro groups are twisted out of the molecular plane. One torsion angle is -9.9° the second one is 20.9°.

### Energetic properties

The performance data of the compounds were calculated using the EXPLO5 program (version 6.02). The input heats of formation were calculated using the atomization method based on CBS-4 M electronic enthalpies. Table 1 gathers the energetic

the maximum electrostatic potential of the human body (20 mJ).<sup>[23]</sup> The detonation pressures and detonation velocities are compared to standard explosives TNT (6950 ms<sup>-1</sup>, 21 GPa) and RDX (hexogen) (8750 ms<sup>-1</sup>, 35 GPa).<sup>[24]</sup> Most of the synthesized compounds have calculated detonation velocities between 5300 and 6800 ms<sup>-1</sup> which are lower than the ones of TNT and RDX. Compound **3** however has a calculated detonation velocity of 7087 ms<sup>-1</sup> which is slightly better than that of TNT. Conspicuously the biperoxides have detonation velocities between 5300 and 6000 ms<sup>-1</sup> and by this perform weaker than the monoperoxides. The total difference is quite small, however this general tendency can be recognized. The difference can be explained with the lower densities of the biperoxides. Compound **3** has the highest detonation pressure of all

the synthesized compounds with a calculated value of 20 GPa. This is close to the detonation pressure of TNT but only about 60% of the detonation pressure of RDX. The synthesized compounds have decomposition points in a temperature range between 125 and 164 °C. While compound **4** features a decomposition point of 125 °C which is in the normal although higher range for an organic peroxide, the other decomposition points determined, especially for **3**, **7** and **8** with more than 160 °C are remarkable high for compounds containing a peroxide backbone.

## Conclusions

Eight new and one literature known peroxy anhydrides namely bis-4-nitrobenzoyl peroxide (**1**), bis-3-nitrobenzoyl peroxide (**2**), bis-3,5-dinitrobenzoyl peroxide (**3**), 3-nitrobenzoyl-4-nitrobenzoyl peroxide (**4**), 3,5-dinitrobenzoyl-3-nitrobenzoyl peroxide (**5**), 3,5-dinitrobenzoyl-4-nitrobenzoyl peroxide (**6**), bis-4-nitrobenzoyl-terephthaloyl peroxide (**7**), bis-3,5-dinitrobenzoyl-terephthaloyl peroxide (**8**) and bis-3-nitrobenzoyl terephthaloyl peroxide (**9**) were prepared following an established synthetic procedure as well as a slight modification of it and tested regarding their sensitivities towards outer stimuli. Some of the prepared compounds can find possible application as radical initiators. Compounds **2** to **6** are as sensitive or slightly less sensitive as commercial available **1**. Compounds **7**, **8** and **9** however are too sensitive for a possible application. They are also the weaker performing energetic materials, although they feature two and not just one peroxy group, what can be explained by the lower density. Moreover the thermal stability of most synthesized compounds is remarkable high for organic peroxides and in contrast to most other peroxides they are long-term stable at room temperature. The monoperoxides also feature only low sensitivities toward friction. Another striking advantage is the remarkable density which is mainly based on the contained nitro groups and the accumulation of many heavy hetero atoms in the peroxy anhydride moiety. The CO (OO)CO moiety is also oxygen rich. These properties make alternative peroxy anhydrides potentially suitable for application as energetic materials especially in the oxidizer sector, where high oxygen contents are needed but the requirements to thermal stability and detonation performance are not extreme. However the high sensitivity towards impact is a significant drawback for possible application as an energetic material even though the compounds only decompose without any noticeable sound and do not detonate.

## Supporting information

Full experimental details and characterization data are included in the SI. A table about crystallographic details with CCDC numbers is also part of the SI as well as NMR spectra and calculation details.

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