



## An effective and regioselective bromination of 1,4,5,8-naphthalene-tetracarboxylic dianhydride using tribromoisocyanuric acid



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### ABSTRACT

A highly efficient and cost-effective reagent for the bromination of 1,4,5,8-naphthalenetetracarboxylic dianhydride under mild reaction conditions is reported. Bromination of 1,4,5,8-naphthalenetetracarboxylic dianhydride using tribromoisocyanuric acid (TBCA) in concentrated  $H_2SO_4$  is very effective and regioselective. 1,4,5,8-Naphthalenetetracarboxylic dianhydride was brominated smoothly under optimized reaction conditions to give mono-, di- and tetra-brominated products in good to excellent yields using TBCA. As a proof of principle, the potential of this bromination methodology is demonstrated by converting brominated naphthalenetetracarboxylic dianhydrides into N-imide and core functionalized 1,4,5,8-naphthalenetetracarboxylic diimides by treating with *n*-butylamine to yield corresponding mono-, di- and tetra-(*n*-butylamino)-naphthalene diimides in good yields in one-step reactions.

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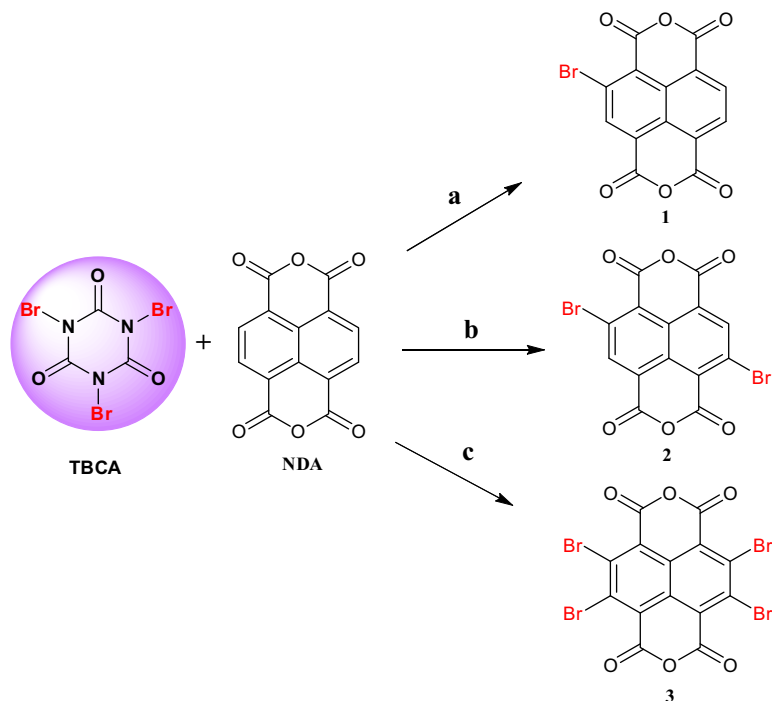
Naphthalene diimides (NDIs) are the rapidly emerging class of aromatic compounds with significant implications in organic, bio-supramolecular chemistry, biomedicine and materials science owing to their remarkable electronic, spectroscopic and self-assembly properties.<sup>1</sup> The imide substituted NDIs and core substituted NDIs (cNDIs) have been shown to have wide-ranging applications in the field of supramolecular chemistry<sup>1,2</sup> and biomedicine that is generation of nanostructures,<sup>2,3</sup> DNA intercalation,<sup>4</sup> supramolecular chirality,<sup>5</sup> artificial photosynthesis,<sup>6</sup> self-cleaning,<sup>7</sup> sensors,<sup>8</sup> organic solar cell applications,<sup>9</sup> host-guest systems,<sup>10a,b</sup> synthetic ion channels<sup>10c</sup> and *n*-type organic field effect transistors (OFETs).<sup>11</sup> Functionalization through imide nitrogens or via core substitution (substitution on the naphthalene core) produces analogues that alter their electrical, optical and redox properties.<sup>12</sup> Varying the nature of substituents either electron donating or withdrawing on cNDIs has been shown to exhibit colourful rainbow fluorescence.<sup>13</sup> The versatility in structure and properties of NDIs is responsible for its wide spread application in various fields.

The bromo-derivatives of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) serve as precursors for the preparation of numerous functionalized NDIs. The area of NDIs has been witnessing a rapid progress due to interesting properties and novel functional applications of N-imide and core functionalized NDIs. The availability of precursor materials in abundance to prepare functionalized NDIs accelerates the ongoing research activities

on NDIs including supramolecular chemistry, organic electronics and biomedicine. Therefore developing an efficient and economical brominating reagent for the regioselective synthesis of bromo-derivatives of NDA is of high priority. Various bromination methods known till date in the literature for bromination of NDA involve (i) molecular bromine as a brominating reagent in the presence of catalytic amount of iodine either in oleum or mixture of conc.  $H_2SO_4$  and oleum as a solvent,<sup>14</sup> (ii) use of sodium bromide (NaBr) as a brominating agent in oleum<sup>15</sup> and (iii) dibromoisocyanuric acid (DBI) in oleum as a source of bromine.<sup>16</sup> However all these literature methods suffer from many drawbacks like molecular bromine involved reactions produce low yields and handling bromine is a difficult task due to its toxicity and high vapour pressure. Moreover, hazardous and corrosive nature of molecular bromine makes it difficult to handle as a brominating reagent under milder reaction conditions. Furthermore, prolonged reaction time and high reaction temperatures were needed to carry out the reaction (i.e., the tetra-bromo NDA was synthesized at 140 °C). The NaBr method required harsh reaction conditions and a special equipment to carry out the reaction.<sup>15</sup> DBI is highly expensive, not readily available in large quantities, reactions were performed at high temperature (130 °C)<sup>16b</sup> and gave mixture of brominated products.<sup>16d</sup> Moreover, purification and isolation of the bromo-derivatives of NDA have not been described with full details in the literature reports. All the above discussed methods typically report purification and characterization of bromo-derivatives of NDAs by converting them into corresponding imides. These drawbacks further reiterate the need for

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**Scheme 1.** Reagents and conditions: (a) **TBCA** (0.5 equiv), concd  $\text{H}_2\text{SO}_4$ , rt, 8 h, 70%; (b) **TBCA** (1 equiv), concd  $\text{H}_2\text{SO}_4$ , rt, 12 h, 76%; (c) **TBCA** (2.5 equiv), concd  $\text{H}_2\text{SO}_4$ , rt, 8 h then at 80 °C, 8 h, 87%.

**Table 1**  
Optimized reaction conditions for the bromination of NDA using **TBCA** as a reagent.

Compound	TBCA (equiv)	<sup>a</sup> Solvent (mL)	Reaction time (h)	Reaction temperature (°C)	<sup>d</sup> Crude yield (%)	<sup>e</sup> Yield after recrystallization (%)
<b>1</b>	0.5	25	8	<sup>b</sup> rt	89	70
<b>2</b>	1.0	25	12	rt	92	76
<b>3</b>	2.5	25	<sup>b</sup> 8 + <sup>c</sup> 8	rt and <sup>c</sup> 80	98	87

<sup>a</sup>Concentrated  $\text{H}_2\text{SO}_4$ .

<sup>b</sup>rt = room temperature.

<sup>c</sup>Heating.

<sup>d</sup>After product precipitation.

<sup>e</sup>Recrystallized from dimethylformamide.

developing an efficient brominating reagent for the rapid and regioselective bromination of NDA to preferred bromo-products in high yield and purity. In addition, research in our laboratory is focused on exploring the potential of functionalized NDIs for their self-assembly, optical and chiroptical properties with the aim of developing biomimetic systems and materials for optoelectronic, chiroptical and biomedical applications.<sup>2,5,7</sup> Therefore we intended to develop an efficient and regioselective bromination methodology to obtain mono-, di- and tetra-brominated NDAs in high yield and purity. Recently, we have developed a 5,5-dimethyl-1,3-dibromohydantoin (DBH) reagent for the regioselective bromination of NDAs.<sup>17</sup> However, the DBH method requires relatively prolonged reaction times, fairly high reaction temperature and excess brominating reagent to give bromo-NDAs with relatively low yields. These shortcomings and our desire to develop a superior bromination method for NDA in terms of bromine-atom economy, reaction efficiency and cost effectiveness motivated us to develop newer and effective brominating reagent. For this purpose we chose **TBCA** as the potential brominating reagent due to its inexpensive synthesis from isocyanuric acid (\$22/25 g, www.sigma-aldrich.com) in large quantities and high atom-economy with respect to transferable bromine atoms compared to other brominating reagents.

**TBCA** is a white solid which is less toxic and expected to be a safe brominating reagent that can be easily synthesized in bulk from isocyanuric acid and NaBr in the presence of Oxone<sup>®</sup>.<sup>18a</sup> **TBCA** has been used for the bromination of simple alkenes and aromatic substrates<sup>18</sup> but has not been exploited for bromination of NDA. Thus we performed bromination of NDA using **TBCA** which was prepared by following the literature procedure<sup>18a</sup> and optimized the reaction conditions for regioselective preparation of mono-, di- and tetra-brominated NDA core. Further it should be noted that **TBCA** is particularly advantageous because of high atom-economy as it can transfer three  $\text{Br}^+$  to one substrate which accelerates the rate of reaction compared to any currently used brominating reagents including dibromoisocyanuric acid (DBI). Easy and straight forward synthesis of **TBCA** reagent<sup>18</sup> in large quantity makes it an industrially viable reagent for the bromination of NDA while DBI is highly expensive and not readily available in bulk quantity. The bromination reactions of NDA using **TBCA** were fast, required low equivalents of **TBCA** and performed under milder conditions compared to any other brominating reagent reported in the literature. Interestingly mono-, di- and tetra-bromination of NDA core was performed at ambient conditions by varying equiv of **TBCA**. It should be noted that the reaction time of tetra-bromination of NDA was greatly reduced by heating the reaction mixture towards

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